

**DEVELOPMENT OF HIGH STRENGTH CONCRETE USING
DIFFERENT POLYCARBOXYLATES AND DIFFERENT CEMENT
TYPES**

BY

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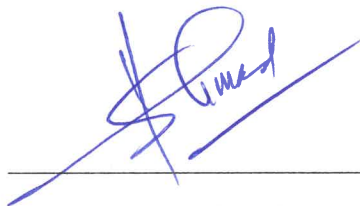
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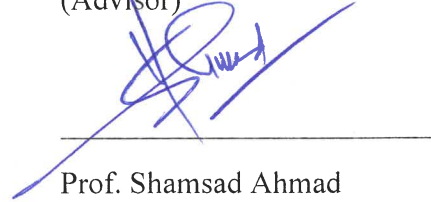


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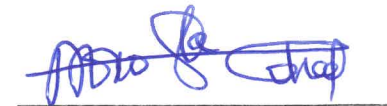
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Dedicated to

My late father, may Allah have mercy on him,

My respected mother, may Allah bless her life,

My brothers, and sisters, may Allah make them successful in their lives.

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In the name of ALLAH, the most beneficent and the most merciful. All thanks and praise belong to him, the lord of the worlds, who has bestowed upon me the strength, power, and guidance to reach this level of knowledge and science.

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ABSTRACT

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Alternative building materials, that not only fulfill the strength and durability requirements but also mitigate the negative environmental impact caused by the growing production of ordinary Portland cement (OPC), are in high demand nowadays. Limestone calcined clay cement (LC3) is a low-CO₂ binder being considered as an alternative to ordinary Portland cement with comparable structural and durability properties. This study presents the outcomes of an experimental investigation on the development of high-strength LC3 concrete using two types of polycarboxylate-based high-efficiency superplasticizers (Fluidum PC314 and PCE CT50) at 0.5, 1, and 2% by binder mass. Experimental results showed that the developed LC3 concrete mixture had a 7-and 28-day compressive strength of about 70 and 90 MPa, respectively, which was comparable to that of the control mixture made of OPC alone at the same water-to-cement ratio as well as the same dose and type of superplasticizer. A relatively lower strength was observed for the concrete mixture made with the PCE CT50 compared to that made with the Fluidum PC314 type superplasticizer. The results of tests pertaining to calorimetry (conducted at 23, 30, and 40 °C), workability, hardened properties (compressive strength, tensile strength, water absorption, density, chloride migration, and shrinkage), and microstructural (SEM) analyses as well as the estimates for activation energies confirmed

the beneficial effect of the Fluidum PC314 type superplasticizer in producing high-strength LC3 concrete. The outcomes of this study validate the research hypothesis recommending LC3 binder for use in the construction industry requiring high-strength concrete.

ملخص الرسالة

الاسم الكامل: احمد معين ابدالى

عنوان الرسالة: تطوير خرسانة عالية القوة باستخدام أنواع مختلفة من البولي كربوكسيلات والأسمنت.

التخصص: ماجستير العلوم فى الهندسة المدنية

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٤

المواد البنائية البديلة التي تلبي متطلبات القوة والمتانة وتقلل من الأثر البيئي السلبي الناتج عن الإنتاج المتزايد للأسمنت البورتلاندي العادي (OPC) هي محل طلب كبير في الوقت الحاضر. يعتبر أسمنت الطين الجيري المكلس (LC3) مادة بناء منخفضة الانبعاثات من ثاني أكسيد الكربون، يُنظر إليها كبديل للأسمنت البورتلاندي العادي مع خصائص هيكلية ومتانة مماثلة. تقدم هذه الرسالة نتائج تحقيق تجريبي حول تطوير خرسانة LC3 عالية القوة باستخدام نوعين من الملدنات الفائقة الكفاءة القائمة على البولي كربوكسيلات (Fluidum PC314 و PCE CT50) بنسبة ٠,٥ و ١ و ٢% من كتلة الأسمنت. أظهرت النتائج التجريبية أن خليط الخرسانة LC3 المطور حقق قوة ضغط عند ٧ و ٢٨ يوماً تبلغ حوالي ٧٠ و ٩٠ ميجا باسكال، على التوالي، وهو ما كان مماثلاً للخليط المصنوع من OPC وحده عند نفس نسبة الماء إلى الأسمنت وكذلك نفس الجرعة ونوع الملدن الفائق. لوحظت قوة أقل نسبياً لخليط الخرسانة المصنوع مع الملدن الفائق PCE CT50 مقارنة بتلك المصنوعة مع نوع Fluidum PC314. أكدت نتائج الاختبارات المتعلقة بالكالوريمتري (التي أجريت عند ٢٣ و ٣٠ و ٤٠ درجة مئوية)، والقابلية للتشغيل، وخصائص المادة المتصلدة (قوة الضغط، قوة الشد، امتصاص الماء، الكثافة، مقاومة الكلوريد، والانكماش)، والتحليلات الميكروسكوبية (SEM) وكذلك تقديرات طاقة تنشيط التفاعل على استخدام الملدن الفائق من نوع Fluidum PC314 في إنتاج خرسانة LC3 عالية القوة. تؤكد نتائج هذه الرسالة صحة الفرضية البحثية التي توصي باستخدام LC3 في صناعة البناء التي تتطلب خرسانة عالية القوة.

CHAPTER 1

INTRODUCTION

1.1 General

The demand for advanced construction materials that can fulfill the requirements for modern structures and architectural concrete constructions has motivated the research area of high-strength concrete. High-strength concrete was first developed in the 1950s with a compressive strength of more than 34 MPa. Later, the high-strength concrete was identified by the American Concrete Institute (ACI) in 2005 as a concrete with a compressive strength of 55 MPa or greater [1].

To continue developing high-strength concrete, one of the promising chemical admixtures that can be incorporated is polycarboxylates [2]. Polycarboxylates can either be in the form of powder or as a dissolved material in superplasticizer solvents. Its advantages are beyond other admixtures such as lignosulfonate-based, melamine-based, and naphthalene-based superplasticizers. With a low dose of polycarboxylates (0.5% of the cement's weight) and a low water-to-cement ratio, high-strength concrete is produced without affecting the workability of the mix.

Today, since carbon dioxide (CO_2) emissions released from Portland cement manufacturing account for 5-7% of the total released carbon emissions to the atmosphere, there is an increased demand for sustainable structures that have high strength and improved durability which allows the use of less material and smaller sections [3].

To describe this issue more, it is worth mentioning that Carbon Dioxide (CO₂) is a greenhouse gas that is mainly released from the burning of fossil fuel and cement production. Based on the International Energy Agency (IEA), the CO₂ emissions due to industrial manufacturing and combustion reached 36.3 Gt in 2021 and 37.6 Gt in 2023 which shows a 3.5% increase in 3 years. It had a 5.1% reduction in 2020 due to the Coronavirus effect on industrial and economic activities. Then, the recovery of economic activities, industrial production, and the energy to fulfill human needs increased the trend of CO₂ emissions in the world.

Many severe problems root back to CO₂ emissions, for instance, greenhouse gas emissions cover the earth and trap the heat from sun radiation which causes global warming and climate change (Figure 1). Nowadays, the world is getting warmer faster than any time ever. This warming interrupts the usual circumstances of life and nature on earth and leads to disasters such as droughts, floods, storms, forests fire, and overflow of the oceans into the continents. Moreover, CO₂ is known as a prominent factor for respiratory and cancer diseases in human life. The effects of CO₂ remain unsafe to all forms of life on Earth [4].

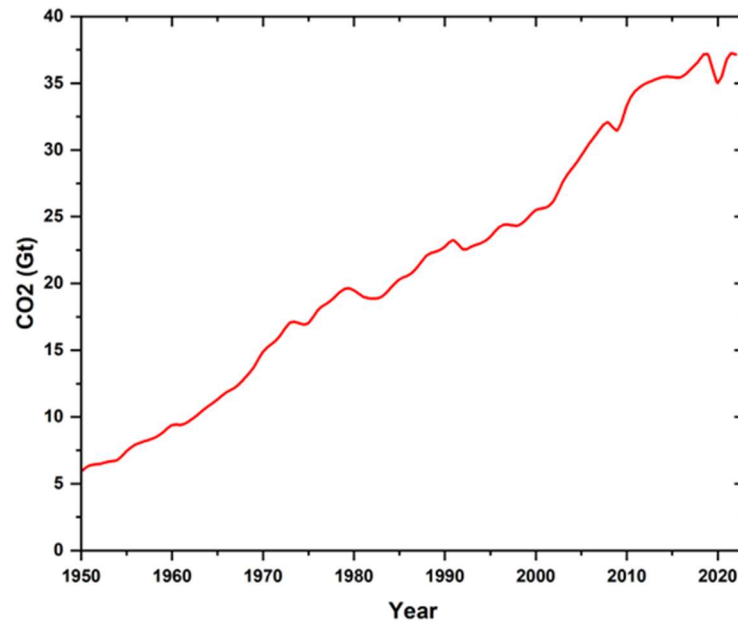


Figure 1. Total CO₂ emissions in the world in Gigatons [5].

As mentioned earlier, CO₂ emissions are the primary concern due to their vast effect on global climate change. The emissions distribution shows considerable variation across the countries and regions. Based on the recent information, these five countries had the most production of CO₂ since the industrial revolution namely the USA, China, Russia, Germany, and the UK (Figures 2 and 3). However, in 2021, the largest CO₂ emissions were from China, the USA, India, Russia, and Japan, respectively. China is the biggest emitter of CO₂ in the world, producing 11.397 Gt in 2021. The next emitter is the United States with 5.05 Gt, then India, Russia, and Japan account for 2.83 Gt, 1.65 Gt, and 1.054 Gt, respectively [6].

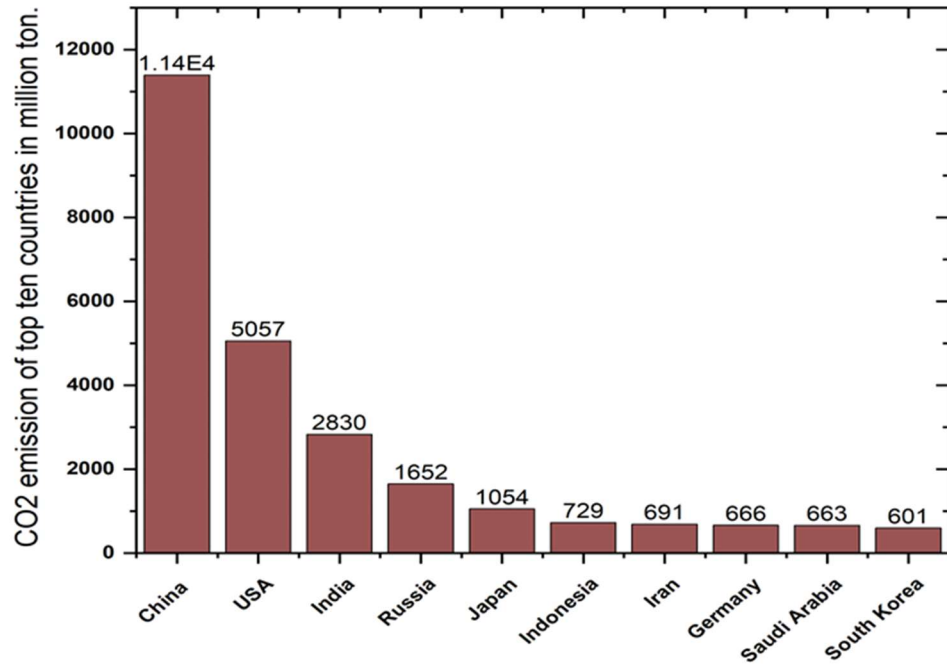


Figure 2. Top ten emitters of CO₂ in 2022 [6].

Graphical representation of CO₂ emitter all around the world

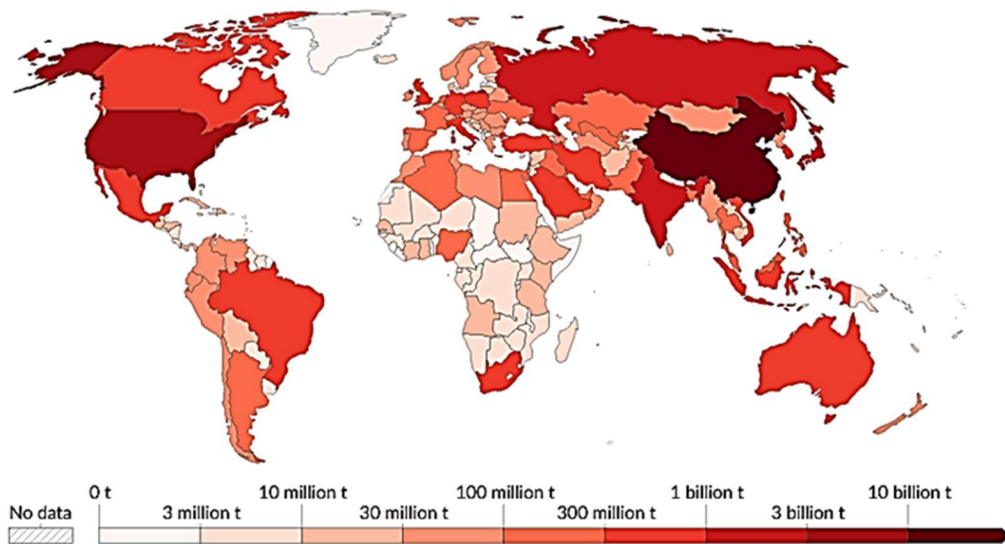


Figure 3. CO₂ emissions in the world [7].

A major contributor to CO₂ emissions globally is Portland cement production. The production of 1000 kg of cement adds 900 kg of carbon dioxide (CO₂) to the environment. This is due to the production process of Portland cement as limestone is heated and mixed with a variety of other components to produce what we call clinkers. In 2014, cement production was 4.3 billion tons and the new developing countries like China, India, and some other Asian countries had a share of 81% of the total cement production in the world [8]. USA, Europe, and Japan produced 9% of the world's total [8]. The cement industry is responsible for approximately 5-8% of global CO₂ emissions [9].

Many solutions are suggested for reducing CO₂ emissions due to Portland cement. For instance, low energy processes for cement manufacturing and industrial energy production through renewable sources [9], and using SCMs like slag and fly ash as partial replacements which can serve as a substitute for cement up to 70% and 25%, respectively [10]. Among all, a particularly promising, viable, and available solution is using limestone calcined clay as a partial substitute for the OPC clinker [6, 7]. It is a good performance and practical material with a lower carbon footprint compared to ordinary Portland cement [11].

The formula behind LC3 is using limestone and calcined clay (CC) which can reduce a considerable amount of clinker [12]. The use of LC3 causes a 40% reduction in CO₂ emissions [11]. The fundamental reason for this massive reduction is that calcined clay does not require exceptionally high temperatures like those of the rotary kiln in clinker manufacturing [12]. Therefore, LC3 can be addressed as one of the best sustainable solutions for reducing carbon emissions and carbon footprint in the cement industry [11]. Thus, this research would also incorporate the limestone calcined clay cement at optimum calcination temperatures either as the main or supplementary cementitious material.

LC3 is composed of limestone, calcined clay, cement, and gypsum. The proportion of cement replacement by SCMs has a profound impact on its properties [8]. This amount of replacement is measured by a ratio called the clinker factor. It is the proportion of the clinker's weight to the overall weight of the binders. This ratio can be as low as 50% to not compromise the overall properties of concrete including durability and strength. In return, it reduces CO₂ emissions as well as the cost of the production of concrete [13].

In a recent study [10], three different types of calcined clay with three substitution ratios of 30, 50, and 70% showed no notable impact on the compressive strength of concrete up to 50% replacement of cement. However, to compare it with the control mix, the mix with a clinker factor of 70% was comparable in terms of compressive strength. The control mixture had 43 MPa compressive strength whereas the mixture with 30% replacement had 36 MPa compressive strength [10]. The optimum recommended mix for LC3 can be stated as 70% cement, 19% calcined clay, 9.5% limestone powder, and 1.5% gypsum [10].

Parashar [14] conducted experiments on the efficiency of various methods to find the reactivity level of mixes with SCMs. It was done on calcined clay, slag, fly ash, and limestone. Substitution of half of the cement content by calcined clay and limestone resulted in a reactive and economical material that is similar to that of LC3 [14].

1.2 Need for this research

The need to utilize locally available natural or waste materials to produce high-strength concrete with a 28-day compressive strength of more than 55 MPa is essential. This could be achieved with the proper incorporation of Polycarboxylates (PC), which can reduce water requirements and improve the performance of the produced concrete. However, the common SCMs that are used in concrete like fly ash and silica fume are not locally available, so the

PCE along with locally available limestone calcined clay cement are promising and need extended investigation in producing high-strength concrete. High-strength concrete can be used in new or repaired constructions.

This research on the development of high-strength concrete incorporating polycarboxylates on different cement types including OPC, limestone calcined clay cement at different calcination temperatures as full, and supplementary cementitious material would contribute to the design of high-strength concrete needed in the concrete industry. In addition, this research is also contributing to the environmental and economic benefits due to the incorporation of limestone calcined clay cement as full, and supplementary cementitious material as well as in reducing cement requirements.

1.3 Research objectives

The primary goal of this study is to examine the impact of polycarboxylates on the production of high-strength concrete for use in new or repair constructions using different cement types. The research findings are expected to provide a solid experimental basis for the design of concrete with various cement types and different polycarboxylate types.

The particular objectives of this research are outlined as follows:

1. To study the effect of different polycarboxylates and different types of binder on the rate of hydration reaction, maximum hydration heat, and morphology (SEM).
2. To model the heat of hydration equations at different temperatures and estimate the activation energies.
3. To study the fresh and hardened properties (mechanical, shrinkage and durability) of the developed concrete mixtures.

1.4 Novelty of the research

The novelty of this research is briefly described as follows:

1. Testing limestone calcined clay cement (LC3) at different calcination temperatures as full, and supplementary cementitious material modified by polycarboxylates to produce high-strength cement composites.
2. Modeling the heat equations at different temperatures of hydration of the selected binders.
3. Modeling the activation energies of hydration of the selected binders.

The results of this research would contribute to the construction industry for possible applications of the developed concrete mixtures in new or repair constructions.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Since carbon dioxide emissions released from Portland cement manufacturing account for 5-8% of the total carbon emissions released to the open atmosphere [15] , an increased demand for alternative sustainable structural materials that satisfy the structural strength and durability properties exists. It is worth mentioning that the production of 1 kg of Portland cement releases about 0.9 kg of CO₂ into the open atmosphere [15] . The effects of increasing CO₂ emissions remain unsafe and are still considered as the primary cause of global climate [10, 15, 16]

The current literature reveals various innovations in sustainable concrete technology that include but are not restricted to the use of alkali-activated binders (geopolymers) that are made of natural materials, e.g., natural pozzolan [15] , clay, and limestone [16] , in addition to the use of supplementary cementitious materials (SCMs) such as fly ash, and blast furnace slag that can substitute Portland cement by 70% [10] as well as the use of nanomaterials such as carbon nanotubes, nano-cellulose, nanographene, graphene oxide, and silica nanoparticles in reinforcing and modifying the concrete matrix [17, 18] , and the use of CO₂ injection (CarbonCure) in concrete [19, 20]. However, the potential for CO₂ reduction through these technologies is limited, and not all places worldwide have access to these technologies locally [10]. Thus, it is feasible to substitute Portland cement in significant quantities with clay and limestone because of their widespread availability worldwide [10, 21].

2.2 Hydration of LC3

LC3, or limestone calcined clay cement, is a sustainable substitute for OPC. It is a ternary blend including calcined clay, clinker, and limestone. The hydration mechanism of LC3 is unique and it is due to the interactions among these components which results in enhanced mechanical and durability properties. [22] Calcined clay which is in the form of metakaolin is a very reactive material due to its amorphous structure. Its microstructure is made during the de-hydroxylation of kaolinite in calcination furnace [23]. In a pozzolanic reaction, the metakaolin reacts with portlandite (CH) which is a byproduct of clinker hydration, and forms calcium-alumino-silicate-hydrate (C-A-S-H) gels. This reaction is extremely advantageous for the enhancement of the strength and durability of the concrete by increasing the C-A-S-H gel and reducing the free lime which can negatively impact the durability of the concrete [24].

The other part of the pozzolanic reaction is the Carboaluminate formation from limestone. Basically, limestone consists of calcium carbonate (CaCO_3) which reacts with the aluminate contents of clinker and metakaolin. The products of this reaction are carboaluminate hydrates namely hemicarboaluminate and monocarboaluminate [25]. Furthermore, the existence of both calcined clay and limestone not only results in the formation of carboaluminates but also produces a more refined microstructure which is due to the synergistic effect of calcined clay and limestone [26].

The heat of hydration of limestone calcined clay cement (LC3) is different from OPC because of its ternary composition and pozzolanic reactions. As stated [25], the LC3 heat flow is lower than OPC in the initial stage because there is less clinker in it. However, the

pozzolanic reactions between limestone and calcined clay add another calorimetric peak to the heat evolution curve which is attributed to the formation of carboaluminate products. Although, many studies have been done on the heat evolution and accumulated heat of LC3. Still, the activation energy of this binder needs to be studied more.

2.3 Effect of LC3 contents on properties of LC3 concrete

As mentioned earlier, LC3 is a ternary blended binder consisting of clinker, calcined clay and limestone. The proportion of its contents highly influences the fresh, mechanical and durability properties of LC3 concrete [21]. Starting with fresh properties, increasing the calcined clay content raises the water requirement of the LC3 matrix due to its fine particle size and high specific surface area which needs more water compared to OPC [24]. Higher water demand necessitates the use of additional dosages of superplasticizer to reach the same workability as OPC concrete, as stated in [13]. The setting times of LC3 are also affected by calcined clay and gypsum. A higher calcined clay amount extends setting times due to a slower pozzolanic reaction compared to clinker [24]. Conversely, a higher gypsum amount tends to accelerate the setting time by enhancing the early hydration products such as ettringite [27]. Therefore, a proper proportioning of LC3 content is essential to ensure adequate workability and sufficient setting times which are applicable for construction purposes [13, 27].

As stated previously, by increasing the clay content of LC3, the water requirement of the binder also increases due to the high specific surface area of clay [10, 28]. It can also be concluded from the literature that a high amount of calcined clay in the LC3 mixture extends the initial and final setting times [29]. The primary reason behind this delay in setting could be attributed to the slower pace of the pozzolanic reaction and the delayed formation of the

C-S-H gel [10]. However, other studies reported interesting results when the incorporation ratio of calcined clay to limestone in the LC3 was decreased from 3 to 1 [28]. The results showed the alternation in the initial and final setting times. It was reported that as calcined clay was increased in the mixture, the induction period decreased [30], and the setting took place earlier [28, 30], whereas when the limestone was increased in the mix, a delay in the setting was observed. More mixing fluidity was gained in the fresh mixtures [28]. This could be justified by the flocculation [29] and relatively high water absorption of clay [29, 31].

A study shows that a 50% replacement of clinker by calcined clay and limestone achieves a comparable longer-term compressive strength [13]. Similarly, other studies mention that 50% clinker gives comparable long-term compressive strength while it reduces the early strength of the LC3 concrete [24, 27]. Another issue is the proportion of calcined clay and limestone which significantly influences the binding capacity and LC3 concrete properties. High replacement of limestone can reduce the overall strength while the reactive calcined clay is the opposite [13, 24].

Another recent study [10] examined three different types of calcined clay with varying replacement ratios by binder mass. These clay types included two Saudi clays (yellow and white) and one Ukrainian clay. The white, yellow, and Ukrainian clays contained 53, 30, and 35% kaolinite, respectively. The optimal binder mixture was 70% conventional Portland cement, 19% calcined clay, 9.5% limestone powder, and 1.5% gypsum by mass. Overall, the compressive strength decreased and was delayed as clay replacement increased. However, virtually all three types of clays utilized at varying replacement ratios had a 28-day compressive strength of at least 28 MPa.

Furthermore, the literature discusses the impact of calcined clay and limestone on the rheological characteristics of LC3 [32, 33]. They noted that the quantity of clay in LC3 is the major cause of increased plastic viscosity, dynamic and static yielding stress, as well as cohesion [32]. This property of clay arises from its layered microstructure, which, as previously indicated, provides it with a high specific surface area and a high mixing water need [33]. Aside from that, the drying shrinkage [10, 34] and carbonation rate [21] of LC3 were larger than that of the control mixture made from conventional Portland cement. Studies believed the drying shrinkage was only larger in the early stages of curing, but it would experience reduced shrinkage over time [10, 34]. It was discussed that the higher carbonation rate of LC3 can be controlled by the amount of calcium in the mature matrix [21, 35]. It was also suggested that the most efficient way to enhance the carbonation resistance of LC3 is to ensure sufficient curing and hydration before exposing it to the open atmosphere [21].

Another important durability aspect of LC3 concrete studied in the literature is chloride permeability [10, 30, 36]. The chloride penetration in the LC3 mixtures depended on the amount of the produced hydrates, i.e., C-A-S-H lowers the ingress rate and delays reinforcement corrosion [10]. A recent study reported the results of rapid chloride permeability test conducted on a series of different types of LC3 made with three different clays at varying replacement ratios [10]. Except for LC3 combinations created from clays with low alumina concentrations, nearly all LC3 mixes demonstrated greater resistance to chloride penetration when compared to the control mixture made from ordinary Portland cement (OPC). The high resistance in the two other types of clay, which contained higher alumina, was due to newly formed structures by limestone and calcined clay contents [10]. Another

study reached a similar conclusion about the chloride permeability of the LC3 and showed that as clay content increases, the chloride resistance increases [36].

2.4 Development of HSC concrete using LC3

High-strength concrete (HSC) as the forefront of advancements in construction materials, drawing considerable attention for its potential to enhance the construction industry by providing outstanding mechanical properties. Nowadays, the utilization of supplementary cementitious materials (SCMs) has become an effective way, not only to enhance strength but also to overcome environmental issues and concerns. This section highlights the recent available research that has significantly contributed to the development of HSC by utilizing LC3.

In a recent study [37], the high-strength concrete was developed using LC3 by targeting two strength levels of 70 MPa, and 40 MPa with clinker content of 500 kg/m³ and 370 kg/m³. The binder was LC3 with 50% clinker replacement and calcined clay to limestone ratio of 2:1. It is worth noting that silica fume was also used in this experiment as 8% by the weight of the binder. The highest compressive strength achieved was 70 MPa at 28 days which is comparable to OPC mix. The durability of LC3 concrete has 45% more resistance to moisture ingress and chloride penetration in comparison to OPC concrete. These results arise from the synergy between limestone and calcined clay which refined the microstructure, reduced the permeability, and made a suitable material for the development of high-strength concrete.

In another study [36], LC3 was used to produce durable and high-strength concrete. The LC3 with 50% clinker replacement and a calcined clay-to-limestone ratio of 2:1. The kaolinite content of the clays varied between 40% to 90%, and the focus of the study was to assess its impact on mechanical and durability characteristics. The compressive strength of 40% kaolinite contained was 42 MPa, 70% kaolinite contained mix was 48 MPa and 90% kaolinite contained mix was 56 MPa. Which shows a direct relationship between kaolinite content and concrete performance. Additionally, the LC3 concrete showed good durability and significant chloride resistance. This study highlights LC3's potential for producing high-strength concrete.

As stated, a limited number of studies developed high-strength concrete using LC3 alone [37]. This also confirms that more studies are required in this field. Thus, the major goal of this study was to evaluate the feasibility of using clay and limestone with various polycarboxylates at variable dosages in the production of high-structural strength LC3 concrete. The specific objectives of this research exploring the possibility of producing high-strength concrete using LC3 were: i) to study the evolved heat, the rate of reaction, and maximum accumulated heat, ii) to model the heat of reaction at different temperatures (23, 30, and 40 °C), and estimate the activation energies, iii) to study the fresh (slump), and hardened (tensile strength, compressive strength, density, water absorption, chloride migration, and shrinkage) properties, and iv) to analyze the microstructure (SEM) of the developed LC3 mixtures, and compare it with the control mixture made from the plain OPC.

The inclusion of the calorimetric tests at different temperatures, estimation of the activation energy, and assessment of the mechanical performance and durability

characteristics of the LC3-based high-strength concrete add novelty to this research. The results of current study would help in the application of LC3-based high-strength concrete to the construction industry in new constructions and for repairing and strengthening of the existing concrete structures.

CHAPTER 3

METHODOLOGY

3.1 Materials

The materials utilized in this experimental study consisted of conventional Portland cement, limestone powder, calcined clay, coarse aggregate, fine aggregate, and two types of polycarboxylate superplasticizers at varying dosages. Locally available materials (clay and limestone powder) were used as a partial replacement for cement.

3.1.1 Ordinary Portland cement (OPC)

Conventional Portland cement was used in this study. Its composition satisfied the ASTM C 150 [38], as shown in Table 1. The freshly produced cement was purchased from a nearby vendor and then preserved in the laboratory for use throughout the experimental study. Figure 4 shows the ordinary Portland cement (OPC) that was used in this experiment.

Table 1. Chemical composition of the cementitious materials.

Materials	Chemical compounds (weight %)									
	SO ₃	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Na ₂ O	NiO
Clay	-	0.21	28.65	59.45	0.36	0.64	3.83	6.86	-	-
LSP	-	7.44	-	14.4	-	77.8	-	0.33	-	0.03
Gypsum	41.3	0.78	-	-	-	57.72	-	0.21	-	-
OPC	2.6	1.8	6.5	19.9	0.6	64.7	-	2.1	0.3	-



Figure 4. Ordinary Portland Cement (OPC).

3.1.2. Calcined clay

The white (raw) clay was obtained from Al-Kharj, Saudi Arabia. Its original form was large fragments of about 50 mm in size. It was ground into powder passing ASTM sieve #200 (0.075 mm) using the grinder. Fine powder of clay was calcined in the furnace at a temperature of 700 °C for one hour. The calcination temperature and duration were optimized after initial trials. The calcination temperature and duration used are believed to be economical and energy-saving and satisfy the ones suggested in the literature [39]. After calcination, the white clay color changed from grayish to brownish. The chemical composition of the clay used in this study is given in Table 1. Figures 5 and 6 show the calcined clay used in this experiment.

3.1.3. Limestone powder (LSP)

Limestone is a locally available material in the eastern region of Saudi Arabia. The limestone powder used in these experiments was obtained from quarries along the Abu Hadriyah highway in Dammam, Saudi Arabia. Its original form was a light yellow color. It had a specific gravity of 2.60, and its chemical composition is shown in Table 1. It was sieved to pass through ASTM sieve #200 (0.075 mm) before being added to the developed mixtures.

Table 1 shows the chemical composition of the LSP used in this study. Figure 7 shows the limestone powder used in this experiment.

3.1.4. Gypsum

Gypsum (calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was obtained from a local store in Dammam, Saudi Arabia. Its original form was powder with a white appearance, and its chemical composition is shown in Table 1. The purpose of using gypsum in LC3 mixtures was to control the setting time and enhance the binder's homogeneity [10]. The gypsum was used at 1.5% of the total binder mass [10]. It was also sieved to pass through ASTM sieve #200 (0.075 mm) before being added to the developed mixes. The chemical composition of the gypsum used in this study is given in Table 1.

3.1.5. LC3 (Limestone calcined clay cement)

The LC3 used in this experiment series was a mixture of ordinary Portland cement, calcined clay, limestone powder, and gypsum. The percentage of partial cement replacement by LC3 materials was chosen based on the optimum percentage available in the literature, which was 30% [10]. The optimum mixture of the LC3 used in the present study consisted of 70% Ordinary Portland cement, 19% calcined clay, 9.5% limestone powder, and 1.5% gypsum (by mass). Figure 8 shows the LC3 that was used in this study.



Figure 5. Calcined and uncalcined clay.



Figure 6. Calcination of clay at 700 °C.



Figure 7. LSP for the calorimetry samples.



Figure 8. LC3 ingredients

3.1.6. Mixing water

Potable water was used to mix the LC3 pastes and concrete ingredients. Distilled water was used to prepare the pastes for the calorimetry analysis.

3.1.7 Aggregate

Two types of aggregates were used i.e., coarse and fine aggregates. The particle size distribution of aggregate conforming to ASTM C 33 [40] was used to prepare the concrete mixtures.

The coarse aggregates used in these experiments were crushed limestone obtained from a local quarry. The maximum nominal size of the aggregate was 12.5 mm. The gradation also consisted of 9.5 mm, 4.75 mm (#4), and 2.36 mm (#8) aggregates, as shown in Table 2, Figures 9 and 10. It had a saturated surface dry specific gravity of 2.61 and an oven-dry specific gravity of 2.58. The water absorption of the coarse aggregate was 1.1% by mass. The gradation of the coarse aggregate used is presented in Table 2.



Figure 9. Coarse aggregate of 1/2 in, 3/8 in, 3/16 in, and 3/32, clockwise respectively.

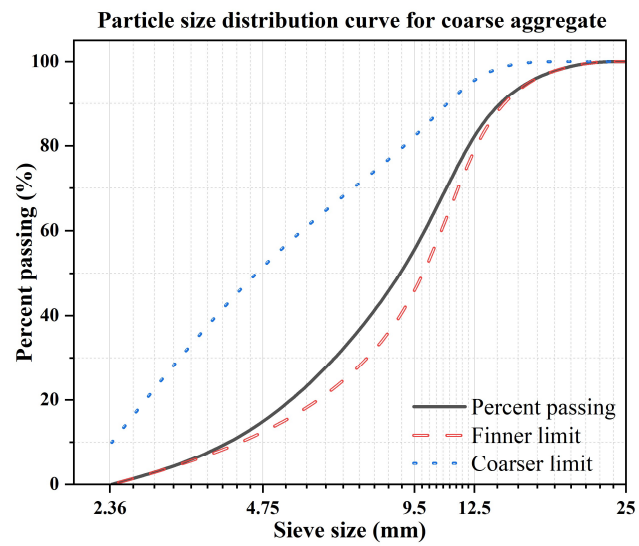


Figure 10. Coarse aggregate gradation curve.

Table 2. Gradation of coarse aggregate.

Sieve size (in)	Sieve size (mm)	Percent retained by weight (%)
1/2	12.5	10
3/8	9.5	40
3/16 (#4)	4.75	40
3/32 (#8)	2.36	10

The fine aggregates used in the experiments were locally available dune sand. Its gradation is shown in Table 3, Figures 11 and 12. It had a fineness modulus of 2.23, a specific gravity of 2.55, and a water absorption of 0.5%.



Figure 11. Fine aggregate.

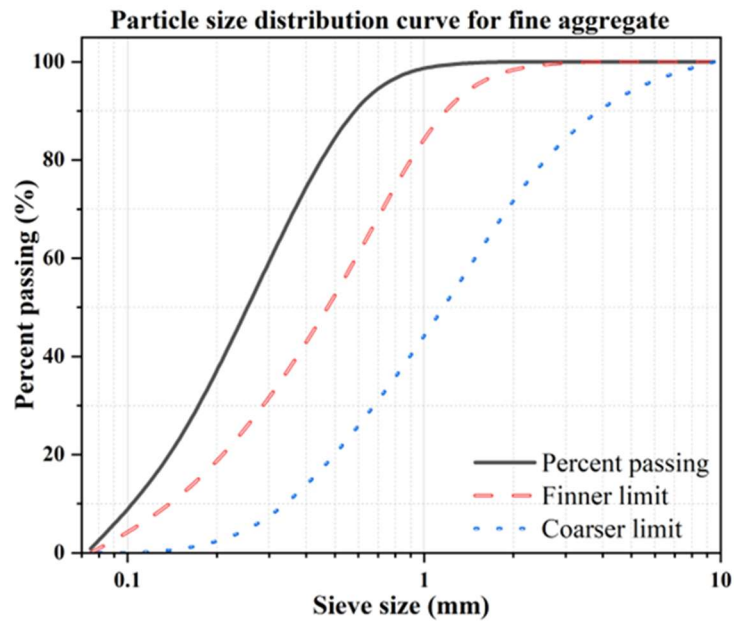


Figure 12. Fine aggregate gradation curve.

Table 3. Gradation of fine aggregate

Sieve size	Sieve size (mm)	Percent passing by weight (%)
#8	2.36	100
#16	1.2	100
#30	0.6	96.1
#50	0.3	59.9
#100	0.15	19.9
#200	0.075	0.8
F. Modulus		2.23

3.1.8 Superplasticizers

Two types of polycarboxylate-based superplasticizers at varying dosages (0.5 to 2%) were used in this study. The first type was the Fluidum PC314 which is shown in Figure 14. According to its technical data sheet, its composition was based on modified carboxylate polymers with high efficiency in increasing the workability, retaining the slump, and improving the cohesion of the concrete. It is a brownish viscous liquid with 1.1 specific gravity at 20°C. The maximum allowable dosage of Fluidum PC314 was 3%, by weight of the binder. Overdose of this material could create segregation and bleeding of concrete and increase the setting time.

The other type of superplasticizer was PCE CT50 which is shown in Figure 13. It is a polycarboxylate-based superplasticizer with a 50% polymer concentration. Its specific gravity is between 1.085 to 1.12, and its pH is 2 to 5.5. It is a white to light yellow liquid with a viscosity of less than 2000 cP at 25 °C. Both used superplasticizers do not have any chloride in their composition and satisfy ASTM C 494 [41].



Figure 13. PCE CT50.



Figure 14. PCE fluidum PC314.

3.2 Test Methods

3.2.1. Calorimetry

The thermal analysis of the binders was performed using calorimetry to study the peaks of the heat of hydration reactions, the rate of heat flow, and the accumulated heat of different binders. Three variables were considered for the thermal analysis of the binders. The first variable was the binder type, including Type I Portland cement (control), and LC3. The second variable was the type of polycarboxylate superplasticizer, which was either Fluidum PC314 or PCE CT50, added in varying dosages of 0, 0.5, 1, and 2% by the weight of binders. The third variable was the varying temperature, (23, 30, or 40 °C) at which hydration of binders was allowed to take place. The total weight of the binder was 50 grams, and a water-to-cement ratio of 0.5 (by mass) was used for each sample. Two samples were tested for each mixture, and their average was taken as a representative value. A total of 14 different mixtures were tested initially at 23 °C (Table 4) and based on the results obtained from the calorimetry analysis at 23 °C, 6 mixtures were selected and tested at higher temperatures, of 30 and 40 °C (Table 4). At the higher temperatures, two samples were tested for each mixture, and their average was taken as a representative value. Using the data on accumulated heat, a model was used to predict the ultimate accumulated heat of hydration and the reaction rate, and the activation energies. The model is discussed and presented later.

A high-precision calorimetry (Calmetrix 8000) was used to conduct the thermal experiments. It was set up and calibrated using standard (reference) sand. The heat was measured for a minimum duration of three days. The testing procedure involved weighing 50 grams of the binder and 25 grams of water with and without PCE according to the mix design

(Table 4). The pastes were mixed for two minutes, capped, and inserted into the calorimetry device. Then, the calorimetric device was operated, and its software showed the corresponding voltage in terms of "volt," heat flow in terms of "Watt" or "Watt/gram of binder," and accumulated heat in terms of "Joules" or "Joules/gram of binder." The test was conducted for a minimum duration of three days. The results, including the hydration profile and accumulated heat, were obtained for each set of specimens (8 specimens) at a time. The following photos (Figures 15 to 19) show a complete round of the calorimetry test for one batch.



Figure 15. Measuring the weight of the dry sample before mixing.

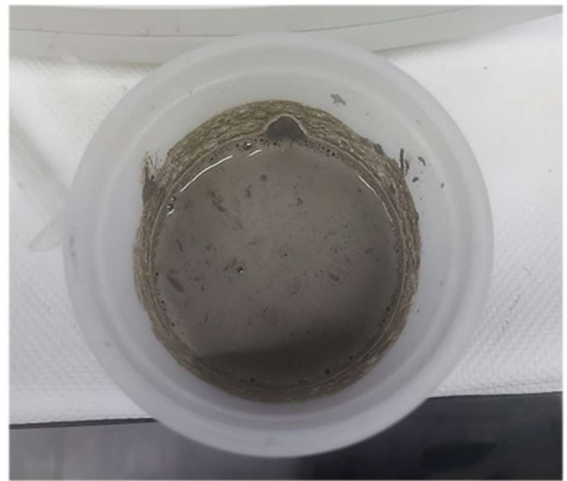


Figure 16. The mixed paste sample was ready for testing after two minutes of mixing.



Figure 17. Calorimetry after finishing the first set of samples.

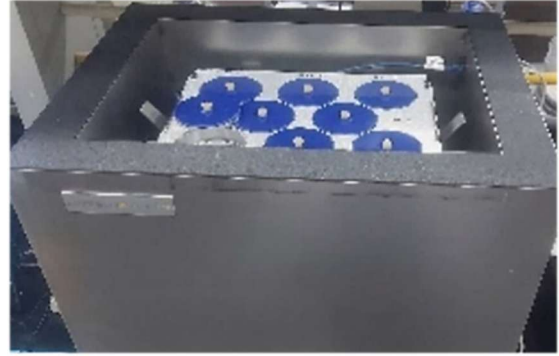


Figure 18. Entering the specimens into the calorimetry device.

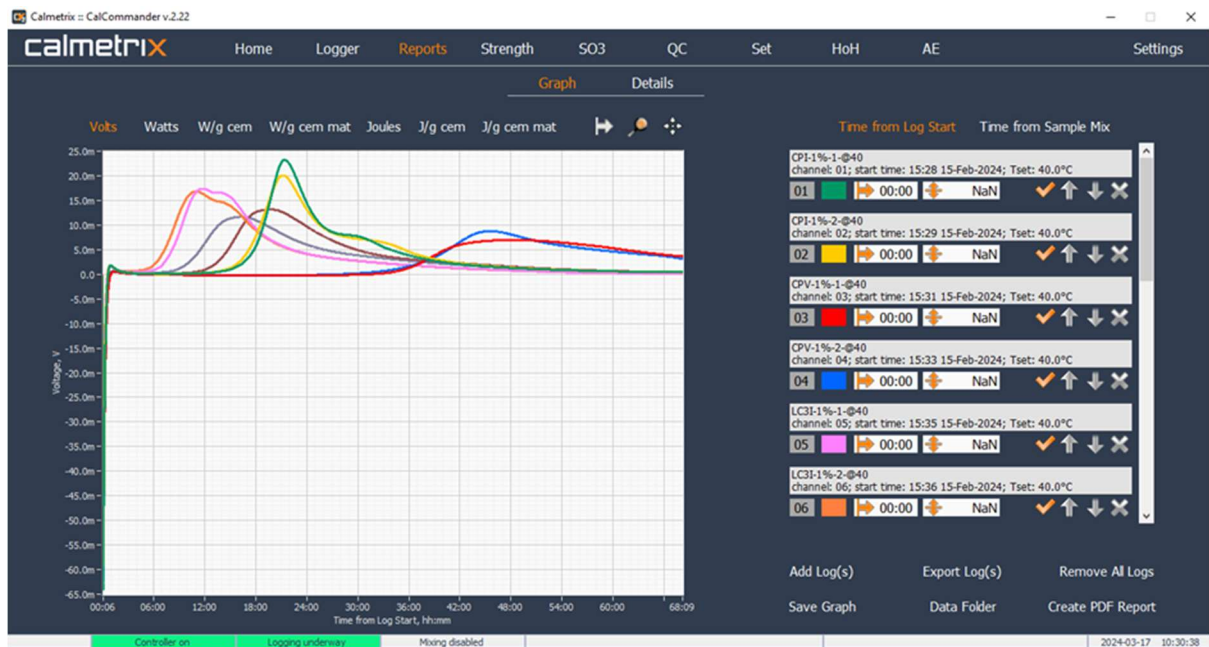


Figure 19. Calmetrix program connected to calorimetry, displaying and recording the heat of reaction for eight samples at a time.

Table 4. Mixture proportions of pastes for calorimetry tests at 23, 30, and 40 °C.

ID	Mixture designation	Binder (g)	PCE (% by mass of binder)	PCE Type	Water (g)	Temp (°C)
1	OPC	50	0	-	25	23
2	OPC-PC0.5	50	0.5	Fluidum PC314	25	23
3	OPC-PC1	50	1	Fluidum PC314	25	23
4	OPC-PC2	50	2	Fluidum PC314	25	23
5	LC3	50	0	-	25	23
6	LC3-PC0.5	50	0.5	Fluidum PC314	25	23
7	LC3-PC1	50	1	Fluidum PC314	25	23
8	LC3-PC2	50	2	Fluidum PC314	25	23
9	OPC-CT0.5	50	0.5	PCE CT50	25	23
10	OPC-CT1	50	1	PCE CT50	25	23
11	OPC-CT1	50	2	PCE CT50	25	23
12	LC3-CT0.5	50	0.5	PCE CT50	25	23
13	LC3-CT1	50	1	PCE CT50	25	23
14	LC3-CT2	50	2	PCE CT50	25	23
15	OPC	50	0	-	25	30 and 40
16	OPC-PC1	50	1	Fluidum PC314	25	30 and 40
17	LC3	50	0	-	25	30 and 40

18	LC3-PC1	50	1	Fluidum PC314	25	30 and 40
19	OPC-CT1	50	1	PCE CT50	25	30 and 40
20	LC3-CT1	50	1	PCE CT50	25	30 and 40

3.2.2. Preparation of LC3 mixtures

Cement and LC3 pastes and concrete mixtures were prepared at a water-to-binder ratio of 0.4 (without superplasticizers) and 0.3 (with superplasticizers), as shown in Tables 5 and 6, respectively. In the case of the pastes, the polycarboxylate-based superplasticizers were 1% (by mass of binder). This quantity of polycarboxylates was decided based on preliminary flowability tests. However, in plain OPC and LC3 concrete mixtures, the polycarboxylate amounts were increased to 2% (by mass of binder) to ensure the homogeneity of the mixtures. Once all the materials were weighed based on the mix designs (Table 6), the dry mixing of coarse and fine aggregate was done. Then, the binder was added to the aggregates with half of the quantity of the mixing solution, and the mixer was sealed and allowed to rotate slowly. Finally, the remaining solution was added (including the polycarboxylates according to the mix design), and mixing was continued at a medium speed until a homogenous mixture was achieved. The total number of mixtures was five with and without polycarboxylates (Fluidum PC314 or PCE CT50). Following mixing, the mixtures were poured into the molds and compacted using a vibration table. The specimens (cubes and cylinders) were de-molded after 24 hours of casting (Figure 20 to 22), and water-cured in the lab environment until the day of testing. Tests on hardened pastes and concrete were conducted to determine the compressive strength, split tensile strength, water absorption, density, chloride migration, drying

Shrinkage, and Scanning Electron Microscope (SEM) analyses using the specimens and standards given in Table 7.



Figure 20. One-inch cube specimens.



Figure 21. 75 × 150 mm cylindrical specimens.



Figure 22. 75 × 150 mm cylindrical specimens (Sulfur capped before compressive testing).

Table 5. Mix design of the pastes.

ID	Compressive strength of the pastes			
	Mixture designation	w/b ratio	PCE (% by mass of	PCE type
			binder)	
1	OPC	0.4	0	-
2	OPC-PC1	0.3	1	Fluidum PC314
3	LC3-PC1	0.3	1	Fluidum PC314
4	OPC-CT1	0.3	1	PCE CT50
5	LC3-CT1	0.3	1	PCE CT50

Table 6. The proportion of the concrete mixtures.

I D	Cement Type	Binders (kg)				w/b ratio	PCE	PCE Type	CA (kg)	FA (kg)
		OPC	Calcine d Clay	LSP	Gypsum		(% by mass of binder)			
1	OPC	544	0	0	0	0.40	0	-	1068	647
2	OPC-PC2	544	0	0	0	0.3	2	Fluidum PC314	1068	647
3	LC3-PC2	381	103	52	8	0.3	2	Fluidum PC314	1068	647
4	OPC-CT2	544	0	0	0	0.3	2	PCE CT50	1068	647
5	LC3-CT2	381	103	52	8	0.3	2	PCE CT50	1068	647

Table 7. Summary of the tests conducted.

Test name	ASTM designation	Specimen size
Heat of hydration (Calorimetry)	ASTM C 1702 [42]	75 grams
Slump	ASTM C 143 [43]	
Compressive strength (Cement pastes)	ASTM C 109 [44]	One-inch cubes
Compressive strength	ASTM C 39 [45]	75 × 150 mm cylinders
Elastic modulus	ASTM C469 [46]	75 × 150 mm cylinders
Split tensile strength	ASTM C 496 [47]	75 × 150 mm cylinders
Water absorption	ASTM C 642 [48]	75 × 150 mm cylinders
Density	ASTM C 138 [49]	75 × 150 mm cylinders
Chloride migration	NT Build 492 test [50] (An alternative to ASTM C 1202 [51])	100 × 50 mm disks
Drying Shrinkage	ASTM C 157 [52] and ASTM C 596 [53]	25 × 25 × 285 mm prisms
SEM	Morphology	

3.2.3. Workability

The slump test to measure the workability of the fresh concrete was conducted in accordance to ASTM C 143 [43]. Figures 23 and 24 show the slump for the concrete mixture without superplasticizer (SP) and the slump flow of the LC3 mixture with SP.



Figure 23. Slump test of the mixture without SP.



Figure 24. Slump flow test of the developed mixture with SP.

3.2.4. Compressive strength

One-inch cubical specimens of 25 mm size and cylindrical specimens of size 75 × 150 mm were tested using a MATEST compression testing machine (Figure 25) in accordance to ASTM C 109 [44] and ASTM C 39 [45] to determine the compressive strength of the cement pastes and concrete mixtures after 7 and 28 days of curing, respectively. Three replicate specimens were tested for each mixture, and the average of their failure loads was taken as the representative value.



Figure 25. MATEST compression machine.

3.2.5. Modulus of elasticity

The standard test method for determining concrete's static modulus of elasticity (Eq.1) in compression (ASTM C469 [46]) specifies that measurements should be taken within 40% of the ultimate concrete strength or breaking load of the specimen. Three replicate specimens were tested using the MATEST machine to determine the elastic modulus for each mixture and the average values were considered as the modulus of elasticity of the mixture. To record the deformation, the LVDTs were placed between two parallel rings positioned 75 mm apart. The LVDTs were attached to the lower ring, with their sensitive ends in contact with the upper ring bearing platforms. This arrangement allowed for precise measurements of the axial deformation from the initial loading phase up to ultimate failure. During the test, both the loads and the associated deformations were recorded using a data logger. The stress versus strain curves were then plotted using the average deformation recorded by the LVDTs and the

load readings from the load cell. Figures 26-a and 26-b show a concrete specimen and the data logger during the test.

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - 0.00005} \quad (\text{Eq. 1})$$

In this equation, "E" stands for modulus of elasticity (MPa), " σ_2 " is the stress (MPa) at 40% of the ultimate load, " σ_1 " is stress (MPa) at 0.00005 of strain along the length of the sample, and " ε_2 " is the strain due to " σ_2 " stress.



a)



b)

Figure 26. a) Elastic modulus setup b) Data logger

3.2.6. Tensile strength

The test for split tensile strength of the concrete mixtures conducted according to ASTM C 496 [47] after 28 days of moist curing using the MATEST machine as shown in Figures 27 and 28. Three specimens were tested for each mix, and the average of their failure loads was taken as the representative splitting tensile load. (Eq.2)

$$f_t = \frac{2P}{\pi l d} \quad (\text{Eq. 2})$$

Where " f_t " is the tensile strength in (MPa), P is the average splitting load in (N), " l " is the loading length in (mm), and " d " is the diameter of the specimen (mm).



Figure 27. A cylinder specimen under split tensile test.



Figure 28. Specimen after breaking.

3.2.7. Water absorption

The test for water absorption was conducted on concrete cylindrical specimens of size 75×150 mm according to ASTM C 642 [48]. After 28 days of moist curing, the concrete specimens were kept in an oven at 110°C for 24 hours to remove any moisture and become completely dry. Subsequently, the dry weight for each specimen was taken, and all specimens were submerged in water for 48 hours. After that, the specimens were removed from the water bath, their surfaces were dried, and their saturated surface dry weights were recorded. Finally, the percentage of the water absorption of each specimen was calculated. The average water

absorption for three replicate specimens was taken as a representative value for each mixture. Figures 29-a and 29-b show the samples used for measuring water absorption.



Figure 29. a) Oven drying of concrete specimens was set at 110 °C for 24 hours. b) Concrete specimens in SSD condition.

3.2.8. Density

The 28-day hardened densities (unit weights) of concrete mixtures were measured in accordance with the ASTM C 138 [49]. The mass and volume of each specimen were measured. Then, the density of each specimen was calculated as the ratio of its mass to its volume and expressed in kilograms per cubic meter (kg/m^3). A representative value for the density of each mixture was determined by averaging the densities of three specimens.

3.2.9. Chloride migration

The chloride migration (the rapid chloride permeability) test was done according to the NT Build 492 [50] (an alternative to the ASTM C 1202 [51]). To conduct the test, 100 mm $\times$ 200 mm concrete cylinders were cast and epoxy-coated after 28 days of moist curing shown in Figures 30 and 31. Then, they were sliced into disks of 100 mm $\times$ 50 mm (Figure 32) and later placed inside the cells and exposed to the electrical current for 24 hours (Figure

33). The test setup comprised of two wires, one submerged in a 0.3 M (NaOH) solution and the other in a 3% NaCl solution. The electrical current was applied maintaining a constant voltage, usually 20 to 35 V, across the specimens throughout the test. The current passing through each specimen was recorded along the time duration of the test, and then the total charge transmitted through each specimen was calculated. Also, the penetration depth for each specimen was measured after slicing and applying the silver nitrate (AgNO_3) to the specimens collected from the chloride migration test (Figure 34). Further, the non-steady-state migration coefficient, D_{nssm} , was calculated for each specimen using (Eq. 3). A representative value for each mixture was determined by averaging three specimens.

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t} \left(X_d - 0.0238 \sqrt{\frac{(273+T)LX_d}{U-2}} \right) \quad (\text{Eq. 3})$$

where "T" is the temperature in °C, "U" is the absolute value of applied voltage (V), " X_d " is average penetration depth (mm), "L" is the thickness of the specimen (mm), and "t" is the duration of the test (hour).



Figure 30. (100 × 200) mm, cylindrical specimens for chloride migration test.



Figure 31. Applying epoxy on the specimen for chloride migration test.

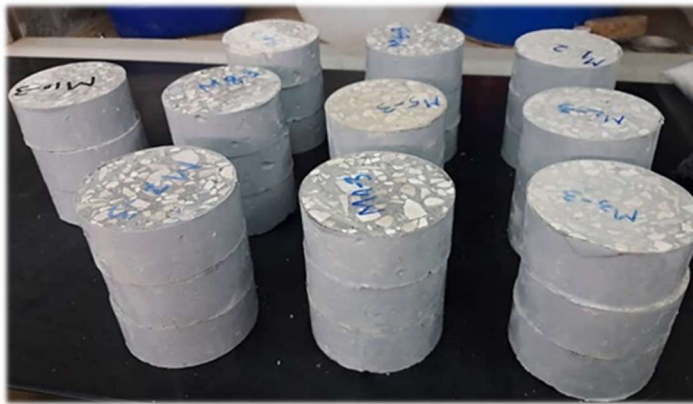


Figure 32. Specimens of size 100 × 50 mm disks



Figure 33. Setting up the disks for running the chloride migration test



Figure 34. Slicing and applying the silver nitrate (AgNO_3) for measuring the penetration depth after 24 hours of running the chloride migration test.

3.2.10. Drying shrinkage

Prisms of $25 \times 25 \times 285$ mm, as shown in Figures 35-a and 35-b were used to measure the drying shrinkage of the selected mortar mixtures in accordance to ASTM C 157 [52] and ASTM C 596 [53] after three days of moist curing in a saturated lime solution. The specimens were air-cured after three days of the saturated lime moist curing.

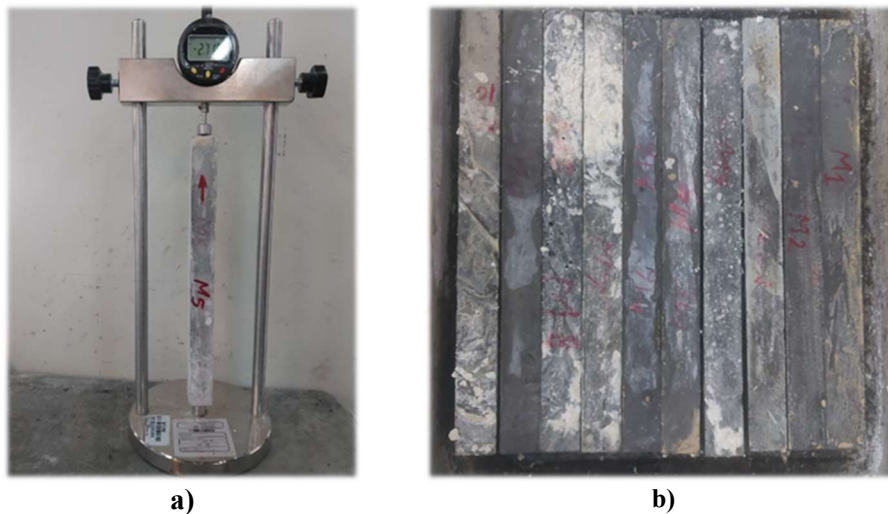


Figure 35. a) Test setup of the drying shrinkage, b) Prismatic mortar specimens to determine the drying shrinkage

3.2.11. Morphology

The microstructures of LC3 concrete were examined using SEM. Fragmented samples were placed on the SEM plate as shown in Figure 36 and scanned. Then, images were captured and analyzed. These tests aimed to evaluate the influence of the limestone and calcined clay in the developed LC3 concrete.



Figure 36. The SEM plate with various paste samples.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Heat flow, accumulated heat, and activation energies

The heat produced by the exothermic processes, cement hydration, and the pozzolanic reaction of clay and limestone were determined to study the reaction kinetics [54, 55]. The isothermal calorimetry was used to indirectly analyze the influence of the superplasticizers, i.e., Fluidum PC314 and PCE CT50, at their varying dosages, i.e., 0, 0.5, 1, and 2% (by mass of binder) in plain cement or LC3 systems. As shown in Figures 37-a to 38-b, increasing dosages of the superplasticizers affects the reactivity of the paste systems. According to Figure 37-a for cement pastes with Fluidum PC314 and Figure 37-b for cement pastes with PCE CT50 at varying dosages of 0, 0.5, 1, and 2% (by mass of cement), the main peak of reaction is decreased and delayed as the dose of each superplasticizer increase. The same observation is noted in Figure 38-a for LC3 pastes with Fluidum PC314 and Figure 38-b for LC3 pastes with PCE CT50 at varying dosages of 0, 0.5, 1, and 2% (by mass of binder). However, the effect of the Fluidum PC314 type superplasticizer altered the main course of the reaction in the cement and LC3 systems. It resulted in lower main peaks in the heat flow curves (Figures 37-a to 38-b) and slower reaction rates ($1/\tau$) compared to the control cement and LC3 pastes and compared to the series of pastes with PCE CT50, as shown in Table 8. Figures 39-a to 40-b illustrate the released cumulative heat of the reaction in the various cement and LC3 systems with and without superplasticizers. According to Figures 39-a to 40-b, the measured cumulative heat of all pastes for three days is lower than that of the control paste or LC3 system. However, it is anticipated that the total cumulative heat may be higher at a later age.

To determine the ultimate accumulative heat of the process in the paste systems, exponential modeling [54, 55] was carried out using the first-order model of reaction kinetics in solid-state systems (Eq. 4). After finding the reaction rate ($k=1/\tau$) at various temperatures and applying the Arrhenius equation, the activation energies [55] of the paste systems were estimated.

$$H_{(t)} = H_u * e^{-\left(\frac{\tau}{t}\right)^\beta} \quad (\text{Eq. 4})$$

Where $H_{(t)}$ is the accumulated heat after time t in (J/gram), H_u is the ultimate accumulated heat in (J/gram), τ is the hydration time parameter (hr), and β is the hydration shape parameter.

The model-derived reaction kinetics (Table 8) confirm the calorimetry test results (heat flow and accumulative heat) for plain OPC and LC3 pastes with varying Fluidum PC314 and PCE CT50 concentrations. It can be seen from Table 8 and Figures 37-a to 38-b, increasing the concentration of Fluidum PC314 or PCE CT50 lengthened the induction period and reduced the height of the main reaction peak. However, increasing the Fluidum PC314 or PCE CT50 dose causes the reaction to proceed at higher cumulative heat at later ages. This is supported by reaction kinetics modeling, which shows that the cumulative heat of the reaction (H_u) increased, and the reaction rate (k or $1/\tau$) decreased (Table 8) when increasing the superplasticizer content. The results also show that the reaction accelerates at higher temperatures (Figures 41-a and 41-b).

The apparent activation energy (E_a) was calculated using the calorimetric data presented in Tables 8 through 11. The effect of Fluidum PC314 and PCE CT50 on E_a values was comparable (Table 11 and Figure 42), with lower E_a found for plain and LC3 pastes

containing Fluidum PC314 or PCE CT50 than those without the superplasticizer. However, pastes containing PCE CT50 produced the lowest activation energies.

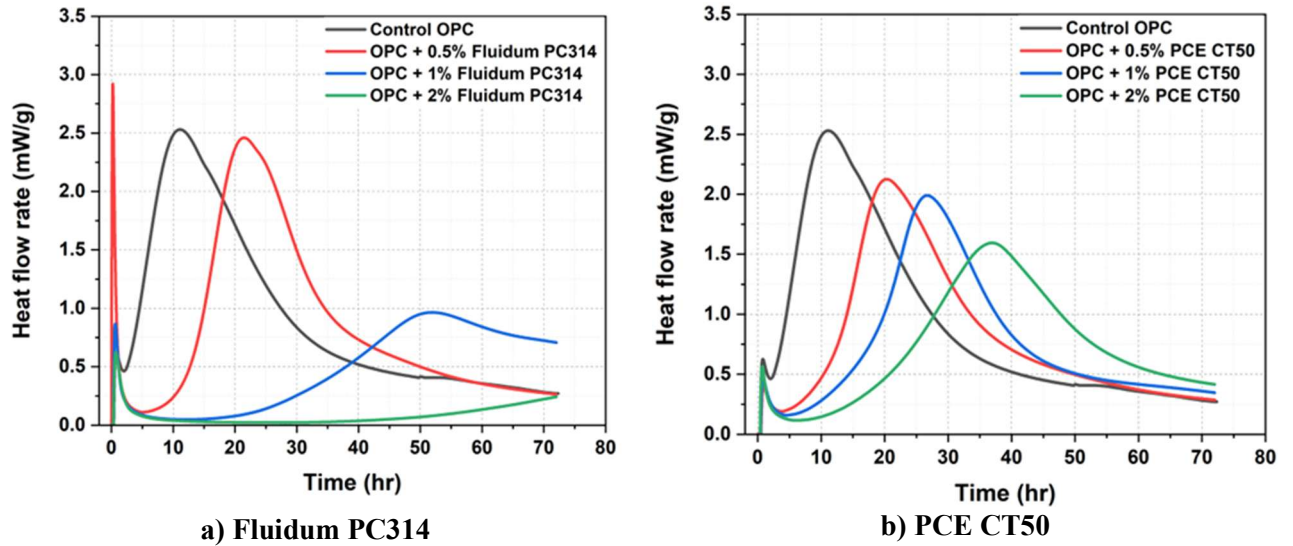


Figure 37. Heat flow rates of OPC paste with various concentrations of superplasticizer.

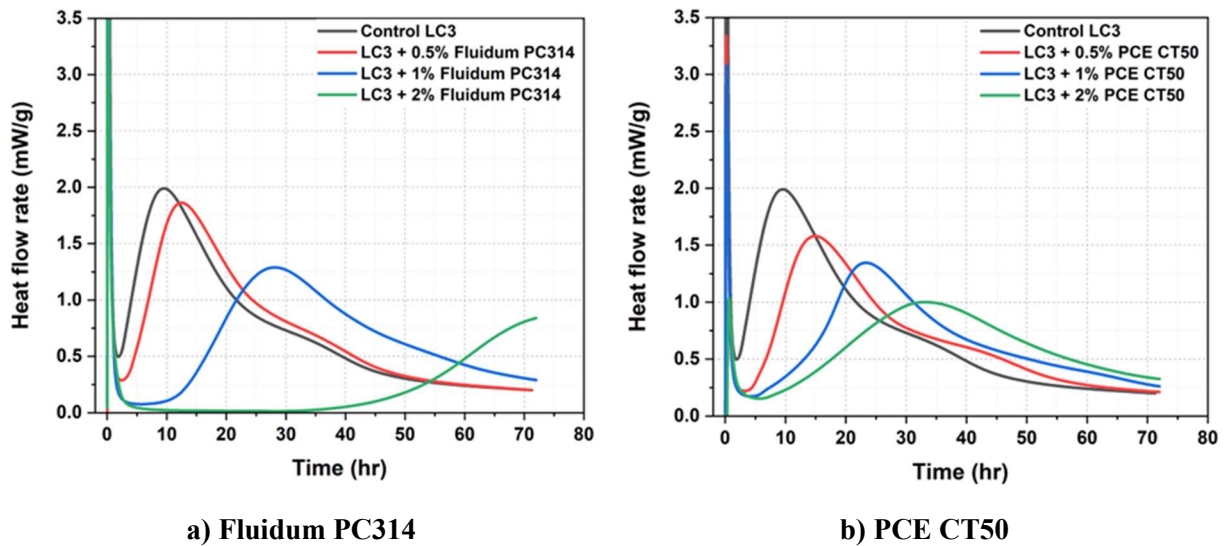
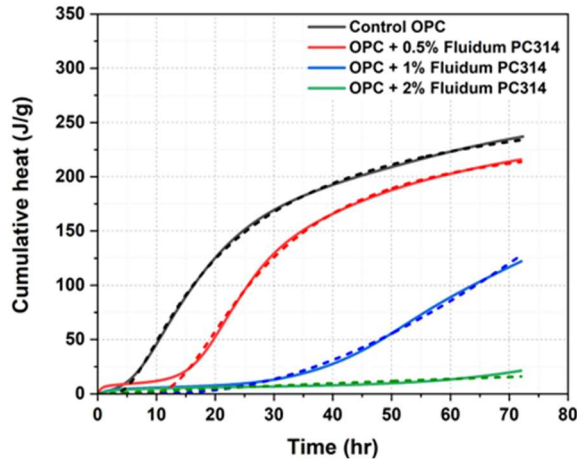
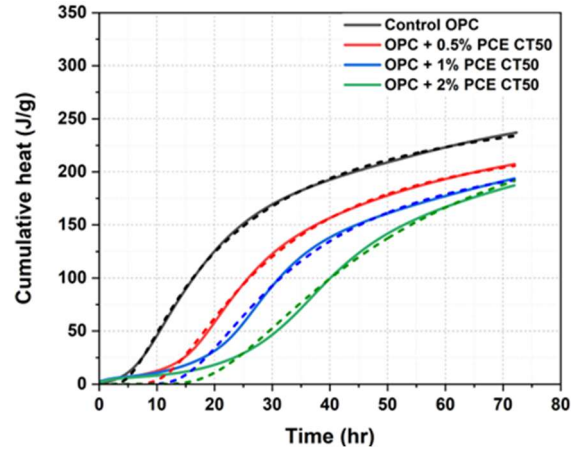


Figure 38. Heat flow rates of LC3 pastes with various concentrations of superplasticizer.

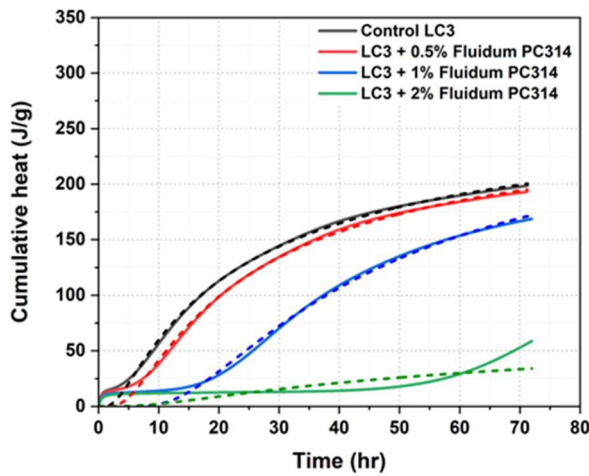


a) Fluidum PC314

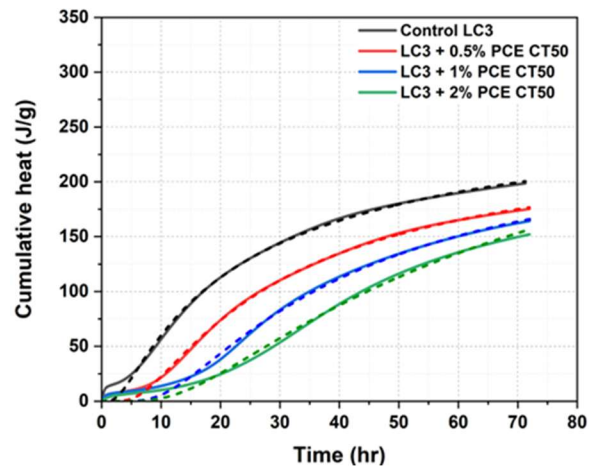


b) PCE CT50

Figure 39. Cumulative heat of reaction of OPC pastes with various concentrations of superplasticizer. Dashed lines represent the reaction kinetics model.



a) Fluidum PC314



b) PCE CT50

Figure 40. Cumulative heat of reaction of LC3 pastes with various concentrations of superplasticizer. Dashed lines represent the reaction kinetics model.

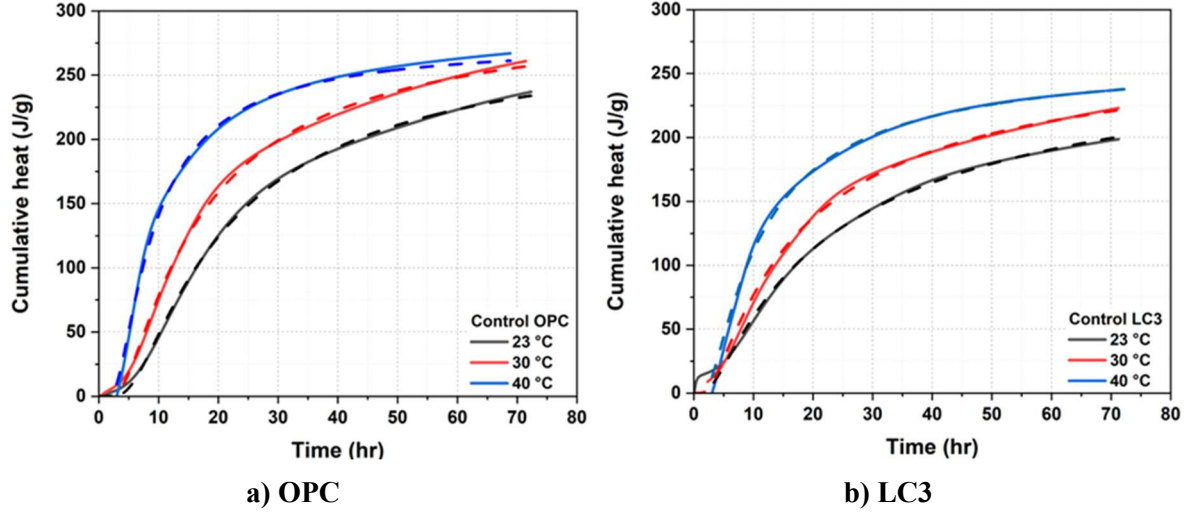


Figure 41. Cumulative heat of reaction of pastes at different temperatures. Dashed lines represent the reaction kinetics model.

Table 8. Heat of hydration parameters at 23 °C.

ID	Mixture designation	H_u	τ	β	R^2
1	OPC	288.16	17.08	1.09	0.99
2	OPC + 0.5% Fluidum PC314	240.31	24.01	1.95	0.99
3	OPC + 1% Fluidum PC314	738.85	130.82	0.98	0.99
4	OPC + 2% Fluidum PC314	68.90	221.45	0.38	0.76
5	LC3	289.56	18.47	0.74	0.99
6	LC3 + 0.5% Fluidum PC314	267.85	19.94	0.90	0.99
7	LC3 + 1% Fluidum PC314	275.90	38.32	1.19	0.99
8	LC3 + 2% Fluidum PC314	89.15	68.11	0.68	0.51
9	OPC + 0.5% PCE CT50	244.58	24.30	1.61	0.99
10	OPC + 1% PCE CT50	231.09	28.56	1.83	0.99
11	OPC + 2% PCE CT50	288.68	41.60	1.62	0.99

12	LC3 + 0.5% PCE CT50	249.42	24.44	0.99	0.99
13	LC3 + 1% PCE CT50	255.98	33.69	1.10	0.99
14	LC3 + 2% PCE CT50	358.88	58.55	0.91	0.99

Table 9. Heat of hydration parameters at 30 °C.

ID	Mixture designation	H_u	τ	β	R^2
15	OPC	303.68	13.32	1.06	0.99
16	OPC + 1% Fluidum PC314	213.87	40.01	4.26	0.99
17	LC3	284.01	13.75	0.85	0.99
18	LC3 + 1% Fluidum PC314	218.72	26.48	1.84	0.99
19	OPC + 1% PCE CT50	235.70	21.74	2.12	0.99
20	LC3 + 1% PCE CT50	222.13	20.47	1.58	0.99

Table 10. Heat of hydration parameters at 40 °C.

ID	Mixture designation	H_u	τ	β	R^2
21	OPC	275.07	7.40	1.33	0.99
22	OPC + 1% Fluidum PC314	246.49	24.60	3.52	0.99
23	LC3	250.91	8.50	1.22	0.99
24	LC3 + 1% Fluidum PC314	237.71	18.42	2.30	0.99
25	OPC + 1% PCE CT50	252.76	20.72	2.33	0.99
26	LC3 + 1% PCE CT50	237.88	19.59	1.66	0.99

Table 11. Activation energy for the selected mixes.

ID	Mixture designation	E_a (kJ/mol)	R^2
1	OPC	38.40	0.98
2	OPC + 1% Fluidum PC314	32.53	0.75
3	OPC + 1% PCE CT50	21.01	0.98
4	LC3	35.36	0.99
5	LC3 + 1% Fluidum PC314	32.97	0.99
6	LC3 + 1% PCE CT50	23.39	0.74

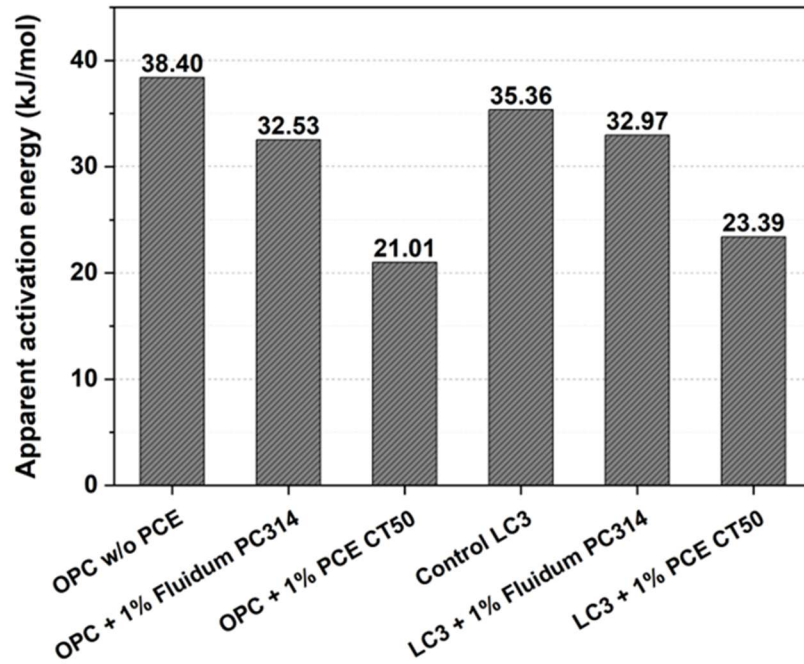


Figure 42. Apparent activation energies as calculated for the OPC and LC3 paste mixtures using the exponential approach.

4.2. Slump

The measured average value of slump of the OPC without PCE concrete made at a water-to-cement ratio of 0.4 was about 50 mm. However, Figure 43 and Table 12 show the slump flow of the plain OPC and LC3 concrete mixtures made at a water-to-cement ratio of 0.3 and with a 2% dosage of superplasticizers. The values of slump flow, as shown in Figure 43 and Table 12, indicated that all four developed concrete mixtures belonged to flowable concrete. However, the plain OPC concrete showed more flowability than the LC3 concrete (540 to 610 mm versus 440 to 450 mm). Overall, the Fluidum PC314 type superplasticizer provided slightly less flowability to the mixtures than PCE CT50.

Table 12. Slump of fresh OPC and LC3 concrete.

Mixes	Slump (mm)	Type of slump
OPC w/o PCE	50	True
OPC+ 2% Fluidum PC314	540	Slump flow
LC3 + 2% Fluidum PC314	440	Slump flow
OPC+ 2% PCE CT50	610	Slump flow
OPC + 2% PCE CT50	450	Slump flow

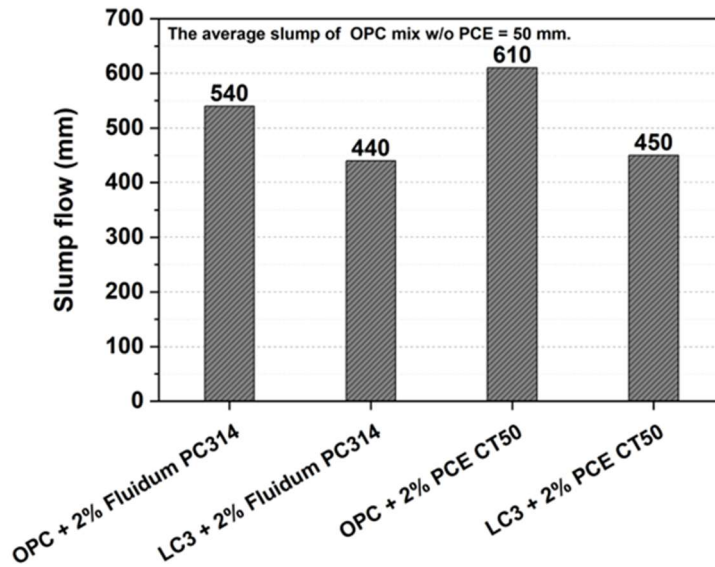
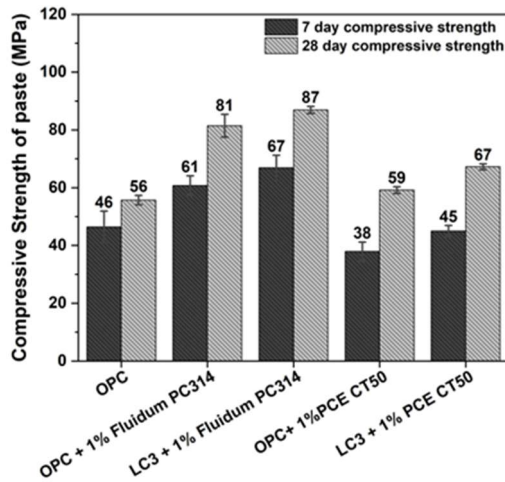


Figure 43. Slump flow of the OPC and LC3 concrete.

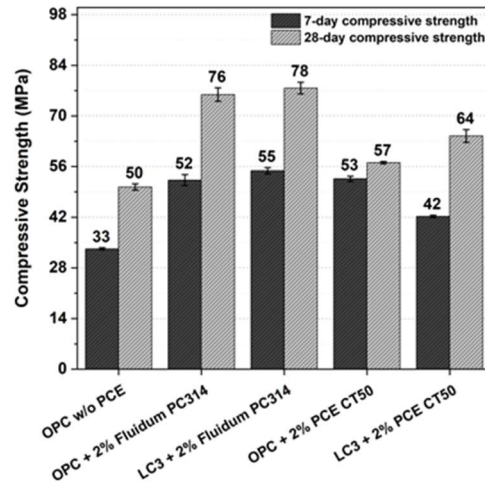
4.3. Strength

Figures 44-a through 44-c illustrate how superplasticizers (Fluidum PC314 and PCE CT50) affect compressive and split tensile strengths. Mixtures containing Fluidum PC314 outperform PCE CT50. The LC3 paste containing 1% Fluidum PC314 exhibited the highest 7-day compressive strength in the series, at 67 MPa (Figure 44-a). It is also worth mentioning that the 28-day compressive strength of LC3 paste was 87 MPa, compared to 56 MPa for the OPC paste without superplasticizer. The 7 and 28-day concrete compressive strengths are shown in Figure 44-b. The OPC mixture with a w/c ratio of 0.4 and without superplasticizer reached a 28-day compressive strength of 50 MPa. All other four mixtures had a higher 28-day compressive, reaching 78 MPa, which signifies the usefulness of both superplasticizers (Fluidum PC314 and PCE CT50) at a 2% dosage. Figure 44-b indicates that among all mixtures, the mixtures with Fluidum PC314 performs better than PCE CT50. It is also worth mentioning that the LC3 mixtures had higher compressive strength than the OPC mixtures.

The 28-day split tensile strength results confirmed the effect of binders and superplasticizers on tensile strength similar to that for compressive strength. The LC3 concrete mixture with the 2% dosage of Fluidum PC314 revealed a maximum split tensile strength of 4.9 MPa (Figure 44-c). However, pastes containing Fluidum PC314 produced higher activation energies than those containing the PCE CT50 type superplasticizer (Table 11 and Figure 44-a), but this was not reflected in the strength data. Comparing the results shown in Figures 44-a and b, it can be noted that, for plain OPC and LC3 mixtures, the Fluidum PC314 is more effective as a superplasticizer than PCE CT50. Among all five mixtures, the minimum compressive strength was noted for the OPC mixture without a superplasticizer, which was 33 MPa (Figure 44-b). The same observation was noted for the split tensile strength results (Figure 44-c). There is an acceptable correlation between the tensile strength and compressive strength in all the mixtures that were tested.



a)



b)

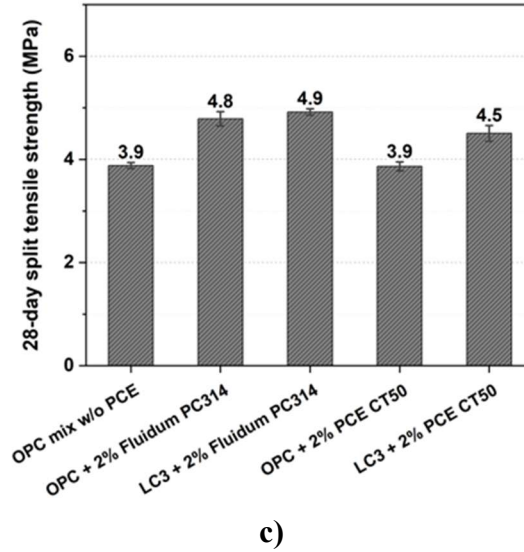
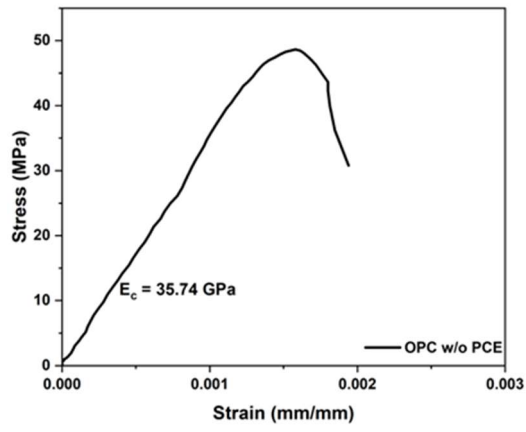


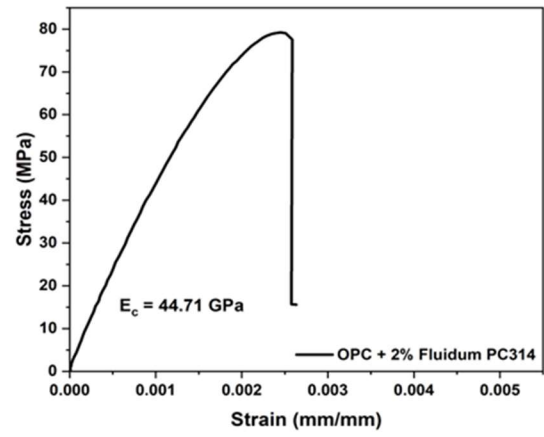
Figure 44. a) compressive strength of paste, b) compressive strength of concrete, and c) split tensile strength of concrete for OPC and LC3 mixtures.

4.4 Modulus of elasticity

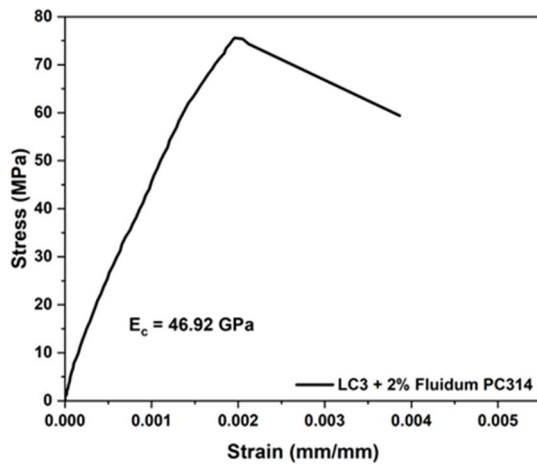
The modulus of elasticity was determined for the LC3 and OPC mixtures after 28 days of moist curing. The OPC mixture without PCE superplasticizer had the lowest elastic modulus of 35.7 GPa. The mixtures with Fluidum PC314 content had a higher elastic modulus than PCE CT50-contained mixtures, and LC3 mixtures had better performance in terms of modulus of elasticity than the OPC mixture. The elastic modulus correlated with tensile strength and compressive strength. Figures 45-a through 45-e show the stress versus strain curves, and Figure 46 shows the average elastic modulus for each of the five mixtures.



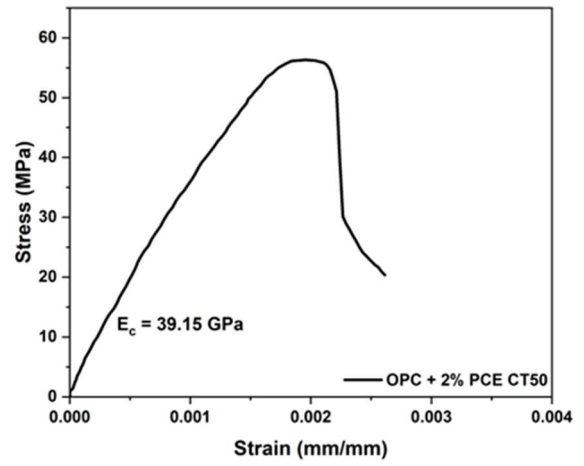
a)



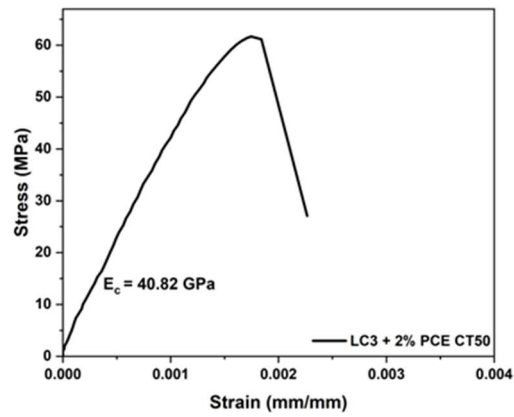
b)



c)



d)



e)

Figure 45. Stress-strain curve for a) OPC without PCE, b) OPC with 2% Fluidum PC314, c) OPC with 2% PCE CT50, d) LC3 with 2% Fluidum PC314, and e) LC3 with 2% PCE CT50.

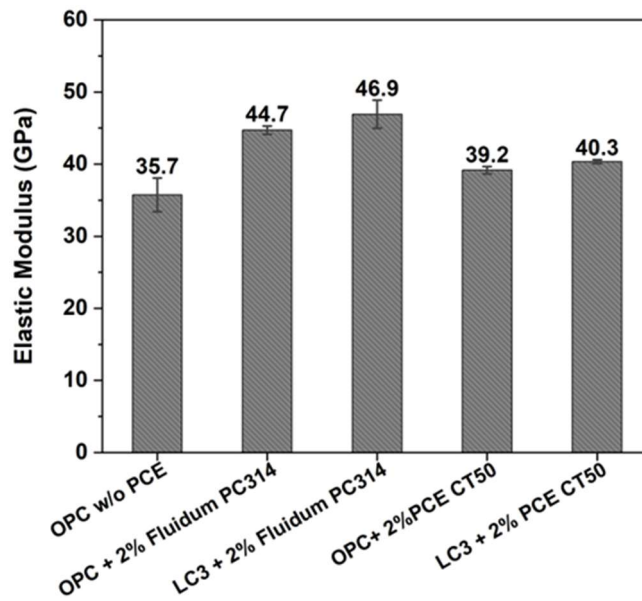


Figure 46. The elastic modulus for OPC and LC3 concrete.

4.5. Water absorption

The water absorption of the five selected concrete mixtures, achieved by testing 28-day moist cured specimens, is shown in Figure 47. As illustrated in Figure 47, LC3-containing mixtures (LC3 mixture with 2% Fluidum PC314 and LC3 mixture with 2% PCE CT50) had a water absorption of about 2%. The plain concrete mixtures (OPC mixture with 2% Fluidum PC314 and OPC mixture with 2% PCE CT50) had a higher % water absorption of about 3%. These four mixtures still retained a water absorption that was less than the control mixture without a superplasticizer, which was 4% (Figure 47 and Table 13).

Table 13. Water absorbtion of OPC and LC3 concrete.

Mixture	No.	SSD Weight (g)	Dry weight (g)	Absorption (%)	Average absorption (%)
OPC	1	1672	1608	3.98	4.01
	2	1710	1643	4.08	
	3	1677	1613	3.97	
OPC + 1% Fluidum PC314	1	1730	1680	2.98	2.94
	2	1705	1656	2.96	
	3	1742	1693	2.89	
OPC + 1% PCE CT50	1	1657	1620	2.28	2.26
	2	1696	1659	2.23	
	3	1711	1673	2.27	
LC3 + 1% Fluidum PC314	1	1651	1598	3.32	3.29
	2	1659	1603	3.49	
	3	1682	1632	3.06	
LC3 + 1% PCE CT50	1	1682	1646	2.19	2.20
	2	1665	1628	2.27	
	3	1716	1680	2.14	

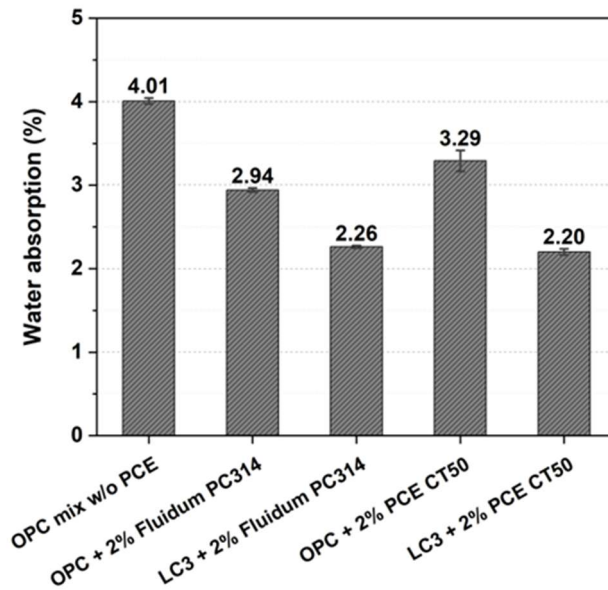


Figure 47. Water absorption of the OPC and LC3 concrete.

4.6 Density

The measured density of hardened concrete mixtures, achieved by testing 28-day moist cured specimens, ranged from 2350 to 2440 kg/m³, as shown in Figure 48. As can be seen from Figure 48, mixtures with Fluidum PC314 (OPC mixture with 2% Fluidum PC314 and LC3 mixture with 2% Fluidum PC314) had a hardened density of at least 2400 kg/m³. However, mixtures with PCE CT50 (OPC mixture with 2% PCE CT50 and LC3 mixture with 2% PCE CT50) had a hardened density of 2350 to 2390 kg/m³. These four mixtures maintained a hardened density equal to or greater than the control mixture without a superplasticizer of 2360 kg/m³ (Figure 48 and Table 14).

Table 14. Density of hardened concrete

Mixture	No.	Length (mm)	Diameter (mm)	Weight (g)	Volume (mm³)	Density (kg/m³)	Average Density (kg/m³)
OPC	1	153.4	76.7	1672	708771	2359	2363
	2	155.0	77.5	1710	731181	2339	
	3	152.8	76.4	1677	701404	2391	
OPC +1%	1	151.5	76.9	1730	704563	2455	2444
Fluidum	2	150.9	76.7	1705	697220	2445	
PC314	3	150.3	77.9	1742	716347	2432	
OPC + 1%	1	152.0	76.4	1657	696819	2378	2399
	2	153.0	76.5	1696	704160	2409	
	3	151.4	77.2	1711	709598	2411	
LC3 + 1%	1	150.1	76.7	1651	694428	2377	2387
Fluidum	2	151.3	76.6	1659	697477	2379	
PC314	3	152.1	76.5	1682	699334	2405	
LC3 + 1%	1	154.9	76.7	1682	715702	2350	2347
	2	153.4	76.9	1665	713075	2335	
	3	154.9	77.3	1716	728118	2357	

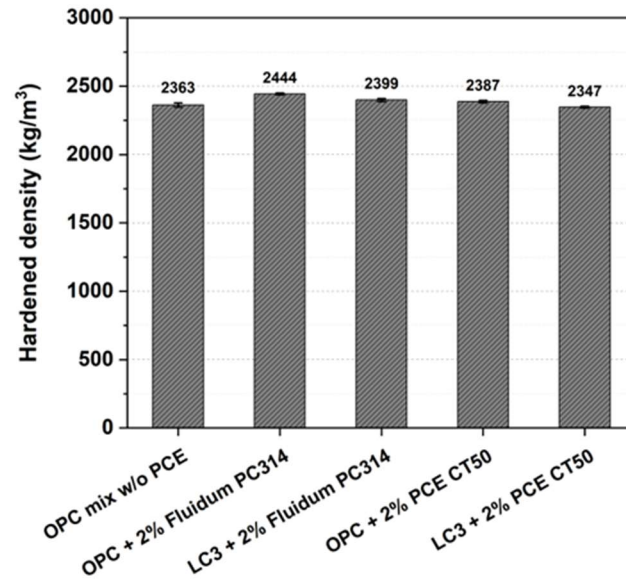


Figure 48. Hardened density of the OPC and LC3 concrete.

4.7. Chloride migration

The rapid chloride permeability results of the five selected concrete mixtures, achieved by testing the 28-day moist cured specimens, are demonstrated in Figure 49-a. It is illustrated in Figure 49-a that the LC3-based mixtures (LC3 mixture with 2% Fluidum PC314 and LC3 mixture with 2% PCE CT50) had significantly lower rapid chloride permeability compared to the plain OPC mixtures (OPC mixture with 2% Fluidum PC314, OPC mixture with 2% PCE CT50 and the control mixture OPC without a superplasticizer). The LC3-based mixtures (LC3 mixture with 2% Fluidum PC314 and LC3 mixture with 2% PCE CT50) had a total charge passed of less than 1000 Coulombs (Table 15). However, the plain concrete mixtures (OPC mixture with 2% Fluidum PC314 and OPC mixture with 2% PCE CT50) had a total charge passed in the range of 3510 to 3630 Coulombs, which was similar to the control mixture without a superplasticizer. The control concrete mixture was without a superplasticizer

maintained at 3580 Coulombs (Figure 49-a, Table 15). Comparing the results shown in Tables 16 and 17, Figures 49-a and 49-b, a logical correlation exists between the total charge passed and the calculated non-steady state chloride migration coefficient of the OPC and LC3 for all of the tested mixtures.

Table 15. Chloride ion penetration classification.

Specimens		Charge passed	Average Charge, Cb	Classification
OPC	3	3581	3580	Moderate
OPC +1%	1	3156.61		
Fluidum	2	3079.36	3633	Moderate
PC314	3	4664.69		
OPC + 1%	1	1141.11		
PCE CT50	2	994.44	993	Low
	3	842.29		
LC3 + 1%	1	2990.78		
Fluidum	2	4083.54	3511	Moderate
PC314	3	3457.5		
LC3 + 1%	1	863.43	855	Low
PCE CT50	2	845.69		

Table 16. Coefficient of chloride migration.

Specimens		CL-Penetration depth (mm) out of 40 mm	Voltage (V)	Temp. °C
OPC	3	20.00	20	20
OPC +1%	1	16.67	20	20
Fluidum	2	18.00	20	20
PC314	3	25.50	30	20
OPC + 1%	1	12.00	35	20
PCE CT50	2	12.14	35	20
	3	12.00	35	20
LC3 + 1%	1	26.75	35	20
Fluidum	2	25.40	35	20
PC314	3	20.25	30	20
LC3 + 1%	1	13.00	35	20
PCE CT50	2	15.63	35	20
	3	13.50	35	20

Table 17. The Coefficient of chloride migration for different mixes.

ID	Mixture designation	Average CL^- penetration depth (mm) out of 40 mm	Voltage (V)	Temp. ($^{\circ}C$)	Average non-steady state migration coefficient ($\times 10^{-12} m^2/s$)
1	OPC without PCE	20.00	20	20	11.21
2	OPC + 2% Fluidum PC314	20.06	20 to 30	20	9.60
3	LC3 + 2% Fluidum PC314	12.05	35	20	3.71
4	OPC + 2% PCE CT50	24.13	30 to 35	20	8.12
5	LC3 + 2% PCE CT50	13.25	35	20	4.11

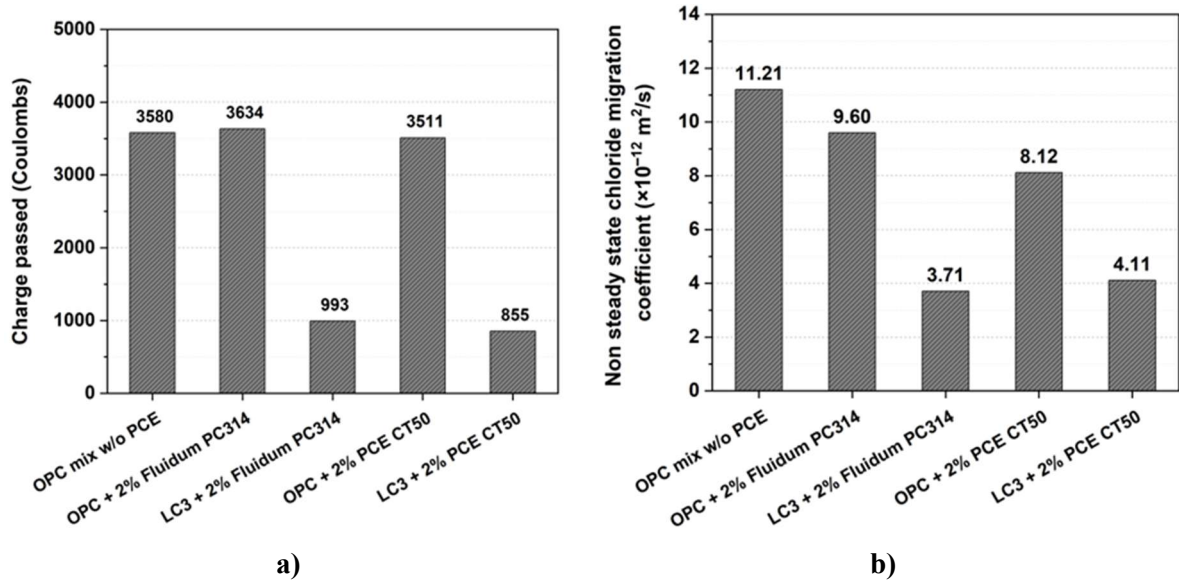


Figure 49. a) Rapid chloride permeability for, b) Non-steady state chloride migration coefficient of the OPC and LC3.

4.8. Drying shrinkage

The measured drying shrinkage over a month for the five selected mixtures is shown in Figure 50. All five selected mixtures were moist-cured in a saturated lime solution for three days. The specimens were air-cured after three days of the saturated lime moist curing. As can be seen from Figure 50, after about a month of air exposure, the LC3-based mixtures (LC3 mixture with 2% Fluidum PC314 and LC3 mixture with 2% PCE CT50) had a drying shrinkage in the range of 203 to 213 microns. However, the plain concrete mixtures (OPC mixture with 2% Fluidum PC314 and OPC mixture with 2% PCE CT50) had a drying shrinkage in the range of 278 to 310 microns, which was close to the control mixture without a superplasticizer. The control concrete mixture without a superplasticizer maintained a drying shrinkage of about 343 microns. Based on these findings, it is evident that the LC3 mixtures have a higher resistance against drying shrinkage.

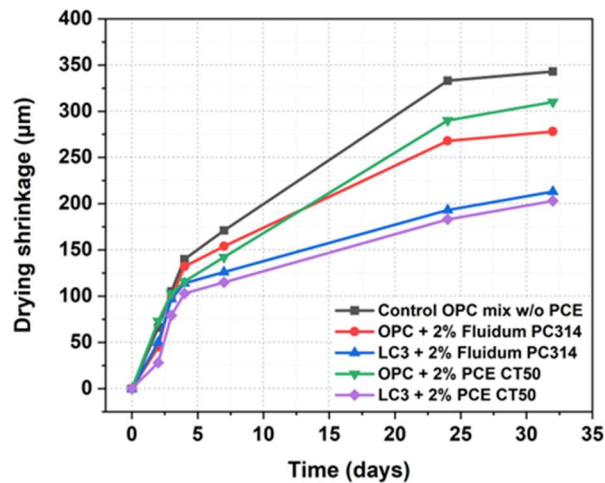
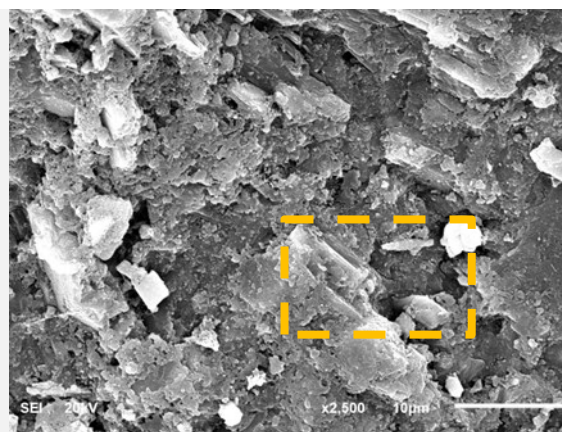
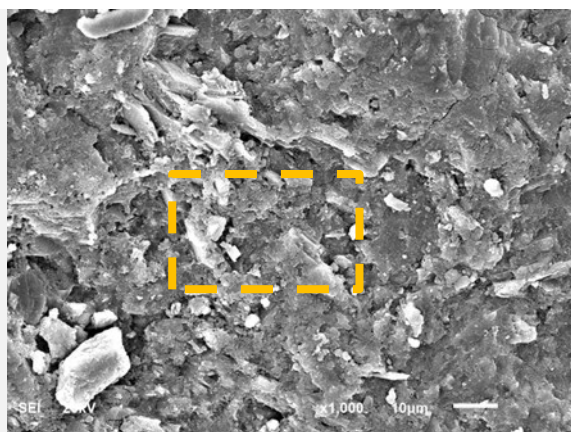
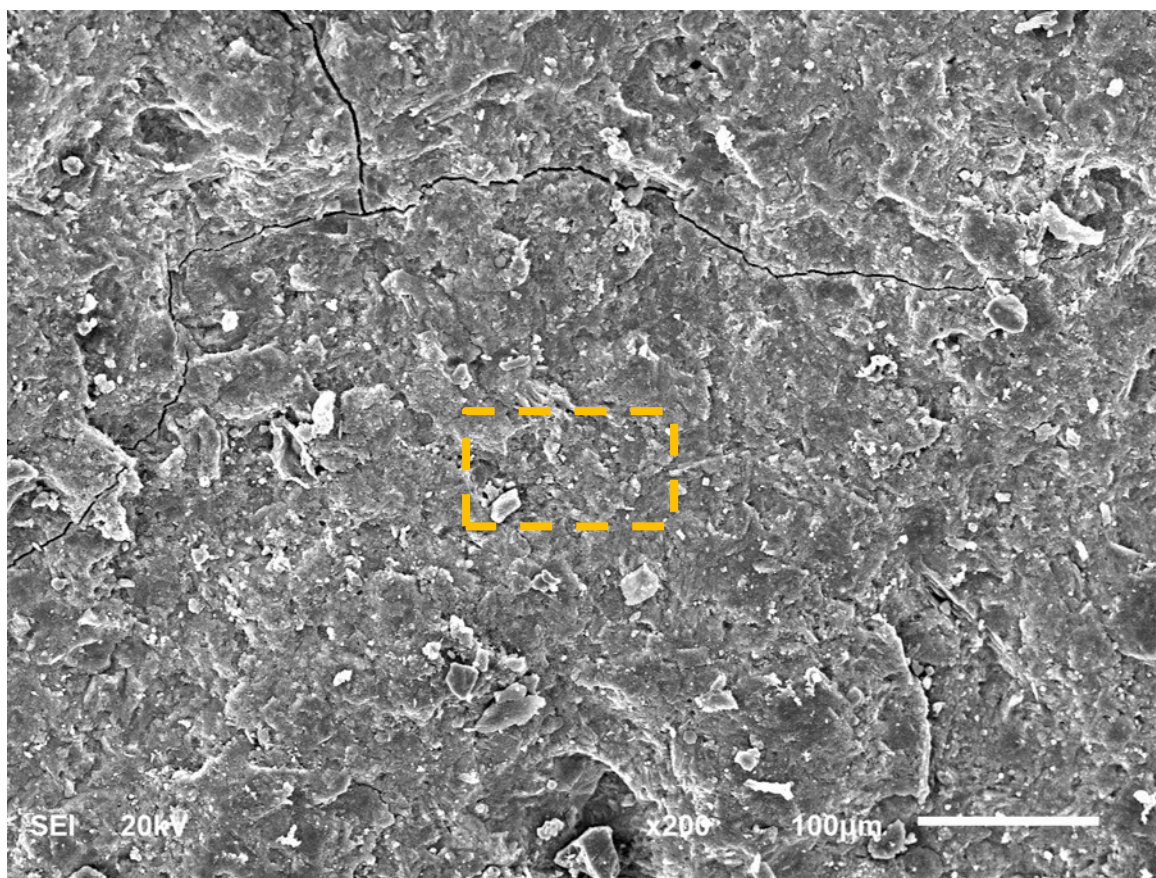


Figure 50. Drying shrinkage of the OPC and LC3 mortars.

4.9 Morphology

Figures 51 through 55 show the morphology of OPC paste without PCE, OPC paste with 1% Fluidum PC314, LC3 paste with 1% Fluidum PC314, OPC paste with 1% PCE CT50, and LC3 paste with 1% PCE CT50, respectively. It is noted that the microstructure of OPC paste with 1% Fluidum PC314 and LC3 paste with 1% Fluidum PC314 mixtures was denser and improved compared to the other three mixtures, i.e., OPC paste without PCE, OPC paste with 1% PCE CT50, and LC3 paste with 1% PCE CT50. An overall observation that could be drawn is the improved matrix of the LC3 mixtures (Figures 53 and 55) compared to the other three OPC cement mixtures with or without superplasticizer (Figures 51, 52, and 54). The denser microstructure of the LC3 mixtures is responsible for their superior performance compared to the ordinary OPC mixtures, as illustrated by the morphological analysis.



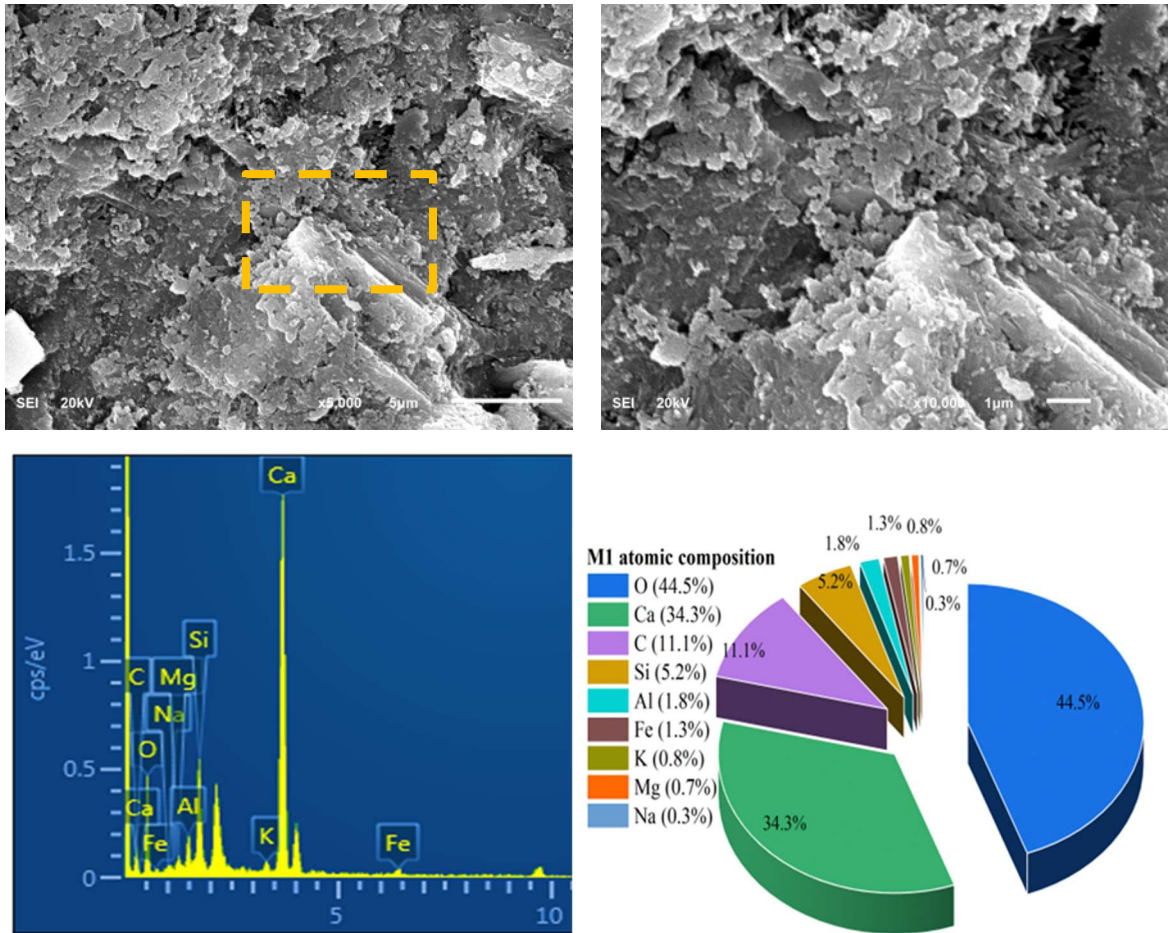
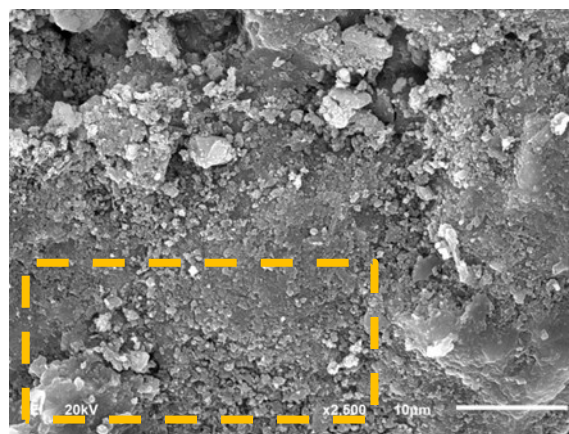
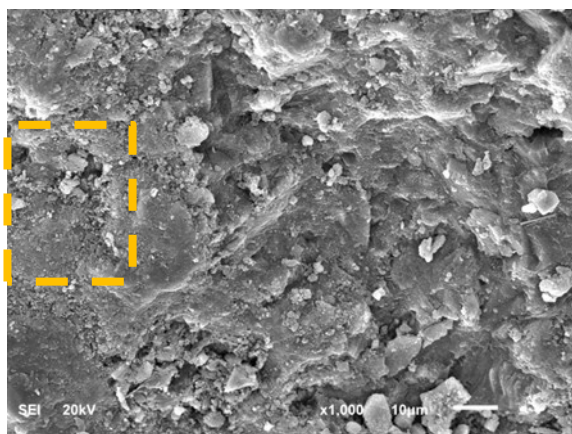
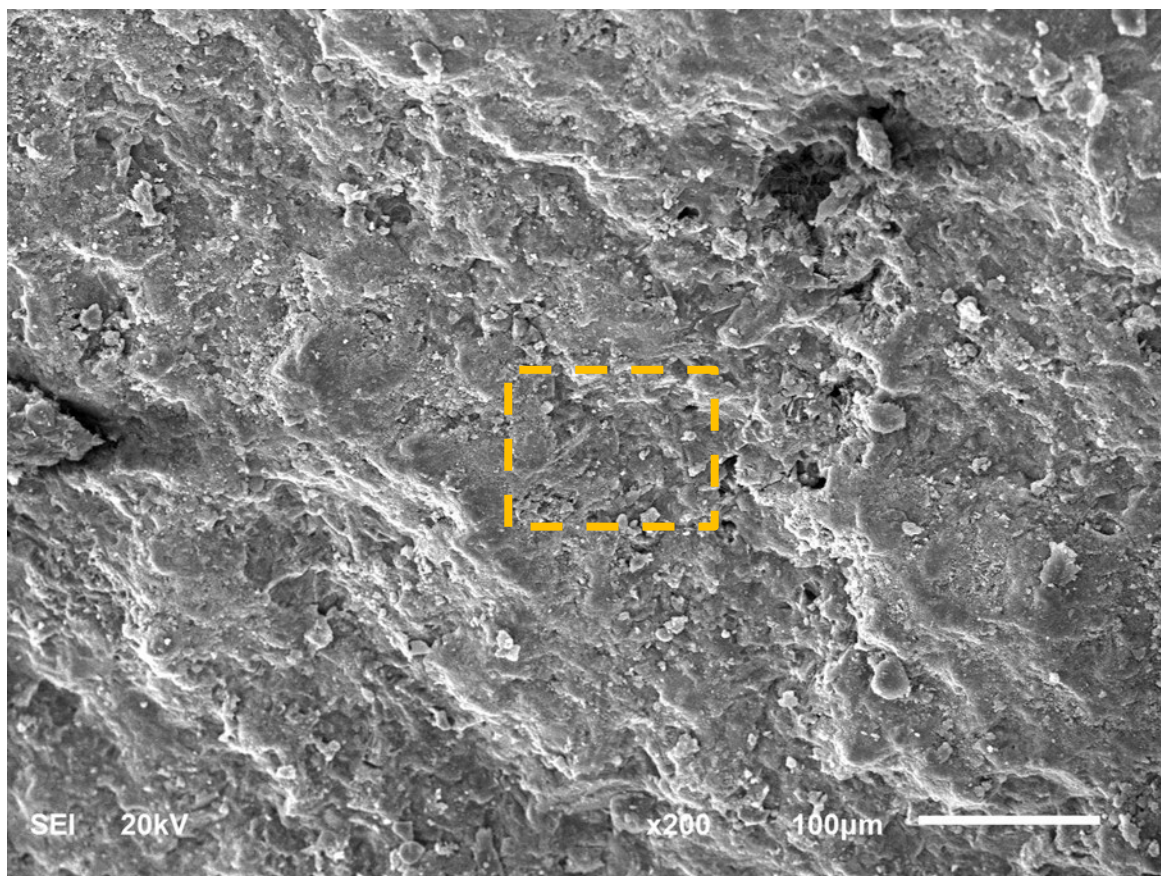


Figure 51. SEM micrograph and EDS of OPC without PCE.



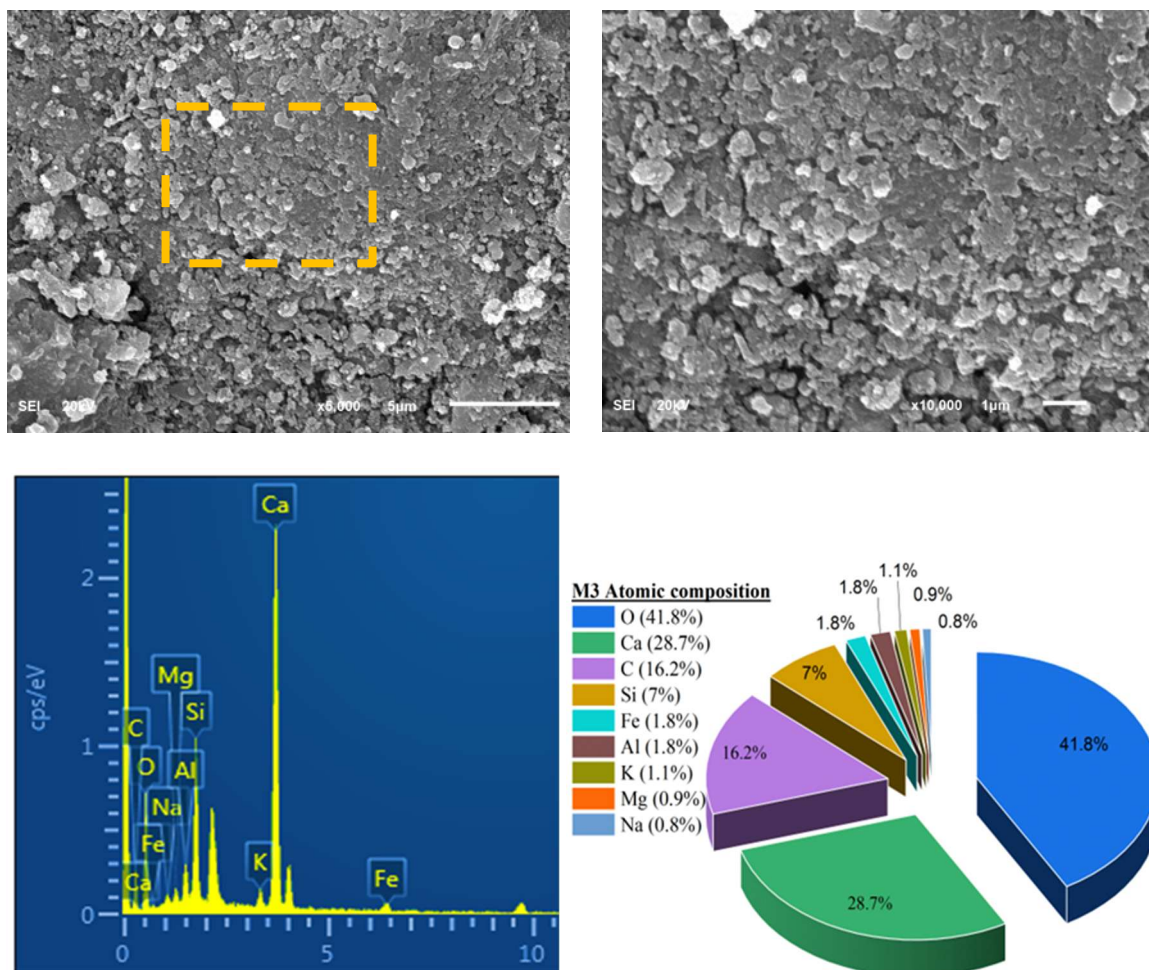
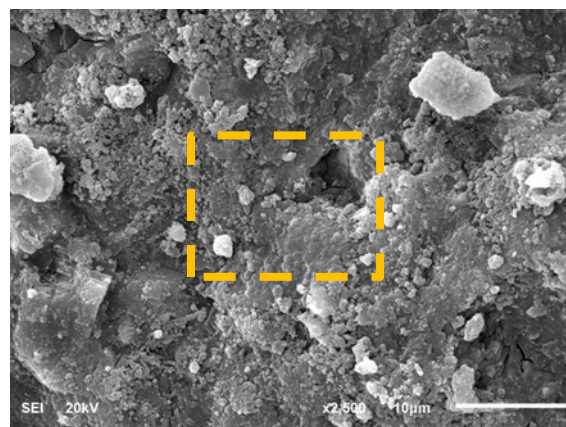
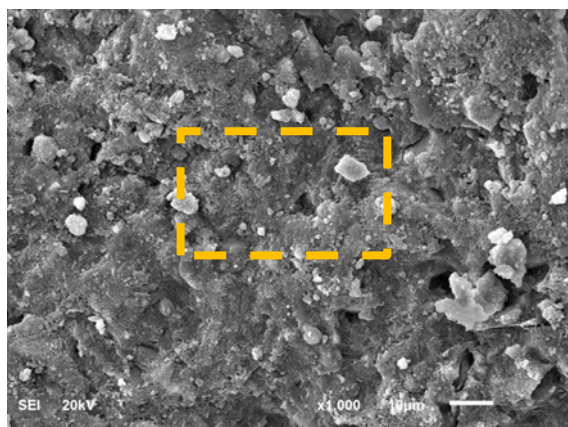
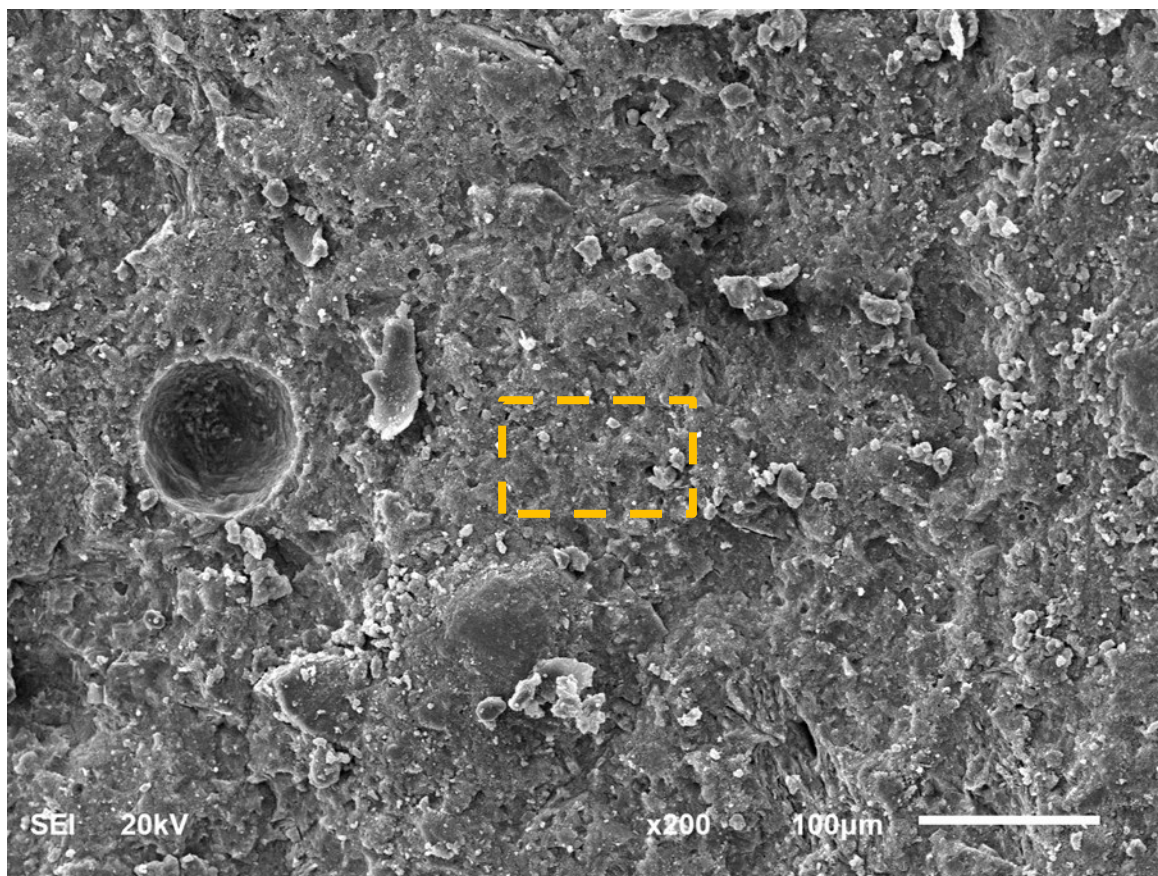


Figure 52. SEM micrograph and EDS of OPC paste with 1% Fluidum PC314.



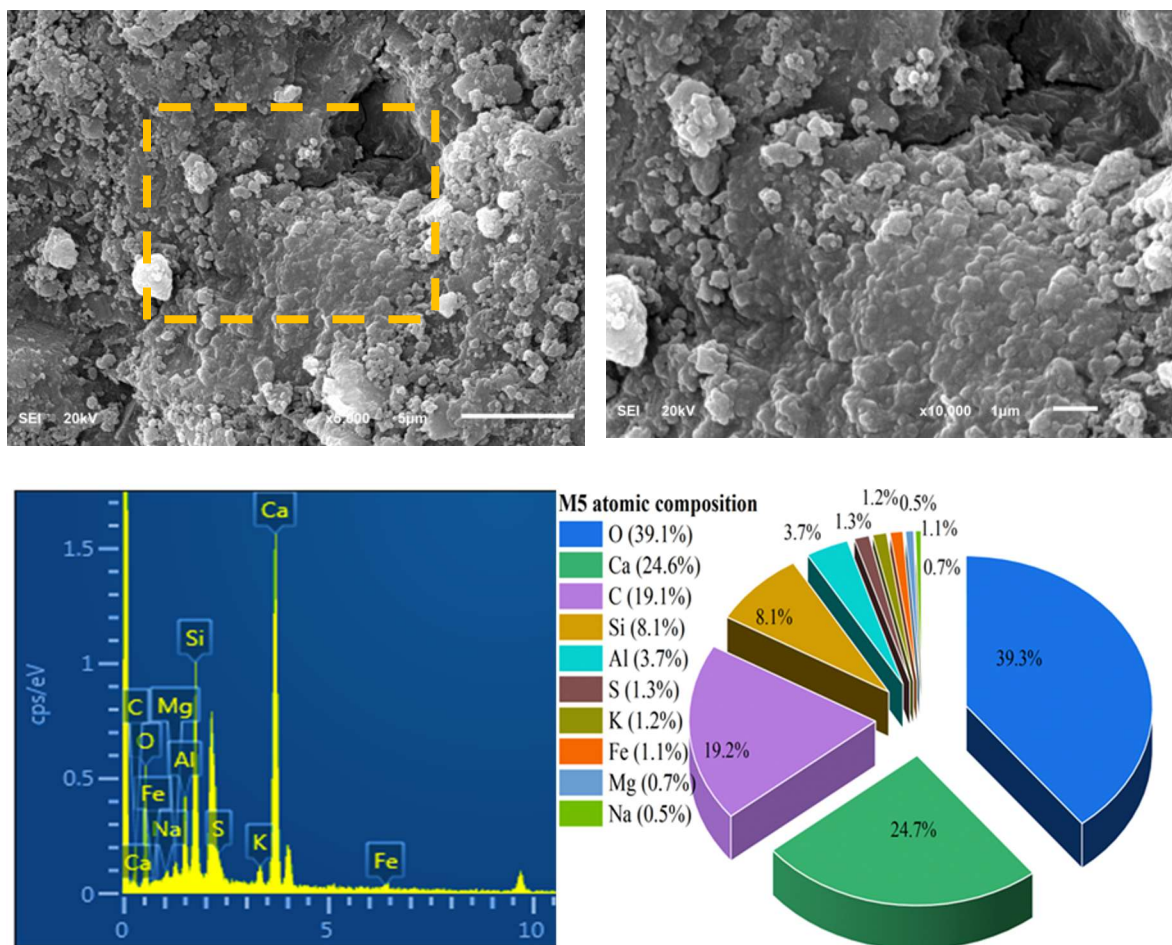
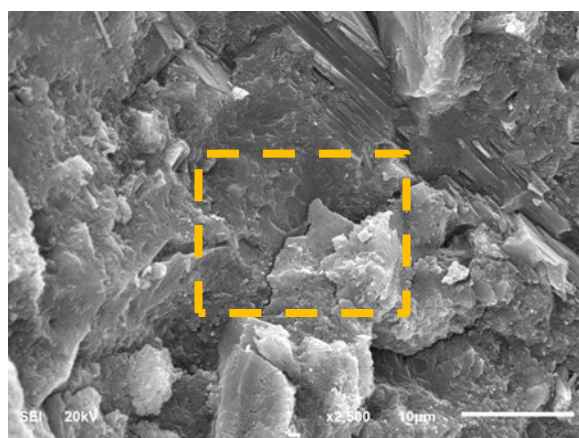
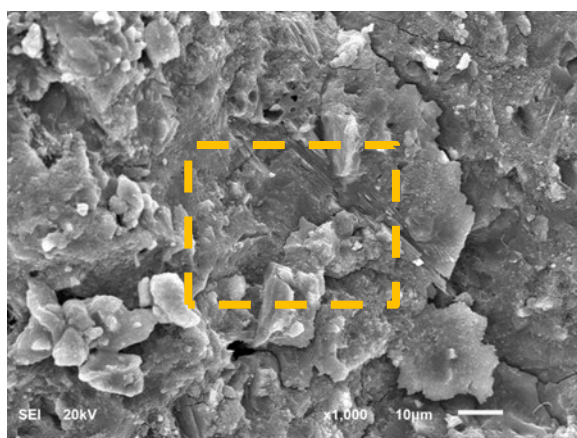
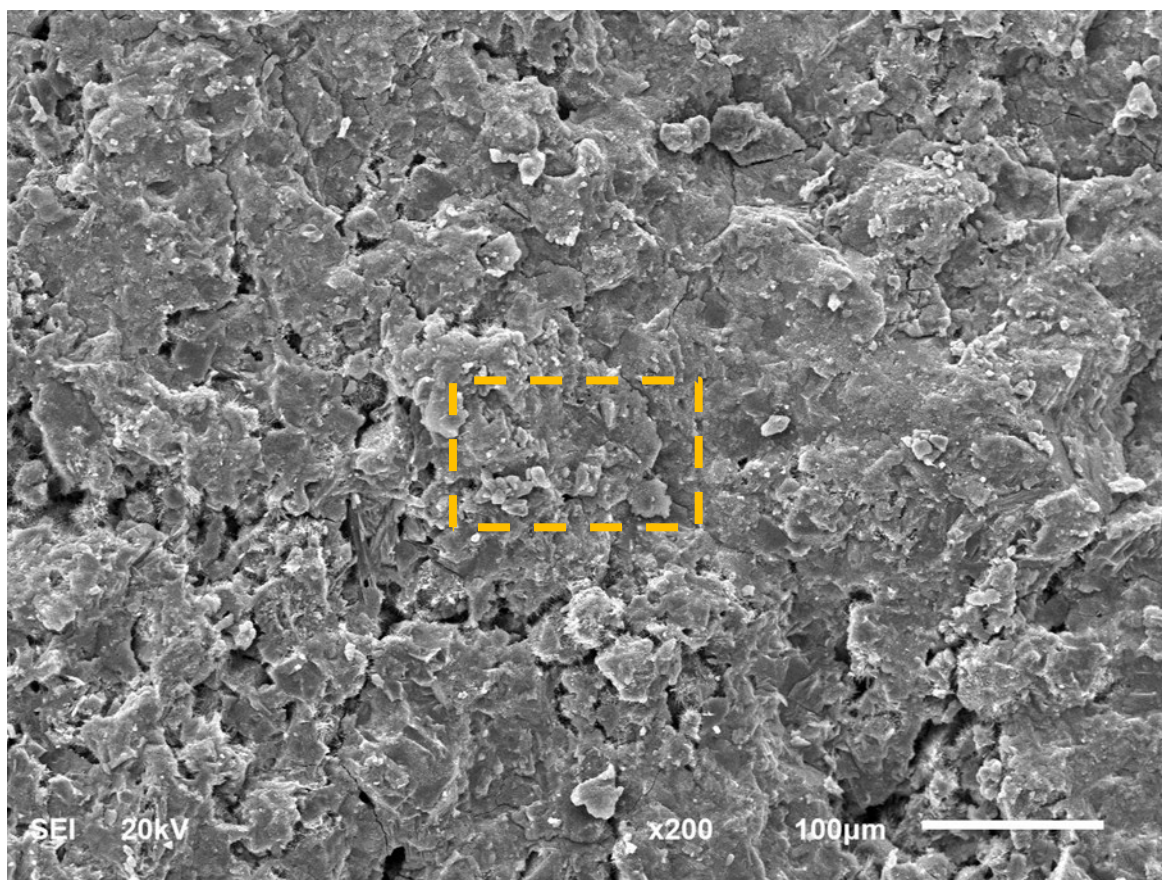


Figure 53. SEM micrograph and EDS of LC3 paste with 1% Fluidum PC314.



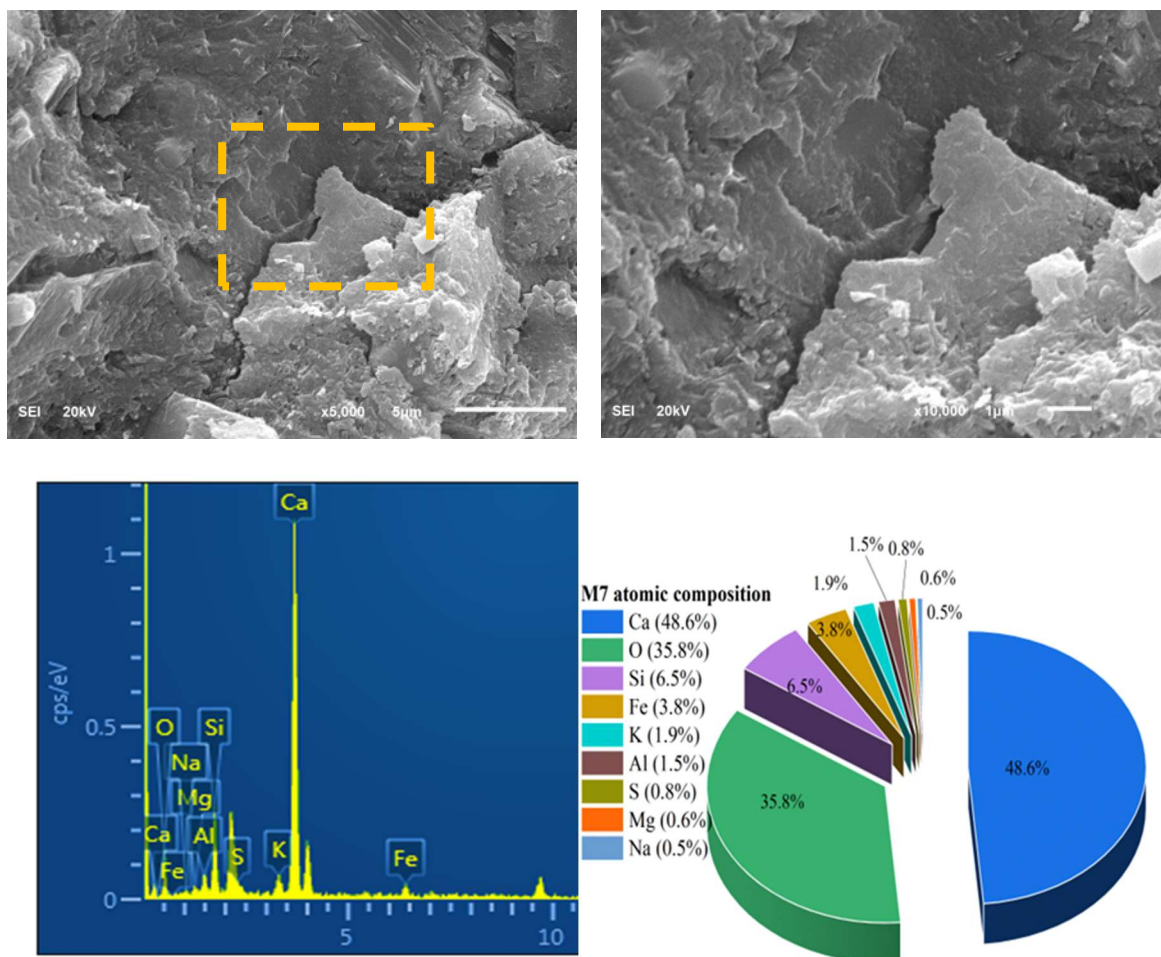
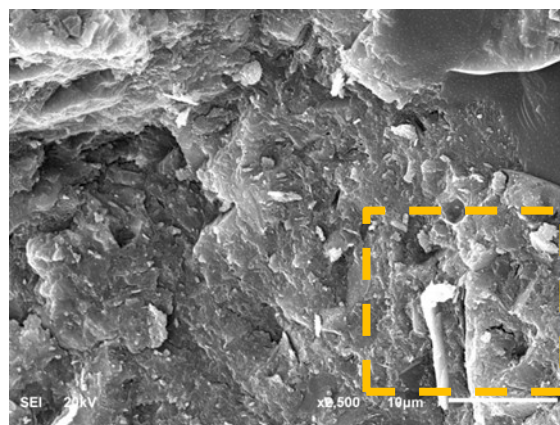
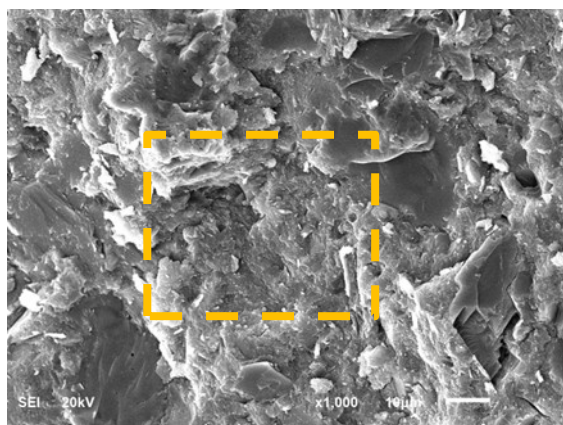
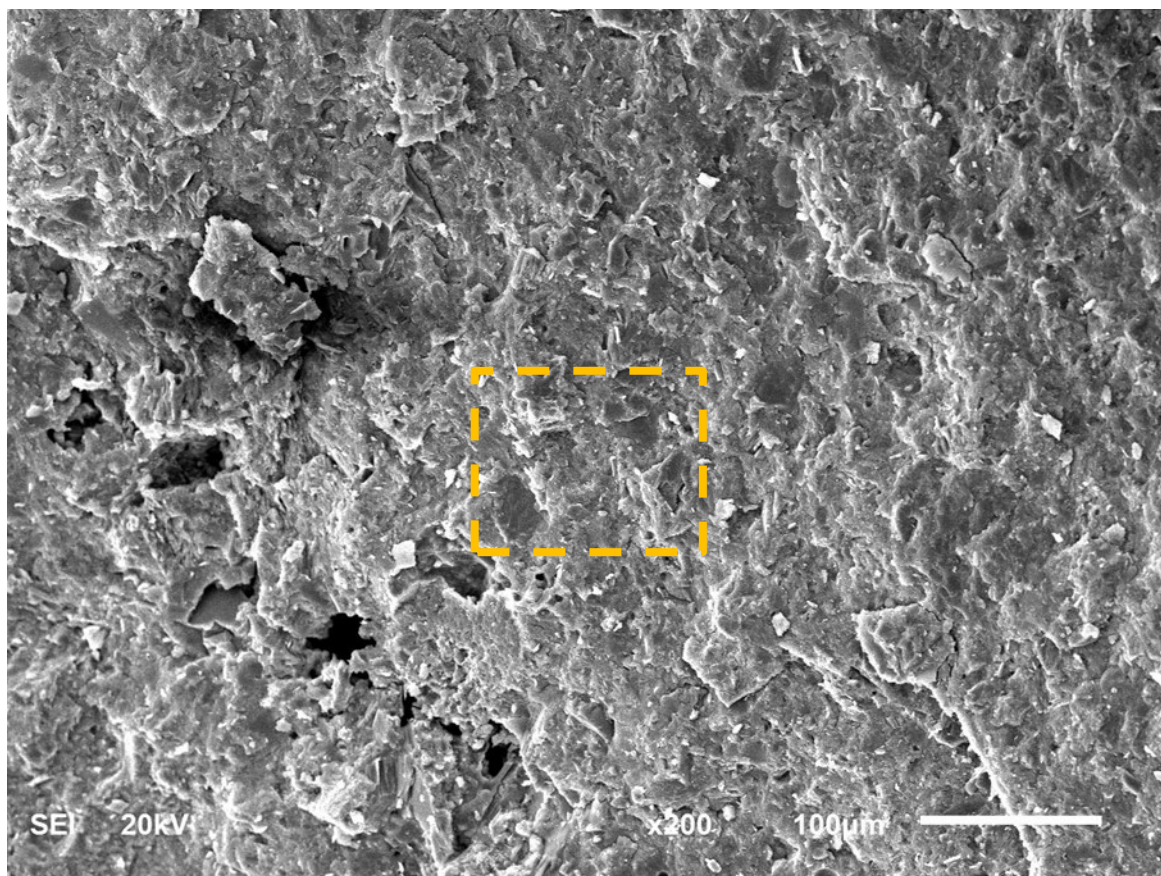


Figure 54. SEM micrograph and EDS of OPC paste with 1% PCE CT50.



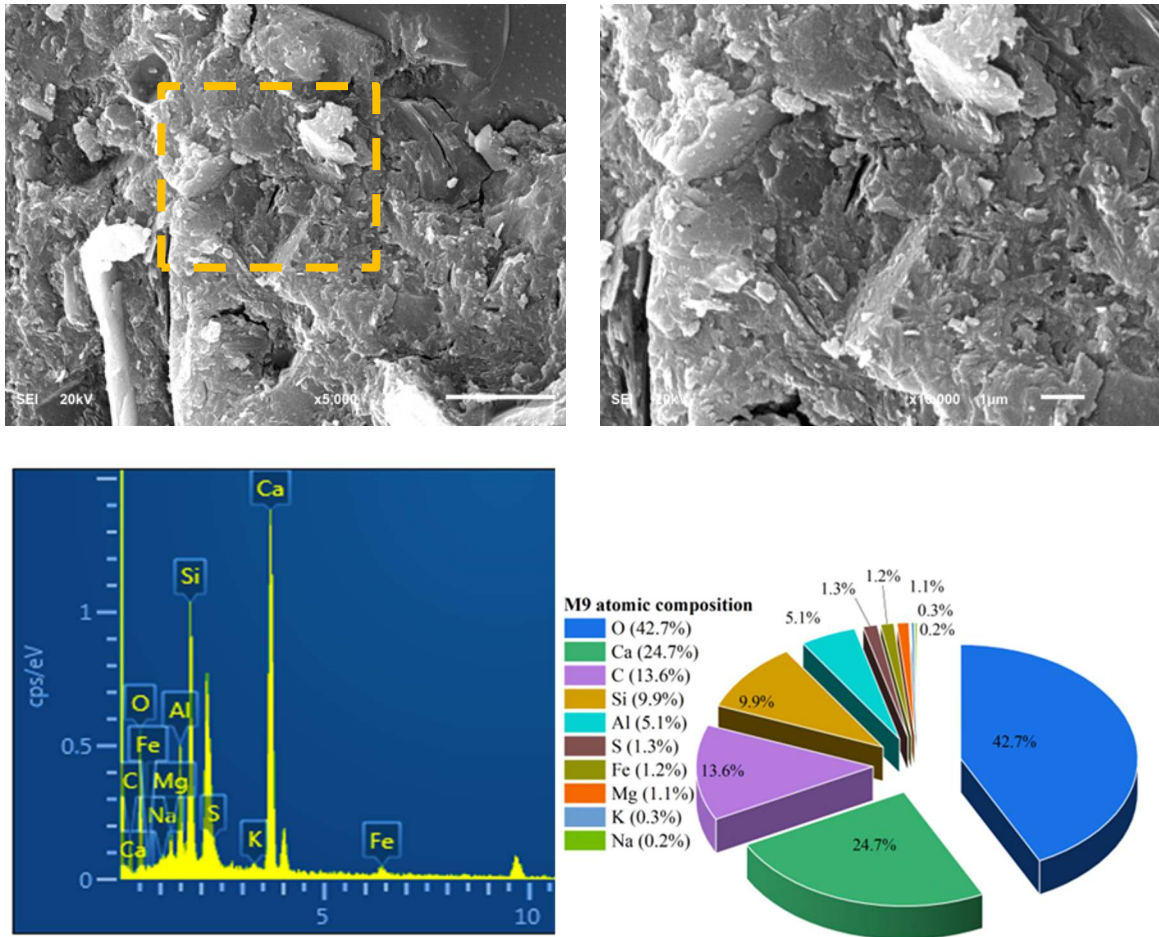


Figure 55. SEM micrograph and EDS of LC3 paste with 1% PCE CT50.

CHAPTER 5

FINDINGS, CONCLUSIONS AND FUTURE RECOMMENDATIONS

5.1 Findings

The findings regarding the reduced peak of heat flow and delayed hydration correlate with a previously done study [56], which reported a similar impact of superplasticizers on LC3 hydration kinetics. However, our study extends these findings by indicating the effect of different dosages of and types of superplasticizers, remarking that Fluidum PC314 outperformed PCE CT50. This difference in performance can be attributed to the various molecular composition and chemical structures that affect the hydration process differently. This is aligned with another study that investigated the effect of PCEs with different molecular structures on the hydration of cementitious materials [57].

The observations that 30% substitution of OPC with LC3 component does not significantly affect the compressive strength of the concrete is aligned with a previously done study [58]. A higher replacement percentage like 50% can affect compressive strength negatively, so 30% was chosen for this study. The LC3-based concrete has a slightly lower density because Calcined clay and limestone powder are lighter than cement, but there are some factors like the superplasticizer effect that increase the hydration time and allow more reaction, compaction, and settlement. Besides that, the combined effect of calcined clay and limestone powder led to a pozzolanic reaction and enhanced the packing of the particles and a refined microstructure [36]. Other mechanical properties like tensile strength and elastic modulus are proportional to compressive strength.

The LC3-based concrete has superior durability, especially in terms of chloride migration and water absorption which is in line with the findings by Maraghechi [36]. As stated in this study, this improvement in chloride migration is mainly due to the refined pore structure leading to lower water absorption which increases the durability of LC3-based mixtures.

The total drying and autogenous shrinkage of LC3 is lower than OPC as was reported in a study [34] which is aligned with this study. It elaborates that shrinkage is mostly influenced by the water-to-cement ratio of the concrete, but LC3 has an overall lower shrinkage than plain cement. This reduction is largely due to a more refined microstructure which is the result of limestone filler effects and pozzolanic reactions of calcined clay. Similarly, another study indicated that LC3 concrete showed improved shrinkage resistance, especially when a low water-to-cement ratio was combined with superplasticizers [58]. These comparisons reinforce our findings, highlighting the role of LC3 in reducing drying shrinkage, making it a viable option for applications requiring dimensional stability.

This study not only supports existing findings regarding the properties of LC3 concrete but also provides detailed insights into how superplasticizers can be used to enhance these properties. This comprehensive study, backed by comparisons with similar works in the field, provides a strong framework for future research and practical applications, particularly in sustainable construction practices that require high-performance concrete with minimal environmental impact.

5.2 Conclusions

This study explored the possibility of producing high-strength concrete using LC3 binder along with various polycarboxylates at variable dosages. It included studying the evolved heat, rate of reaction, and maximum accumulated heat of the developed LC3 mixtures, modeling the heat of reaction at different temperatures (23, 30, and 40 °C), and analyzing the fresh and hardened properties of the developed LC3 mixtures and comparing the results with those for OPC mixtures as control ones.

Based on the findings of the present work, the following conclusions can be drawn:

- The increasing dosages of the superplasticizers affected the reactivity of the binders. The main peak of the hydration reaction decreased and was delayed as the dosage of each superplasticizer increased. However, the effect of the Fluidum PC314 type superplasticizer altered the main course of the hydration reaction of the plain OPC and LC3, resulting in lower main peaks in the heat flow curves and slower reaction rates.
- The model-derived reaction kinetics parameters confirmed the calorimetry test results for plain OPC and LC3 binders with varying Fluidum PC314 and PCE CT50 dosages. The effect of Fluidum PC314 or PCE CT50 on activation energy values was comparable, with lower activation energy values found for plain OPC and LC3 binders containing Fluidum PC314 or PCE CT50 than those without superplasticizers. However, binders admixed with PCE CT50 produced the lowest activation energies.
- All four concrete mixtures showed the behavior of flowable concrete, but the plain OPC concrete showed more flowability than the LC3 concrete. Further, the Fluidum PC314 type superplasticizer provided slightly less flowability to the mixtures than PCE CT50 type superplasticizer.

- As compared to plain OPC concrete mixtures, the LC3 concrete mixtures showed a slightly higher compressive strength, tensile strength, and modulus of elasticity.
- Both superplasticizers (Fluidum PC314 and PCE CT50) affected compressive and split tensile strengths. Mixtures containing Fluidum PC314 outperformed PCE CT50-type superplasticizers. The LC3 mixture containing Fluidum PC314 exhibited the highest compressive strength in the series, at 55 MPa and 78 MPa after 7 and 28 days of moist curing, respectively. The effect of the superplasticizers on 28-day split tensile strength was found to follow a trend similar to that for compressive strength. The LC3 concrete mixture with Fluidum PC314 attained a split tensile strength of 4.9 MPa.
- The LC3-based mixtures had a water absorption of about 2%, while the plain OPC concrete mixtures had a higher water absorption of about 3%. The addition of superplasticizers resulted in reduction of water absorption.
- The rapid chloride permeability results showed that the LC3 concrete mixtures had a total charge passed of less than 1000 Coulombs, which was much lower than that of the plain OPC concrete mixtures indicating lesser risks of reinforcement corrosion in the case of LC3 mixtures.
- After a month of air curing, the LC3 mixtures had the higher resistance against drying shrinkage in the range of 203 to 213 microns.
- The better densification of the microstructure of the LC3 concrete mixtures was observed through the analysis of the SEM micrographs, that is attributed as the main reason behind better performance of the LC3 mixtures as compared to that of the plain OPC concrete mixture.

This study provides valuable insights into the feasibility of using clay and limestone with various polycarboxylates as superplasticizers to produce high-strength LC3 concrete having better mechanical properties, durability characteristics, and shrinkage resistance.

5.3 Future recommendations

To further highlight the sustainability of LC3 concrete, a thorough Life Cycle Assessment (LCA) is recommended. This should involve the effects of LC3 components on the environment including CO₂ released from the extraction of raw materials, calcination, transportation, and concrete production. Then, its advantages over OPC can be better understood.

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