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PERFORMANCE AND SUSTAINABILITY OF ULTRA-HIGH PERFORMANCE CEMENTITIOUS COMPOSITES WITH NATURAL POZZOLANS

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Sustainable ultra-high-performance concrete (UHPC) is an advanced cementitious composite known for its exceptional strength, ductility, and durability. However, its high cement content contributes significantly to the carbon footprint, and the addition of cementitious materials is recommended to address this. In this regard, research on metakaolin, a natural pozzolan, is important. However, metakaolin has been mainly used in combination with silica fume or with silica fume and other pozzolans like fly ash and slag. Studies on binary compositions of UHPCs with metakaolin are scarce in the literature. In the present study, compositions with varying cement contents, containing 15 – 25 % metakaolin, were investigated. The study also considered two other natural materials with some pozzolanic reactivity, zeolite and limestone powder, to understand their effectiveness. These mixtures are compared to pozzolan-free compositions and a conventional composition containing only silica fume. The main evaluations of the study focus on the mechanical strength performance, permeability properties, such as water absorption, pore permeability, sorptivity, acid resistance, chloride penetration, and carbonation. In addition, factors, such as the GWP, carbon footprint and cost, were analysed to assess the environmental sustainability of UHPFRC compositions incorporating metakaolin.

INTRODUCTION

The use of concrete in construction is growing rapidly due to industrialisation and accelerated urban growth worldwide. Recognising the impact of the carbon footprint and global warming potential (GWP) of concrete and construction, efforts are being made to find solutions to reduce or mitigate the environmental effects of cement and concrete use. One such effort is to promote the use of sustainable, high-strength, and high-performance compositions to decrease the number of components in cement and concrete production, while ensuring a longer service life and reducing the overall lifecycle cost of infrastructure projects.

Ultra-high performance concretes (UHPCs), with their outstanding strength, ductility and energy absorption capacity apart from the inherent durability in terms of the very low permeable porosity and corrosion resistance, are establishing themselves as the material of choice in both structural and architectural construction practices. Concrete compositions of strengths up to 130 MPa are generally recognised as very high-performance concretes (VHPCs), while those between 130 – 150 MPa (Type Z) and those between 150 – 250 MPa (Type S) are categorised as ultra-high performance fibre reinforced concretes (UHPFRCs) by the French standard NF P 18-470 [1]. UHPCs inherently require a significantly higher cement content of between 800 and 1300 kg·m^{-3}, which naturally results in higher CO_2 emissions and a considerable environmental impact. UHPCs also require high-performance supplementary cementitious materials (SCMs), such as silica fume or calcined clays (metakaolin), which not only help in reducing the carbon emissions, but also improve the strength and durability of the concrete. Metakaolin, which is the primary material under investigation presently, is an anhydrous aluminosilicate obtained by calcining the natural kaolinite clay at temperatures ranging from 500 to 800 °C. During this process, dihydroxylation occurs, resulting in the loss of structural water and the formation of a disordered, amorphous structure. Due to its high reactivity, metakaolin is widely used as a pozzolan in cementitious materials for enhancing the strength and durability [2].

Investigations on ultra-high performance concrete containing natural pozzolans like metakaolin (MK) are rare. Concrete mixes containing 828 kg·m^{-3} of cement and 207 kg·m^{-3} of silica fume (SF) or metakaolin (MK), modulated with steel fibre and quartz F or metakaolin (MK), along with steel fibres [3, 4]. The compressive and flexural strengths achieved were 155 and 29 MPa for the SF mix, and 146 and 30 MPa for the MK mix,

respectively. They also looked at the durability aspects in terms of the absorption, porosity, permeability, diffusion, carbonation and leaching. Also, the X-ray diffraction (XRD) analysis revealed the presence of quartz, anhydrous clinker phases, and Portlandite, providing insight into the hydration and pozzolanic activity of the mixes.

Huang et al. studied compositions containing 575.6 kg·m^{-3} of cement along with 134 kg·m^{-3} of SF or calcined clay (CC) and achieved a compressive strength of 165 MPa [5]. They reported a compressive strength variation with time and the degree of reactions, apart from the cost and carbon footprint aspects. Rong et al. studied concretes with 10 % SF and 35 % fly ash (FA), with 55 % of the cement being replaced by 6 to 14 % metakaolin, achieving compressive and flexural strengths of 160 and 40 MPa for fibre-reinforced concretes, while normal concrete resulted in 95 and 19 MPa [6]. The effect of 90 kg·m^{-3} of silica fume or MK and their combination on the concrete mixtures containing 754 kg·m^{-3} of cement and 306 kg·m^{-3} of fly ash resulted in strengths of around 155 MPa [7]. The study also reported a chloride migration depth of about 7 mm. Investigating the effects of 55 – 220 kg·m^{-3} of replacement of metakaolin in 1100 kg·m^{-3} of binder with 332 kg·m^{-3} of limestone powder, Mo et al. found a maximum strength of about 105 MPa [8]. The improvement in the microstructure due to the addition of MK has been demonstrated through studies such as the differential thermal analysis (DTA), XRD, and pore size distribution analysis using Mercury Intrusion Porosimetry (MIP). In a further investigation into concrete samples containing 55 – 110 kg·m^{-3} of metakaolin, with and without 332 kg·m^{-3} of limestone powder, resulted in a strength of around 105 MPa at 90 days when cured at 90 °C [9]. The corresponding flexural and tensile strengths were around 13 – 15 MPa. Mo et al. later published two additional studies discussing the high--temperature mechanical and microstructural properties of the same compositions previously mentioned [10, 11].

The replacement of cement with 120 kg·m^{-3} of MK resulted in a compressive strength of about 120 MPa and improvements in other mechanical strengths as well in a cement-silica fume system [12]. The shrinkage, water and chloride permeability also improved. Other SCMs, like fly ash and slag, could not result in the same level of improvement. Zhang et al. studied compositions keeping the cement and SF contents constant at 729.3 and 269.8 kg·m^{-3}, while replacing cement with MK and MgO from 0 to 15 %, respectively [13]. The compositions resulted in strengths ranging from 100 to 140 MPa at 28 days. They investigated several other parameters related to the microstructure as well as the fibre bond and flexural strength.

In a composition containing 900 kg·m^{-3} of cement mixtures with SF, ground granulated blast furnace slag (GGBS), fly ash and MK replacements were investigated by Abdellatief [14]. It was observed that increasing the levels of GGBS and FA marginally reduced the strength, while the addition of MK showed no significant change. Durability in terms of the sorptivity and chloride permeability, along with the microstructure and life cycle assessment, was presented. Compositions containing cement at 1081 kg·m^{-3} and SF at 94 kg·m^{-3} were compared with those in which cement was replaced by calcined clay and limestone powder (LP) at different levels. They were investigated for the strength, XRD, and DT-TGA characteristics to understand hydration as well as porosity [15]. The highest strength of about 140 MPa at a combination of 150 kg·m^{-3} of MK and 328 kg·m^{-3} of LP was observed. A combination of cement (CEM II 52.5) and limestone powder (LP) was modulated by an SF, MK mixture of 300 kg·m^{-3}, resulting in concrete strengths ranging from 120 – 140 MPa at 28 days [16]. The flexural strengths ranged from about 17 to 22 MPa. They also investigated the microstructural and interfacial transition zone (ITZ) compositions of the mixtures.

Abbas et al. studied three compositions with a control mix containing 850 kg·m^{-3} of cement and 270 kg·m^{-3} of SF, which was modified through recycled glass powder, calcium carbonate powder, and metakaolin, achieving a compressive strength of about 150 MPa compared to 160 MPa for the control mix [17]. The effects of these modifications on the chloride ion penetration resistance and the global warming potential (GWP) were found to be significant. Hong studied UHPC compositions with a binder content of 1000 kg·m^{-3} while replacing cement with different percentages of SF and MK [18]. The highest strength of about 170 MPa was obtained for a composition containing 210 kg·m^{-3} of MK. The mixtures resulted in chloride penetration depths ranging from 4 to 19 mm. Concretes containing 890 kg·m^{-3} of cement with 89 kg·m^{-3} of SF modified with an additional fly ash and metakaolin or diatomaceous earth combination achieved a strength of around 100 MPa at 7 days [19]. The composites cured at 90 °C for 7 days resulted in an improved strength of about 135 MPa.

The effects of a nano metakaolin (NMK) addition to concretes containing 800 kg·m^{-3} of cement and 80 kg·m^{-3} metakaolin resulted in a strength of about 160 MPa [20]. It was noted that NMK reduced the fluidity of the mix, which may be due to the additional fine clay and, more importantly, due to the ultrafine particles requiring higher wetting water, but did not lead to any significant improvement in the strength characteristics. The observation that the addition of nano materials will primarily influence the thixotropy of the mixture and may not lead to any significant improvement in strength is noteworthy. Abdelmelek studied strength reduction rates of low cement compositions of 480 kg·m^{-3} with MK replacement at elevated temperatures [21]. They observed a strength increase from about 100 – 120 MPa at 300 °C.

This brief summary on UHPC compositions containing MK shows that most researchers preferred to use MK only in combination with silica fume, or silica fume and a few lower efficiency pozzolans [3-20]. Very few studies [3, 21] are available on the effectiveness of MK alone for realising UHPCs, probably with the doubt that it may not be possible to achieve very high strengths with it alone as the SCM. Also, most of these investigations reported only strengths reaching around 120 – 150 MPa, suggesting that there is a need for augmenting the pozzolanic reaction through SF in most cases. Considering this, a specific study aimed at investigating the effectiveness of metakaolin as the main SCM has been proposed

EXPERIMENTAL

After carefully reviewing the UHPC compositions used by previous researchers, it was decided to include MK at a level of approximately 15 – 25 %, similar to silica fume in most cases. The proportions of the different components of the proposed UHPC mixtures were finalised after several preliminary studies, starting with the American Society for Testing and Materials (ASTM) standard mortar and its modifications with silica fume and metakaolin. It is important to note that all the materials were locally sourced, and the production, processing, and testing methods used are described below. The goal is to develop a non-proprietary ultra-high performance cementitious composite that can meet modern durability standards without sacrificing the strength or performance.

Constituent material characteristics

Ordinary Portland Cement (OPC) Type I from an Indian manufacturer, with a fineness of 320 kg·m^{-3} and a strength class of 36 MPa at a water-cement ratio of 0.485 (which is equivalent to C32.5 grade as per the Euro standard) was adopted as the primary binder. Calcined metakaolin clay (MK) containing 52 % SiO_2 and 46 % of alumina with a fineness of 12000 m^2·kg^{-1} was the pozzolanic additive. A locally available lower-grade silica fume (SF) with only 90 % SiO_2 content was chosen for comparison. Apart from these two other natural materials, zeolite (Z) and limestone powder (LP) are also studied for a broad understanding of their efficiency in concrete. The other constituents were quartz powder (QP) passing 2000 mesh and fine quartz sand (QS) conforming to ASTM standard aggregate [22]. To achieve a water-binder ratio of around 0.2 required for producing the UHPCs, a polycarboxylate ether-based superplasticiser (SP) manufactured by Sika was adopted. Brass-coated micro steel fibres (MSFs), 0.2 mm in diameter and 13 mm in length, were added to enhance the ductility and energy absorption characteristics in a few mixtures. The water content of each mixture was adjusted to achieve a viscous, near-flowable matrix for ease in compaction and not to lose strength due to inadequate compaction. The chemical compositions of the different constituents primarily chosen from locally available materials are given in Table 1.

The details of the different concrete mixtures studied are presented in Table 2. The table also includes the proportions of the ASTM standard mortar and its modifications (Mixes 1-3). A UHPC type composition without any pozzolanic additive (Mix 4), as well as a general UHPC composition with 180 kg·m^{-3} (20 %) SF (Mix 5) also form a part of the study. These variations help in understanding and evaluating the efficiency of the cement, plasticiser and pozzolanic mixture combinations adopted. Considering the lower-grade OPC cement used (Euro 32.5 grade), a cement content of 900 kg·m^{-3} was adopted primarily and was later modulated to around 600 and 1200 kg·m^{-3}. The metakaolin content varied from 135 – 225 kg·m^{-3} (15 to 25 %). In fact, several preliminary trials were conducted with different cement and metakaolin contents before finalising these mixtures. Apart from these two other mixtures, the first

Table 1. Physical and chemical characteristics of the constituents.

Chemical composition	Cement (C)	Silica fume (SF)	Metakaolin (MK)	Zeolite (Z)	Limestone powder (LP)	Quartz powder (QP)	Quartz sand (QS)
CaO (%)	61.85	0.75	0.09	0.70	48.0	0.03	0.01
SiO_2 (%)	20.07	90.20	52.0	73.0	12.4	99.72	99.02
Al_2O_3 (%)	5.32	1.10	46.0	15.0	4.6	0.13	0.77
Fe_2O_3 (%)	4.62	1.38	0.60	0.70	2.7	0.05	0.22
MgO (%)	2.54	0.40	0.03	0.03	0.9	0.00	-
SO_3 (%)	2.34	0.50	-	-	-	0.03	-
Loss on ignition (%)	2.41	2.50	0.50	11.00	34.2	0.09	0.8
Fineness (m^2·kg^{-1})	320	18500	12000	19200	345	2000 (mesh)	ASTM sand
Specific gravity	2.83	2.65	2.6	1.6	2.68	2.65	2.68

Table 2. UHPC mixture proportions investigated.

Mix no.	Mix type	Mix name	C	PZ	QP ($kg \cdot m^{-3}$)	QS	SP	MSF	w/b
1.	ASTM mortar	N56S0P0	565	-	-	1554	0	0	0.485
2.	and	N56S0P2	565	-	-	1554	11.3	0	0.485
3.	modifications	N47S20P.5	470	90	-	1554	2.3	0	0.425
4.	Plain UHPC	N9S0P2	900	-	337	963	18.0	0	0.35
5.	UHP-FRCs	U9S20M1	900	180	180	954	18.0	78	0.23
6.		U9K15M1	900	135	135	1044	18.0	78	0.29
7.		U9K20M2	900	180	180	954	21.6	156	0.22
8.		U9K25M2	900	225	225	900	11.7	156	0.24
9.		U6K20M2	600	120	120	1404	6.0	156	0.27
10.		U12K20M2	1200	240	240	408	12.0	156	0.21
11.		U9Z20M1	900	180	180	954	16.2	78	0.40
12.		U9LP20M2	900	180	180	954	9.0	156	0.25

containing zeolite (Z) and another containing limestone powder (LP) at 180 $kg \cdot m^{-3}$ (20 %) are also studied to understand the behaviour of the other natural powders in the UHPC compositions. Zeolites, used as catalysts and adsorbents of nutrients in feed applications mostly, are a group of microporous, crystalline alumino-silicate minerals having interconnected channels of meso--cavities. The aluminosilicate with this highly interconnected porosity helps in promoting the supplementary cementitious activity. The details of the final mixture compositions studied are presented in Table 2.

All the concrete mixtures were prepared in a Hobert type mixer, with the ingredients being intimately mixed in stages for almost 15 minutes, till the resulting compound arrives at a thixotropic state with a near flowing consistency. The mixtures are transferred into steel moulds of 40 × 40 × 160 mm in size and are compacted with a handheld vibrator in layers. After the mixture attains some rigidity, the top surface is finished level and then covered with plastic sheet. The concrete is never allowed to dry by replacing the plastic sheet with a moist cloth immediately after about four hours to ensure an appropriate initial curing practice.

Workability and strength characteristics

The slump flow values of the UHPC mixes were obtained using a frustrum of a cone as per the ASTM C 230 recommendation [23], which are presented in Table 3. The concrete samples were demoulded and placed in a water tank at 27 °C in the laboratory until the age of testing. Both the flexural tensile strength and compressive strength were determined according to EN 196-1 [24]. A loading rate of 0.05 mm/sec as was chosen for the compressive strength test after several initial trials. This rate was also suggested by Way and Wille earlier [25]. The specimens were tested immediately after removing from the curing tank in a saturated surface dry condition and the average strength of three samples was reported after removing the outliers. The split tensile strength of the concretes was also recorded. The ultrasonic pulse velocities of these composites were all measured before conducting the compressive strength test at a frequency of 50 kHz at three points distributed across the specimen using a coupling agent as prescribed [26].

Durability characteristics

The degradation of concrete is predominantly influenced by the ingress of harmful chemicals through the permeable pore space during the life of the structure. In the present context, the durability characteristics have been established through the water absorption and chemical degradation studies as described.

Absorption and permeable pore space

The water absorption rate in the permeable pore system of the UHPC composite was measured in accordance with the recommendations of ASTM C 642 [27]. The mass of a concrete sample oven-dried at a temperature of 105 °C for 72 hours was first recorded. The 72-hour drying period, it was found to be appropriate for considering the specimen to be fully dry, with almost no further weight-loss observed after another 6 to 12 hours drying in the hot air oven. The samples were then immersed in water, and the weight gain due to water absorption was measured every 30 minutes, then every hour for up to six hours. Measurements were made every 6 hours for up to 72 hours later. The 30-minute absorption value as a percentage of its original weight is obtained and compared with the recommendations for evaluating the concrete quality for durability by the CEB recommendations [28]. Also, the permeable pore space (PPS) of the concrete sample is calculated by using the mass of the sample after 72 hours using the formula:

$$\text{PPS}\ (\%) = \frac{M_S - M_D}{M_S - M_A} \qquad (1)$$

where, PPS is the permeable pore space or permeable porosity (%), M_s is the mass of the saturated surface dry sample (gms.), M_D is the mass of oven dry sample (gms.) and M_A is the apparent or submerged mass of the sample in water (gms.), which, in fact, represents the volume of the sample.

Surface capillary rate of the absorption (sorptivity) characteristics

The capillary water absorption characteristics from the surface of the porous concrete is a very good indicator of the porosity and pore connectivity in general. The rate and quantity of water absorption in the initial stage will present an idea of the saturation in larger capillary pores while the later absorption characteristics depicts the absorption into the micro capillary system associated with the concrete composites. ASTM C 1585 [29] presents a methodology for evaluating these sorptivity characteristics. These measurements were conducted on samples that had been dried in an oven at 105 °C for 72 hours and then cooled in a desiccator to prevent the absorption of atmospheric moisture during the cooling period. The mass change of the sample was recorded first at 30 minutes followed by measurements every hour until 6 hours which formed the initial absorption period. Later, the measurements were continued every 6 hours up to 72 hours and were designated as the secondary absorption. The capillary absorption which is calculated as the mass change per unit area of the exposed cross section of the test specimen is considered for evaluation.

$$\text{Capillary absorption (\%) } I = \frac{M_t}{a * \rho} \qquad (2)$$

where, I is the capillary absorption, M_t is the mass change at a given time, a is the cross-sectional area and ρ is the density of the water. The limits for the volume of the water absorption per unit area per second during the initial 30 minutes for establishing the quality of concrete were suggested by CEB recommendations [28]. The methodology of obtaining this was by using the test recommended for the determination of the initial surface absorption in BS 1881: Part 208 [30]. However, the initial 30 min. absorption obtained earlier by using the ASTM C 1585 will also be nearly the same and is probably more appropriate for this evaluation and was used for assessing the quality of the concrete presently.

Chemical attack

The chemical degradation of the concrete compositions, particularly due to the acidic medium, is still matter of concern. This effect is being determined presently through the degradation of the concrete specimens exposed to a 5 % sulfuric acid solution. To ensure that the concentration of the acid solution is not to altered during the exposure period, the ratio of the volume of the specimens exposed to the volume of the solution is kept at a minimum of 1:5 ratio with enough gap all around. Even so, the entire solution is replaced after 15 days. The exposed specimens are rinsed in freshwater and weighed before they are replaced back in the solution. The test performed is generally in line with ASTM C 1898 [31]. The deterioration in terms of mass loss, surface characteristics, dimensional changes have all been recorded at regular intervals up to 28 days. The final effect of the acid attack in terms of strength degradation was measured after 28 days through the compressive strength test.

Corrosion characteristics

Steel corrosion in concrete is mainly influenced by the pH drop near the rebars, which depassivates the steel, or by the conductivity associated with the penetration of environmental chlorides, which breaks the passivation layer. Permeability and diffusion play a critical role in the corrosion phenomenon, which is primarily an electrochemical mechanism. Chlorides in particular permeate from the concrete surface, eventually reaching the embedded steel, where they depassivate the protective oxide layer, initiating corrosion. This leads to rust formation, expansion, cracking, and ultimately spalling of the concrete, thereby weakening the structure. The possibility of corrosion of the steel in these compositions was assessed through the alkalinity, carbonation and the chloride diffusion characteristics. These durability and corrosion characteristics can be used as factors for assessing the efficacy and sustainability of these compositions. Though the porosity and permeability discussed earlier also play a significant role even in the corrosion characteristics, their understanding through a few directly related tests responsible for corrosion was felt essential.

Alkalinity

In all cementitious compositions, particularly those involving the effects of supplementary cementitious materials as at present, it would be prudent to have a definite fix on the pH levels of each of the composites produced to ensure that there are no problems associated with the corrosion of steel in these composites due to the lowering of pH from the pozzolanic activity. The pH values were measured using a pre-calibrated digital pH meter on a 1:5 mixture of the powdered concrete sample collected from different locations of the concrete specimen and distilled water.

Chloride diffusion

An effective estimate of the chloride diffusion capability of the different cementitious compositions can be studied through the test presented by NT Build

443 [32]. The test involves the preparation of a 2.8 % NaCl solution of enough quantity for the complete submergence of all the samples. The exposure period for chloride diffusion was to be not less than 35 days as per the recommendations of the code. To ensure that the UHPCs with its dense microstructure will have sufficient time for the diffusion effects of the chlorides to be assessed with measurable depth levels, the exposure period was presently extended to 90 days. After the exposure period, the specimens were removed from the solution and were split open to study the depth of chloride ingress. The chloride ingress was measured by the visible whitish or greyish white band at the exposed surface, after spraying with 0.1 M silver nitrate solution. The chloride penetration depth of all the samples was recorded to the nearest 0.5 mm.

Carbonation

The effects of carbonation from environmental exposure in concrete was assessed by exposing the concrete specimens to an atmosphere containing 3 % carbon dioxide and at a relative humidity of 65 % in a carbonation chamber at a temperature of 27 °C according to NT Build 357 [33]. The samples are left in the chamber at 65 % RH at 27 °C initially for 14 days to ensure that the samples attain the required humidity before exposing them to the carbon dioxide. The test according to NT Build 357 requires that the concrete samples be exposed to the CO_2 environment for 35 days. However, this period was also extended to 90 days due to the UHPC concretes being tested as in the chloride diffusion study. After the 90-day exposure period, the samples were removed from the chamber and the average carbonation depth was measured by spraying a phenolphthalein indicator solution on a freshly fractured surface of the specimen.

Assessment criteria for establishing the concrete quality

It is indeed possible to achieve a fairly accurate understanding of the capabilities of cementitious compositions through the mechanical, durability, and corrosion evaluations outlined above. In fact, many international organisations have developed these test methods to assess the properties of cementitious compositions, providing solid evidence of the effectiveness of the results and their interpretation. However, it is also true that organisations such as the CEB (Comité Euro-International du Béton) have used only a few of these parameters to rate the quality of concrete; these criteria are shown in Table 3. The limits proposed by the CEB were also used to explain and categorise the compositions studied in this research.

Table 3. Assessment criteria for establishing the concrete quality (CEB, 1989).

Concrete quality	Ultrasonic pulse velocity ($km \cdot s^{-1}$)	30 min. water absorption (%)	30 min. capillary absorption ($mL \cdot m^{-2}s^{-1}$)
Very good	> 4.0		
Good	3.5 – 4.0	< 3.0	< 0.17
Average	3.0 – 3.5	3.0 – 5.0	0.17 – 0.35
Poor	< 3.5	> 5.0	> 0.35
Very poor	Hollow sound		

Note: * - (Presently utilised only)

X-ray diffraction studies

The X-ray diffraction (XRD) studies were performed on concrete samples cured for 90 days. The ground sample powders passing through a 200-mesh sieve are pre-dried in a vacuum desiccator before the test. The XRD studies were conducted using a SmartLab device manufactured by Rigaku. The tests employed CuKα radiation at 40 kV and 50 mA, with a step size of 0.01° and a duration of 0.2 seconds per step (3° per minute) over a 2θ range of 3° to 90°. The phase identification was performed using the International Centre for Diffraction Data (ICDD) database, as was earlier attempted by Lee et al. [34]. Subsequently, the XRD data was analysed quantitatively using Rietveld analysis of the SmartLab device for detailed characterisation of the crystalline materials. This analysis involves refining a theoretical model to match the observed diffraction pattern, allowing for the extraction of the various microstructural parameters.

Efficiency, sustainability and environmental impact

In the present context, the global warming potential (GWP) per unit mass of the composite, the effectiveness of cementitious materials (binder intensity or efficiency), CO_2 emissions or CO_2 intensity per unit strength as well as the cost efficiency of these UHPC compositions are considered for evaluation. These factors have been proposed and discussed by a few earlier researchers in some of their investigations [35-37]. These concepts as earlier proposed have been utilised in the present investigation as well.

RESULTS AND DISCUSSION

The experimental investigations on UHPC compositions and the appropriate control concretes containing metakaolin as the supplementary cementitious material are presented in terms of their mechanical, durability and corrosion characteristics in the following paragraphs. The investigations are directed to study the effect of the natural pozzolan, metakaolin at different percentages and in compositions with different cement contents. One mixture containing the most commonly used

SCM, silica fume is also included, apart from two other compositions containing natural pozzolans, zeolite and limestone powder. Finally, the microstructural characteristics as well as the sustainability parameters were discussed.

Figure 1. Specimens of the UHPC concrete with metakaolin.

Workability and strength characteristics

Concrete compositions in the UHPC range have extremely low water contents and, naturally, its workability has a significant influence on the compaction and, thus, the compressive strength. The need for a highly thixotropic yet flowing matrix that can be compacted easily at the very low water contents of UHPCs is dependent on not just the water content and the water cement ratio, but is also influenced by the particle size distributions of the different consti. tuents. It can be seen that all the UHPC compositions (Mixes 5 − 12) exhibit slump flow values exceeding 200 mm, while the corresponding control UHPC mix without any pozzolanic material (Mix 4) and the ASTM standard mortar and its modifications (Mixes 1 − 3) show negligible slump flow (Table 4). The primary factor for this could be the missing additional fineness contributed by the pozzolanic admixtures.

The compressive strengths of the UHPC compositions along with the ASTM standard mortar and its modifications and control concrete, at 28 and 90 days are summarised in Table 4. The ASTM mortar (Mix 1) exhibited a compressive strength of 36 MPa at 28 days, indicating that the cement confirms to the C 32.5 grade of the Euro code. The modified compositions of the ASTM mortar (Mixes 2 and 3) indicate that the compatibility of the superplasticiser and pozzolanic admixtures like SF in general, resulting in strengths of 58 and 63 MPa, respectively. Also, the UHPC control mix without any pozzolanic addition (Mix 4) containing about 900 kg·m^{-3} cement reached a strength of 85 MPa at 28 days. The specimens of UHPC compositions containing MK are shown in Figure 1. The compositions containing metakaolin (MK) at the different dosage levels of 135, 180, and 225 kg·m^{-3}, (15, 20, and 25 %) have all resulted in strengths exceeding 150 MPa except, while that containing 600 kg·m^{-3} of cement (Mix 8), which resulted in a strength of 119 MPa only. This clearly shows the need for an increase in the cement content to achieve strengths in the range of 150 MPa. Also, the highest compressive strength of about 190 MPa was achieved for the composition containing 225 kg·m^{-3} (25 %) of MK with 900 kg·m^{-3} of cement. This also shows that metakaolin percentage has a great influence on the compressive strength of these compositions. Also, while a minimum cement content is necessary, cement contents beyond a limit may not help in increasing the compressive strength (Mix 10). These effects can be associated with the complex interaction of the cement - metakaolin ratios and the cement saturation effects of the excessive cement content used in the composition. The results also show an excellent pozzolanic participation of MK on the strength development in UHPC, which

Table 4. The mechanical strength characteristics of the compositions studied.

Mix no.	Concrete composite	Average slump flow (mm)	Compressive strength (f_c)* 28 days (MPa)	90 days (MPa)	Split tensile strength (f_t)* 90 days (MPa)	Flexural tensile strrength (f_b)* 90 days (MPa)	Pulse velocity 90 days (km/sec)
1.	N56S0P0	100	36.04 (2.0)	43.43 (3.2)	6.60 (0.3)	2.40 (0.3)	4.7
2.	N56S0P2	100	58.64 (2.1)	59.51 (2.5)	5.35 (0.4)	4.29 (0.2)	4.8
3.	N47S20P.5	100	63.76 (1.6)	66.23 (1.8)	3.41 (0.2)	3.71(0.3)	4.8
4.	N9S0P2	131	85.04 (3.6)	102.00 (2.9)	9.49 (0.4)	5.59 (0.3)	5.3
5.	U9S20M1	233	139.9 (2.4)	146.6 (2.3)	15.47 (0.6)	11.70 (0.5)	5.0
6.	U9K15M1	222	167.9 (2.9)	170.16 (2.7)	18.24 (0.5)	16.88 (0.6)	5.0
7.	U9K20M2	229	135.25 (2.1)	151.78 (2.2)	16.15 (0.4)	14.51 (0.3)	5.0
8.	U9K25M2	207	167.1 (1.7)	188.19 (2.1)	23.13 (0.6)	15.53 (0.5)	5.0
9.	U6K20M2	217	108.65 (3.2)	118.74 (3.5)	-	10.76 (0.7)	5.0
10.	U12K20M2	203	156.51 (2.3)	161.7 (1.8)	20.42 (0.7)	16.97 (0.4)	4.7
11.	U9Z20M1	185	92.2 (1.8)	88.78 (1.6)	11.86 (0.4)	6.34 (0.3)	4.3
12.	U9LP20M2	229	125.86 (2.7)	141.49 (2.3)	20.06 (0.6)	10.48 (0.6)	4.7

*The values in brackets are the standard deviations.

may be attributed to its high aluminate (Al_2O_3) content. An earlier reported study [3], however, resulted in a strength of only 146 MPa at 28 days for a concrete containing 225 kg·m^{-3} (25 %) addition of metakaolin (MK). It is also to be noted that the composition containing zeolite, another natural clay, (Mix 11) resulted in a strength of only 90 MPa indicating and lower pozzolanic reactivity. However, the mix containing limestone powder (Mix 12) resulted in strengths almost similar to silica fume and metakaolin.

To better understand the current situation, the results of previous studies (references 3-21) are tabulated and analysed. It is important to note that most of the researchers used metakaolin as the supporting pozzolan, combined with silica fume as the primary SCM in the composition, resulting in ternary mixes. Some researchers even used more SCM, leading to quaternary or higher-order mixes. The complex interactions of different SCMs, especially regarding efficiency and water requirements which depend on the fineness and wetting surfaces are difficult to evaluate, to say the least. Despite this, we attempted to analyse the relationships between the water/binder ratio and strength across these studies, which naturally produced a wide range of strengths for each water/binder ratio. The results of our current experimental studies are overlaid on the data and shown in Figure 2 below. A careful review of the graph clearly indicates that the strengths from the binary mixes in this study are at the upper end of the strength spectrum for any particular water/binder ratio. The best-fit curve from our data yields a power equation displayed in the graph (expt. fit). To account for some of the maximum strengths achieved by previous researchers at different water/binder ratios, we have slightly adjusted this power equation, as shown in the graph (expt. fit–proposed). It is also important to note that compaction issues and resulting porosity tend to reduce strength at very low water/binder ratios, typically less than 0.20, as illustrated in the figure.

The split tensile and flexural tensile strengths are also given in Table 4. The relationships associated with the variation of these tensile strengths with the compressive strength is depicted in Figure 3. The relationships show that the variations are primarily linear even with the compressive strengths varying from 40 to 190 MPa. The ultrasonic pulse velocities of all these concrete compositions, including the ASTM mortar and its modifications, show values far exceeding 4.0 km·s^{-1} (most of them reaching 5.0 km·s^{-1}) indicating them to be concretes of very good quality as per the CEB recommendations given earlier (Table 3). This clearly indicates that the workability and compaction procedure adopted resulted in a highly compact mass without any discontinuities or voids even with the low water contents associated with the mixtures.

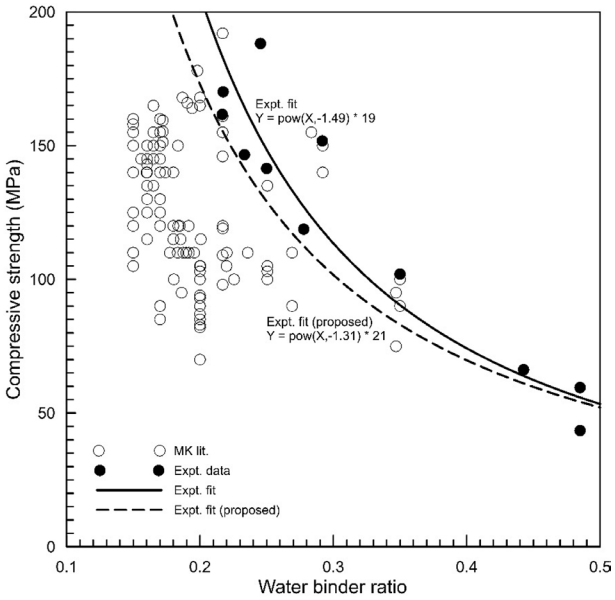

Figure 2. Strength to water binder ratio relationships of the metakaolin concretes.

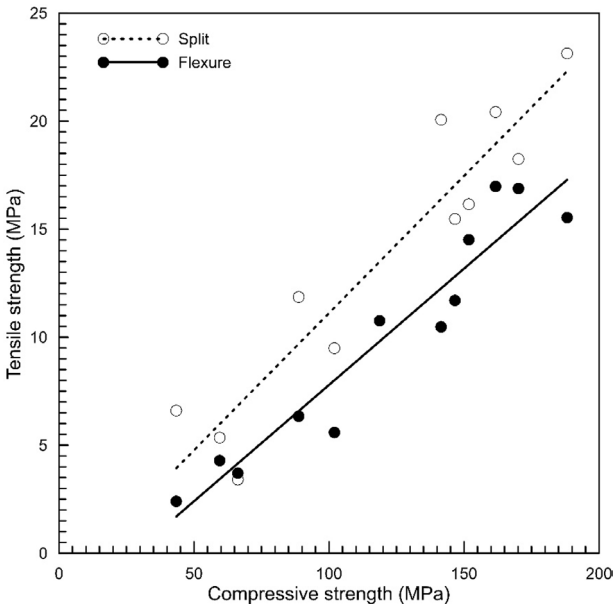

Figure 3. Compressive and flexural tensile strength of the UHPC composites with metakaolin.

Permeability characteristics

The durability of cementitious composites is largely influenced by the porosity and the pore structure of the matrix, which plays a critical role in governing both the strength and performance of the material. The key permeability characteristics, including the permeable pore space (PPS), absorption, capillary absorption, initial and secondary sorptivity coefficients, of these mixtures are presented in Table 5. These parameters provide a good insight into the potential

Table 5. Permeability characteristics of the cementitious composites studied.

Mix no.	Concrete comporite	Permeable pore space [27] (vol. %)	30 min. water absorption [27] (wt. %)	72 h. water absorption [27] (wt. %)	30 min. capillary absorption [29, 30] ($mL \cdot m^{-2}s^{-1}$)	Initial rate of surface absorption [29] (mm/√sec)	Secondary rate of surface absorption [29] (mm/√sec)
1.	N56S0P0	14.29	4.44	6.81	0.46	0.0225	0.0001
2.	N56S0P2	10.59	3.29	5.16	0.31	0.0112	0.0002
3.	N47S20P.5	10.97	2.66	4.80	0.18	0.0050	0.0009
4.	N9S0P2	9.04	2.94	4.34	0.30	0.0103	0.0012
5.	U9S20M1	4.37	1.01	1.93	0.07	0.0022	0.0006
6.	U9K15M1	4.38	1.00	2.03	0.07	0.0015	0.0009
7.	U9K20M2	5.49	1.25	2.88	0.03	0.0010	0.0003
8.	U9K25M2	5.00	1.23	2.50	0.12	0.0029	0.0008
9.	U6K20M2	2.86	0.48	1.26	0.01	0.0009	0.0006
10.	U12K20M2	5.42	0.88	2.34	0.06	0.0020	0.0009
11.	U9Z20M1	14.07	3.70	7.11	0.22	0.0051	0.0027
12.	U9LP20M2	7.05	1.54	3.72	0.15	0.0051	0.0026

for environmental ingress that influences the durability and long-term performance, particularly in aggressive environmental conditions.

In simple terms, it is clear from Table 5 that most UHPC compositions containing metakaolin (Mixes 6 – 10) show a significant improvement in all the characteristics associated with the permeability characteristics, and with the values decreasing by almost about half or even a third compared to the ASTM standard mix and its modifications (from a PPS of about 14 % to about 4 % or less typically). However, the mixtures containing zeolite, in particular, as well as limestone powder did not yield the same improvement, which can be easily associated with the lower strengths that were obtained in both cases.

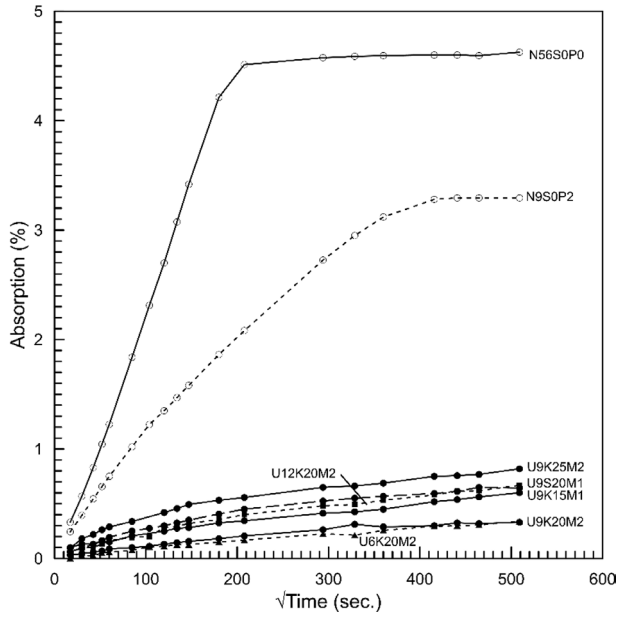

Figure 4. Typical capillary permeability characteristics of the metakaolin compositions.

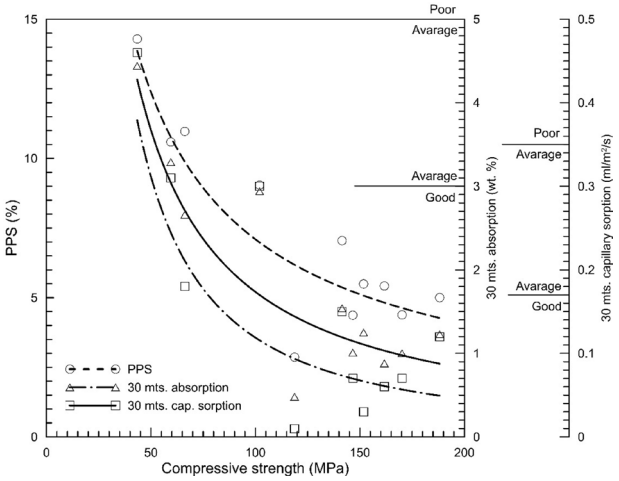

Figure 5. Variation in the PPS and absorption characteristics with the strength.

The typical capillary absorption or permeability characteristics with time as required under ASTM C 1585 are presented in Figure 4. The initial rate of change of these relationships until 6 hours (slope of this portion of the curve) is the initial rate of surface absorption and the slope of it from 24 to 72 hours is the secondary rate of surface absorption are both given in Table 5. In fact, the direct absorption characteristics of these compositions are also very similar to what has been depicted in Figure 4, and as such are not being presented.

Apart from this, limits for establishing the concrete quality for the absorption value at 30 min. as well as the capillary permeability in 30 min. have already been prescribed by the CEB recommendations, given in Table 3 earlier. To have a clear picture of the concrete quality status of these compositions the variations of the PPS, the absorption and the capillary permeability values with the concrete compressive strength for the ASTM and the metakaolin composi-

tions are all presented in Figure 5. The figure also depicts the limits on concrete quality clearly for direct interpretation. It can also be seen that these variations follow a power relationship in general, however, there could be variations as can be associated with any porosity and permeability assessments.

Also, comparing the results of the metakaolin compositions (Mixes 6 – 10) with the composition containing silica fume (Mix 5) in Table 5, it is clear that metakaolin (MK) is a highly reactive supplementary cementitious material (SCM) and could serve as an effective alternative to silica fume (SF). One can also observe that even the 72 hours absorption value for full saturation are below the limit of 3 % prescribed for 30 min. water absorption in all the UHPC mixes containing metakaolin, indicating its excellent performance.

The reactivity of the cementitious composites in an acidic environment is a complex factor influenced by the cement content, which is the most reactive component in the mix, as well as the porosity and strength, which affect the environmental penetration. Currently, the reactivity in an acidic environment was studied by exposing the samples to a 5 % H_2SO_4 solution. The mass loss at different intervals and the final reduction in compressive strength were recorded to assess the material's resistance to chemical attack. This reactivity is presently measured in terms of weight and strength loss after 28 days, as shown in Table 6. The weight loss generally ranges from 30 to 40 % and appears to depend on the cement content and the type and percentage of pozzolan used. However, the strength loss varies widely, influenced by both the cement and pozzolan contents, as well as the initial strength.

Corrosion characteristics

The risk of steel corrosion in these compositions was evaluated by analysing the effects of the environmental factors, primarily the chlorides and CO_2, on the alkaline concrete system. In this context, the pH, chloride penetration, and carbonation properties of all the concrete mixes were examined using relevant tests specified by various standards, as previously mentioned. The results of these assessments are shown in Table 6. They directly reflect the durability of these compositions.

In the first place, the alkalinity of the studied concrete mixes ranged from about 11.5 to 12.5, indicating a stable passivating layer on the steel surface. The silica fume, metakaolin mixtures containing about 900 $kg \cdot m^{-3}$ of cement (Mixes 5 – 8) all showed pH values around 12.0 and the MK mix with the lower cement content of 600 $kg \cdot m^{-3}$ (Mix 9) resulted in a slightly lower pH of about 11.5. The chloride ingress assessed using the silver nitrate solution showed a significantly lower chloride penetration depth of only 2 – 4 mm for all the metakaolin concretes (Mixes 6 – 10), which had significantly lower permeability depths of about 2 – 4 mm compared to all the others, probably due to the chloride binding effects of the aluminates in it. The ASTM standard mortar (Mixes 1 – 2) showed the highest permeability depths at approximately 40 mm. The silica fume (SF) concretes also exhibited relatively higher chloride penetration compared to compositions containing metakaolin. The carbonation depth is shown in Figure 6. and measured using a phenolphthalein indicator after CO_2 exposure, which also showed that the MK-based concretes exhibit lower carbonation

Table 6. Corrosion characteristics of the UHPC.

Mix no.	Concrete composite	90 day comp. strength (f_c)* (MPa)	pH value	Chloride migration depth (mm)	Carbonation depth (mm)	Chemical attack (28 day)	
						wt. loss (%)	strength loss (%)
1.	N56S0P0	43.43 (3.2)	12.31	40	6	32	42
2.	N56S0P2	59.51 (2.5)	12.25	40	5	31	43
3.	N47S20P2	66.23 (1.8)	11.71	7	4	46	35
4.	N9S0P2	102.00 (2.9)	11.54	7	0	36	55
5.	U9S20M1	146.6 (2.3)	12.13	12	2	39	41
6.	U9K15M1	170.16 (2.7)	11.77	4	0	25	37
7.	U9K20M2	151.78 (2.2)	12.26	2	1	35	76
8.	U9K25M2	188.19 (2.1)	12.02	2	1	27	58
9.	U6K20M2	118.74 (3.5)	11.57	3	1	31	82
10.	U12K20M2	161.7 (1.8)	-	2	0	23	62
11.	U9Z20M1	88.78 (1.6)	12.21	10	4	41	45
12.	U9LP20M2	141.49 (2.3)	-	8	0	26	60

*The values in brackets are the standard deviations.

Figure 6. Carbonation depth measurement of the MK based UHPC with the addition of fibres.

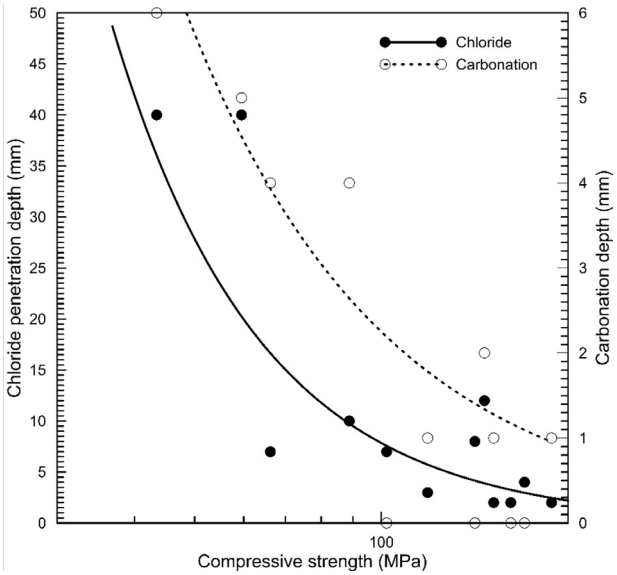

Figure 7. Variation in the chloride migration and carbonation depths with the strength.

depths compared to the SF and ASTM mortars. In fact, the values follow a very similar trend to that observed in the chloride migration. These results are plotted against the compressive strengths achieved and are presented in Figure 7, which shows a reasonable correlation.

X-ray diffraction characteristics

The X-ray diffraction characteristics of the concrete constituents are given in Figure 8. The XRDs show the diffraction peaks representing the constituent chemicals in each of these concretes.

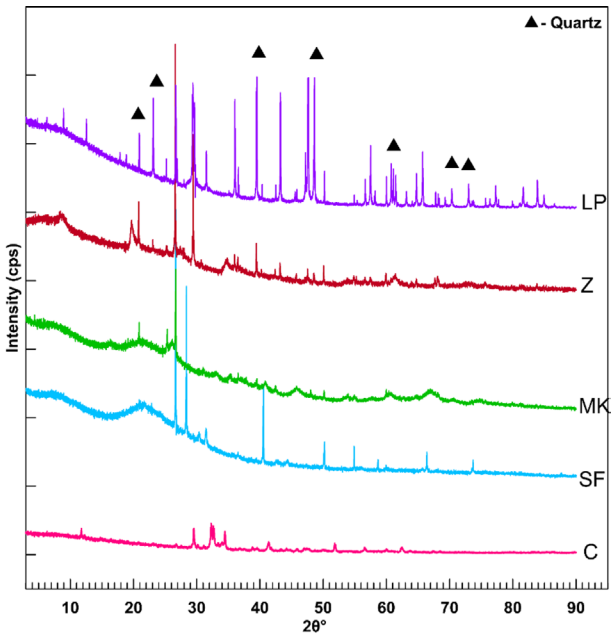

Figure 8. X-ray diffraction characteristics of the concrete constituents.

However, a notable and significant observation, especially for pozzolanic materials, is the presence of a diffused band seen as a hump in the curve at a 2θ of about 22°, as clearly visible in the case of SF shown in Figure 8. This indicates the presence of amorphous silica, which is highly reactive in alkaline environments of cement compositions [38]. Besides SF, a similar but smaller hump is also seen in the case of MK, indicating the presence of reactive silica. Metakaolin and zeolite show minimal crystalline phases compared to the silica fume. Naturally, the LP, QP, and QS display abundant crystalline phases of silica, which are observed as quartz in later concretes.

The XRD patterns of the different cementitious compositions studied are presented in Figure 9. The crystalline phases of quartz (SiO_2), portlandite (CH), tobermorite (CSH), ettringite (Aft), hydrogarnet (CAH), alite (C_3S), belite (C_2S), and celite (C_3A) were analysed using the Rietveld refinement technique. A higher amount of unhydrated clinker (C_3S) was found in Mix 10, probably due to its higher cement content compared to Mix 9 and 10. Among these, Mix 9 showed greater hydration of the alite and belite phases. Mix 8 exhibited relatively low levels of unhydrated phases and achieved the highest compressive strength of approximately 190 MPa, even when using only metakaolin as the binary component. In comparison, the composition with SF only reached about 146 MPa. This indicates that silica fume, as the primary SCM, and MK as a ternary additive are not strictly necessary. The phase composition analysis revealed that the highest calcium hydroxide (CH) content was present in Mixes 1, 6, and 10, mainly due to the high cement content of the concrete (mix 10) or the limited or absent pozzolan content in Mixes 6 and 1.

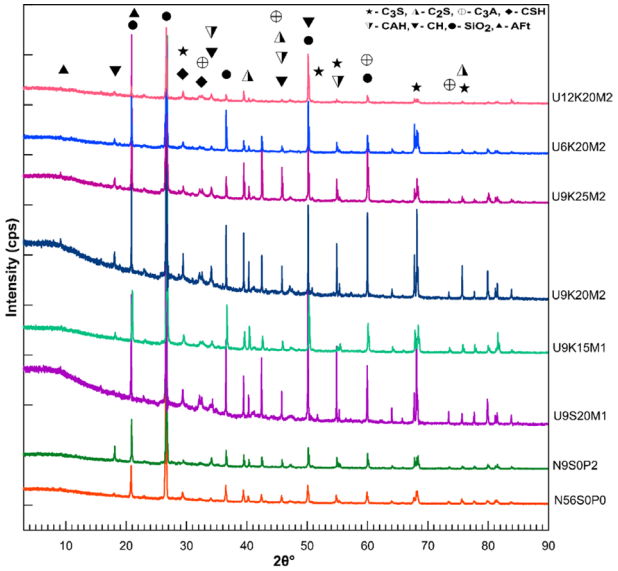

Figure 9. X-ray diffraction characteristics of the concrete compositions.

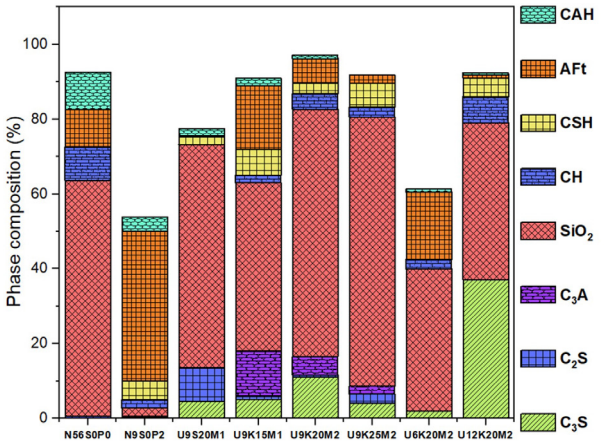

Figure 10. Phase composition of the investigated concrete compositions.

The phase composition of these cementitious composites was analysed using Rietveld refinement, which quantifies the mineralogical phases present in the hydrated matrix (Figure 10). Due to the low water binder ratio and high cement content, unhydrated clinker phases were observed in Mixes 7 and 8 in small amounts, while a relatively higher proportion was detected in Mix 10. In contrast, Mix 9, containing 600 kg·m^{-3} of cement, showed minimal unhydrated phases, indicating nearly complete hydration. Additionally, the formation of C-S-H gel was confirmed across all the mixes, with mix 8 exhibiting the highest content, correlating with its favourable hydration conditions.

Sustainability characteristics

The sustainability of the cementitious compositions is assessed by their global warming potential (GWP), carbon intensity (GWP/MPa), embodied energy (EE), and cost. These factors are mainly affected by the cement content, fibre volume, and superplasticiser percentage, as producing them consumes the most energy. It is more relevant to analyse these parameters based on their contribution per unit of strength rather than their direct impact to better demonstrate their usefulness in construction practice. In this context, Table 7 shows various environmental parameters, the cost per unit of strength, and binder efficiency. A close look at this table clearly indicates that most studied cementitious compositions have values similar to those of conventional concrete mixes currently in use. The CO_2 intensity is notably lower in most metakaolin-based UHPC compositions, while the embodied energy per unit of strength remains nearly the same. However, the cost per MPa seems to depend on the fibre content in the matrix and may be comparable to, or even lower than, that of traditional fibre mixes. Ultimately, it is evident that using metakaolin as a supplementary cementitious material is effective; the binder intensities calculated for UHPFRC compositions are certainly lower than those of most conventional mixes.

Table 7. Efficacy and sustainability aspects of the studied cementitious compositions.

Mix no.	Concrete composite	CO_2 intensity per MPa [35, 36] (kg CO_2/m^3/MPa)	EE/MPa [37] (MJ/kg/m^3/MPa)	Cost per MPa (Euro/m^3/MPa)	Binder intensity [36] (kg/m^3/MPa)
1.	N56S0P0	14.44	65.38	1.16	12.99
2.	N56S0P2	10.67	51.18	1.05	9.48
3.	N47S20P2	8.36	36.90	0.92	8.52
4.	N9S0P2	8.44	48.96	0.87	8.82
5.	U9S20M1	7.72	46.36	1.85	7.72
6.	U9K15M1	6.72	61.13	1.53	6.16
7.	U9K20M2	9.06	58.60	2.94	7.12
8.	U9K25M2	7.27	46.89	2.32	5.98
9.	U6K20M2	9.49	58.13	3.36	6.06
10.	U12K20M2	9.77	63.48	2.78	8.91
11.	U9Z20M1	15.16	75.61	3.10	12.16
12.	U9LP20M2	9.11	57.38	2.83	7.63

CONCLUSIONS

The present study on the development of sustainable ultra-high-performance concrete (UHPC) incorporating metakaolin emphasises its potential as an effective supplementary cementitious material. It was observed that MK compositions delivered significantly higher strengths and performances than the commonly used silica fume composition. Based on this extensive research on the strength, porosity, permeability, chemical resistance, corrosion characteristics, and environmental sustainability parameters, binary cementitious mixtures containing metakaolin perform well and serve as effective alternatives to silica fume, the most commonly preferred SCM. The main findings to date are as follows.

- The binary cementitious compositions containing MK demonstrated superior efficiency, achieving a peak compressive strength of approximately 190 MPa, while the commonly adopted silica fume combination could realise only about 146 MPa.
- Considering the fairly large number of investigations utilising metakaolin along with the results of the present study an overall water binder ratio to strength relationship was proposed.
- It is also seen that the flexural and tensile strengths of all the studied compositions, including the conventional compositions, are very low particularly proportional to the compressive strength of the cementitious compositions. All the investigated compositions had a very good compaction level as indicated by the ultrasonic pulse velocities of over 4.5 $km \cdot s^{-1}$.
- The permeability characteristics like the water absorption and capillary permeability of the MK based compositions indicate a highly dense and very low porosity system. This is clear from the host of investigations and studies based on several international test methods performed and compared with the durability benchmarks of the CEB recommendations.
- All the compositions exhibited pH levels of around 11.5, suggesting no significant depletion in the pH of the compositions due to the large pozzolanic participation of metakaolin.
- The chemical resistance as well as the chloride permeability and carbonation depth were observed to be very low particularly in MK concretes, affirming their superior corrosion resistance and long-term durability.
- The XRD analysis, supported by Rietveld refinement, showed increased formation of calcium silicate hydrate (C-S-H) in the 25 % MK mix. Complete hydration was observed in Mix 9 with 600 $kg \cdot m^{-3}$ cement, while Mix 10 with 1200 kg·m-3 cement showed unhydrated clinker, revealing compositional and hydration efficiency differences.
- From a sustainability perspective, MK concretes offer promising environmental benefits. However, a higher fibre volume and cement content could result in a higher Global Warming Potential (GWP), Embodied Energy (EE), and cost.

Overall, metakaolin proved itself to be a highly effective and sustainable pozzolan and could be an excellent alternative to silica fume, delivering exceptional results in terms of the strength, durability, and long-term performance, while aligning with eco-conscious concrete design goals.

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