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Influence of Ultrafine Metakaolin in Improving the Compressive Strength and Durability Properties of Concrete Reference S. W. M. Supit, R. Rumbayan, and A. Ticoalu, "Influence of Ultrafine Metakaolin in Improving the Compressive Strength and Durability Properties of Concrete," Advances in Civil Engineering Materials 10, no. 1 (2021): 210-222. <https://doi.org/10.1520/ACEM20180059> ABSTRACT This research reports on the effects of using ultrafine metakaolin to improve the durability properties of concrete. The particle size of ultrafine metakaolin was obtained using high-energy milling with 2 h of grinding.

An experimental investigation was carried out by replacing portland composite cement with 5 % and 10 % ultrafine metakaolin. The results show that the optimum amount of ultrafine metakaolin in concrete mixes is 10 % by weight. For instance, the compressive strength of the concrete specimens with 10 % ultrafine metakaolin (UM-10) improved the compressive strength by 123 % at 3 days, 85 % at 7 days, and 53 % at 28 days, respectively. The results from water sorptivity and volume permeable void tests also confirmed the significant effects of ultrafine metakaolin in terms of it improving the durability resistance and increasing the density of the concrete.

The water sorptivity value of the UM-10 sample was found to be 76 % and 68 % lower compared to the control concrete (PC). The percentage of the volume of the permeable voids in UM-10 was also reduced at about 70 %, indicating the modification of the pore size distribution because of the ultrafine sizes of the metakaolin. The results were confirmed by microstructure analysis such as scanning electron microscopy/backscattered electron image, X-ray diffraction, and differential thermal analysis/thermogravimetric analysis conducted on hardened cement paste with and without ultrafine metakaolin.

It was concluded that the addition of ultrafine metakaolin influences the pore modification and reduces the calcium hydroxide (CH) content, thus initiating the formation of calcium silicate hydrate gel as one of the beneficial effects of amorphous ultrafine metakaolin that results in the enhancement of the performance of the cement concrete composites with ultrafine metakaolin. Keywords ultrafine metakaolin, compressive strength, durability, water sorptivity, volume of permeable voids, microstructure Introduction The durability of concrete depends largely on the materials used when producing it.

The use of economical materials including the use of local natural resources as supplementary cementitious material is one way of improving the cost-effectiveness of a construction project. Among the many supplementary cementitious materials that have been extensively investigated such as fly ash, silica fume, rice husk, and slag, kaolin clay is one of the materials that also exhibits cementitious properties with a high silica and aluminum content. According to ASTM C618-19, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, 1 kaolin is classified as a natural pozzolan (class N).

Materials classified as pozzolans may not have cementitious properties or only have a few cementitious properties, but their very small particle size means that they can undergo chemical reactions with calcium hydroxide (CH) at a regular temperature and in the presence of moisture as part of forming cementitious mixtures.² Supit, Rumbayan, and Ticoalu³ reported that kaolin has a particle size range from 0.5 to 2 μm and is a highly reactive pozzolan. To obtain metakaolin, kaolin clay is calcined at a temperature approximately between 500°C and 800°C,⁴⁻⁶ with the reaction as expressed in the following formula: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$ (1) Based on some of the previous experimental works, the addition of metakaolin has the potential to produce more economical cement concrete mixtures by reducing permeability, increasing strength, and influencing the durability of the cementitious materials.

An early study on the effect of metakaolin by Curcio, DeAngelis, and Pagliolico⁷ indicated that superplasticized mortars with 15 % metakaolin (by weight of cement) exhibited a 15 % higher 28-day compressive strength compared to mortar without kaolin. In another study, Sayamipuk⁸ found that mortar containing 30 % metakaolin exhibited the highest compressive strength, whereas Batis et al.⁹ reported that 10 % metakaolin contributed to the strength improvement of the cement mortar. Similar findings were also reported in Supit, Rumbayan, and Ticoalu³ who recently investigated early and later age compressive strength because of the addition of 10 % metakaolin to the concrete.

It was found that the compressive strength of 10 % metakaolin concrete exhibited 50, 45, and 25 % higher compressive strengths at 3, 7, and 28 days, respectively, in comparison to typical concrete. Additionally, the addition of up to 10 % metakaolin in pozzolan portland cement concrete mixes has been shown to produce a high compressive strength, greater durability, and less water permeability. In mortar, the use of 5-20 % metakaolin for partial cement replacement also improved the flexural strength by up to 16 %, which is higher than the control mortar according to Yazv?c?, Arel, and Anuk.¹⁰ The reaction products that are due to metakaolin addition densified the interfacial transition zone, with a decrease in the volume of the pores (Poon, Kou, and Lam¹¹).

In recent years, the use of ultrafine materials including nanomaterials has been considered in the application of construction materials especially in mortar and concrete. The characteristic of very fine particle sizes can increase the surface area (per unit mass) and result in a corresponding increase in chemical reactivity (Sobolev et al.¹²; Charmichael, Prince, and Arulraj¹³). This provides a denser microstructure, reduces porosity, and improves strength (Supit and Shaikh¹⁴).

The development of new techniques to characterize materials at the ultrafine scale has inspired many ideas when it comes to studying the properties of the cement composites that are due to the addition of ultrafine particles. One of the advancements made was the discovery that the addition of metakaolin (in ultrafine size) can improve the mechanical properties of mortar and concrete. Karthikeyan and Dhinakaran¹⁵ reported the performance of concrete with 5, 10, and 15 % SiO₂ and metakaolin obtained using a planetary ball mill for an optimum period of 1 h.

Their experiments showed that the increase in the compressive strength and corrosion resistance of the concrete specimens was due to the addition of 10 % SiO₂ and 5% metakaolin. Their results concluded that the performance of concrete with ground metakaolin was better than that of concrete with SiO₂. On the use of nano-metakaolin, Morsy, Alsayed, and Aql¹⁶ reported that the increase in the compressive and tensile strength of the mortars was to the addition of 8 % nano-metakaolin of 49 % and 8 %, respectively.

Aiswarya, Arulraj, and Narendran¹⁷ found that the compressive strength of the concrete at 28 days has increased approximately by 30 % for samples where there was a 10 % replacement of cement with nano-metakaolin. Furthermore, in their study, a significant improvement was also observed in the split tensile strength results. The experimental result from Abo-El-Enein et al.⁶ similarly reported on the beneficial effect of replacing

cement with 10 % nano-metakaolin in normal cement concrete, whereas Morsy et al.¹⁸ reported the enhancement of the compressive and flexural strength of the cement mortar with 15 % nano-metakaolin under thermal treatment. The study by Morsy et al.¹⁸ revealed that the compressive and flexural strength increased when the temperature reached 250°C and then decreased as the exposure temperatures increased up to 800°C.

The reduction is suggested to be due to the occurrence of microcracks and macrocracks in the mortars because of the high temperature. Recently, the utilization of nano-metakaolin as an additive in ultrahigh performance concrete has been reported by Muhd Norhasri et al.¹⁹ They found that the 1 % inclusion of nano-metakaolin with a particle size of 176 nm was obtained using high-energy milling.

They charted the optimum effect in relation to the compressive strength when combined with 10 % micro-metakaolin (by weight of cement). The result showed that the filling effect of the nano-metakaolin particles contributed to the strength development at 3-7 days and the pozzolanic reaction started at 14 days of age. In their study, it was also observed that the compressive strength of the nano-metakaolin specimen was increased and showed a better strength compared to the ordinary portland cement and micro-metakaolin concrete samples.

A similar observation was also reported by Fadzil et al.²⁰ In the study by Shoukry et al.,²¹ the effectiveness of nano-metakaolin was found more beneficial as mineral additives in terms of improving the microstructure and flexural strength of fiber-reinforced cementitious composites. In their study, they also found that the CH content of the cement paste with 10 % nano-metakaolin had decreased to 42 % because of the pozzolanic activity of the nano-metakaolin, and they remained relatively constant when the nano-metakaolin replacement ratio was higher than 10 %.

Despite the positive influence of using micro- and nano-metakaolin in relation to the mechanical properties of mortar and concrete, the effects of ultrafine metakaolin (UM) on the durability of cement concrete and its microstructure characterization has not been intensively explored. This experimental investigation focuses on the compressive strength development, water sorptivity, and volume percentage of the permeable voids of the cement concrete containing UM. Materials Portland composite cement (PCC) and UM were used as the main materials in all mixes. The kaolin was obtained from Toraget Village, Minahasa Region in North Sulawesi Province, Indonesia.

It was sun/air dried for about 8 h and then the sample was dried in the oven at 110°C for 24 h. After drying, the lumped kaolin clay was milled and later it was sieved using

stainless steel sieve with No. 100 openings. Afterward, it was calcined in an incinerator at 800°C with constant temperature for 6 h. The metakaolin was then refined to an ultrafine size by using high-energy milling. Before grinding, the metakaolin powder was dried at 105°C for 2 h and then were crushed using high-energy milling type E3D. The milling time was set for 2 h and conducted at CV Nanotech Indonesia.

The chemical analysis and physical properties of cement and UM from Toraget Village are summarized in Table 1. Moreover, the characteristics of ultrafine metakaolin based on X-ray diffraction (XRD) analysis is shown in figure 1. The XRD pattern shows that UM used in this experiment is amorphous material and is relatively less crystal leading to reaction with lime and hence makes a good synthetic pozzolan (Yanguatin, Tobo'n, and Ramírez22). The particle size distribution of the UM was measured using a Delsa Nano Particle size analyzer.

Based on the particle size analysis, it was found that the average size of UM used in this experiment was 196 nm with the SiO₂ content in UM is 47 %, which is more than in PCC. Experimental Program Four parts of the experimental program were conducted where the variations of mortar and concrete mixtures were prepared as in Table 2. FIG. 1 X-Ray diffraction of ultrafine metakaolin. TABLE 1 Chemical Composition of PCC and ultrafine metakaolin

Chemical Analysis	PCC, %	Ultrafine Metakaolin, %
SiO ₂	8.43	47.00
Al ₂ O ₃	1.65	32.00
Fe ₂ O ₃	4.81	3.43
CaO	73.12	2.53
MgO	...	...
K ₂ O	...	1.10
Na ₂ O	...	...
SO ₃	2.71	1.9

TABLE 2 Mixture proportions of cement mortar and concrete with different percentages of ultrafine metakaolin (kg/m³)

	Mortar	Concrete	Materials	PCC	UM-3	UM-5	UM-10	PCC
UM-5	UM-10	Portland composite cement (PCC)	450	436.5	427.5	405	553	526
498		Ultrafine-metakaolin (UM)	0	13.5	22.5	45	0	28
55		Fine aggregate	1,125	1,125	1,125	1,125	1,125	1,125
565		Coarse aggregate	0	0	0	0	976	976
976		Water	207	207	207	207	223	223
223								

The first part determined the optimum dosage of UM based on the compressive strength development of cement mortar at 7 and 28 days. In this part, PCC was replaced by UM at 3, 5, and 10 % (by weight) of binders.

In the second part, the optimum content of UM that exhibited the strongest resistance on compression in the mortar was used in the concrete mixture to evaluate the compressive strength development at 3, 7, and 28 days. For each age, three specimens were tested, and the mean value of these measurements is reported. The third part evaluated the effects of UM addition on durability properties of cement concrete by means of water sorptivity and volume permeable voids tests at 7 and 28 days.

The microstructure and phase changes on cement paste containing UM was analyzed in

part 4 based on scanning electron microscopy (SEM) image, XRD, and differential thermal analysis/thermogravimetric analysis (DTA/TGA) analysis. Experimental Methods A Hobart mixer was used for mixing all types of mortars at an ambient temperature of approximately 25°C using a water/binder ratio of 0.46 and a sand/binder ratio of 2.5. Before pouring into the mixer, the raw powder materials including cement and UM were weighed and dry mixed by hand until a homogeneous consistency was obtained.

Dry sand, cement, and UM were then mixed in a high-speed Hobart mixer for approximately 2-3 min. Water was added thereafter and mixed for another 2-3 min. The 50-mm mortar cubes were cast into 50-mm cube molds and demolded after 24 h. The mortar samples were **cured in water at room temperature** until the testing days. In concrete mixes, cement, UM, and aggregates were dry-mixed uniformly, then the mixture of water and superplasticizer was poured in and stirred for several minutes. Mixtures were then cast into a standard cylinder having a diameter of 100 mm and a height of 200 mm **and cured in water at room temperature** and **demolded 1 day after** testing.

COMPRESSIVE STRENGTH The compressive tests **of mortar and concrete** specimens were performed using a universal testing machine in the concrete laboratory at Manado State Polytechnic, Indonesia. To accomplish the tests, ASTM C109/C109M, **Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)**,²³ was followed for defining the compressive strength of mortar and ASTM C39/C39M-20, **Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens**, for **the compressive strength of concretes**.²⁴ **WATER SORPTIVITY** This experiment follows ASTM C1585-20, **Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes**,²⁵ where the sorptivity value of each type of mixes was obtained.

The specimens of 100 mm in **diameter and 50 mm in** thick disks were measured to determine the rate of water absorption **after 7 and 28 days of** water curing. The principal of this test is to regularly measure the increase in the mass of a specimen resulting from absorption of water as a function from 1 min to the first 6 h (initial absorption). The testing setup **can be seen in figure 2**, where one surface of the specimen supported on rods is in free contact with water (no more than 5 mm above the base of the specimen), whereas the others are sealed with nonabsorbent coating.

The absorption can be calculated by dividing the mass changed with the cross-sectional area of the test specimen and the density of water. **The cumulative water absorption (I) increases as the square root of elapsed time (t)**, therefore the sorptivity value (S), can be computed by $S = I/t^{1/2}$. **FIG. 2 Schematic illustration of sorptivity test setup. VOLUME**

OF PERMEABLE VOIDS This test adopted ASTM C642-13, **Standard Test Method for Density, Absorption, and Voids in Hardened Concrete**,²⁶ to determine the density and voids in hardened concrete containing UM.

The 50-mm cut cylinder specimens were prepared after curing, **dried in the oven** at 110°C for 24 h, and then immersed in water for 48 h. After being removed from water, the weight **of the saturated surface dry** specimens were measured and then put in a water bath at 105°C for 5 h of boiling. The weights of the boiled specimens were then recorded with dried mass and mass in water to calculate **the volume of permeable pore space**.

SEM/BACKSCATTERED ELECTRON IMAGES The analysis of the morphology **of the cement paste** samples was conducted through SEM/backscattered electron (BSE) images analysis using 10 µm in width and 1,000x magnification. The cut paste samples were mounted in resin, polished using water-free lubricant, and covered by a layer of platinum to ensure that the samples were electrically conductive. The image contrast of **BSEs can be generated** by the composition of the different phases relative to their average atomic number and by the differential brightness in the image.

The residual cement grains and the unhydrated phases are the brightest feature, followed by CH, carbonate aggregate, calcium silicate hydrate (C-S-H), and pores for the black color. **XRD** This test was conducted to analyze the crystalline phases **of cement paste samples** based on its diffraction image. The sample for this analysis was prepared at approximately 3 g of cement paste powder with particle sizes of 10-20 µm that grinded using laboratory porcelain mortar after curing days. The analysis was conducted at a speed of 0.5°/min with 2θ angle from 10° to 50° using a D8 Advance Diffractometer (Bruker-AXS). The voltage of and current used for the analysis were fixed at 40 kV and 30 mA, respectively. At every testing date, the cement paste samples were cast and refined for the analysis.

DTA/TGA ANALYSIS In this analysis, the 50 mg of the well-powdered sample in a 110-µL platinum crucible was heated from ambient to 1,000°C at 20°C per minute in a nitrogen atmosphere flowing at 100 mL per minute. The Linseis instrument type STA PT 1600 was used to measure heat flow and weight changes in a material **as a function of temperature of time in a controlled atmosphere**. This experiment can also determine the amount of uncarbonated CH in percent on cement paste with and without UM using simple formula (Taylor²⁷): Percentage of CH = % loss of water mass x Molecular weight of CH / Molecular weight of CH₂ (2) **Results and Discussion** **EFFECT OF UM ON COMPRESSIVE DEVELOPMENT OF MORTAR AND CONCRETE** The effect of UM **on the compressive strength of cement mortar** and concrete is shown in figure 3A and 3B.

Figure 3A shows that the compressive strength of mortar containing 10 % UM exhibited higher strength compared to samples without UM (control sample) and samples with 3 % and 5 % UM, respectively. The UM-10 sample achieved a compressive strength of 31 MPa and 40 MPa at 7 and 28 days, respectively. The increase is about 121 % at 7 days, and at 28 days, the strength improvement is obtained, which is about 100 % higher than the reference PCC mortar. The error bars lie within one standard deviation as measured based on three mortar samples in each type of mix. An increase of strength development can be also observed on mortars containing 3 % and 5 % (UM-3 and UM-5).

However, the compressive strength development of UM-3 and UM-5 mortars does not show any significant improvement as seen in UM-10 mortar. The similar trend can be found in concrete with UM, as illustrated in figure 3B. Replacing PCC with 5 % and 10 % UM was found to increase the FIG. 3 Compressive strength of cement (A) mortar and (B) concrete containing UM at 7 and 28 days. compressive strength of concrete and confirms that the optimum dosage of UM in these mixes is 10 % by weight of cement. The compressive strengths of concrete containing 10 % UM reaching the value of 29, 37, and 46 MPa at 3, 7, and 28 days, respectively.

This is about 123, 85, and 53 % higher than the reference PCC concrete at 3, 7, and 28 days, respectively. Abo-El-Enein et al.⁶ also found the effectiveness of using UM with particle sizes ranging from 50-200 nm at 10 % replacement (by weight), whereas Fadzil et al.²⁰ found the optimum replacement of nano-metakaolin obtained by milling for 24 h was at 7 %. The beneficial effects of UM are suggested because of the physical filler characteristics of UM and also the pozzolanic reaction between amorphous aluminosilicate in UM and free CH liberated during cement hydration, which produces extra C-S-H that has a low calcium/silicon ratio and calcium aluminates hydrate phases that filled in the pore system.¹⁸ However, a percentage of replacement higher than 10 % will decrease the compressive strength because of the dilution effect of cement content, which has more hydraulic properties than UM.²⁸

EFFECT OF UM ON WATER SORPTIVITY OF CONCRETES Figure 4A and 4B illustrate the cumulative water absorption of all types of concretes cured at 7 and 28 days, against the square root of time.

The three lines in the figures refer to the average of three samples tested from each type of mix. It can be observed that the inclusion of UM has reduced the rate of water absorption of concrete at both 7 and 28 days. The figures also present the effect of curing time on the sorptivity of concrete samples. Furthermore, according to the summarized sorptivity values on Table 3, the water sorptivity of concrete with 10 % UM is 6 and FIG. 4 Water absorption of cement concrete mixes containing UM at (A) 7 days

and (B) 28 days.

TABLE 3 Sorptivity value of various concretes containing UM Sorptivity Value ($\times 10^{-4}$ mm/s $^{1/2}$) Type of Mixes 7 Days 28 Days PCC 25 16 UM-5 7 5 UM-10 6 5 5 ($\times 10^{-4}$ mm/min $^{1/2}$) at 7 and 28 days, respectively, which is 76 % and 68 % lower compared to the sorptivity value of cement concrete. A similar trend is also noticed on concrete with 5% UM. This is an indication that the usage of UM in concrete has densified the microstructure and has increased the density, thus providing greater resistance to the water absorption by capillary suction.

Similarly, Ramezaniapour²⁹ reported that the positive effect of metakaolin in reducing the water absorption by capillarity is due to the finer pores structure. This result is also in line with the experiment conducted by Samimi et al.³⁰ It was reported that replacing cement with metakaolin decreased the conductivity of concrete and refined the pore structure of concrete. Therefore, the finer particle sizes of metakaolin will optimize the filler effect in making a denser paste matrix, thus reducing the sorptivity values of concretes with UM.

The results are further confirmed by microstructure analysis through backscattered scanning electron images showing the less pores initiated in cement paste containing UM. EFFECT OF UM ON VOLUME OF PERMEABLE VOIDS OF CONCRETES The influence of UM on the volume of permeable voids (VPV) of concrete is shown in figure 5. It can be observed that the addition of 5 % and 10 % UM significantly reduced the VPV of concrete samples. Based on the VPV results, a low volume of voids is achieved by concrete with 10 % UM (by weight), where the percentages of VPV reduced from 13 to 4 % at 7 days and 11 to 2 % at 28 days.

Because the permeability of concrete is influenced by the degree of hydration, the usage of UM has dramatically modified the entire pore size distribution and has thus decreased the volume proportion of large voids. Furthermore, because of its ultrafine size, UM addition in cementitious concrete may improve the interfacial zone, fill the voids between cement grains, and enhance the microstructure of UM cement pastes. MICROSTRUCTURAL ANALYSIS OF CEMENT PASTE CONTAINING UM The examination of cement paste microstructure containing 10 % UM was conducted at 28 days and compared with the image of the cement paste sample.

The composition of different phases was generated through BSE FIG. 5 Volume of permeable voids of cement concrete mixes containing UM at 7 and 28 days. images contrasted based on the differential brightness in the images. The anhydrous cement appears brightest, followed by CH and C-S-H, and the darkest part is voids or pores.

Based on figure 6A and 6B, it can be observed that many white and black areas in the cement paste sample indicate the unhydrated cement particle and voids, respectively.

On the other hand, the unhydrated cement particle and voids are less in the sample containing 10 % UM. In the UM-10 paste sample, the presence of voids was minimal, and more amorphous C-S-H gels were visible. They are represented by the large number of grey to dark areas around the remaining unhydrated parts of cement grains, which indicate the hydration products and the consumption of CH, hence triggering the strength development of cement paste samples. The filling effect of UM particles also minimizes the internal capillary pores and makes the microstructure of the hardened cement paste uniform, compact and dense. Fan et al.³¹ also reported similar observations where the addition of kaolinite clay was found to reduce the average pore diameter because of its filler effect and accelerator of cement hydration.

Furthermore, the results from the microstructural analysis confirm the results from compressive tests and water absorption tests. XRD ANALYSIS OF CEMENT PASTE WITH UM The crystalline phases occurring during cement hydration after curing for 7 and 28 days are studied through XRD analysis. An analysis of 2 θ angle from 10° to 70° was carried out at a speed of 0.5°/min. XRD peaks of cement pastes with and without 10 % addition are shown in figure 7. As can be observed in the XRD scale, the CH has a high peak pattern located at 2-theta angle of 18°, 34°, and 47°. The peak at 2-theta = 29° is related to the calcite phase.

In this analysis, this CH peak is regarded as an important sign of the performance of the samples. By analyzing the amount of CH in XRD patterns, the C-S-H concentration can be indirectly determined. From figure 7, it can be seen that the intensity of CH peaks in the cement paste sample FIG. 6 SEM/BSE images of cement paste samples containing UM at 7 and 28 days. FIG. 7 XRD patterns of blended cement mortar with UM at (A) 7 days and (B) 28 days. containing 10 % UM was decreased compared to the intensity in cement paste without UM.

The significant reduction can be seen at 2-theta angle of 18° and 34°, where the intensity of CH in cement paste at 7 and 28 days decreased for about 70 % after the UM addition. As the curing time was increased, the peaks intensities of CH were also increased (see fig. 7B). This can be indicative as due to the low rate hydration of calcium silicates (C2S and C3S) with the formation of C-S-H and liberation of CH as also reported by El-Diadamony et al.²⁸ Moreover, the presence of calcium carboaluminate can also be observed and suggested as the results of UM-pozzolanic cement hydration formed by the reaction of atmospheric carbon dioxide (CO₂) with C-A-H.³² However, because the peak characteristic of calcite is overlapped with C-S-H gel, the intensity of C-S-H could

not be clearly determined.

DTA/TGA ANALYSIS OF CEMENT PASTE CONTAINING UM DTA/TGA measurement has been performed on 7 and 28 days of cement paste samples with and without UM to investigate the presence of phases from hydration reaction during test conditions. Three major endothermic peaks in DTA thermograms of cement paste containing UM are shown in the figure 8. The first peak is located at around 110°C-130°C and is associated with the decomposition of C-S-H/ettrin- gite (AFt). The second peak is located at around 470°C-479°C and is related to the decomposition of CH, whereas the third peak is located at around 700°C-800°C and is related to the decarbonation of calcite (CaCO_3).

It can be observed from the figure that the intensities peaks for CH and CaCO_3 were increased as the curing time increased up to 28 days because of the hydration progress. Comparing the curves of the PC sample with those of the UM-10 FIG. 8 TGA/DTA analysis of (A) cement paste and (B) UM-10 samples at 7 days. FIG. 9 TGA/DTA analysis of PCC and UM-10 paste samples at 7 days and 28 days. TABLE 4 Calcium hydroxide content in cement pastes containing ultrafine metakaolin Amount of CH, % Type of Mixes 7 Days 28 Days PCC 6.18 9.01 UM-10 4.04 4.22 sample at 7 and 28 days, it can be observed that the dehydration intensity of CH at 473°C is less in the UM-10 paste sample. This indicates CH consumption that is due to UM addition through the formation of C-A-H and C-A-S-H on the expense of C-S-H.²⁷ On the other hand, TGA curves in figure 9 show the changes in mass of cement paste containing UM that are due to heating from room temperature to about 900°C.

The mass changed can be used to assess CH content based on the Taylor formula, as explained in the section "DTA/TGA Analysis." As can be observed from the results presented in Table 4, the CH content at 7 days was 6.18 % and 4.04 %, whereas at 28 days, the CH content was in the value of 9.01 % and 4.22 % for PC and UM-10 samples, respectively. These results are supported by the results gained in the experiment conducted by El-Diadamony et al.²⁸ It was reported that metakaolin acts as a nucleating agent and a filler that can accelerate the hydration rate and lead to a decrease in porosity.

At 28 days, the amount of CH in UM-10 decreased in weight at 479°C, indicating the consumption of CH as it either turned into C-S-H or absorbed CO_2 to form calcite. According to the calculation, the CH amount of PCC and UM-10 samples are 9.01 % and 4.22 %, respectively. The CH amount in UM-10 paste is 30 % lower than the CH amount of cement paste, indicating that the mass loss and the reduction of CH content at 28 days are due to 10 % UM addition. The DTA/TGA results also confirmed the XRD results, showing the reactivity of 10 % UM in acting as nucleating agent, which accelerates the

hydration rate of PCC. Conclusions Conclusions of this experimental study are as follows:
1.

The usage of UM in mortar and concrete was effective in increasing the compressive strength of samples tested at 3, 7, and 28 days, respectively. The optimum compressive strength was achieved by mortar and concrete containing 10 % UM (by weight). It was observed that the improvement of compressive strengths in concrete with UM were approximately 123 %, 865 %, and 53 % higher compared to the compressive strength of control samples after 3, 7, and 28 days of curing. This indicates the influence of UM in promoting the hydration process, thus improving the compressive strength at early and later ages of concrete. 2.

In terms of water sorptivity and VPV results, the addition of 5 and 10 % UM have shown a positive contribution, increasing the density of cement concrete. The result shows that UM-10 concrete has sorptivity values of 6 and 5 ($\times 10^{-4} \text{ mm/min}^{1/2}$) at 7 and 28 days, which is 76 % and 68 % lower compared to the sorptivity of concrete without UM. On the other hand, the VPV of UM-10 concrete is only 4 % and 2 % at 7 and 28 days, respectively. It infers that UM particles have filled the internal capillary pores and make the microstructure uniform, compact, and dense. 3.

The results from SEM/BSE and XRD analysis confirm the influence of UM in improving the microstructure of cement pastes. The pore structure of UM-10 paste is denser than the control paste. Additionally, the intensity counts of CH in cement paste with 10 % UM at 7 days decreased significantly from 257 to 84 at theta angle of 18.18° , 252 to 89 at 34.24° , and 117 to 721 at 47.28° . A similar trend is also observed in the intensity counts of the UM-10 paste sample at 28 days. The reduction of CH indicates that the formation of more C-S-H in the system increases the compressive strength of UM mortar and concrete samples. 4.

The DTA/TGA results show the reactivity of 10 % ultra-metakaolin in reducing the CH content in the samples. Based on the Taylor formula, the amount of CH in the UM-10 paste sample at 28 days is 30 % lower than the CH amount of control samples, indicating that the mass loss and the reduction of CH content is due to the presence of 10 % UM. ACKNOWLEDGMENTS The authors wish to acknowledge the financial support from DIKTI through INSINAS 2016 Scheme, Indonesian Government. References 1.

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