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Performance of Cement Mortar Containing Micro and Ultrafine Metakaolin Binders

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***Abstract*— Research into the usage of locally available construction material is essential and beneficial in ensuring a cost-effective construction project. One of the natural resources that be used as supplementary cementitious material is metakaolin. This research aims to investigate the performance of mortar reinforced with micro- and ultrafine metakaolin based on compressive strength and water absorption tests. Locally sourced metakaolin was mixed in cement mortar after calcined at 800°C with a variation amount of 0%, 5%, and 10% by wt. The tests were conducted on the 50mmx50mmx50mm cube specimens after water curing at 7 and 28 days, following the ASTM-standards. Results show that specimens containing 10% of micro- and ultrafine-metakaolin (MK-10 and UM-10) exhibited the highest compressive strength and better water-resistance characteristics when compared to control mortar. In this case, the addition of 10% ultrafine metakaolin (UM-10) reached the highest compressive strength value with approximately 121% and 100% higher than the compressive strength of control mortar on the 7th and 28th day, respectively. Additionally, the water absorption of UM-10 at 28 days was found to be 86% and 30% lower than PCC and MK-10, respectively. Furthermore, X-Ray Diffraction (XRD) and Thermogravimetric graphs of pastes with micro- and ultrafine-metakaolin indicate a reduction of CH; therefore, the production of more CSH gel. The densification of cement paste with ultrafine-metakaolin is also confirmed by nitrogen adsorption analysis indicating ultrafine-metakaolin's inert filler effect in forming a denser matrix.**

***Keywords*—Metakaolin; compressive strength; water absorption; X-Ray diffraction; nitrogen adsorption.**

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I. INTRODUCTION

Portland cement (PC) in various compositions has been commonly used as the main binder in mortar and concrete mixture. When mixed with water, cement undergoes the hydration process, which will cause it to harden over time. Materials having this behavior are referred to as pozzolanic materials. Although cement is an excellent binder, cement production has become an issue of cost, high energy consumption, and pollution. Therefore, it is essential to invest in the research into minimizing the adverse effects of cement production while maintaining enough production for the demand. One of the options is to replace cement with pozzolanic materials that are more economical and environmentally-friendly. This research aims to investigate the replacement of a certain percentage of cement with metakaolin (MK), obtained from the calcination of kaolin clay. Kaolin clay consists of one tetrahedral (Si-O), and one octahedral (Al-O) layer with stoichiometric formula is $Al_2Si_2O_5(OH_4)$ [1]. It is deposited and can be found in several provinces in Indonesia, including North Sulawesi. Kaolin clay is normally calcined at a specific temperature of about 500-800^{0}C to obtain reactive metakaolin [2], [3].

According to ASTM C618 [4], metakaolin is one of the natural pozzolans (Class N) with a particle size around 0.5 to 2μm. This classification confirms the effectiveness of metakaolin. It has a cementitious property that reacts chemically with calcium hydroxide formings cementitious mixtures at a specific temperature in the presence of moisture [5].

Studies on the partial substitution of cement with metakaolin in cement composites reported a positive contribution to the improvement of mechanical properties of mortar and concrete [6]-[11]. The amount of MK that gives the optimum value of compressive strength differs from several studies. Vu [5] and Narmatha and Felixkala [7] reported that 15% is the optimum substitution at 28 days, while Sayamipuk in [8] has found that 30% MK has resulted in the highest compressive strength of mortar. Batis *et al.* [9]

also reported that the optimum percentage of cement replacement by metakaolin in mortar mixtures was 10%. A similar percentage, 10% replacement, improved the compressive strength of normal concrete and achieved high strength concrete [10], [11]. Research on water absorption characteristics of mortar and concrete specimens with metakaolin shows that the water resistance is improved. Supit *et al.* [6] found that the substitution of MK has increased the water resistance capacity of concrete specimens. This finding supports the result investigated in Duan *et al.* [12], which showed the microstructure improvement on the pore system and Interfacial Transition Zone (ITZ) of concrete.

Recently, scholars have recognized and studied nanomaterials due to its unique properties in improving the performances of cement-based materials. According to the previous studies, nanoparticles' inclusion is beneficial to the microstructure because of the nanoparticles' fineness and reactivity. They accelerate calcium hydroxide consumption and promote an additional calcium silicate hydrate condensed gel that makes the microstructure denser, which effectively decreases the permeability [13]. The addition of 10% ultrafine-metakaolin in concrete improved the 7^{th} day tensile and flexural strength by 21% and 15%, respectively [14]. The studies mentioned previously have provided important information that was used as the basic knowledge for this experimental study where the effect of ultrafine-metakaolin was considered. However, fewer reports on the water absorption and microstructure characterization of cement composites with micro- and ultrafine metakaolin are available. This research aims to experimentally investigate the performance of mortar containing micro- and ultrafine metakaolin, focusing on the water absorption and microstructural analysis. The results are expected to contribute to advancing future research in optimizing the use of metakaolin in the countries where this material is available.

II. Material and Method

A. Materials

This research uses metakaolin (MK), sand, water, and Portland-Composite Cement (PCC). The kaolin clay was calcined at 800^0C in the high-temperature refractory for 6 hours and finally converted into Metakaolin (MK). The micro-size metakaolin was then refined into ultrafine sizes using High Energy Milling apparatus for two hours of grinding (see Fig. 1). From the grinding process, the size of ultrafine-metakaolin (UM) was found to be 196 μm while the size of micro-metakaolin was around 10μm.

Table 1 shows the chemical composition of PCC and the micro and ultrafine-metakaolin. Based on the table, the total amounts of SiO_2+Al_2O_3+Fe_2O_3 in micro-metakaolin and ultrafine-metakaolin are 72.52% and 82.43%, more than 70%, thus can be used to replace cement partially, based on ASTM C618. Figure 2 shows the X-Ray Diffraction spectra of the ultrafine-metakaolin which was used to confirm its characteristic as an amorphous material.

The river sand with a fineness of modulus 2.3 and tap water was prepared before mixing. Superplasticizer type F used for the mixtures was Sikacim Concrete Additive supplied by PT. Sika Indonesia. The dosage was kept constant at 0.8% by the weight of cement.

TABLE I
CHEMICAL COMPOSITION OF MATERIALS (%)

Chemical Analysis	PCC	Metakaolin	Ultrafine-metakaolin
SiO_2	8.43	40.48	47.00
Al_2O_3	1.65	31.17	32.00
Fe_2O_3	4.81	0.87	3.43
CaO	73.12	1.20	2.53
MgO	-	3.65	-
K_2O	-	0.73	1.10
Na_2O	-	12.32	-
SO_3	2.71	2.59	1.9

Fig. 1 High energy milling apparatus

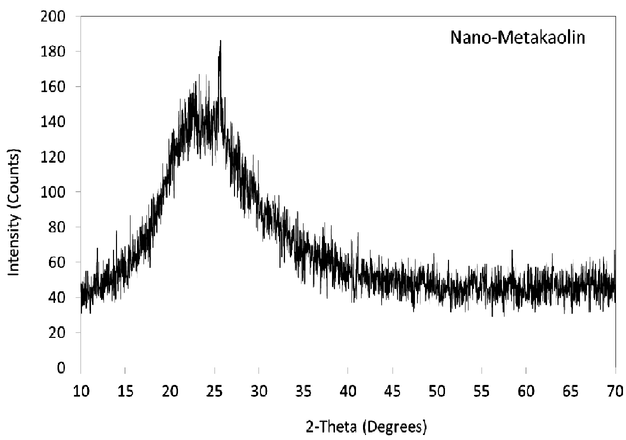


Fig. 2 XRD pattern of ultrafine-metakaolin

TABLE II
MIXTURE PROPORTIONS OF BLENDED CEMENT MORTARS (KG//M^3)

Mix	PCC	MK	UM	FA	W
PCC	450	-	-	1125	207
MK-5	428	22	-	1125	207
MK-10	405	45	-	1125	207
UM-5	428	-	22	1125	207
UM-10	405	-	45	1125	207

Notes: PCC=Portland-Composite Cement; FA=Fine Aggregate; W=Water

In this experiment, the study was conducted on mortars with 5% and 10% micro- and ultrafine-metakaolin (by wt.). The sand to binder ratio was kept constant at 2.5. As listed in Table II, the variation of mortar mixtures was cast in 50mmx50mmx50mm cube specimens for compressive strength and water absorption tests at 7 and 28 days after water curing. In the mixture proportions table, the control mixture is labeled PCC (denoted as Portland Composite Cement, which contains no metakaolin), while mortar mixture MK and UM are labeled as micro-metakaolin and ultrafine-metakaolin.

B. Flow Table Test

All mixture components are mixed with a pan mixer with the ratio of water/binder 0.46. Soon after mixing, the mortar's consistency is measured using Flow Table, as specified in ASTM C230 [15]. The flow table has a diameter of 255 mm, and the conical mold used to cast the flow specimen has dimensions of height 50 mm, a diameter of top opening 70 mm and bottom opening 100 mm, and thickness 5 mm. The flow of mortars was observed according to ASTM C 1437 [16]. Fig. 3 shows the test on the consistency of cement mortars with and without metakaolin using Flow Table.

For each variation, the value from the Flow Table is measured and recorded. When the consistency is right, the mortar is cast into (50 x 50 x 50) mm metal molds. After casting, specimens are then demoulded after 24 hours and submerged for 7 and 28 days of water curing.

Fig. 3 A flow test to measure the consistency of mortar using a flow table.

C. Compressive Test

Compressive strength is tested using an ELE Compressive Testing machine with a maximum compression load of 300 kN. The testing procedures were followed by ASTM C109 [17]. The average of compressive strength values from three mortar specimens on each mixture was taken as the compressive strength result.

D. Water Absorption Test

Water absorption of the specimens is measured by following the procedure on ASTM C1403-1 [18]. The specimens are weighed and then placed in a flat and watertight container (see Fig. 4). The samples are removed and weighed at selected times based on the standard and replaced again in water for the chosen period. The coefficient of capillary absorption *(k)* was calculated by dividing the amount of water that was absorbed in the concrete piece (A, gram) with the cross-sectional area (cm^2) multiplied with the square root of tested time in second.

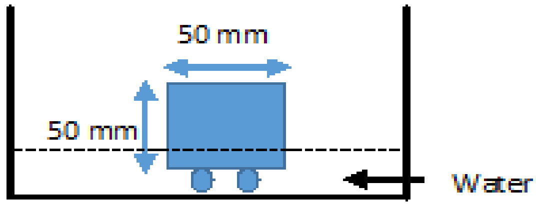


Fig. 4 Water absorption test set-up

E. X-Ray Diffraction

The crystalline phases of cement paste samples containing micro- and ultrafine-metakaolin were investigated through XRD test. The D8 Advance Diffractometer (Bruker-AXS) was used for this analysis using the speed of 0.5^o/min with 2θ angle from 10^o to 50^o. Each phase's intensity, such as calcium hydroxide, calcium silicate, and calcium silicate hydrate, can be obtained based on the diffraction image.

F. Thermogravimetric Analysis

The measurement of the heat flow and weight changes of cement phases were conducted through TGA analysis. The Linseis instrument type STA PT 1600 was used to measure the paste powdered sample heated from ambient to 1000°C at 20°C per minute in a nitrogen atmosphere flowing at 100 ml per minute. Through this analysis, the amount of CH can also be determined and calculated using the Taylor formula [28]: Percentage of CH = % loss of water mass x (Molecular weight of the CH / Molecular weight of H_2O).

G. Nitrogen Adsorption Analysis

The Brunauer-Emmett-Teller (BET) theory was conducted to analyze the gas adsorption data and calculate the powdered sample's surface areas. In this analysis, nitrogen was used as the adsorbate gas in the relative pressure range of 0.05 to 0.3. After the analysis, the surface area and pore volume of the powdered samples' variation with and without metakaolin can be determined.

III. RESULTS AND DISCUSSION

A. Consistency of Micro- and Ultrafine-Metakaolin Mortars

Consistency of mortar specimens as measured with Flow Table is given in Table III. It can be seen that the flow table results decrease as the metakaolin content increases indicating that the water-tightness at the water to binder ratio of 0.46 was performed because of the characteristics of metakaolin inclusive of small particle size and high surface area. Ling *et al.* [19] reported a related observation of how metakaolin increased the concrete's cohesiveness; therefore, the superplasticiser dosage should be increased to achieve the workability as required. The use of metakaolin requires more water in the mortar mixtures due to its high pozzolanic reactivity and the fact that it consumes water very early. Similarly, Fan *et al* [20], reported a reduction in slump values with increasing MK content.

Additionally, the lower workability values of mortar with ultrafine-metakaolin is also observed lower than MK mortar samples. This trend is suggested because of the small particle sizes of ultrafine metakaolin and its high surface area. Fat *et al* [21] mentioned that the relationship between the addition of clay percentage and the decrease in flowability is linear. However, metakaolin's characteristic with finer particle sizes benefits in controlling water-tightness that can enhance the resistance to permeability and durability of ultrafine-metakaolin cement-based binders.

TABEL III
FLOW TABLE RESULT BASED ON THE VARIATION OF MIXTURE

Mixture ID	Flow table result (mm)
PCC	180
MK-5	170
MK-10	165
UM-5	155
UM-10	145

B. Compressive Strength of Micro- and Ultrafine-Metakaolin Mortars

Fig. 5 shows a 50-mm mortar cube under compressive loading, presenting the comparison of compression load resistance of mortar mixtures at 7 and 28 days. The inclusion of micro- and ultrafine metakaolin increases the resistance on compression load, as anticipated. The highest increase of compressive strength was achieved by UM-10, which recorded approximately 121% higher than the compressive strength of PCC sample at 7 days and 100% higher at 28 days.

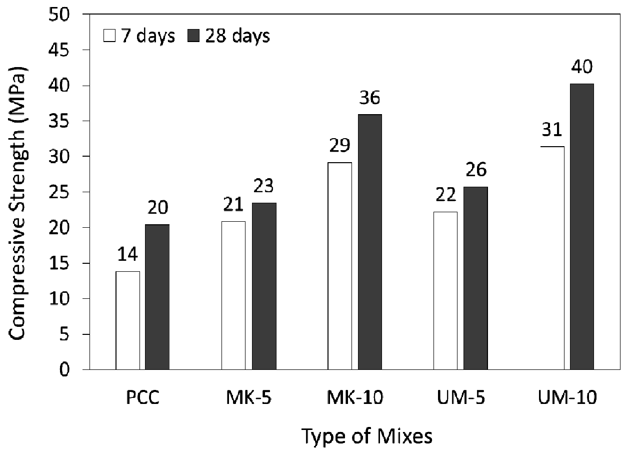
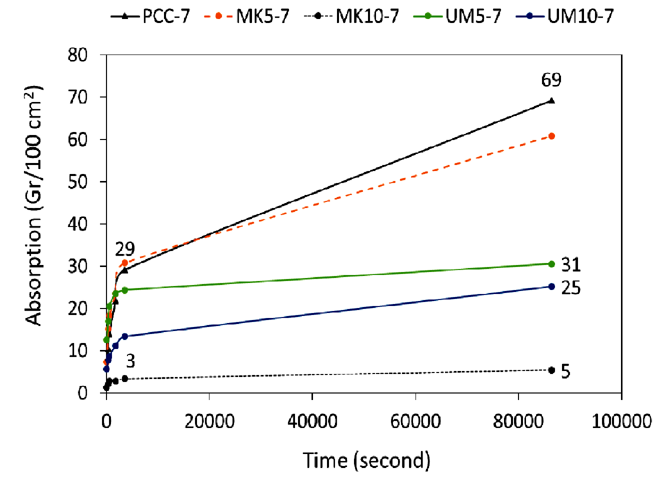


Fig. 5 Compressive strength of mortar mixtures at 7 and 28 days

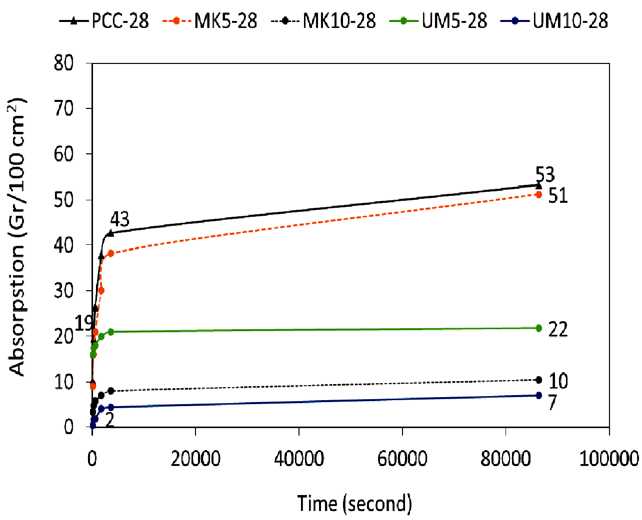
It can be inferred from this finding that the substitution of ultrafine-metakaolin in cement mortar has provided better bonding characteristics and accelerate the pozzolanic reaction compared to micro-metakaolin. The optimum level of 10% ultrafine-metakaolin as the cement replacement found in this study was also in line with the study reported in [22]. In this work, metakaolin with a size of 100 nm was used and achieved a compressive strength of up to 40 MPa at 28 days after replacing the cement by 10%. The increased performance of mortar with ultrafine-metakaolin is observed due to the physical packing effect of very fine metakaolin that can increase density as well as compressive strength. Moreover, due to the thermal calcination, the ultrafine-metakaolin has a high level of pozzolanic activity, initiating the formation of alumina-silicate structures that can react with calcium hydroxide that was not fully removed during the hydration period. From the reaction, an additional Calcium Silicate Hydrate can be formed and effectively increased the strength development. [23], [24].

C. Water Absorption of Micro- and Nano- Metakaolin Mortar

The water absorption rate vs. time of 7 days and 28 days specimen is presented in Fig. 6a and b, respectively. In Fig. 4, it can be observed that at 7 days, MK-10 showed a slight increase in water-absorption rate compared to the other variation. UM-10 showed little increase and UM-5, while MK-0 and MK-5 showed higher increases, especially after 40000 seconds.



(a)



(b)

Fig. 6 Absorption rate vs time of micro- and ultrafine-metakaolin mortars tested at a) 7th and b) 28th day

It can be concluded that metakaolin reduces water-absorption of the mortar specimens, hence increasing water-resistance at 7th day curing age. However, the water absorption of UM-10 was found higher than MK-10 at 7 days. This result is due to the great amount of surface energy of the ultrafine particles during hydration that promotes agglomeration, thus preventing complete cement hydration in a mortar matrix. Meanwhile, the water-absorption rate vs time of specimens at 28th day shows a more acceptable trend where the water absorption of UM-10 is lower than MK-10 while a higher rate of increase is shown by MK-0 and MK-5 samples before 20000 seconds. The water absorption of UM-10 was found to be 86% and 30% lower than PCC and MK-10 mortars, respectively. In this case, the ultrafine-metakaolin enhanced the bond between the cement paste and sand due to the filler effect, thus reducing water absorption, especially at 28 days. This behavior improves water absorption resistance, thus extending the service life of the cement-based system and improving durability properties [25].

D. X-Ray Diffraction (XRD)

The crystalline phases that occurred during cement hydration on the 7th and 28th day are studied through XRD analysis. The XRD peaks of cement pastes containing 10% micro- and ultrafine are shown in Fig. 7, as well as the control cement paste sample.

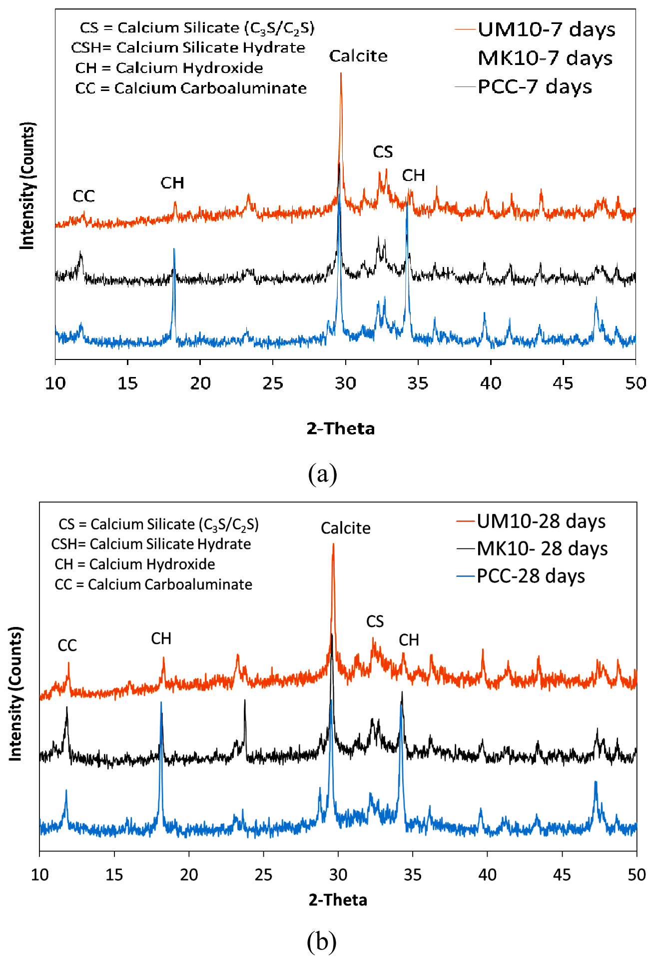


Fig. 7 XRD of cement pastes with and without 10% metakaolin at a) 7th day and b) 28th day

The analysis on the peak intensity of calcium hydroxide (CH) is selected since CH is a poor crystalline material produced from the reaction between cement and water, and its reduction can indicate the better performance of cement paste mixtures. The peak of CH can also indirectly determine the presence of CSH concentration in paste samples. The presence of CH can be identified at a 2-theta angle of 18º, 29°, 34.2°, and 47°, while the peak of Calcite phase can be found at 2-theta = 29°. From Fig.7, the lowest peak intensity of CH among the cement paste mixtures is found on UM10 sample. When looking at all days of the sample ages, the CH intensity in cement paste containing 10% ultrafine-metakaolin decreased for about 70% as also seen in 2-theta angle of 18° and 34.2° (see Fig. 5). Figure 8 clearly shows the reduction of CH peak intensity at a 2-theta angle of 34.2° after using 10% ultrafine-metakaolin. This result can be suggested due to the low rate hydration of calcium silicates (C_2S and C_3S), CSH formation, and liberation of CH [26]. Moreover, the presence of calcium carboaluminate can also be observed and suggested as the results of metakaolin-pozzolanic cement hydration formed by the reaction of atmospheric CO_2 with CAH [27]. However, the intensity of CSH could not be clearly determined since the peak characteristic of CSH is overlapped with calcite.

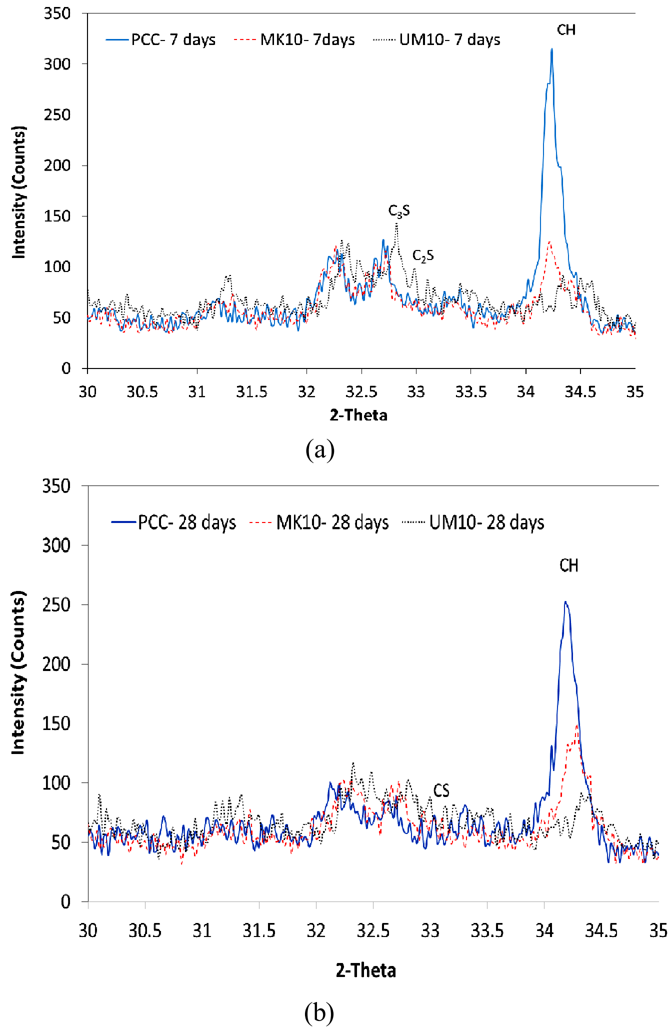
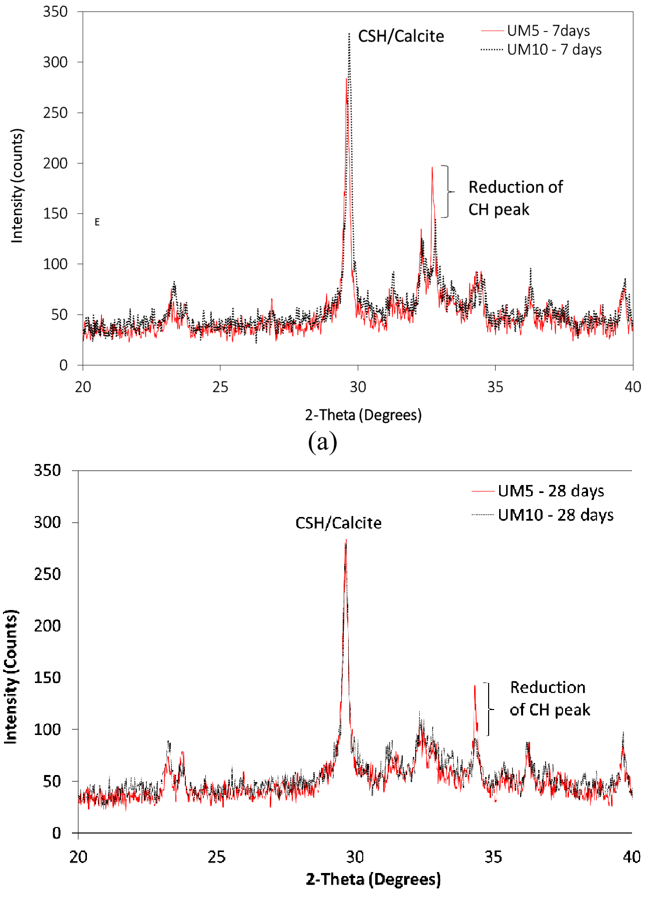


Fig 8. Intensity peak of different mixes at a) 7th day and b) 28th day

Comparing the intensity counts of CH peaks at 7 and 28 days between UM-5 and UM-10 paste samples, the lower level of CH peaks can be found in cement paste sample added with 10% ultrafine-metakaolin, even when dilution is accounted for (see Fig.9). For example, after 7 and 28 days, the intensity peak of CH at 2-theta=34.2° decreased from 195 to 145 and 140 to 90, respectively. This result indicates that the additional hydration products are more effective in a mixture containing 10% UM compared to 5% UM. These results support the study reported in [28]. From this experimental work, it was reported that metakaolin has a pozzolanic nature that contributes to the consumption of CH, lower Ca/Si and potentially higher CSH phase. However, there are no significant changes in CH intensities at 28 days of curing. The trend can also explain the compressive strength difference between UM-5 and UM-10, as described earlier in section IIIB.



(a) (b)

Fig. 9 Intensity peak of UM5 and UM10 pastes at a) 7th day and b) 28th day

E. TGA Analysis of Micro- and Ultrafine- Metakaolin Pastes

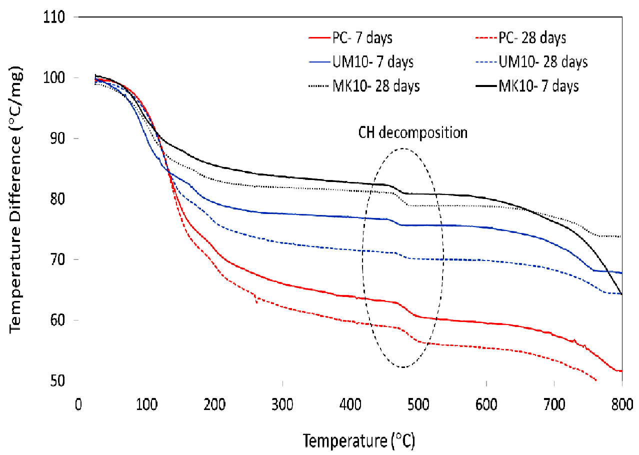


Fig. 10 TGA of cement pastes with 10% MK and UM at a) 7th day and b) 28th day

Fig. 10 shows the mass changes through the TGA curve of cement paste containing micro- and ultrafine-metakaolin after treated at room temperature to about 800°C. It can be seen that the reduction in mass that is assigned to the decomposition of CSH gel takes place up to around 200°C while CH decomposition at 480°C and the decomposition of crystalline calcite or $CaCO_3$ at 675°C.

Based on the calculation using the Taylor formula, the CH content in all mixtures can be revealed. The results report that CH's amount on cement paste containing 10% UM is lower than the CH amount of 10% MK. For instance, the CH content in UM10 sample on the 7th day was 4.01%, while in MK10 was 6.18%. On the 28th day, the CH amount of MK-10 and UM-10 pastes is 9.01% and 4.22%, respectively. Additionally, the calcite decomposition in the UM pastes was smaller than the MK pastes, which confirms the low amount of CH available for carbonation due to the very fine sizes of the ultrafine metakaolin [23]. Overall, the CH content of pastes with micro- and ultrafine-metakaolin was found lower than the CH content of PPC paste sample. The CH content in PCC paste samples at 7 and 28 days were 11.76% and 10.93%, respectively.

F. Nitrogen Adsorption Analysis of Cement Paste Containing Ultrafine-Metakaolin

Table IV shows the surface area and pore volume of mixes containing PCC and 10% ultrafine metakaolin at 7 and 28 days. A lower surface area means low porosity. The surface area and pore volume of UM-10 paste at 7 days were 45.948 m^2/g and 0.156 cc/g while at 28 days decreased to 42.420 m^2/g and 0.13 cc/g (approximately 35% and 18% lower when compared with the surface area and pore volume of cement paste sample. This result indicates that the particle size distribution is modified due to ultrafine-metakaolin's addition, leading to an increase in the solid volume, thus refining the pore structure of cement paste. The similar observation was also reported that the addition of nanomaterials reduced the pore volume and modified the paste pore structure [29].

TABLE IV
SURFACE AREA AND PORE VOLUME OF CEMENT PASTES WITH 10% ULTRAFINE-METAKAOLIN

Type of Mix	BET Surface Area (m^2/g)	Pore Volume (cc/g)
PCC-7 days	71.569	0.164
PCC-28 days	55.276	0.160
UM10-7 days	45.948	0.156
UM10-28 days	42.420	0.130

IV. CONCLUSION

Metakaolin sourced from the Toraget Village, Indonesia is suitable as a partial substitution of cement with a dosage of 10%. Ultrafine-metakaolin with the size of 196 nm exhibited higher strength (121% increase from PCC at 7 days and 100% at 28 days) due to the smaller particle size and higher surface area of ultrafine-metakaolin. The 7 and 28-days water-resistance was improved by partial replacement of PCC by ultrafine-metakaolin. At 28 days, the capillary water absorption of UM-10 sample was 86% and

30% lower than PCC and MK-10, respectively. The XRD patterns of powder paste sample with micro- and ultrafine-metakaolin show the reduction of calcium hydroxide and increase CSH formation and additional CAH that enhance the compressive strength and more dense of the microstructure of cement paste combined with 10% micro- and ultrafine-metakaolin. Through Taylor formula, the TGA analysis reports the reduction of calcium hydroxide content in UM 10, indicating the effect of very fine particles in contributing to the acceleration of pozzolanic reaction and for an additional CSH phase. Nitrogen adsorption analysis shows that the pore structure of UM-10 sample is smaller than the cement sample, which means the ultrafine-metakaolin matrix is denser. Therefore, low permeability can be expected, and consequently, high durable properties can be achieved.

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