

Effect of Ternary Cementitious System on Microstructure and Strength Behaviors of Concrete

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Abstract

The effect of two local pozzolan, fly ash (FA) and metakaolin (MK) on the performance of the ternary system concrete was reported in this paper, particularly on modification of microstructure and strength properties. Different performances of individual material proved to benefit the other's weakness. Additional FA improved workability and provided more uniform microstructure while MK strongly increased early age strength. The combination yielded the better performance of fresh and hardened concrete. The MK/FA ratio significantly affected compressive and flexural strength. Some forms of unstable compounds were found during 7-28 days of the modified mixtures, their effects were still unclear. The denser microstructures of ternary system also significantly improve the abrasion resistance. Weight loss appeared to reduce about half of the control. The proper ratio of MK and FA (10:10) appeared to have strong combination effects on workability improvement, slump loss as well as providing marked and continuous effect on long term strength.

1. Introduction

During the past decade, the use of local lignite fly ash (FA) as pozzolan in Thailand's concrete industry has been increasingly gaining acceptance. Cost effectiveness has been of primary concern in addition to the capability of improving workability and long term strength from effect

of particle shape, pozzolanic reaction and micro filling. However, some disadvantages of low early age strength was recognized.

Metakaolin (MK) from the process of heat treatment of natural local kaolin is reported as a potentially good quality and effective pozzolanic material [1,2,3 and 4]. The significant reactivity and early strength development character have been reported, however, its particle shape and high surface area substantially reduced concrete workability, in term of slump and slump loss.

Since the beneficial properties of both local pozzolan are recognized [5,6,7] the combined use in a simple mean, by mixing the separately batched material, may be the effective way to utilize these two materials [8]. The benefit of increased early strength from metakaolin, improved long term strength and workability of fresh concrete from the effect of round particle shape of fly ash are expected to improve the overall concrete performance. However, the actual performance of these ternary system materials needs to be investigated.

2. Research Significance

The result from this study provides information of the ternary cementations system for the better quality or high performance concrete. The understanding of microstructure which influences concrete properties is essential for the prediction of structural performance.

3. Experimental Investigation

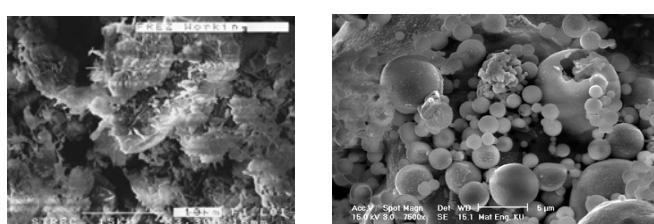
3.1 Materials

The ground Ranong metakaolin (MK) from proper heating process for 6 hours under 800°C [3,4] and Mae-moh fly ash (FA), were used throughout this study. The chemical compositions and physical properties are shown in Table 1. Particle shape of Metakaolin and local fly ash are shown in Figure1.

The 28 day target strength of normal and metakaolin concrete were 45 MPa and 50 MPa, the target slump was 75 ± 25 mm. The percentage pozzolan cement replacement of 20 was kept constant and the studied ratio of MK to FA (MK/FA) varied in the range of 20 to 0 percent. Crushed limestone with maximum size of 9 mm. and coarse river sand were used as coarse and fine aggregate.

Table 1 Compositions and properties of metakaolin, cement and fly ash

Chemical composition (%)	N*	F*	C*	MK	FA	OPC
SiO ₂ (%)				58.26	47.65	21.16
Al ₂ O ₃ (%)				35.18	18.51	5.09
Fe ₂ O ₃ (%)				0.97	10.29	3.01
CaO (%)				0.03	11.94	66.22
SO ₃ (%)	4	5	5	0.03	2.69	2.42
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃ ≥ (%)	70	70	50	94.41	76.45	29.26
LOI< (%)	10	6	6	1.20	0.5	0.98
Spgr.	2.1-2.58			2.51	2.64	3.15
Blaine fineness , cm ² /g	2,400-4,800			13800	4045	



(a) metakaolin

(b) Fly ash)

Figure 1 Microstructure of pozzolan material

3.2 Specimens Preparation

The small sample sizes of 75x75x75 mm and 62.5x62.5x300 mm. were chosen for compressive and flexural strength tests due to the limited capacity of mixer and variation reduction between mixes. For abrasion resistance investigation, concrete samples of 150x150x75 mm. from similar mixes were cast and water cured after demolding until the test age. Weight loss was measured according to ASTM C944-90a.

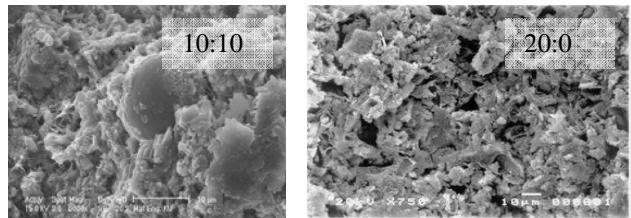
3.3 Items of Investigation

In this study, the properties and microstructure of material and paste incorporating various ratios of MK to FA at a constant 20 percent of cement replacement were investigated, using SEM and XRD Analysis. Both materials were added as cement replacement during concrete mixing. Then, mechanical properties of concrete focusing on strength and abrasion resistance were investigated.

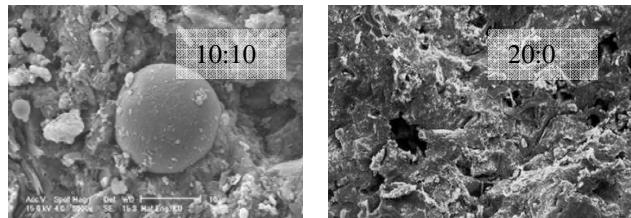
4. Experimental Results and Discussions

4.1 Material and microstructures

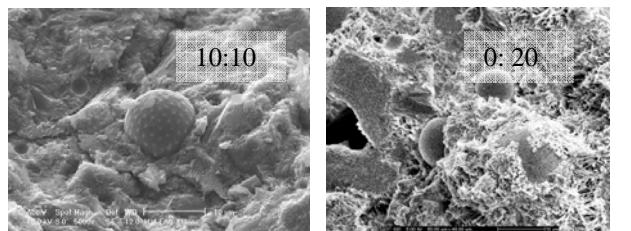
The rather loose, porous and irregular shape plate like of metakaolin particles as well as their high surface area, as shown in Figure 1 (a), significantly reduced workability. This confirmed the results from previous study [4], while the round shape of local fly ash in Figure 1 (b) improved workability[9]. The comparison of microstructure changes of metakaolin-fly ash-cement paste of total percentage pozzolan replacement 20, with different MK/FA of 10:10 and of 20:0 are shown in Figure 2. The loose and porous structure was shown during the early age 3-14 days. However, the denser structure of the combined mixture was observed, compared to those of metakaolin-cement paste alone (20:0) and of fly ash-cement paste alone [10].



(a) 3 days (left: MK-FA cement paste, Right MK-cement paste)



(b) 28 days (left: MK-FA cement paste, Right MK-cement paste)



(c) later age (left: MK-FA cement paste 91 days, Right FA-cement paste 8 month[10])

Figure 2 Microstructure of metakaolin- fly ash paste (10:10 and 20:0) at different ages

As the maturity gained, the depletion of CH and dense microstructure were observed. The continuous developed products was still seen on the surface of fly ash particles in the ternary system at 91 days. From previous study[10], FA-cement paste at the later age of 8 months, ettringite needle was observed in a small amount, compared to the uniform dense and irregular matrix with rare ettringite observation of MK-FA cement mixture on the left of Figure 2(c).

The comparison results of XRD of the combined mixtures and of metakaolin mixture at different ages, from

1 day to 91 day, as shown in Figure 3 at the end of the paper. The significant calcium hydroxide (CH) depletion was observed during 14 day in metakaolin concrete, especially during the first three days. At 91 days CH almost disappeared entirely, differed from the mixtures with only fly ash which has slower pozzolanic reaction and the clear depletion occurred at later age of 91 days. Incorporating 10% fly ash yielded slightly high calcium hydroxide intensity at the early age. The XRD results were comparable at the later age, interestingly. During 7-28 day ages of the ternary system samples, some forms of unstable compound were found. The identified compounds of calcium aluminum oxide carbonate hydroxide hydrate; $\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3)0.5(\text{OH})11.5\text{H}_2\text{O}$ and Calcium aluminum oxide carbonate hydrate; $\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_311\text{H}_2\text{O}$, were found at 2 Theta angles of 10.5 and 23 degree in metakaolin-fly ash matrix but not for the control or fly ash paste as shown in Figure 4 at the end of the paper. The same finding was also found in one research work, to investigate hydration of C_3A under controlled condition [11]. However, their effects were still unclear.

4.2 Fresh concrete

Fly ash significantly improved workability, slump loss while more water requirement and the marked effect on slump loss were observed in concrete with metakaolin alone, compared to those of control mix with similar slump. However, additional round shape fly ash produced different effects. The remarkably increase workability and reduce water requirement was shown in Figure 5. The retained workability in term of slump loss was significantly improved. As the percentage replacement of fly ash increased, the decrease in slump loss was more pronounce. This effect may reason from the slow pozzolanic reaction of fly ash.

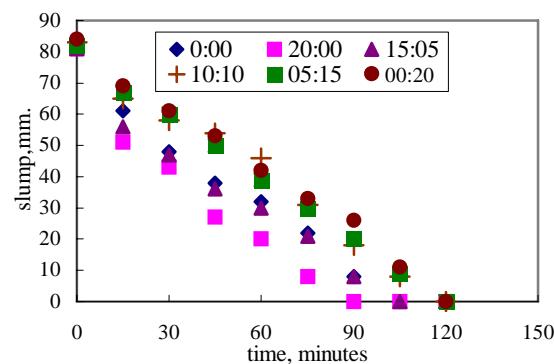


Figure 5 Workability performance of metakaolin concrete
(Note MK:FA 0:0)

4.3 Hardened concrete

4.3.1 Compressive strength

As shown in Table 2, strength of Metakaolin concrete increased by about 10-13% both at early and later age from direct and indirect effect as suggested by previous study [1] even the W/B increased. For Fly ash concrete, the improved in later age strength was observed, compared to that of the control.

However, different reactivity of each pozzolan noticeably improved strength development of the ternary system, compared to those of the binary system. Although the 1 day, compressive strength of all mixes were lower than that of the control (2-12%). During 7-28 day ternary blended samples gained strength between -9% to +12%, depended on MK to FA ratio. With the proper percentage fly ash-metakaolin replacement, the mixture could provide the greater long term strength compared to normal, Fly ash and Metakaolin concrete. It would expect that some unreacted fly ash particles may provide the nucleation site of the developed product in the system. The 24 percent higher strength than that of control mix was observed from the mix with MK/FA of 10/10. The noticeably dense and continuous matrix of the mixture, compared to cement-fly ash system in figure 2c strongly supported the evidence of strength improvement.

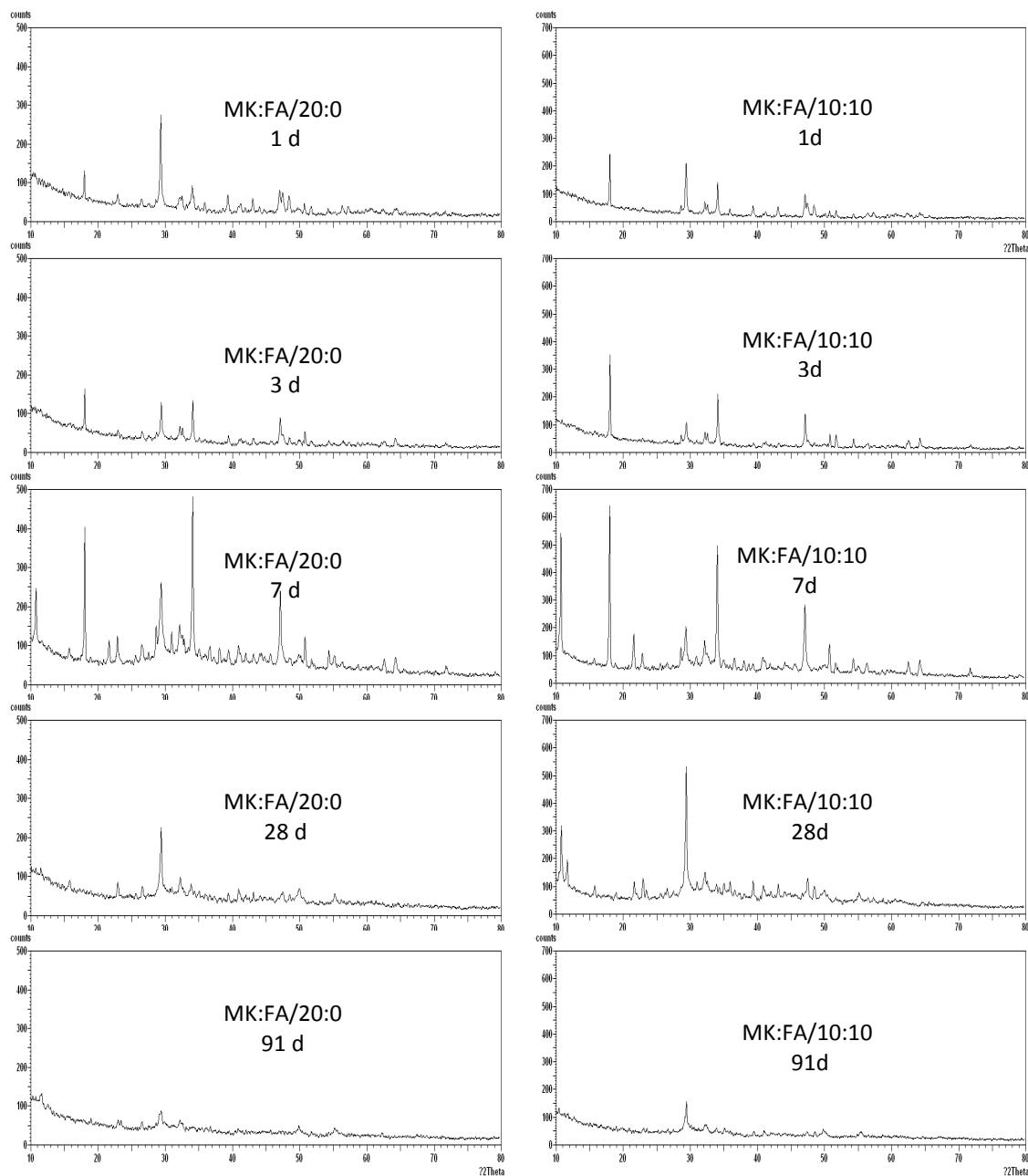


Figure 3 XRD results of metakaolin- fly ash paste of 20:0 and 10:10.

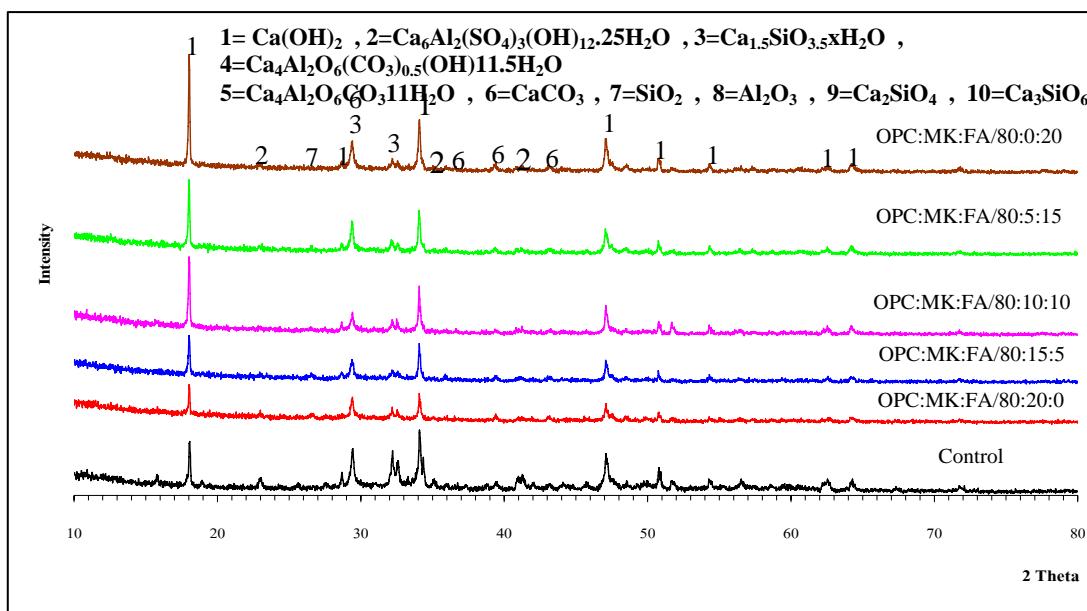


Figure 4 XRD results of metakaolin-fly ash paste of different pozzolan ratios at 7 days age.

Table 2- Compressive strength of concrete mixtures at different age

Mix	W/B	Compressive strength ,MPa				
		1d	7d	28d	56d	91d
Control	0.48	25.6	37.0	47.8	49.0	50.7
MK:FA20:0	0.52	25.7	41.8	53.7	54.9	55.3
MK:FA15:5	0.51	23.2	41.4	49.1	51.3	52.0
MK:FA10:10	0.48	22.7	39.3	49.6	56.5	62.7
MK:FA5:15	0.46	25.3	33.7	46.2	51.0	53.3
MK:FA0:20	0.44	24.5	35.5	44.7	57.7	57.9

4.3.2 Flexural strength

Similar to compressive strength, flexural strength at 1 day of all ternary system samples was lower than that of the control, up to 10%. However, after 7 day ternary blended samples gained strength at least similar or even better than that of the control, up to 10%, depended on MK to FA ratio. The lower percentage increase indicated the different failure mechanism. The denser microstructure improved

both type of strength, but single weak point strongly affected flexural strength compared to compressive strength. The effect of MK on early age strength improvement and of FA on later age strength improvement were clearly shown from the binary mixture samples but the proper percentage MK/FA of 10/10 in ternary system yielded the best result.

4.3.3. Abrasion resistance

The significant increase abrasion resistance at 28 days and 56 days of metakaolin-fly ash and fly ash concrete was observed, compared to those of normal concrete. The increased resistance slightly depended on pozzolan ratio but not the strength gained, as shown in Table 3. The test results implied the pronounced influence of additional

pozzolan both binary and ternary on the change of void system in both short and long term as shown in Fig.2,3 and 4. Focusing on abrasion resistance, ternary system appeared to perform much better than that of control mix although slightly poorer than that of binary system, either metakaolin-cement or fly ash-cement.

Table 3 Abrasion resistance of different mixes

Mix Description	W/B	Weight loss/ abrasive area, $\times 10^{-4}$ g/mm ² [strength, MPa]	
		28 day	56 day
Control	0.48	7.76,[47.8]	7.55,[50.7]
MK:FA20:0	0.52	5.11,[53.7]	3.44,[55.3]
MK:FA15:5	0.51	5.16,[49.1]	4.05,[52.0]
MK:FA10:10	0.48	5.51, [49.6]	4.63,[62.7]
MK:FA5:15	0.46	5.56,[46.2]	4.50,[53.3]
MK:FA0:20	0.44	5.41, [44.7]	3.62,[57.9]

5. Conclusions

From this study, conclusions could be drawn as followings.

1. Incorporated local fly ash in metakaolin concrete substantially increased workability and later age strength gain even in mixes with slightly higher W/B ratio, slump loss behavior was also improved.
2. Additional fly ash yielded slow calcium hydroxide depletion of metakaolin concrete at the early age due to its slow pozzolanic reaction, compared to that of the cement-metakaolin mixtures in which the depletion occurred during the first 14 days. The depletion depended on percentage replacement. Some forms of unstable calcium aluminum oxide carbonate hydrate compounds were found during 7-28 day of the ternary system mixtures and their effects were still unclear.
3. The denser and more uniform microstructure on

hardened concrete improved strength gain, both compressive and flexural at different level.

4. The replacement ratio of metakaolin to fly ash of 10:10 appeared to be most effective for strength development and workability improvement.

5. Regardless of the pozzolan type, their effects on long term void improvement were more pronounced than those of compressive strength. High abrasion resistance was observed, compared to the same level of strength.

6. The potential of ternary system, incorporating fly ash and metakaolin as a low cost local-supplement material for high strength and durable concrete was confirmed.

6. Acknowledgement

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