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Synergistic effect of metakaolin and fly ash on properties of concrete

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HIGHLIGHTS

- Synergy of cement, metakaolin and fly ash on cementitious system was investigated.
- Phase composition, microstructure and long term concrete behaviors were studied.
- It improved workability, mix uniformity, dense matrix and performance of concrete.
- Better understanding of synergy on properties of this ternary system was proposed.

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ABSTRACT

This paper reports the effects of the interaction between metakaolin and fly ash on the microstructure and property development of concrete. X-ray diffraction analysis revealed unstable hemicarboaluminate and calcium monocarboaluminate compounds in most mixtures during 7–28 day curing periods, the relative amounts depending on the metakaolin to fly ash ratio. The mix with the highest peaks of the monocarboaluminate phase yielded the highest long-term strength. Significant improvements in terms of durability, abrasion resistance, chloride permeability and steel corrosion risk were observed. A proportion of cement:metakaolin:fly ash as 80:10:10 yielded marked improvements on slump, slump loss and long- term strength. Synergistic action in the ternary blend significantly improved the workability of fresh concrete and yielded a more uniform mix, denser microstructure and better performance of the hardened concrete.

1. Introduction

Due to its improvement of concrete properties, the use of fly ash as pozzolan in the Thai concrete industry has increased significantly during the past decade. The responsible mechanism for the improvement has been well documented [1–3]. Since the microstructure and properties development of concrete at the time of exposure to the surroundings are critical in determining long-term performance, the typically slow early strength gain by local fly ash concrete probably affects concrete durability significantly, particularly in marine environments. The still-developing microstructure in the early stages of curing provides insufficient chloride penetration resistance, resulting in low protection of steel reinforcement. In an attempt to overcome some of these issues, attention has now turned to the use of ternary systems, containing two types of compatible and reactive pozzolans [4]. The resulting changes in reactivity rate and hydration processes affected phase compositions and microstructures of the cement pastes [5]. The benefits from the synergy of pozzolans in cementitious systems, such as higher early strength, have been widely reported [6–8]. Some observed specific compounds such as calcium mono- or hemicarboaluminate were reported in fly ash-limestone systems and corresponded well with the better compressive strength improvement [8,9].

Metakaolin, produced by heating and grinding of natural kaolin, has been reported to be a good and effective pozzolanic material [10,11]. The faster strength development and denser microstructure formation during the early stages of curing of this material compensate for the drawbacks in fly ash concrete mentioned earlier as well as improve concrete durability, in particular, chloride permeability [12].

Metakaolin and fly ash are aluminate-rich pozzolans. Improved concrete performance is expected from the combined addition of these two materials to concrete. The pozzolanic reactions from these materials provide additional aluminates to the system which

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react with hydration products and produce more phases containing alumina in addition to CSH and reportedly enhance strength gain [13]. Little information on the actual performance of the combined use of these materials is available [14], although synergistic reactions and the improved products of concrete with other systems, e.g., fly ash-limestone powder system have been widely reported [8].

The combination of different pozzolans in cementitious systems changes reaction processes, phase compositions and microstructure development as well as the behavior of the concrete. Studies on the synergistic effects of cement, metakaolin and fly ash on concrete performance are rare. This study aimed to investigate the effect on microstructure and properties, in both early stages of curing and in the longer term of metakaolin-fly ash concrete to provide a better understanding of this synergy. In the first part, phase development of the cement paste incorporating various ratios of metakaolin and fly ash was investigated using X-ray diffraction (XRD) analysis. For the second part, the investigation focused on concrete strength and durability on 1) abrasion resistance, 2) chloride permeability and 3) steel corrosion risk. These results provided information on specific concrete performance for some applications such as in marine environment.

2. Experimental investigation

2.1. Materials

Local metakaolin (MK) and lignite fly ash (FA) were used in this study. Metakaolin was prepared, using the techniques of Sayamipuk [15], by heating raw kaolin at 800 °C for 6 h and grinding in a high-speed ball mill. The chemical compositions and physical properties of the materials are listed in Table 1.

Commercial Type I Portland cement interground with 4% limestone powder [16] was used throughout this study. The small amount of limestone powder benefits cement particle size distribution and workability of fresh concrete, furthermore, it provides more nucleation surface for accelerated hydration reactions [9].

The concrete mixes were designed for a 28 day compressive strength of 45 MPa and a slump of 75 ± 25 mm. The total percentage of cement replacement was kept at 20 wt% with ratios of metakaolin to fly ash varied in 5% increments (20:0, 15:5,10:10, 5:15 and 0:20). Crushed limestone with a maximum size of 9 mm and coarse river sand were used as coarse and fine aggregates. The details of the mix proportions are shown in Table 2. No chemical admixture was used in this system.

2.2. Cement paste specimens

Paste samples at normal consistency (ASTM C 187) were prepared to investigate the phase development during curing. All specimens were moist cured until the age for microstructure examination. The structural development of a mature fly ash-cement paste system (8 months) was used for comparison.

2.3. Concrete specimens

Small specimen sizes of 75 × 75 × 75 mm^3 and 62.5 × 62.5 × 300 mm^3 were used for compressive and flexural strength tests to reduce the number of batches and hence the variation between batches. All specimens were moistly cured for 24 h after casting, then demolded and water cured at room temperature, 28 °C, until test to simulate the practical condition. For the designed target strength and slump, the water to binder ratios (W/B) were varied between 0.44 and 0.52. Weight loss of 150 × 150 × 75 mm^3 concrete samples, according to ASTM C944-90a, was used as an index for abrasion resistance. The Rapid Chloride Permeability Test (ASTM C1202) was conducted at 28 and 56 days curing on 50 mm thick specimens sliced from water-cured cylindrical samples, 100 mm diameter by 200 mm height. For steel corrosion risk investigation, cylindrical specimens (150 mm diameter by 300 mm height) with 9 mm diameter reinforcing steel embedded to a length of 200 mm, were submerged in 3% NaCl solution in order to simulate a marine environment. Direct current voltage of 6 volts was applied throughout the experiment to accelerate the corrosion. Consequently, the corrosion potential was measured, using a copper-copper sulfate half-cell potentiometer. After 90 days and 140 days in the NaCl, specimens were broken and the broken surfaces sprayed with silver nitrate solution for the measurement of chloride penetration depth.

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

Chemical composition (%)/Properties	MK	FA	OPC
SiO_2	58.26	47.65	21.16
Al_2O_3	35.18	18.51	5.09
Fe_2O_3	0.97	10.29	3.01
CaO	0.03	11.94	66.22
SO_3	0.03	2.69	2.42
$SiO_2 + Al_2O_3 + Fe_2O_3$	94.41	76.45	29.26
LOI<	1.20	0.5	0.98
Specific gravity	2.51	2.64	3.15
Blaine fineness, cm^2/g	13800	4045	3320

3. Results and discussion

3.1. Effects on the physical properties of fresh concrete

The morphological features of the metakaolin and fly ash particles are shown in Fig. 1. The metakaolin particles were fluffy and porous, whereas those of fly ash were spherical and ranged in size from 2 μm to 40 μm. Fig. 2 shows the effects of the admixtures on the slump and slump loss with time of concrete. It can be seen that metakaolin increased the water requirement while fly ash decreased it for the given slump. The reason for this was due to the spherical shape of fly ash compared to that of metakaolin. Due to the same reason slump loss also decreased by increasing fly ash substitution level or by decreasing metakaolin inclusion level.

3.2. Phase development

The changes in microstructure with time of the 10:10 metakaolin:fly ash specimens are shown in Fig. 3. A loose and porous structure is observed at an early age, from 3 to 14 days. A decrease in porosity is observed after 14 days.

The results of XRD analysis, shown in Figs. 4–7 indicate the decrease of calcium hydroxide content and the formation of calcium hemicarboaluminate, or tetra calcium dialuminium dodecahydroxide hemicarbonate hydroxide n-hydrate $Ca_4Al_2O_6(CO_3)_{0.5}(OH)11.5H_2O$, (peaks labeled '4') and calcium monocarboaluminate, $Ca_4Al_2O_6CO_3{\cdot}11H_2O$ (peaks labeled '5'). The lower peak intensity of CH after 7 day is somewhat an anomaly, but the phenomenon had been reported [17] and partially explained by the interaction of calcium silicate hydrate and nano sized CH [18,19].

The results present significant changes in the development of the hemi- and monocarboaluminate in the alumina, ferric oxide, monosulfate phase (AFm) of the cement-metakaolin-fly ash system (PC-MK-FA) during 7–28 days. At 7 days, calcium hemicarboaluminate was found in all ternary mixes and binary mix of metakaolin, with a slight increase in the peaks for monocarboaluminate. Of note, this intensity increase appears to be highest in the 10:10 metakaolin-fly ash mix. The formation of both carboaluminate products probably from the small amount of available limestone in the systems did not appear either in cement or in binary cement-fly ash mixtures. The formation of these two products has been widely reported for limestone-cement mixes [13,20,21]. In that system, the hemicarboaluminate formation was found as early as 1–3 days and gradually converted to calcium monocarboaluminate within 7 days [21]. At 14 days, the reduced intensity of the calcium hydroxide peak was evident in the ternary system with high metakaolin percentage. This was due to the pozzolanic activity during the early stages of curing. This was compatible with the results of Wild et al. who found the maximum pozzolanic reaction of metakaolin was at about 14 days [22]. It was observed that the peak intensity of the hemicarboaluminate decreased, but that of the monocarboluminate increased during this early stage of phase development. This supports the previously reported conversion of the hemi- to monocarboluminate phase in the calcite-rich