



Effect of W/B ratios on pozzolanic reaction of biomass ashes in Portland cement matrix

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ARTICLE INFO

Article history:

Received 9 April 2010

Received in revised form 31 August 2011

Accepted 1 September 2011

Available online 10 September 2011

Keywords:

Pozzolanic reaction

Biomass ash

Rice husk–bark ash

Palm oil fuel ash

Thailand

ABSTRACT

In this study, the effects of W/B ratios on pozzolanic reaction of by-product biomass ashes, namely rice husk–bark ash (RHBA) and palm oil fuel ash (POFA), were determined. These biomass ashes were ground to the same fineness as that of Type I Portland cement (OPC) and partially replaced OPC at replacement levels of 10–40% by weight of binder. Water to binder (W/B) ratios of 0.50, 0.575, and 0.65 were used. The compressive strengths of mortars were compared to those of mortars made with OPC partially replaced with ground river sand of similar particle size. The results demonstrate that at the same cement replacement levels, the degrees of pozzolanic reaction of RHBA and POFA increase with W/B ratio. In addition, ground river sand with the same particle size of OPC can be used as a non-reactive material to replace OPC for determining the compressive strength due to pozzolanic reaction of biomass ash.

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1. Introduction

Presently, there are many types of industrial by-products such as silica fume, fly ash, and ground granulated blast furnace slag that can be effectively used as supplementary materials in concrete. Biomass ash is a type of by-product resulting from burning of renewable energy sources viz., agricultural residues and agro-industrial wastes. In Thailand, rice husk–bark ash (RHBA) is a biomass ash resulting from incineration of rice husk and eucalyptus bark in a biomass power plant. Palm oil fuel ash (POFA) is obtained from the burning of palm oil fibers, shells, and empty fruit bunches in a palm oil mill power plant. Many reports [1–6] show that grinding helps improve the pozzolanic properties of these biomass ashes. They can contribute to the strength development and are thus used as a partial replacement of Portland cement. However, there is still lack of investigation on the variation in W/B ratios affecting the actual pozzolanic properties of RHBA and POFA.

Generally, the use of pozzolan as cement replacement contributes to strength development as the results of both chemical and physical effects [7–9]. The chemical effects are associated between normal hydration of Portland cement compounds and water, and the pozzolanic reaction between pozzolanic material, $\text{Ca}(\text{OH})_2$ and water. The mechanical effect is associated with the packing characteristics of mixtures and depends on the particle size of

the pozzolan. Previous study [10] indicates that the compressive strength of mortar mixed with non-reactive material is due to hydration reaction of Portland cement and packing effect of non-reactive material particle. Theoretically, the compressive strength contribution from the pozzolanic reaction of a pozzolan can, therefore, be determined from the difference in compressive strengths between fly ash mortar and mortar containing non-reactive material with same particle size as fly ash.

The objective of this study is to present the effect of W/B ratios on compressive strength of mortar due to pozzolanic reaction of RHBA, POFA, and non-reactive material (river sand). The results provide important information for future utilization of these biomass ashes.

2. Experimental programs

2.1. Materials

Materials used in this research consisted of Portland cement Type I (OPC) in accordance with ASTM 150 [11], pozzolanic materials, and tap water. In addition, graded river sand which passed through sieve no. 16 and retained on sieve no. 100 in accordance with the ASTM C 778 [12] were used as fine aggregate in mortar mixture. Pozzolanic materials were by-products from biomass power plant of Thailand namely rice husk–bark ash (RHBA) and palm oil fuel ash (POFA). Ground river sand was used as a non-reactive material to determine the packing effect and pozzolanic reaction

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[13]. As-received RHBA, POFA, and river sand were ground by ball mill into approximately the same particle sizes as that of OPC and designated as MRHBA, MPOFA, and MGS, respectively. The physical properties and chemical compositions of materials are shown in Tables 1 and 2. The weight of particles retained on a 45 μm sieve of OPC, MRHBA, MPOFA, and MGS were 13.5%, 12.2%, 13.7%, and 12.6% with median particle sizes of 12.1, 10.0, 13.0, and 11.5 μm , respectively. The Blaine fineness of OPC, MRHBA, MPOFA, and MGS were 3580, 9460, 7190, and 6610 cm^2/g , respectively. Fig. 1 shows the particle size distributions. It can be seen that the particle sizes of these materials are within a narrow range and thus may be assumed that their particle sizes are similar. The major chemical composition of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ of MRHBA and MPOFA were 84.91%, and 69.84% and the loss on ignition (LOI) were 3.72%, and 10.05%. Therefore, according to the ASTM C 618 [14] for chemical composition requirement, MRHBA and MPOFA may be treated as class N pozzolanic material. The major chemical composition of MGS was SiO_2 which was 92.86%.

2.2. Mortar proportioning

For mortar, the ratio of a binder (OPC plus pozzolan) or OPC plus non-reactive material to fine aggregate was set at 1–2.75 by weight. The W/B ratios of mortars were 0.50, 0.575, and 0.65. The mortar cube specimens of $50 \times 50 \times 50$ -mm were produced in accordance with ASTM C 109 [15]. The OPC was replaced by MRHBA, MPOFA, and MGS at the replacement levels of 0%, 10%, 20%, 30%, and 40% by weight of binder. All mortar specimens were cast and demolded after 24 h. They were cured in saturated lime water until testing age. Compressive strengths of mortar were tested at 7, 28, 60, and 90 days. 0.50CON, 0.575CON, and 0.65CON were control mortars with only OPC as a binder at W/B of 0.50, 0.575, and 0.65, respectively. For other mortars, the symbols are shown as (W/B) (type of replaced material) (replacement level in percent). For example, 0.575MPOFA30 indicated W/B ratio of 0.575%, and 30% MPOFA replacement of OPC.

3. Results and discussions

3.1. Compressive strength of mortar

Compressive strength and percentage compressive strengths (PCS) of mortars containing MRHBA, MPOFA, and MGS at various ages are shown in Tables 3–5. PCS is defined as a percentage of the compressive strength of mortar with replacement material to that of control mortar. For control mortar or plain OPC mortar, the compressive strength from hydration reaction decreased with the increase in W/B ratio. According to Abrams's law, the compressive strength of concrete varies inversely with the W/C ratio [16,17]. The compressive strength at 28 days of 0.50CON, 0.575CON, and 0.65CON mortars were 46.3, 44.8, and 43.3 MPa, respectively. The use of the same replacement level of MRHBA and MPOFA had different effect on mortar compressive strength especially at the later age. For example, compressive strength at

Table 2

Chemical composition of materials.

Chemical composition (%)	OPC	MRHBA	MPOFA	MGS
SiO_2	20.80	84.75	65.30	92.86
Al_2O_3	5.50	0.16	2.56	3.17
Fe_2O_3	3.16	0.0	1.98	0.27
CaO	64.97	2.78	6.42	0.55
MgO	1.06	2.32	3.08	0.49
Na_2O	0.08	0.37	0.36	0.42
K_2O	0.55	2.57	5.72	0.32
SO_3	2.96	0.60	0.47	0.55
LOI	2.89	3.72	10.05	0.67

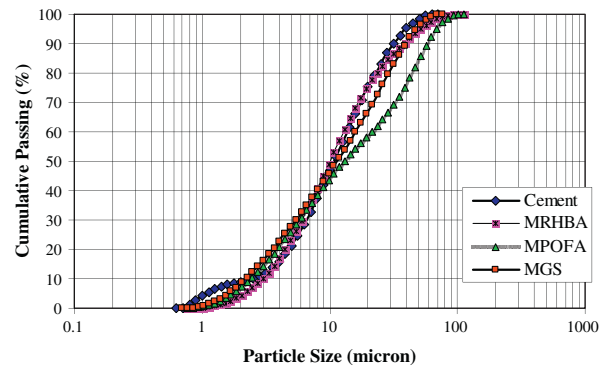


Fig. 1. Particle size distribution of materials.

90 days of 0.50MRHBA20 mortar was 53.5 MPa while that of 0.575MRHBA20 mortar with higher W/B ratio was 55.6 MPa. The results confirmed that the gain in compressive strengths of mortar containing MRHBA and MPOFA was from packing effect and pozzolanic reaction in addition to the hydration reaction of cement. Furthermore, the PCS of MRHBA20 and MPOFA20 mortars at the age of 7 or 28 days ranged between 93.0–109.8% as shown in Tables 3 and 4. Thus MRHBA and MPOFA can be used as pozzolanic materials because they produced strength activity indices in excess of 75% in accordance with ASTM C 618 [14].

From Table 3, the compressive strengths and PCS of mortars containing MRHBA increased with the increased of age. For example, the compressive strengths of 0.50MRHBA10 mortar at 7, 28, 60, and 90 days were 35.3, 47.3, 49.8, and 51.0 MPa with PCS of 94.1%, 102.2%, 104.0%, and 104.3%, respectively. At the early age (7 days), the compressive strength of mortars containing MRHBA decreased with the increase in cement replacement level. This was due to the reduced amount of OPC causing low hydration reaction. The compressive strength from pozzolanic reaction of MRHBA, however, compensated the compressive strength lost. The replacement level between 10% and 20% exhibited the optimum replacement level and gave the compressive strengths at 60 days higher than those of control mortars. Mortars containing more than 20% MRHBA by weight of binder gave lower compressive strength than that of the control mortar for all W/B ratios. However, the compressive strengths at 90 days of 0.50MRHBA30, 0.575MRHBA30, and 0.65MRHBA30 mortars were 48.6, 48.0, and 45.7 MPa or 99.4%, 99.2%, and 98.5% of the control mortars, respectively. These strengths almost equaled to the control mortars at the same age and tended to be higher than the control mortars at the later age.

Table 4 shows the development of compressive strength of mortar with various replacement levels of MPOFA. At the early ages, the compressive strength decreased with the increase in the replacement level of MPOFA. The 7 day compressive strengths of 0.575MPOFA10, 0.575MPOFA20, 0.575MPOFA30, and 0.575MPOFA40 mortars were 34.8, 34.7, 30.9, and 27.0 MPa or 96.9%, 96.7%,

Table 1

Physical properties of materials.

Sample	Specific gravity	Median particle size, d_{50} (μm)	Blaine fineness (cm^2/g)	Retained on a sieve no. 325 (%)
OPC	3.15	12.1	3580	13.5
MRHBA	2.16	10.0	9460	12.2
MPOFA	2.22	13.0	7190	13.7
MGS	2.63	11.5	6610	12.6

Table 3
Compressive strengths of mortars containing MRHBA.

Sample	Compressive strength (MPa) – (percentage compressive strength, PCS) (%)			
	7 days	28 days	60 days	90 days
0.50CON	37.5–(100)	46.3–(100)	47.9–(100)	48.9–(100)
0.50MRHBA10	35.3–(94.1)	47.3–(102.2)	49.8–(104.0)	51.0–(104.3)
0.50MRHBA20	39.1–(104.3)	49.2–(106.3)	51.8–(108.1)	53.5–(109.4)
0.50MRHBA30	32.2–(85.9)	44.8–(96.8)	47.2–(98.5)	48.6–(99.4)
0.50MRHBA40	28.1–(74.9)	40.5–(87.5)	43.2–(90.2)	44.4–(90.8)
0.575CON	35.9–(100)	44.8–(100)	46.8–(100)	48.4–(100)
0.575MRHBA10	34.6–(96.4)	45.7–(102.0)	50.4–(107.8)	53.6–(110.8)
0.575MRHBA20	37.5–(104.6)	49.2–(109.8)	52.9–(113.0)	55.6–(114.9)
0.575MRHBA30	31.5–(87.7)	43.6–(97.3)	46.1–(98.5)	48.0–(99.2)
0.575MRHBA40	27.4–(76.3)	38.1–(85.0)	42.1–(90.0)	43.8–(90.5)
0.65CON	34.5–(100)	43.3–(100)	45.5–(100)	46.4–(100)
0.65MRHBA10	31.6–(91.6)	42.1–(97.2)	46.7–(102.6)	50.0–(107.8)
0.65MRHBA20	33.8–(98.0)	44.9–(103.7)	48.7–(107.0)	52.1–(112.3)
0.65MRHBA30	27.7–(80.3)	38.9–(89.8)	43.1–(94.7)	45.7–(98.5)
0.65MRHBA40	24.3–(70.4)	35.3–(81.5)	40.3–(88.6)	41.8–(90.1)

Table 4
Compressive strengths of mortars containing MPOFA.

Sample	Compressive strength (MPa) – (percentage compressive strength, PCS) (%)			
	7 days	28 days	60 days	90 days
0.50CON	37.5–(100)	46.3–(100)	47.9–(100)	48.9–(100)
0.50MPOFA10	36.5–(97.3)	48.4–(104.5)	51.4–(107.2)	53.2–(108.8)
0.50MPOFA20	35.9–(95.7)	46.7–(100.9)	49.5–(103.3)	50.8–(103.9)
0.50MPOFA30	33.6–(89.6)	42.2–(91.1)	45.6–(95.2)	48.3–(98.8)
0.50MPOFA40	28.2–(75.2)	38.2–(82.5)	41.3–(86.1)	43.0–(87.9)
0.575CON	35.9–(100)	44.8–(100)	46.8–(100)	48.4–(100)
0.575MPOFA10	34.8–(96.9)	44.3–(98.9)	46.9–(100.2)	49.2–(101.7)
0.575MPOFA20	34.7–(96.7)	44.0–(98.2)	47.4–(101.3)	49.5–(102.3)
0.575MPOFA30	30.9–(86.1)	40.1–(89.5)	43.6–(93.2)	46.2–(95.5)
0.575MPOFA40	27.0–(75.2)	35.8–(79.9)	38.8–(82.9)	40.2–(83.1)
0.65CON	34.5–(100)	43.3–(100)	45.5–(100)	46.4–(100)
0.65MPOFA10	34.1–(98.8)	43.7–(100.9)	46.6–(102.4)	49.8–(107.3)
0.65MPOFA20	32.1–(93.0)	41.1–(94.9)	44.3–(97.4)	47.5–(102.4)
0.65MPOFA30	27.4–(79.4)	37.1–(85.7)	39.6–(87.0)	41.8–(90.1)
0.65MPOFA40	23.9–(69.3)	31.4–(72.5)	34.3–(75.4)	36.4–(78.4)

Table 5
Compressive strengths and average percent compressive strengths of mortars containing MGS.

Sample	Compressive strength (MPa) – (percentage compressive strength, PCS) (%)				Average PCS (%)
	7 days	28 days	60 days	90 days	
0.50CON	37.5–(100)	46.3–(100)	47.9–(100)	48.9–(100)	100
0.50MGS10	36.8–(98.1)	45.8–(98.9)	47.0–(98.1)	48.6–(99.4)	98.6
0.50MGS20	32.9–(87.7)	40.5–(87.5)	42.1–(87.9)	43.3–(88.5)	87.9
0.50MGS30	27.7–(73.9)	35.1–(75.8)	36.3–(75.8)	36.5–(74.6)	75.0
0.50MGS40	24.5–(65.3)	31.0–(67.0)	32.1–(67.0)	32.6–(66.7)	66.5
0.575CON	35.9–(100)	44.8–(100)	46.8–(100)	48.4–(100)	100
0.575MGS10	33.0–(91.9)	41.7–(93.1)	43.8–(93.6)	45.4–(93.8)	93.1
0.575MGS20	28.4–(79.1)	37.4–(83.5)	39.9–(85.3)	41.6–(86.0)	83.4
0.575MGS30	25.5–(71.0)	33.4–(74.6)	34.8–(74.4)	35.7–(73.8)	73.4
0.575MGS40	20.2–(56.3)	26.1–(58.3)	27.6–(59.0)	28.7–(59.3)	58.2
0.65CON	34.5–(100)	43.3–(100)	45.5–(100)	46.4–(100)	100
0.65MGS10	27.6–(80.0)	35.4–(81.8)	36.6–(80.4)	36.9–(79.5)	80.4
0.65MGS20	25.2–(73.0)	32.4–(74.8)	33.2–(73.0)	33.3–(71.8)	73.2
0.65MGS30	20.2–(58.6)	28.9–(66.7)	29.6–(65.1)	29.8–(64.2)	63.6
0.65MGS40	16.5–(47.8)	22.2–(51.3)	22.8–(50.1)	23.2–(50.0)	49.8

86.1%, and 75.2% of the control mortar (0.575CON mortar), respectively. After 28 days, the MPOFA mortars at 10%, and 20% replacement levels had high compressive strengths compared to the others replacement levels. In fact, the strengths were higher than that of control mortar at 90 days. It is obvious that for all W/B ratios, MPOFA can be used to replace Portland cement at 20% replacement

level without any adverse effect on the compressive strength of mortar.

The compressive strengths and PCS of mortar containing MGS with W/B ratios of 0.50, 0.575, and 0.65 are presented in Table 5. At the same W/B ratios with the increase in replacement level, the compressive strength of mortar containing MGS decreased.

For example, 0.65MGS10, 0.65MGS20, 0.65MGS30, and 0.65MGS40 mortars had compressive strengths at 60 days of 36.6, 33.2, 29.6, and 22.86 MPa or 80.4%, 73.0%, 65.1%, and 50.1% of control mortar (0.65CON mortar), respectively. In addition, the PCS of mortars containing MGS with the same replacement levels and W/B ratio at various ages were nearly the same as shown in term of average PCS. This result suggested that the PCS of mortars containing MGS did not depend on the curing ages. The result thus confirmed that MGS was non-reactive material.

3.2. Compressive strength from hydration reaction of mortar with various W/B ratios

It was assumed that all silica (or quartz) in MGS was not reactive with no cementing property. The compressive strength of MGS mortar at the same replacement level depended on W/B ratio. In addition, MGS employed in this test had the same particle size as that of OPC. Thus, there were no change in the filler effect [18] and no pozzolanic reaction from the replacement of cement by MGS. The compressive strength of mortar containing MGS was from the hydration reaction of OPC only.

Fig. 2 shows the relationship between the average PCS of mortar due to hydration reaction and replacement level of MGS. This result suggested that the decrease in PCS due to hydration reaction related to the increase in W/B ratio. As a result, the compressive strength due to hydration reaction (C_{CH}) could be established in terms of PCS, percent of replacement level (R), and W/B ratio. The empirical equation could be expressed for mortars with W/B ratios of 0.50, 0.575, and 0.65 as follows:

$$\text{For } W/B = 0.50, \quad C_{CH} = -1.092(R) + 109.3 \quad (1)$$

$$W/B = 0.575, \quad C_{CH} = -1.147(R) + 105.7 \quad (2)$$

$$W/B = 0.65, \quad C_{CH} = -1.014(R) + 92.1 \quad (3)$$

The relationship of the percentage compressive strength due to hydration reaction and percent replacement in Eqs. (1)–(3) could be written as:

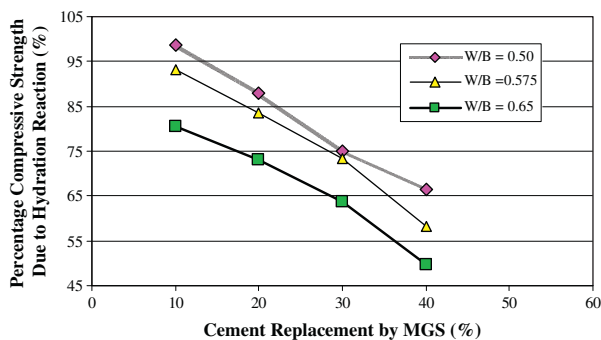
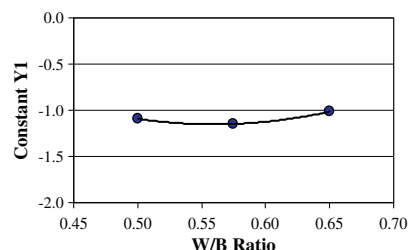
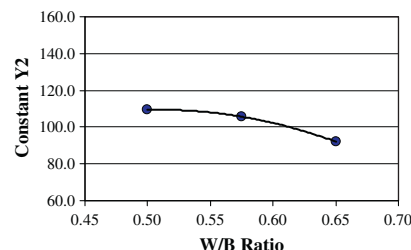


Fig. 2. Relationships between PCS of mortar due to hydration reaction and cement replacement by MGS.



(a) Constant Y1



(b) Constant Y2

Fig. 3. Relationship between constants Y1 and Y2 and W/B ratios.

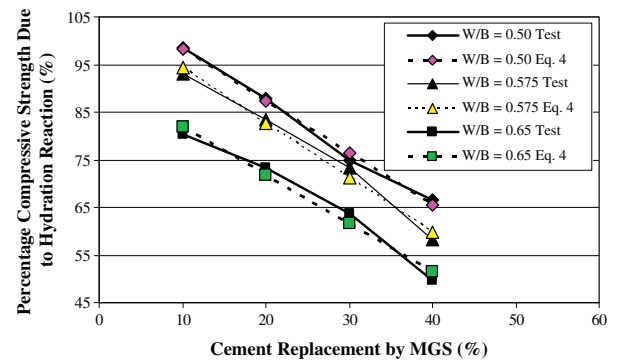


Fig. 4. Comparison the PCS of mortar due to hydration reaction obtained from Eq. (4) and from experiment.

$$C_{CH} = Y1(R) + Y2 \quad (4)$$

where C_{CH} is the compressive strength of mortar due to hydration reaction of OPC (% of the strength of control mortar), $Y1$ is $16.7(W/B)^2 - 18.7(W/B) + 4.1$, $Y2$ is $-888.9(W/B)^2 + 907.5(W/B) - 122.3$, R is the cement replacement level between 10% and 40%.

It should be noted here that $Y1$ and $Y2$ were obtained by curve fitting of the results from Fig. 3 for W/B ratios of 0.50, 0.575, and 0.65. The results of the compressive strength of mortar due to hydration reaction from this equation were very close to the actual test results as shown in Fig. 4. Eq. (4) is, therefore, useful for predicting the compressive strength of mortar due to hydration reaction of OPC mortar and pozzolan mortar at various W/B ratios and cement replacement levels.

3.3. Compressive strength from pozzolanic reaction of mortar with various W/B ratios

In this study, the compressive strengths contributed from filler effect of all mortars were constant due to the same particle sizes of OPC, inert material (MGS), and pozzolanic materials (MRHBA and MPOFA). Therefore, the increase in compressive strength of pozzolan mortar compared to inert material mortar at the same cement replacement level was pozzolanic reaction. Thus, the compressive strengths from pozzolanic reaction were the difference between the compressive strengths of mortars containing MRHBA or MPOFA and MGS as shown in Figs. 5 and 6.

The compressive strength of MRHBA mortar was from pozzolanic reaction as shown in Fig. 5. At the same W/B ratio, the compressive strengths due to pozzolanic reaction of MRHBA mortars increased with age and replacement level. For example, the compressive strengths of 0.50MRHBA20 mortar due to pozzolanic reaction increased from 6.2 MPa at 7 days to 10.2 MPa at 90 days. At 90 days, the compressive strength from pozzolanic reaction of 0.575MRHBA mortar increased from 8.2 MPa for 0.575MRHBA10

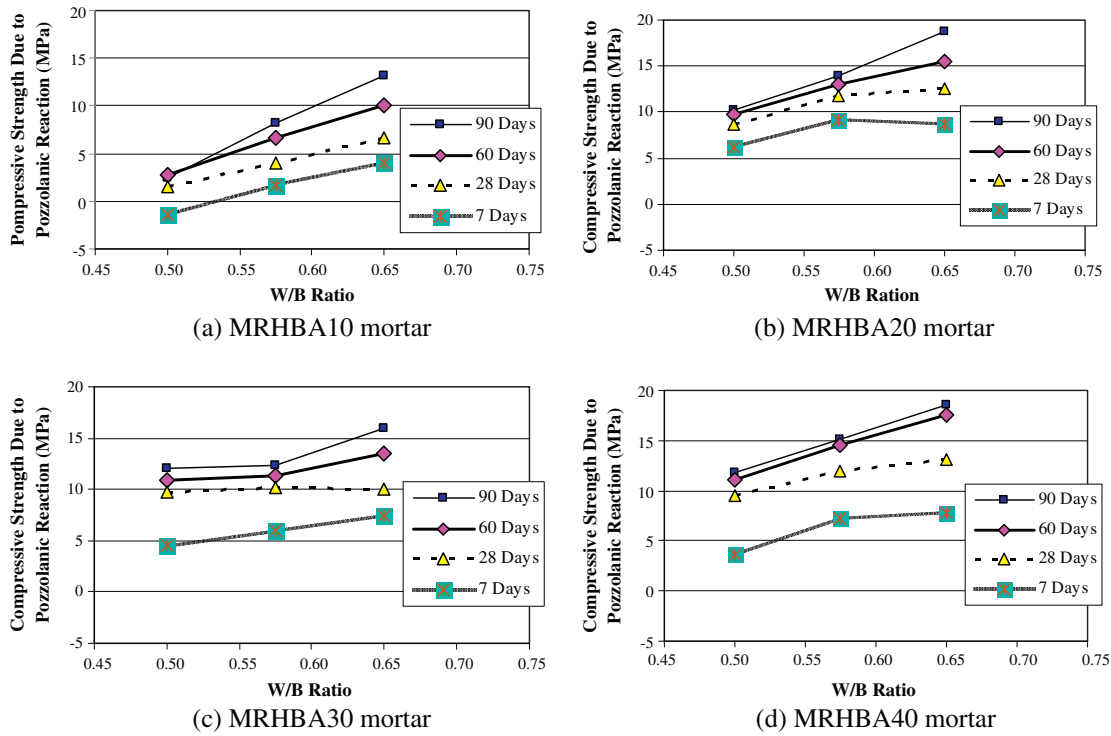


Fig. 5. Relationship between compressive strength of MRHBA mortars due to pozzolanic reaction and W/B ratio.

mortar to 15.1 MPa for 0.575MRHBA40 mortar. In addition, the optimum compressive strength from pozzolanic reaction at the early age occurred at lower replacement level while the optimum at the later age occurred at higher replacement level. At 7 days, 0.575MRHBA mortars had the highest compressive strength from

pozzolanic reaction at 20% of cement replacement (9.1 MPa) while the optimum of 40% of cement replacement (15.1 MPa) was at 90 days.

At the same cement replacement level, the compressive strength from pozzolanic reaction of MRHBA mortars increased

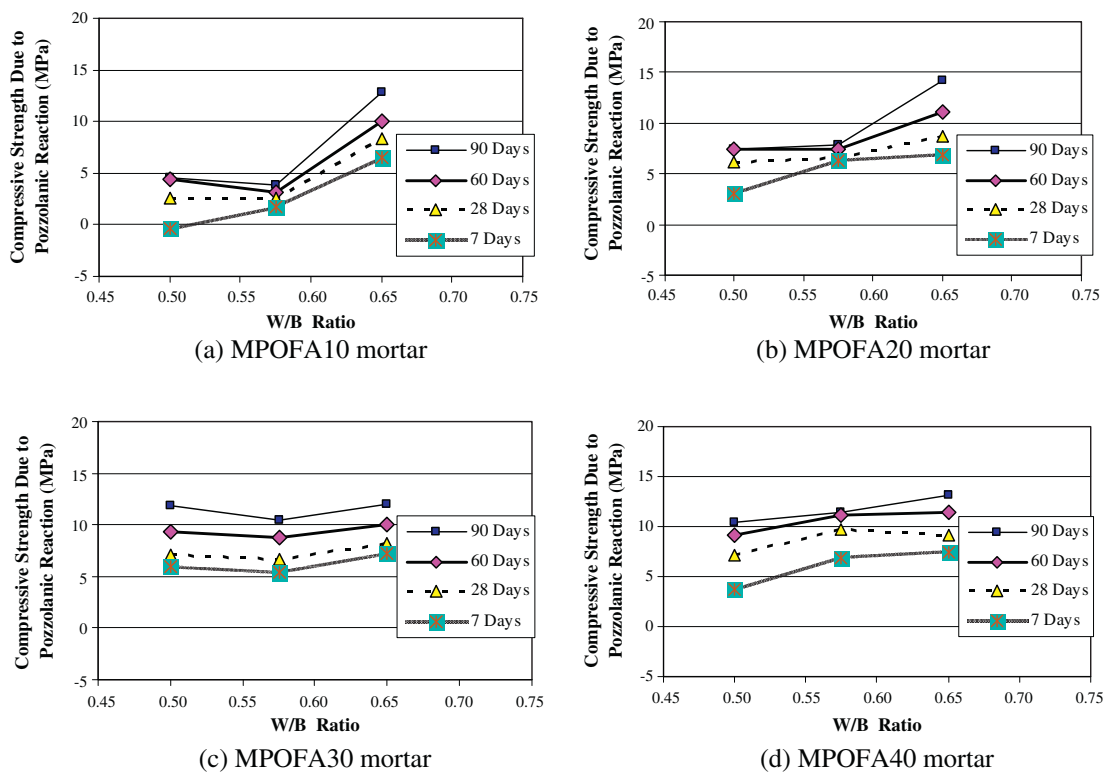


Fig. 6. Relationship between compressive strength of MPOFA mortars due to pozzolanic reaction and W/B ratio.

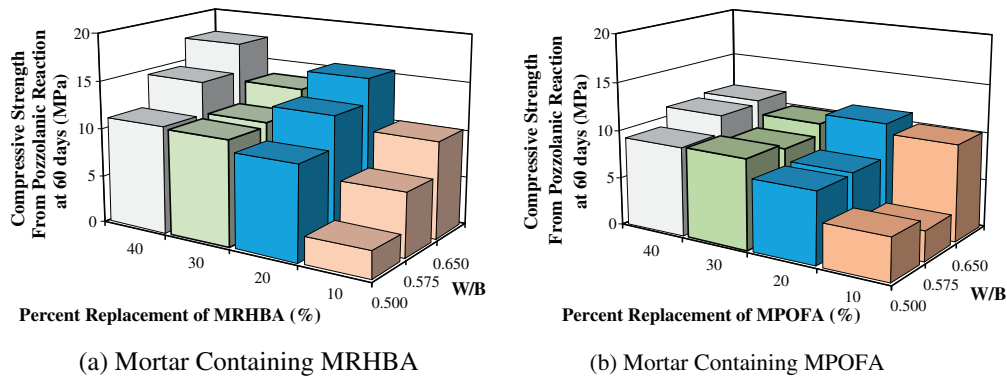


Fig. 7. Relationship between compressive strength of mortars due to pozzolanic reaction at 60 days, cement replacement level, and W/B ratio.

with the increase in W/B ratio. At high W/B ratio (0.65), relatively greater strengths due to pozzolanic reaction were produced. The increasing W/B ratio promotes the compressive strength from pozzolanic reaction since the amount of water at the high W/B ratio was sufficient for the reaction between $\text{Ca}(\text{OH})_2$ and pozzolan to form additional calcium silicate hydrates (CSH) [19]. At 90 days, 0.65MRHBA20 mortar gave the highest compressive strength due to pozzolanic reaction of 18.8 MPa or 40.5% of the control mortar strength (0.65CON mortar).

The compressive strengths of mortars containing MPOFA due to pozzolanic reaction are shown in Fig. 6. The trends of the results were the same as those of MRHBA mortars. However, by comparing the compressive strength from pozzolanic reaction of MRHBA and MPOFA, it was evident that the compressive strengths from pozzolanic reaction of MRHBA were slightly higher than those of MPOFA. At W/B ratio of 0.65, and 90 days, MRHBA mortars had compressive strength due to pozzolanic reaction from 13.1 MPa (28.3%) to 18.6 MPa (40.5%) of 0.65CON mortars strength, while those of mortars containing MPOFA were between 12.0 MPa (25.9%) and 14.2 MPa (30.6%) of 0.65CON mortar strength. This was due to the high major chemical composition ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) and low LOI in MRHBA as compared to MPOFA. These results conformed to previous published data from the study of high-strength concrete [3] which indicated that RHBA is slightly more reactive than POFA.

Fig. 7 presents the relationship between compressive strength of mortars at 60 days from pozzolanic reaction, cement replacement level and W/B ratios. It is evident that the compressive strengths from pozzolanic reaction of mortars containing MRHBA and MPOFA enhanced with the increase in W/B ratio and cement replacement level.

4. Conclusions

This study investigated the effect of W/B ratios on the pozzolanic reaction of MRHBA and MPOFA within OPC-based mortars. Based on the experimental results obtained in this study, the following conclusions can be drawn:

1. Ground RHBA and POFA with the similar particle size to OPC are reactive pozzolanic materials which have strength activity indices at 7 and 28 days between 93.0% and 109.8%; the replacement level between 10% and 20% exhibited optimal results. In addition, the compressive strengths from the pozzolanic reaction of MRHBA were slightly higher than those of MPOFA.
2. Ground river sand with the same particle size of OPC can be used as an inert material to evaluate the compressive strength of mortar from hydration reaction and pozzolanic reaction.

3. The degree of compressive strength of mortar due to hydration reaction depends on the W/B ratio. The higher is the W/B ratio, the lower is the degree of compressive strength of mortar due to the hydration reaction.
4. At same W/B ratio, the compressive strength of mortar due to pozzolanic reaction of MRHBA and MPOFA tends to increase with age and cement replacement level. In addition, at the same replacement level, the degree of compressive strength of mortar due to pozzolanic reaction increases with an increase in W/B ratio.

Acknowledgments

The authors gratefully acknowledge the financial support from the Thailand Research Fund (TRF) under TRF Senior Research Scholar Grant No. RTA5380002 and the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission, through the Advanced Functional Materials Cluster of Khon Kaen University.

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