

Influence of Fly Ash Fineness on Calcium Hydroxide in Blended Cement Paste

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บทคัดย่อ

This research demonstrates the effect of fly ash fineness on calcium hydroxide (Ca(OH)_2) in blended cement paste. The investigation of Ca(OH)_2 quantity was determined by thermogravimetry analysis (TGA). Two sizes of fly ash, original fly ash and classified fly ash were used to replace Portland cement type I paste with water-to-binder ratio (W/B) of 0.35. This was used in all mixtures and the percentages of fly ash to replace Portland cement of 0, 20, and 40% by weight of binder were used in this investigation. Test results indicated that the amount of Ca(OH)_2 in the blended cement pastes containing fly ash is lower than in neat Portland cement paste due to the dilution effect and the pozzolanic reaction of fly ash. The amount of Ca(OH)_2 of the blended cement paste with fly ashes decreased with increasing replacement percentage of fly ash and were lower than that of PC paste. It was found that the fineness of fly ash had an effect on the reduction rate of Ca(OH)_2 . The Ca(OH)_2 of fine fly ash pastes dropped more rapidly than those of coarse fly ash pastes. This may be due to the fact that the particle sizes of fine fly ash are smaller than those of coarse fly ash. This reason is that the fine fly ash has a larger surface area to provide the silica and alumina compounds for pozzolanic reaction. The paste containing finer fly ash showed higher pozzolanic reaction rate than the paste containing coarse fly ash.

คำสำคัญ: Fineness, Fly ash, Calcium hydroxide, Blended cement paste.

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Abstract

This research demonstrates the effect of fly ash fineness on calcium hydroxide ($\text{Ca}(\text{OH})_2$) in blended cement paste. The investigation of $\text{Ca}(\text{OH})_2$ quantity was determined by thermogravimetry analysis (TGA). Two sizes of fly ash, original fly ash and classified fly ash were used to replace Portland cement type I paste with water-to-binder ratio (W/B) of 0.35. This was used in all mixtures and the percentages of fly ash to replace Portland cement of 0, 20, and 40% by weight of binder were used in this investigation. Test results indicated that the amount of $\text{Ca}(\text{OH})_2$ in the blended cement pastes containing fly ash is lower than in neat Portland cement paste due to the dilution effect and the pozzolanic reaction of fly ash. The amount of $\text{Ca}(\text{OH})_2$ of the blended cement paste with fly ashes decreased with increasing replacement percentage of fly ash and were lower than that of PC paste. It was found that the fineness of fly ash had an effect on the reduction rate of $\text{Ca}(\text{OH})_2$. The $\text{Ca}(\text{OH})_2$ of fine fly ash pastes dropped more rapidly than those of coarse fly ash pastes. This may be due to the fact that the particle sizes of fine fly ash are smaller than those of coarse fly ash. This reason is that the fine fly ash has a larger surface area to provide the silica and alumina compounds for pozzolanic reaction. The paste containing finer fly ash showed higher pozzolanic reaction rate than the paste containing coarse fly ash.

Keywords: fineness, fly ash, calcium hydroxide, blended cement paste.

1. Introduction

Concrete is a composite material which has a complex microstructure and exhibits a wide range of scale lengths from nanometers to millimeters. Aggregates are the biggest materials in concrete and have particle size in millimeters. At the micrometer

scale, the cement paste is a composite of unhydrated residues of cement grains and hydration products (C-S-H, $\text{Ca}(\text{OH})_2$, and capillary pore). The availability of $\text{Ca}(\text{OH})_2$ is one of the factors affecting the pozzolanic reaction rate since it is the main compound in pozzolanic reaction. It is known that replacing cement with fly ashes results in lower amount of $\text{Ca}(\text{OH})_2$ in paste. Many researches have established its effect of fly ashes on the physical properties and pozzolanic reaction of paste, mortar and concrete. However, the $\text{Ca}(\text{OH})_2$ changes due to differences in fly ash fineness are not well established. The present paper, therefore, attempts to provide essential information on the $\text{Ca}(\text{OH})_2$ of blended cement with fly ash of two finenesses.

2. Experimental Methodology

2.1 Material

Fly ash from Mae Moh power plant in the north of Thailand, Portland cement type I (PC) and tap water were used in this study. The chemical composition of PC, original and classified fly ashes (OFA and CFA) are given in Table 1. The total amount of the major components SiO_2 , Al_2O_3 , and Fe_2O_3 in OFA and CFA are 81.54% and 79.44%, respectively. They can be classified as class F fly ash in accordance with ASTM C 618. It should be noted that there is no significant difference in the chemical composition of OFA and CFA. Two fly ash sizes of OFA with median particle size of 19.1 microns and CFA with median particle size of 6.4 microns were used to replace Portland cement. Physical properties of PC, OFA, and CFA are shown in Table 2 and particle size distributions are shown in Figure 1. Particle shapes of PC, OFA, and CFA by SEM are shown in Figure 2.

Table 1. Chemical Composition of Portland Cement Type I and Fly Ashes

Chem. Composition (%)	PC	OFA	CFA
SiO ₂	20.90	45.69	44.72
Al ₂ O ₃	4.76	24.59	23.69
Fe ₂ O ₃	3.41	11.26	11.03
CaO	65.41	12.15	12.67
MgO	1.25	2.87	2.63
SO ₃	2.71	1.57	1.28
Na ₂ O	0.24	0.07	0.07
K ₂ O	0.35	2.66	2.87
LOI	0.96	1.23	1.42

Table 2. Physical Properties of Portland Cement Type I and Fly Ashes

Sample	Median Particle Size (micron)	Retained on a Sieve No. 325 (%)	Specific Gravity	Blaine Fineness (m ² /kg)
PC	14.1	4.8	3.15	360
OFA	19.1	31.0	2.33	300
CFA	6.4	0	2.54	510

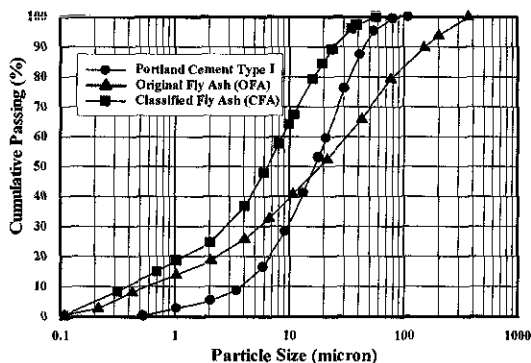
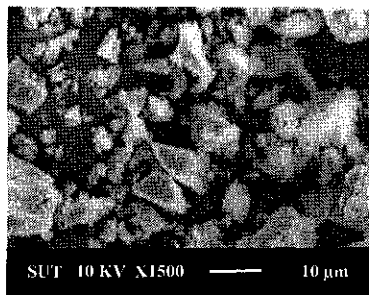
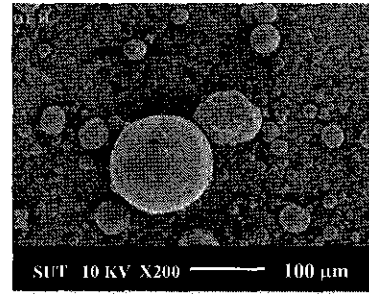


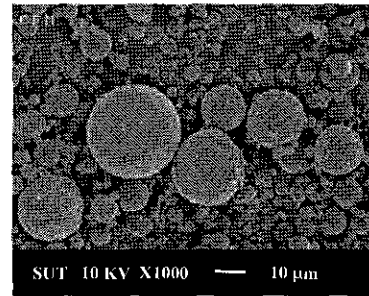
Figure 1. Particle size distribution of PC type I and fly ashes



(a) PC type I (PC)



(b) Original fly ash (OFA)



(c) Classified fly ash (CFA)

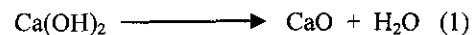
Figure 2. SEM of PC type I and fly ashes

2.2 Mix Proportions and Specimens

Fly ashes were used to replace portland cement at dosage levels of 0, 20, and 40% by mass of binder. A constant water to binder ratio (w/b) of 0.35 was used throughout the investigation. The pastes were mixed in a mechanical mixer and the specimens were cast in 50 mm cube moulds. The fresh samples were covered with polyethylene sheet to prevent evaporation. After 24 hours, the samples were removed from the mould and cured in saturated lime water.

2.3 Thermal Gravity Analysis (TGA)

The Ca(OH)₂ content in blended cement paste is the result of the product between Portland cement and water. Consumption of Ca(OH)₂ by pozzolanic reaction of fly ash can be observed by the reduction in Ca(OH)₂ content. TGA test as shown in Figure 3 has been widely accepted as an accurate method for the determination of crystalline Ca(OH)₂ content and other hydration (loss of water), including C-S-H, ettringite (Aft phases), gypsum, and so on [1]. The Ca(OH)₂ content was calculated based on the weight loss between 450°C and 580°C, [2, 3, 4] and express as a percentage by weight of ignited sample. When heating the cement paste at the temperature between 440-580 °C, Ca(OH)₂ will be decomposed into calcium oxide (CaO) and water as in equation 1.



The amount of calcium hydroxide measured directly by TGA method is the amount of calcium hydroxide occurring at that particular time, which results from hydration reaction and the pozzolanic

reaction. This amount of calcium hydroxide is called "the measurable amount of calcium hydroxide". The amount of calcium hydroxide due to the hydration reaction can be found by using TGA method in normal cement paste. The amount of calcium hydroxide due to the hydration reaction in fly ash cement paste can be known by the direct comparison with the proportion of cement used in mixing. However, as a matter of fact that fly ash causes the pozzolanic reaction, which decreases the calcium hydroxide. This decreasing calcium hydroxide known as "percent consumption of calcium hydroxide in pozzolanic reaction" can be found by comparing the amount of calcium hydroxide from normal cement paste with that of fly ash cement paste as shown in equation 2.

$$P = H*(1-R/100) - F \quad (2)$$

When P = calcium hydroxide used in pozzolanic reaction (%)

R = fly ash replacement of cement by weight (%)

H = calcium hydroxide measured from normal cement paste (%)

F = calcium hydroxide measured from fly ash cement paste (%)

TG curve is the graph referring to the weight loss during each peak compared with the original weight of substances prior to the test. Due to the heat, the water lost, causing the decrease in overall weight. This water can be measured, thus the amount of calcium hydroxide from this water can be calculated by the equation 1. According to the calculation, it is pointed out that the amount of the calcium hydroxide loss refers to the amount of water measured multiplying by the constant value, which equals to 4.11 [2, 3].

All samples was cured for the specified ages (7, 28, 60 and 90 days). Cube specimen was crushed into fragmented samples and the freeze-dried samples as prepared for MIP. Prior to testing, the dried sample pastes were ground in a ball mill and sieved through 100 mesh (150 μm). TGA analysis of the samples was performed using thermal analyzer. Dry N₂ atmosphere has been used for TGA analysis. Approximately 10-20 mg of the sample was taken for the analysis. The rate of heating has been maintained to 10°C/min and the sample was heated up to 1,000 °C.

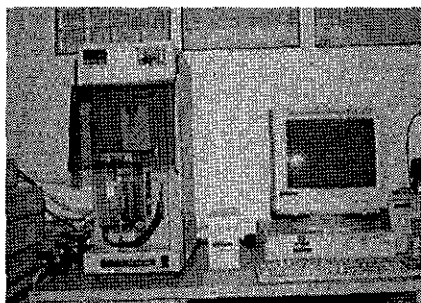


Figure 3. Thermal Gravity Analysis (TGA)

3. Results and discussion

3.1 Calcium Hydroxide in Blended Cement Paste

Table 3 shows percentage of Ca(OH)₂ in each mix proportion and Figure 4 shows a comparison of Ca(OH)₂ of PC paste and pastes containing fly ashes with different fineness. From the results of Table 3 and Figure 4, the amount of Ca(OH)₂ in the blended cement pastes containing fly ash is lower than in neat Portland cement paste due to the dilution effect and the pozzolanic reaction of fly ash. The amount of Ca(OH)₂ of the blended cement paste with fly ashes decreased with increasing replacement percentage of fly ash and were lower than that of PC paste. After the Ca(OH)₂ was produced by the hydration reaction, it was consumed by pozzolanic reaction. The content of Ca(OH)₂ were decrease at longer ages in the cases of pastes containing fly ash. It was found that the fineness of fly ash had an effect on the reduction rate of Ca(OH)₂. The Ca(OH)₂ of CFM20 and CFM40 pastes dropped more rapidly than those of coarse fly ash pastes (OFA20 and OFA40). This may be due to the fact that the particle sizes of CFA are smaller than those of OFA. This reason is that the fine fly ash has a larger surface area to provide the silica and alumina compounds for pozzolanic reaction. These compounds reacted and consumed Ca(OH)₂. The Ca(OH)₂ consumption was used as an indicator of pozzolanic action. The reduction of Ca(OH)₂ in all fly ash pastes became subtle with age. It is also found that the fineness of fly ash had an effect on the pozzolanic action rate. The paste containing finer fly ash showed higher pozzolanic reaction rate than the paste containing coarse fly ash.

Table 3. Weight loss during the TG analysis of pastes

Mix	Ages (day)	Weight loss (%)	Ca(OH) ₂ (%)		
			Test	Hydration	Consump.
PC	7	3.93	16.15	16.15	-
	28	4.46	18.33	18.33	-
	60	5.00	20.53	20.53	-
	90	5.08	20.87	20.87	-
OFA20	7	2.79	11.47	12.92	1.45
	28	3.25	13.35	14.66	1.32
	60	3.50	14.39	16.42	2.03
	90	3.54	14.54	16.70	2.16
OFA40	7	2.12	8.72	9.69	0.97
	28	2.19	8.98	11.00	2.01
	60	2.21	9.10	12.32	3.22
	90	2.15	8.83	12.52	3.69
CFA20	7	2.72	11.18	12.92	1.74
	28	3.05	12.52	14.66	2.14
	60	3.02	12.40	16.42	4.02
	90	2.91	11.96	16.70	4.74
CFA40	7	2.05	8.40	9.69	1.29
	28	2.15	8.84	11.00	2.16
	60	2.14	8.79	12.32	3.53
	90	2.02	8.29	12.52	4.23

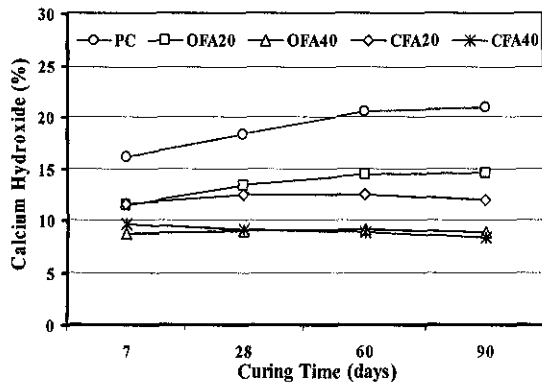


Figure 4. Relationship between $\text{Ca}(\text{OH})_2$ of pastes with curing times

5. Conclusions

Based on the results obtained, the following conclusions can be drawn.

1. The blended cement paste containing original fly ash generally exhibited a lower $\text{Ca}(\text{OH})_2$ than that of Portland cement type I paste.
2. The blended cement paste containing classified fly ash resulted in a lower $\text{Ca}(\text{OH})_2$ than that of the one with original fly ash.

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