FLUIDIZED BED COAL-BARK FLY ASH GEOPOLYMER WITH ADDITIVES CURED AT AMBIENT TEMPERATURE

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ABSTRACT: In this research, the properties of fluidized bed coal-bark fly ash geopolymer mortar containing additives viz., ordinary Portland Cement (OPC) and micro silica (MS) were studied. The fluidized bed coal-bark fly ash was a waste from a power plant boiler in Khon Kaen, Thailand. The geopolymer mortar was made from fluidized bed coal-bark fly ash, sand, sodium silicate solution, NaOH solution, and additives. The additives were used to replace the fluidized bed coal-bark fly ash at the level of 0 - 15 % by weight. The mortars with liquid alkaline/ash ratios of 0.9-1.4, sodium silicate/NaOH ratios of 0.33-3.00, NaOH concentrations of 5-15 molars, OPC and micro silica contents of 0 - 15 % by weight of fly ash, and curing at ambient temperature were tested. The geopolymer mortars with 28-day compressive strengths between 5.5 and 27.0 MPa and densities between 1970 and 2175 kg/m³ were obtained. The addition of OPC and micro silica content of 15 %. It is shown here that the fluidized bed coal-bark fly ash geopolymer mortar containing OPC and micro silica as additives with ambient temperature curing possesses sufficient strength. The use of this product can reduce the energy consumption in cement production and increases the sustainability of construction industry.

Keywords: Coal-bark fly ash, Fluidized bed, OPC, Micro silica, Geopolymer

1. INTRODUCTION

Cement is the main material in construction. In the cement production process, a large amount of limestone is obtained from the limestone mountain. It is processed through washing, grinding, baking and other processes and huge energy is thus used. The temperature up to 1,400 degrees Celsius is needed and a large amount of carbon dioxide (CO₂) is released into the atmosphere. Every 1 ton of Portland cement comes out of the furnace, about 1 ton of CO₂ is produced [1]. This results in an increase in the greenhouse effect.

For this reason, the researches have been conducted to develop alternative materials to substitute cement to reduce the above-mentioned problems. The potential binder to substitute Portland cement is geopolymer materials. Geopolymer is an environmentally friendly binder with binding capacity based on aluminosilicate [2, 3]. It provides high strength in a short time when modulate heat is applied. The temperature used is not very high around 40-80 degrees Celsius [4]. The geopolymer can be used for the production of precast concrete such as pillars, beams, walls and finished flooring which are suitable for work requiring high compressive strength in a short time.

Today, the precast concrete is in high demand in the market because it is convenient and fast to work. However, heat curing also increase the cost of the product. Curing at room temperature causes the geopolymer to develop the strength slowly [4]. The additive materials such as silica fume or micro silica are used to help develop strengths. It helps to improve the compressive strength of the geopolymer cured at room temperature.

In addition, the production of geopolymer can utilize the waste from the manufacturing process in the industrial sector. This includes agricultural products such as rice husk ash, bagasse ash, and other biomass ash; the garbage industry, including waste ash, and the electricity industry, including fly ash and bottom ash.

In this research, fly ash was selected to use. The fly ash was a waste from a power plant boiler in Khon Kaen, Thailand. It used the wood scraps, which are the waste materials from the paper production process. The factory has burned these wood scraps to produce electricity together with the use of sub-bituminous coal in the Fluidized Bed Combustion (FBC).

The fluidized bed combustion uses small scale pulverized coal mixed with limestone, and sprays into the furnace with the hot air. The coal and limestone, which are sprayed into the furnace, are suspended in the hot air. It looks like a boiling liquid while the coal burns, the limestone acts as a sponge trapping sulfur dioxide. This process can reduce the amount of sulfur that is released by combustion by as much as 90% [5]. In addition, the combustion at temperatures below 1,000 °C reduces the amount of pollution caused by nitrogen in the combustion system. However, the fly ash obtained from this system is irregular in shape with high crystallinity because the burnt temperature is not very high. This fly ash can be used as a pozzolanic material but It is not as good as the fly ash obtained from the pulverized burning system. Also, it has high calcium and sulfur content [6] to be used in the work of geopolymer materials. The properties and effects of ash will have to be investigated. The co-burning of coal and biomass is now also practiced in the other country [7, 8]. This co-burning of coal and biomass has recently been applied and thus there is no statistical report on this. In addition, the use of fluidized bed coal-bark fly ash as a binder source is not yet financially supported by the Thai government. The support would promote the use of waste materials and is an essence tool for future use of waste.

Therefore, this research has studied the properties of geopolymer with fluidized bed furnace system ash from burning sub-bituminous coal with wood derived from the paper production at burning temperature below 1,000 °C. It has high calcium and sulfur contents. The purpose is to recycle the waste from the industry for maximum benefit. This is the development of materials for use in the construction which is environmental friendly and sustainable.

2. EXPERIMENTAL PROGRAM

2.1 Materials

In this study, materials consisted of fluidized bed coal-bark fly ash (FCB-FA) was a waste from a power plant boiler in Khon Kaen, Thailand, ordinary Portland cement (OPC) and micro silica (MS) of 0, 5, 10, and 15 % by weight of fly ash, sodium hydroxide (NaOH) of 5, 10, and 15 M, sodium silicate with 15.32% Na₂O, 32.87% SiO₂, and 51.8% water, and river sand. the physical properties of materials are shown in Table 1. The specific gravity of FCB-FA was 2.86 with median particle size of 23.9 μ m. The FCB-FA consisted of a high content of 21.14% SiO₂, 8.02% Al₂O₃, 10.98% Fe₂O₃, and 35.8% CaO with the loss on ignition (LOI) of 0.28% as shown in Table 2. It was,

therefore, a class C in accordance which ASTM C618 [9]. The XRD of MS and OPC as shown in Fig. 1 and the morphology of FCB-FA by SEM as shown in Fig. 2 indicated that the shape of FCB-FA was irregular with some additional small pores.

2.2 Mix proportion

2.2.1 OPC and MS content

To study the effect of OPC and MS content, the OPC and MS contents of 0, 5, 10, and 15 % by weight of fly ash were used in one series. The compressive strength and density of fluidized bed coal-bark fly ash geopolymer were determined.







b. OPC

Fig.1 The XRD of MS and OPC

2.2.2 Mix compositions

In order to obtain adequate data, a number of series of mixes were tested as follows.

Series OPC: To study the effect of OPC content, all mixtures used constant NaOH of 10 M, NS/NaOH ratios of 1.00, aggregate A/FA of 2.75 cured at ambient temperature. L/FA of 0.9, 1.0, 1.1, 1.2, and 1.3 and OPC content of 0, 5, 10, and 15 % by weight were tested.

Series MS: To study the effect of MS content, all mixtures used constant NaOH of 10 M, NS/NaOH ratios of 1.00, A/FA of 2.75 cured at ambient temperature. And varies L/FA of 0.9, 1.0, 1.1, 1.2, and 1.3 and MS content of 0, 5, 10, and 15 % by weight were tested.

Series NS/NaOH: This series was used to study the effect of sodium silicate/NaOH ratios. All mixtures used constant NaOH of 10 M, OPC and MS content of 10 % by weight, A/FA of 2.75 cured at ambient temperature, and NS/NaOH ratios of 0.33, 0.67, 1.0, 1.5 and 3.0.

Series [NaOH]: All mixtures used constant OPC and MS content of 10 % by weight, NS/NaOH ratios of 1.00, A/FA of 2.75 cured at ambient temperature. Three NaOH concentrations viz., 5, 10 and 15 molars were used to study the effect of NaOH concentration.

Series A/FA: This series was used to study the effect of aggregate/fly ash ratio. all mixture used constant OPC and MS content of 10 % by weight, NS/NaOH ratios of 1.00, NaOH of 10 M with cured at ambient temperature. The A/FA of 2.50, 2.75, and 3.00 were tested.



Fig.2 The morphology of FCB-FA by SEM

2.2.3 Details of Mixing

All mixtures were made and cured at ambient temperature. OPC and MS content of 0, 5, 10, and 15 % by weight of FCB-FA, concentration of NaOH of 10, 12.5, and 15 molars, sodium silicate/NaOH ratios (NS/NaOH) of 0.67, 1.00, and 3.00, aggregate/ash ratios of 2.50, 2.75, and 3.00. The mixing was done in a pan mixer with following step:

- FCB-FA, OPC and MS were mixed for 5 min.
- NaOH was added and mixed for 5 min.
- Sand was added and mixed for 5 min.

- Sodium silicate was added and mixed for 5 min.

The fresh fluidized bed coal-bark fly ash geopolymers were placed into 50 x 50 x 50 mm cubes molds according to ASTM C109/C109M-16a [10]. The specimens were wrapped with plastic sheet and placed in a 25 °C controlled room for 24 hours. Finally, the specimens were demolded and stored in a 25 °C controlled room. The textures of fluidized bed coal-bark fly ash geopolymer mortar containing additives are shown in Fig. 3.

Table 1 The physical properties of materials

Materials	MS	OPC	FCB-FA	Sand
Specific gravity	2.16	3.15	2.86	2.61
Median particle size (µm)	13.8	18.7	23.9	-
Fineness modulus	-	-	-	2.65
Unit weight (kg/m ³)	460	1440	875	1360
Water absorption (%)	-	-	-	1.17

Table 2 Chamical composition of materials (by weight)

Chemical compositions (%)	FCB-FA	MS	OPC
SiO ₂	21.14	92.4	20.8
Al_2O_3	8.02	-	4.7
Fe_2O_3	10.98	0.33	3.4
CaO	35.8	2.52	65.3
K ₂ O	5.36	3.13	0.4
Na ₂ O	0.33	-	0.1
SO_3	11.56	0.96	2.7
LOI	0.28	0.21	0.9



Fig.3 The sample of fluidized bed coal-bark fly ash geopolymer mortar containing additives

2.3 Details of Test

2.3.1 Compressive strength and density

The 50 x 50 x 50 mm cube specimens were tested for density and compressive strength. The density was determined at 28 days using the compressive strength specimens as described in ASTM C 138/C138M-14 [11]. The compressive strength was measured after the density

determination. The cube specimens were tested to determine the compressive strength in accordance with ASTM C109/C109M-16a [10]. The reported unit weight and compressive strengths were the average of three samples.

3. RESULTS AND DISCUSSIONS

3.1 Compressive Strength and Density

3.1.1 Series OPC

The results of compressive strength of fluidized bed coal-bark fly ash geopolymer with various L/FA and OPC content are shown in Fig. 4. The compressive strength of fluidized bed coal-bark fly ash geopolymer with additives depended on both L/FA and OPC contents. For the OPC content, the compressive strength increased with increasing OPC content from 0 to 10 % by weight of fluidized bed coal-bark fly ash. This was due to the increased amount of calcium from Portland cement. As a result, the reaction form additional hydration products of C-S-H and C-A-S-H which coexisted with normal geopolymer products and improved compression [12, 13]. For the high OPC replacement level of 15 %, the increase in compressive strength started to cease and in some cases significant decreases were observed. The high OPC content of 15 % resulted in some strength reduction due mainly to the modifications of microstructure of hydration products and the amount of cement is too high to make the mixture dry [14, 15]. For example, the compressive strengths at 28 days of mixes with L/FA of 0.9 with volume of OPC of 0, 5, 10, and 15 % by weight were 9.2, 16.8, 22.9, and 22.0 MPa, respectively.



Fig.4 Compressive strength of series OPC at 28 days

With regards to L/FA, the compressive strength decreased with increasing L/FA. Due to the ratio of liquid to fly ash is too high, the result was bleeding and thus resulted in the reduction in compressive strength [16, 17]. For example, the compressive strengths at 28 days of 15 % OPC with L/FA of 0.9,

1.0, 1.1, 1.2, and 1.3 were 22.0, 20.4, 19.6, 18.4, and 16.4 MPa, respectively.

3.1.2 Series MS

The results of compressive strength of fluidized bed coal-bark fly ash geopolymer with various L/FA and MS contents are shown in Fig. 5. For the MS content, the compressive strength increased with increasing MS content from 0 to 15 % by weight of fluidized bed coal-bark fly ash. The particles of silica fume were very small and highly amorphous phase could react quite quickly [18]. For example, the compressive strengths at 28 days of mixes with L/FA of 0.9 with volume of MS of 0, 5, 10, and 15 % by weight were 9.8, 18.6, 24.5, and 34.5 MPa, respectively.

With regards to L/FA, the compressive strength of fluidized bed coal-bark fly ash geopolymer tended to decrease with increasing L/FA. For the example, the compressive strengths at 28 days of 15 % OPC with L/FA of 0.9, 1.0, 1.1, 1.2, and 1.3 were 34.5, 25.0, 30.5, 20.5, and 4.2 MPa, respectively.



Fig.5 Compressive strength of series MS at 28 days

3.1.3 Series NS/NaOH

The results of compressive strength of fluidized bed coal-bark fly ash geopolymer with various sodium silicate/NaOH ratios and OPC, MS content of 10 % by weight are shown in Fig. 6. It was found that the optimum compressive strength was with sodium silicate/NaOH ratios of 1.00. The increased in silicate/NaOH ratios affect to the pH value and increased the compressive strength [19]. In contrast, for the silicate/NaOH ratios above 1.00, the increase in sodium silicate content also increased the viscosity of mixture and this resulted in the difficulties in casting and adversely affect the compressive strength [20]. For example, the compressive strengths at 28 days of mixes with control and NS/NH of 0.67, 1.00, and 3.00 were 6.7, 15.5, and 11.1 MPa, respectively.

When considering MS and OPC contents; the 10 % MS gave mix with compressive strength higher than 10 % OPC due to MS or micro silica is a very reactive pozzolanic material because of its

extreme fineness and very high amorphous silicon dioxide content [21]. For example, the compressive strengths at 28 days of mixes with NS/NH of 0.67 of control, 10 % OPC and 10 % MS were 6.7, 9.3, and 15.4 MPa, respectively.



Fig.6 Compressive strength of series NS/NaOH at 28 days

3.1.4 Series [NaOH]

The results of the compressive strength of fluidized bed coal-bark fly ash geopolymer with various [NaOH] and OPC, MS content of 10 % by weight are shown in Fig. 7.



Fig.7 Compressive strength of series [NaOH] at 28 days

The increased in NaOH from 10 M to 12.5 M resulted in the increasing compressive strength. For example, the compressive strengths at 28 days with the volume of control with NaOH of 10, 12.5, and 15 M were 15.5, 15.8, and 10.3 MPa, respectively. The low compressive strength with low NaOH due to setting time of paste was short with low NaOH [22, 23]. The NaOH influence the setting time of the geopolymer. At low NaOH, the leaching out of silica and alumina was low but high in Ca2+ and the amount of calcium was sufficient for the precipitation and reacted to form calcium aluminate hydrate and calcium silicate hydrate. Thus, the setting time of geopolymer was related to the amount of available calcium [24, 25]. In contrast, an increased NaOH from 12.5 to 15 M resulted in a decrease in the compressive strength. At high concentration of NaOH, the compressive strength decreased due to the excessive hydroxide ions causing aluminosilicate gel precipitation at the very early stages and resulting in low compressive strength [13, 26, 27].

3.1.5 Series A/FA

The results of compressive strength of fluidized bed coal-bark fly ash geopolymer with various aggregate/fly ash ratio (A/FA) and OPC, MS contents of 10 % by weight are shown in Fig. 8. The increase in aggregate/fly ash ratio resulted in a slightly decrease in compressive strength due to the volume of cementitious materials decreased.

When considering MS and OPC contents; at the same Series NS/NaOH, the compressive strength of 10 % MS was higher than that of 10 % OPC due to MS is a very reactive pozzolanic material.



Fig.8 Compressive strength of series A/FA at 28 days

4. CONCLUSIONS

Based on the obtained data, the following conclusions can be drawn:

1. When considering varies L/FA with OPC and MS contents; the compressive strength increased with the increasing volume of OPC from 0 to 10 % by weight. In contrast, when the OPC increased from 10 to 15 % by weight, the compressive strength decreased. For the volume of MS, the compressive strength increased with the increasing of the volume of MS from 0 to 15 % by weight.

2. For series NS/NaOH; the NS/NaOH of 1 gave the highest compressive strength and apart from this, the strength of geopolymer started to drop. The 10 % MS gave compressive strength higher than 10 % OPC due to MS is a very reactive pozzolanic material.

3. For the control and 10 % OPC samples of series [NaOH], the increase in NaOH from 10 M to 12.5 M resulted in the increasing compressive strength. In contrast, an increase in NaOH from 12.5 to 15 M resulted in a decrease in the compressive

strength. At 10 % MS, the increase in NaOH from 10 M to 15 M resulted in the decreasing compressive strength

4. For series A/FA; the increase in A/FA resulted in a slight decrease in compressive strength and the compressive strength of 10 % MS was higher than that of 10 % OPC.

5. The results showed that the 28-day compressive strengths between 5.5 and 27.0 MPa and densities between 1970 and 2175 kg/m³ were obtained. The addition of OPC and MS enhanced the strength development of geopolymer mortars with the optimum OPC content of 10 % and MS content of 15 %. The use of this product can reduce the energy consumption in cement production and increases the sustainability of construction industry.

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