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INFLUENCE OF Si/Al RATIO ON COMPRESSIVE STRENGTH OF RICE HUSK–BARK ASHES AND FLY ASH-BASED GEOPOLYMER PASTE

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***ABSTRACT**: This paper focuses on the influence of Si/Al ratio on the compressive strength and rate of reaction of fly ash and rice husk-bark ash based geopolymer paste. The test included the effect of curing temperature on both compressive strength and rate of reaction. Geopolymer pastes were cast in cylindrical mold 3 cm diameter and 6 cm height for crushing test. Paste also tested for rate of reaction at the selected times. The results revealed that compressive strength of geopolymer paste increased as the Si/Al ratio increased. When the Si/Al ratio reached 8.28, the compressive strength tended to drop down. Moreover, cracks were found at the mix with Si/Al ratio higher than 8.28, due to dimensional instability. The 28 days highest compressive strength was 510 ksc when cured in room temperature. However, curing at 60 ^{o}C enhanced the higher compressive strength within early ages.*

KEYWORDS : Fly ash, Rice Husk–bark Ash, Geopolymer, Si/Al Ratio, Compressive Strength

1. INTRODUCTIONS

Geopolymer is known in many names such as alkali-activated cement, aluminosilicate material and inorganic polymer. Geopolymers have been widely investigated in every corner of this world also in Thailand [1, 2, 3]. Fly ash from power plant was usually studied as an initial substance, resulting the Si/Al ratio was not much changed. It was the barrier to investigate the wider range of Si/Al of geopolymer properties. Using the rice husk-bark ash with fly ash as the initial monomer, allow us to observe the wide range of Si/Al ratio geopolymer.

2. OBJECTIVES

This work is to study the influence of Si/Al ratio on the compressive strength of fly ash and rice husk-bark ash-based geopolymer.

3. EXPERIMENTAL PROGRAM

3.1 Materials

Rice Husk-Bark Ash (RHBA) is a by-product from power plant process at Thai Power Supply Company Ltd., in Chachoengsao province. RHBA was ground by ball mill till the mass of the fine particles retains on sieve size No. 325 was less than 2%. Fly Ash (FA) is obtained from

Mae Moh power plant in Thailand. The physical properties of RHBA and FA are shown in Table 1. Sodium silicate solutions, Na_2OSiO (15.36% Na_2O and 30% SiO_2) and 18M NaOH solutions (commercial grade) was used.

3.2 Mixed Proportions of Geopolymer Paste

RHBA and FA were pre-mixed in jar. Mixed proportions of geopolymer paste were prepared by the proportion of RHBA to FA. Six ratios were studied as follows: 0:100, 20: 80, 40: 60, 60:40, 80:20, and 100:0 by weight. The ratios of solid (RHBA + FA) to total weight (solid sodium silicate + sodium hydroxide + water) was 0.65 by weight. The ratio of sodium silicate to sodium hydroxide was 2.50 by weight and sodium hydroxide concentration was 18 M. All mixed proportions of geopolymer paste were shown in Table 2.

3.3 Mixing of Geopolymer Paste

The solution of sodium silicate and sodium hydroxide were pre-mixed prepared and allowed it to cool down over night till 27°C. Then the solution was poured into mixing machine and mixed it thoroughly with RHBA and FA for 5 min. The specimens of geopolymer paste (30 mm in diameter, 60 mm in height) were compacted by vibration table for 2 min. The specimens were then wrapped in plastic and cured at room temperature (27°C). For the special specimen 65FA40 18M (2.5), some parts were separated to cure at 60°C for 24 hours and prolonged cured at room temperature until the tested dates. The compressive strength of all geopolymer paste was determined at the different ages as follows: 3, 7, 14, 28, and 90 days, respectively.

3.4 Determination of Reaction Rate

The fine particles of geopolymer paste (0.5 g) were prepared by crushed and sieved through a 100-mesh sieve. They were dissolved with the solution of picric acid (5g) in 30 mL of methanol by stirring machine for 10 min. 20 mL of distilled water was then added and mixed for 30 min. The solution was passed filter-paper and the retainer was heated in an oven to determine the final weight loss of geopolymer paste. Hence, the percentage of weight loss of geopolymer paste is the reaction rate of the initial substance or the reaction rate of geopolymerization. This method was commonly used to analyze the reaction rate of pozzolanic reaction by many researchers [5, 6, 7] Specimens 65FA100 18M (2.5), 65FA40 18M (2.5), and 65FA00 18M (2.5) were determined the reaction rate in this study.

3.5 Microstructure

The pieces of cracked specimens after the compressive strength testing at 28 days were examined by SEM and EDAX. This examination could explain the outstanding characteristic and chemical composition of the specimens.

4. RESULTS AND DISCUSSION

The results of compressive strength of all geopolymer paste specimens were shown in Table 3. For room temperature curing condition, the maximum compressive strength (624 ksc) was obtained from the specimen 65FA40 18 M (2.5) at 90 days. When the same mixture was cured in 60 °C for 24 hour, the early strength increased dramatically. Compressive strength of 492 ksc was at 3 days could be gain. The sample also exhibited compressive strength 728 ksc at 90 days. Besides, the results showed that mixture with using RHBA alone or too little fly ash such as 65FA00 18M (2.5), 65FA20 18M (2.5) and 65FA30 18M (2.5) made geopolymer expanded and finally cracked. Its compressive strength can not be reported.

4.1 Effect of Si/Al Ratio on the Compressive Strength of the Geopolymer Paste

The different ratios of mixed proportion of geopolymer paste clearly changed the chemical ratio of the initial substance, especially, the Si/Al ratio as shown in Table 4. The results showed that the experiments obtained the wide range of the Si/Al proportion from 2.09 to 538.45, achieving the different compressive strengths (see in Table 4).

Figure 1 shows that the compressive strength increased with the Si/Al ratio increasing until the Si/Al ratio reached 8.28 (or at 40% RHBA of mixed proportion). After the ratio passed 8.28, the compressive strength gradually dropped down. This behavior was confirmed by other study [7].

4.2 Rate of reactions

The results from the determination of reaction rate were shown in Table 5 and Figure 2. The test showed the relationship between the reaction rate and ages of samples. When the age of the samples were older, the polymerization degree was raised as time. The result showed that the reaction still continued even though the geopolymer transformed to the solid state at late ages. In addition, it seems that FA was more reactive than that of RHBA. Figure 3 reveals that heat enhanced the degree of reaction which resulting the increase of compressive strength. The development of the compressive strength of samples 65FA40 18M (2.5) and 65FA40 18M (2.5) H were distinguished. The sample curing geopolymer at 60^{o}C quickly gained 492 ksc of compressive strength in 3 days. It spent longer (28 days) when curing at room temperature.

4.4 Microstructure

The cracked specimens after the compressive strength testing at 28 days were examined by SEM camera with EDAX mounted (see Figure 4) which the chemical composition of the specimens can be reported while scanning. The dense random places of the specimens were examined, indicating the end product chemical constitute as shown in Table 6.

The Si/Al ratio of geopolymer paste at 28 days trendily increased as initial Si/Al ratio increased. In fact, the chemical composition of the geopolymer paste for each random place was not the same. The product was not homogenous.

5. CONCLUSIONS

From the results, the following conclusions can be drawn:

1. The compressive strength of geopolymer paste increased as the Si/Al ratio in creasing. When the Si/Al ratio reached 8.28, the compressive strength tended to drop down.
2. When the Si/Al ratio was higher than 8.28, self cracking was found due to dimensional instability.
3. Higher temperature could accelerate the compressive strength of geopolymer paste in short period and activate the reaction faster.

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Table 1 – Chemical composition of RHBA and FA

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	LOI
RHBA	84.7	0.2	-	2.7	0.6	3.7
FA	36.0	20.5	15.9	18.7	2.2	0.0

Table **2** .Mix proportion of fresh Geopolymer paste 1000 g.

MIX ID.*	Mix Proportion (g.)			
	RHBA	FA	Na_2OSiO_2	NaOH
65FA100 18M (2.5)	-	650	250	100
65FA80 18M (2.5)	130	520	250	100
65FA60 18M (2.5)	260	390	250	100
65FA40 18M (2.5) (H)	390	260	250	100
65FA30 18M (2.5)	455	195	250	100
65FA20 18M (2.5)	520	130	250	100
65FA00 18M (2.5)	650	-	250	100

***Note:** The two digits number in front of letter "FA" that represent the ratio between solid and total weight, the two digits number back letter "FA" that represent percent of fly ash replacement by rice husk–bark ash, the two rigid number in front of letter "M" that represent sodium hydroxide concentration, the number in parenthesis is the ratio between sodium silicate and sodium hydroxide and (H) is specimen with curing high temperature.

Table **3**. Compressive strength of geoploymer paste change into volume instead of fly ash with rice husk–bark ash and fly ash.

MIX ID	Compressive Strength (ksc)				
	3 Days	7 Days	14 Days	28 Days	90 Days
65FA100 18M (2.5)	109	170	257	340	353
65FA80 18M (2.5)	134	203	306	404	426
65FA60 18M (2.5)	231	303	361	445	540
65FA40 18M (2.5)	243	335	409	510	624
65FA40 18M (2.5) H	492	492	549	560	728
65FA30 18M (2.5)	232	299	379	422	NA
65FA20 18M (2.5)	196	257	331	393	NA
65FA00 18M (2.5)	NA	NA	NA	NA	NA

H = curing with 60 ^oC for 24 hours after then in room temperature.
NA = The specimen can't test because it expanded and cracked before.

Table **4**. Comparison volume between SiO_2/Al_2O_3 and Si/Al

MIX ID	SiO_2/Al_2O_3	Si/Al
65FA100 18M (2.5)	4.03	2.09
65FA80 18M (2.5)	6.02	3.14
65FA60 18M (2.5)	9.34	4.86
65FA40 18M (2.5)	15.90	8.28
65FA30 18M (2.5)	22.39	11.65
65FA20 18M (2.5)	35.11	18.27
65FA00 18M (2.5)	1034.62	538.45

Table 5. The result of rate of polymerization

MIX ID.	Degree of Polymerization (%)						
	0h	1h	6h	1d	2d	7d	28d
65FA00 18M (2.5)	13.29	30.70	31.52	31.58	37.96	39.10	40.20
65FA40 18M (2.5)	15.57	22.93	28.86	32.14	33.31	35.36	46.25
65FA100 18M (2.5)	23.47	36.44	41.51	55.44	61.46	63.83	65.21

Table **6** The chemical composition and the mole ratio of Si/Al of different proportion paste.

MIX ID.	Na	Si	Al	Si/Al
65FA100 18M (2.5)	14.84	14.61	3.90	3.75
65FA80 18M (2.5)	8.47	17.88	2.97	6.02
65FA60 18M (2.5)	5.67	12.85	5.38	2.39
65FA40 18M (2.5)	6.27	15.64	2.38	6.57
65FA20 18M (2.5)	5.88	21.34	2.97	7.19
65FA00 18M (2.5)	5.44	37.65	-	-

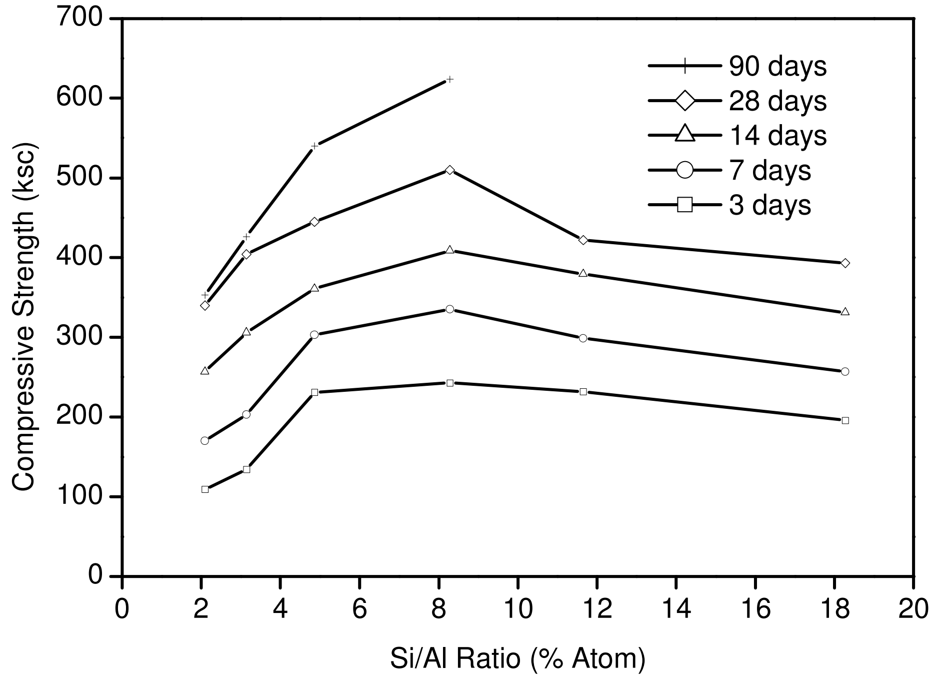

Figure **1.** The affect of proportion Si/Al and compressive strength of paste.

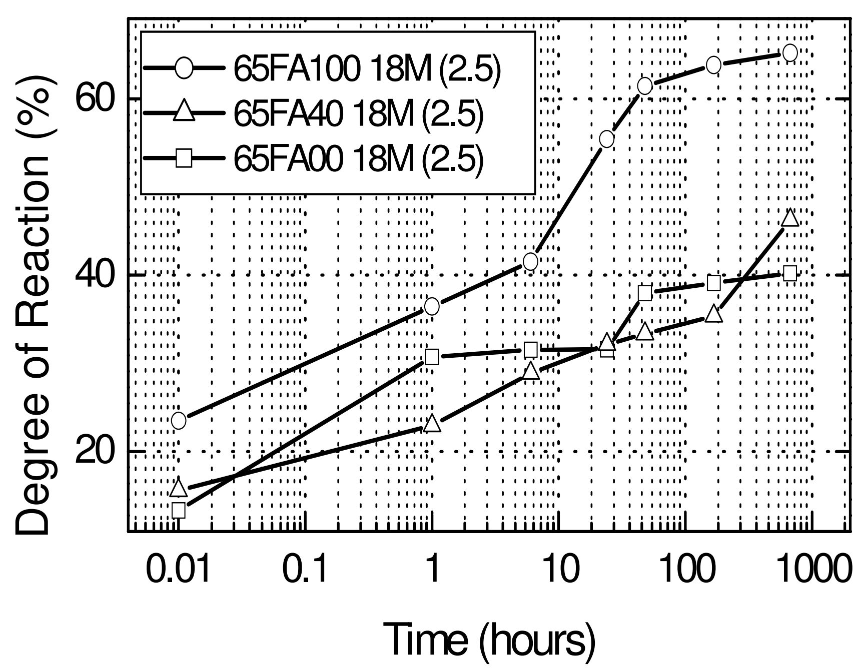

Figure **2.** Relation between time and rate of reaction.

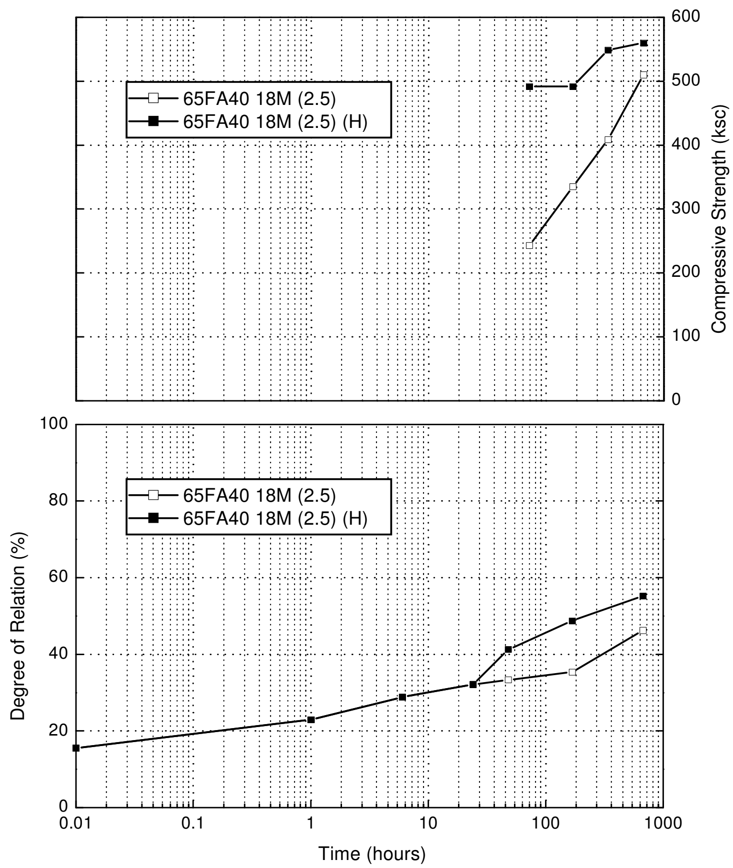

Figure **3.** Relation between compressive strength, rate of reaction and age of paste in different temperature of curing.

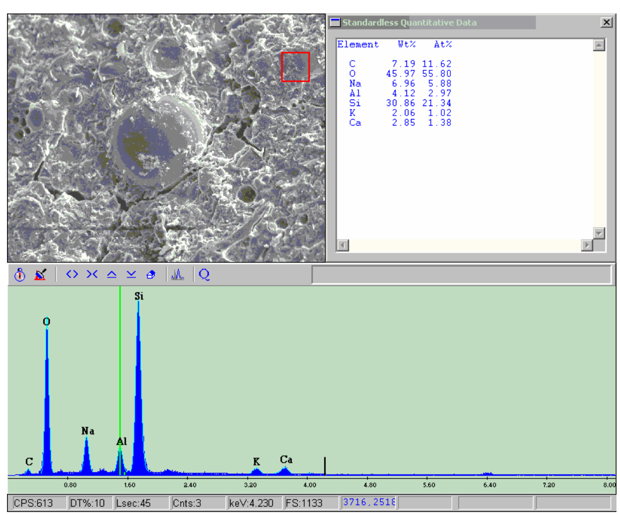

Figure **4.** Scanning electron microstructure zoom 500x and the chemical composition of paste by SEM-EDAX.