

Effect of Low NaOH Concentration on Compressive Strength and Products of High Calcium Geopolymer

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Abstract. *This research aims to study effect of low NaOH concentration on compressive strength and products of high calcium geopolymer. Fly ash was used to be starting material to synthesize geopolymer and mixed with 2 M sodium hydroxide (NaOH) concentrations. Silica fume was also used to be addition of silica in mixture to make different Si/Al ratios. Geopolymer pastes were determined compressive strength at the ages of 7, 14 and 28 days. The products of geopolymer pastes were characterized by Fourier transform infrared spectroscopy (FTIR) and salicylic acid with methanol (SAM solution) leaching test. The products of geopolymer were determined by the FTIR in different patterns before and after SAM solution leaching which is specific for calcium composite gel. It was found that low NaOH solution can produce the highest compressive strength of 15.91 MPa at the age of 28 days. The products of high calcium geopolymer were possible be calcium silicate hydrate (CSH gel), calcium aluminate silicate hydrate (CASH gel), geopolymer (NASH gel) and zeolite which were characterized by FTIR and SAM leaching tests.*

Keywords:

geopolymer, silica fume, FTIR, SAM leaching

1. Introduction

Geopolymer is an aluminosilicate material which can be synthesized by using aluminosilicate materials such as fly ash and metakaolin with alkali hydroxide solution such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). In the geopolymerization reaction, aluminosilicate material is dissolved to form free of tetrahedrons of silica and alumina. To the develop reaction, water is gradually spitted out and tetrahedrons of silica and alumina is linked by sharing oxygen atom [1]. Generally, there are three classes of geopolymer structures, depending on the silica/alumina ratio: polysialate (Si-O-Al), polysialate-siloxo (Si-O-Si-O-Al) and polysialate-disiloxo (Si-O-Si-O-Si-O-Al) which have Si:Al ratios of 1:1, 2:1 and 3:1,

respectively [1]. The products of geopolymer are composed of both amorphous phases and crystalline phases. They are also contributed to the superior mechanical strength of geopolymers.

Fly ash is one of the most famous starting materials of geopolymer. There are two types of fly ash which are Class F and Class C fly ash as described by ASTM C618 [2]. Class F fly ash is more popular to be starting material for geopolymer than Class C fly ash because Class F fly ash has high silica and alumina content [3]. Nevertheless, fly ash in Thailand is classified in Class F fly ash with high calcium content. A few researchers reported that the calcium might be interfered reaction of geopolymer or formed other products in geopolymer [4]. Moreover, it is possible that high calcium in fly ash can be formed calcium hydroxide ($\text{Ca}(\text{OH})_2$) and gave alkali solution (OH^-) to geopolymer pastes. It might be resulted in geopolymer synthesis with decreasing concentration of NaOH in system. In addition, calcium might be formed other products such as calcium silicate hydrate, calcium aluminate hydrate and calcium geopolymer. Some researchers found that calcium in fly ash improves mechanical properties of geopolymer. It accelerates the hardening process and increases the strength [4]. In Thailand, some researchers have used fly ash with high calcium to synthesize geopolymer and obtained high strength [5-8].

NaOH solution is commonly used as an alkali activator in geopolymer production. Alkaline solution (NaOH and/or KOH) is an essential reactant in geopolymerisation. Many researchers found that NaOH concentration between 10 – 14 M produced geopolymer with high compressive strength [9-10]. Somna et al. [8] found that geopolymer mixed with 14 M NaOH presented the highest compressive strength as 23.0 MPa at 28 days. Although the use of a high concentration of sodium hydroxide gave high compressive strength, the mixture is costly due to the sodium hydroxide solution. In addition, high concentration of NaOH has high viscosity which affects workability of geopolymer [10]. The idea of this

research is to use low NaOH concentration to synthesize geopolymer and study the compressive strength test as well as study products of geopolymer.

Thus, the aim of this paper is to study effect of low NaOH concentration on compressive strength and products of high calcium geopolymer. Class F fly ash was synthesized with low NaOH solution. The products of geopolymer were characterized by FTIR and salicylic acid with methanol (SAM solution) leaching test. The compressive strength of geopolymer was also investigated. Utilization of fly ash which is a by-product from electric thermal power plant to synthesize geopolymer is beneficial in environmental management. The geopolymer product would be environmentally friendly cementitious material.

2. Experimental Program

2.1 Materials

Fly ash (FA) was obtained from Mae Moh, Lumpang province, Thailand. To improve the reaction, fly ash was sieved by 200 meshes to obtain particles with size smaller than 100 microns. Silica fume (SF) was purchased under the name of Elkem Company, Chonburi province, Thailand.

The particle size distributions of fly ash and silica fume are shown in Fig. 1 and the chemical compositions of fly ash and silica fume are shown in Table 1.

Table 1: Chemical compositions of fly ash and silica fume

% by wt.	GFA	Silica Fume
SiO ₂	39.47	98.51
Al ₂ O ₃	29.46	-
CaO	13.82	0.54
Fe ₂ O ₃	9.85	0.06
SO ₃	3.66	-
K ₂ O	1.95	0.79
Na ₂ O	-	-
LOI	1.8	-

2.2 Alkali hydroxide solution

Sodium hydroxide (NaOH) solution was used as alkali hydroxide solution. 2 M NaOH concentration was used all mixtures in this research.

2.3 Geopolymer synthesis

Geopolymer samples were prepared by mixing ground fly ash (GFA) with silica fume and 2 M NaOH solution. Silica fume was used to replace fly ash at 5, 10, 20 and

30% by weight. A NaOH solution to solid ratio of 0.55 was assigned to the mix. They were stirred for 5 minutes then, cast in cylindrical mold with 30 mm in diameter and 60 mm in height. The geopolymer pastes were demolded and kept at ambient temperature until the test age. The compressive strength of geopolymer was investigated at the ages of 7, 14 and 28 days. The pastes were ground and characterized by FTIR and SAM solution leaching test. Typical chemical ratios of activated geopolymer pastes are given in Table 2.

Table 2: Typical chemical ratios of activated geopolymer pastes

Sample	FA	SF	Si:Al	Ca:Si	Na:Al
2Si0	100	0	1.54	0.53	0.20
2Si5	95	5	1.76	0.46	0.21
2Si10	90	10	2.00	0.41	0.22
2Si20	80	20	2.56	0.32	0.25
2Si30	70	30	3.29	0.25	0.28

2.4 FTIR technique

Fourier transform infrared spectroscopy was chosen to study the products of geopolymer. FTIR was obtained from PerkinElmer model Spectrum 100. The specimen was prepared by 0.001 mg of sample in 0.04 mg of KBr. Spectra analysis was performed in terms of the wavenumber range

2.5 Salicylic acid with methanol (SAM solution) leaching test

The SAM solution was first introduced by Takashima who used this technique to dissolve alite and belite in Portland cement. It was used to dissolve calcium bearing phase in geopolymer pastes. In this research, SAM leaching test was studied using the steps proposed by Somna and Bumrongjaroen [12]. 7 grams of salicylic acid and 40 ml of methanol were prepared to study products of geopolymer.

The geopolymer pastes were ground and stirred with SAM solution for 3 hours. After that, it was filtered and dried at 100°C. Part of insoluble residue of geopolymer after SAM leaching test was characterized by FTIR technique.

Steps to determine the products of geopolymer are as follows:

1. Fly ash was characterized by FTIR.

2. Geopolymer pastes were characterized by FTIR and subtracted with FTIR spectra of fly ash. The possible products found in resultant FTIR spectra are calcium silicate hydrate gel (CSH gel), calcium aluminate silicate hydrate gel (CASH gel), geopolymer gel (NASH gel) and zeolite.

3. Insoluble residue of geopolymer pastes after SAM solution leaching test was characterized by FTIR. They were subtracted with FTIR spectra of fly ash. The possible products found from FTIR spectra are NASH gel and zeolite.

4. FTIR spectra of CSH gel and CASH gel was obtained by subtracting FTIR spectra obtained from step 2 and step 3.

3. Results and Discussion

3.1 Properties of materials

Chemical compositions of fly ash and silica fume are shown in Table 1. For fly ash, the sum of SiO₂, Fe₂O₃ and Al₂O₃ was 78.78%. The CaO and loss on ignition (LOI) values were 13.85% and 1.8%, respectively. Fly ash was indicated to be Class F fly ash as prescribed by ASTM C 618 [2] with high calcium oxide content. For silica fume, the chemical composition of silica fume had high in SiO₂ content as 98.51%.

The particle size distributions of fly ash, ground fly ash and silica fume are shown in Fig. 1. The particle sizes of GFA were smaller than those of OFA. It is noted that the small particles can react better and faster than the large particles.

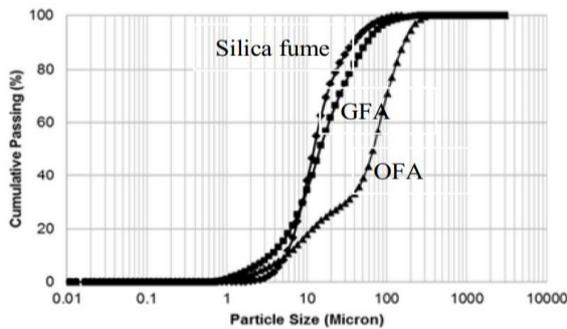


Fig. 1: Particle size distributions of fly ash, ground fly ash and silica fume

3.2 FTIR and SAM solution analysis

Fig. 2 shows FTIR spectra of geopolymer pastes after subtracting by FTIR spectra of fly ash. The remaining FTIR spectra after subtracting by FTIR of fly ash could be those of geopolymer products (CSH gel, CASH gel, NASH gel and zeolite).

FTIR spectra presented the two major peaks at 980 cm⁻¹ which is associated with Si-O in Q₂ units [13] and at 1120 cm⁻¹ which is associated with Si-O in Q₃ units [7]. There is the band characteristic of carbonate group around 1450 cm⁻¹ which was supposed to be CaCO₃. All bands at 1650 and 3460 cm⁻¹, respectively, related to O-H stretching and bending modes of molecular water.

Fig. 3 showed FTIR spectra of insoluble residue of geopolymer after SAM solution leaching test. The products of this part would be NASH gel and zeolite.

Interestingly, peak at 980 cm⁻¹ disappeared. The major peaks of geopolymer shifted to higher wavenumber around 1100-1200 cm⁻¹ which were contributed to Si-O in Q₃ units, typical NASH gel or zeolite. Since salicylic acid is organic acid, many sharp peaks of salicylic were interfered in insoluble residue of geopolymer pastes after SAM leaching test.

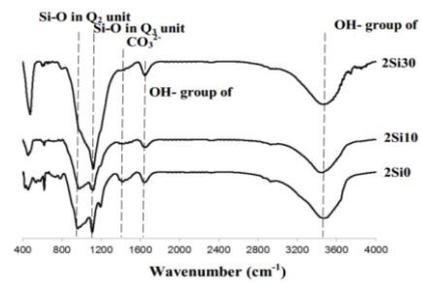


Fig. 2: FTIR spectra of geopolymer pastes after subtracting by FTIR spectra of fly ash

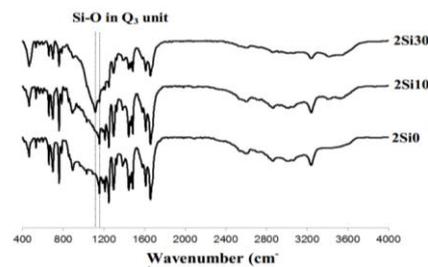


Fig. 3: FTIR spectra of insoluble residue of geopolymer after SAM solution leaching test

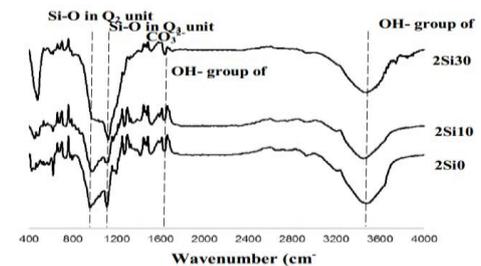


Fig. 4: Subtraction FTIR spectra between FTIR spectra of geopolymer pastes after subtract by FTIR spectra of fly ash and FTIR spectra of insoluble residue of geopolymer after SAM solution leaching test

Fig. 4 showed subtraction FTIR spectra between Fig. 2 and Fig. 3. FTIR spectra of this part would present CSH gel and CASH gel. The major peaks were shifted to lower wavenumber around 970 cm⁻¹ which were contributed to Si-O in Q₂ units, typical CSH gel and CASH gel [14]. Peaks at around 1450 cm⁻¹ also found.

From this part, FTIR technique can used to determine the products of geopolymer with SAM solution leaching test. The products of geopolymer were possible be

CSH gel and CASH gel which were presented with wavenumber at 970 cm^{-1} [13]. In addition, NASH and zeolite were also observed at wave number around $1000 - 1100\text{ cm}^{-1}$. It was described that additional of silica in high calcium geopolymer with 2M NaOH solution can be formed CSH gels products. Some silica and alumina in fly ash can react with calcium to form CASH gel. Moreover, silica and alumina in fly ash can release out to form NASH gel and zeolite under low NaOH concentration.

3.3 Effect of low NaOH concentration on compressive strength

Fig. 5 showed the geopolymer compressive strength test results for different silica fume replacements and curing ages. It was found that silica fume replacement has an effect on the compressive strength of geopolymer pastes. Additional silica fume in system led to increase Si:Al ratio of geopolymer. The compressive of geopolymer increased with increasing the Si:Al ratio in mixture of geopolymer. The compressive strength slightly increased from 7 to 28 days. The compressive strength of geopolymer pastes with silica fume replacements of 5, 10, 20 and 30% at the age of 28 days were 10.28, 11.18, 12.02, 14.27 and 15.91 MPa, respectively. The maximum compressive strength was found to reach 15.91 MPa with 30% silica fume replacement. The compressive strength of 2Si30 was 10.08, 11.00 and 15.91 MPa at the ages of 7, 14 and 28 days, respectively. It was found that addition of SiO_2 to geopolymer led to an increase in compressive strength.

Thus, low concentration NaOH solution mixed with fly ash and silica fume can give the highest compressive strength of 15.91 MPa at the age of 28 days with 30% silica fume replacement which had Si:Al ratio of 3.92. It can be mentioned that high calcium oxide contents in fly ash can react with silica fume to form calcium silicate hydrate. This product would be similar to product obtained from cement hydration reaction which can produce strength.

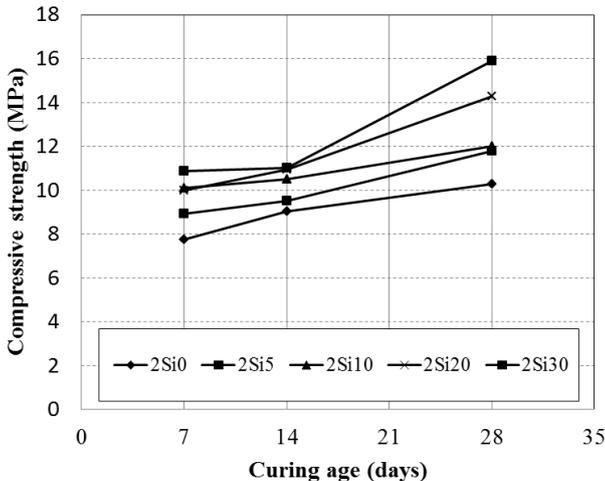


Fig. 5: Compressive strength of geopolymer

4. Conclusion

1. Geopolymer which synthesized by using low concentration NaOH solution, high calcium fly ash and silica fume can produce a high strength. The highest compressive of geopolymer was 15.91 MPa in 2Si30 at the age of 28 days.
2. The Si:Al ratio in mixture of geopolymer increased led to increase compressive strength of geopolymer.
3. The products of geopolymer which characterized by FTIR and SAM leaching were possible be CSH gel, CASH gel, NASH gel and zeolite.
4. High calcium geopolymer can be activated with low alkali hydroxide solution. The pastes provided strength which was closed to the strength obtained from cement hydration reaction.

5. Acknowledgement

The authors would like to thank faculty of engineering and architecture, Rajamangala University of Technology Isan for giving financial support to do this research and faculty of sciences and liberal arts, Rajamangala University of Technology Isan for giving access to FTIR instrument.

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Bibliography



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