

## การศึกษาการชะง่้าถ่านหินลิกไนต์และกำลังอัดของวัสดุจีโอโพลิเมอร์ จากถ่้าถ่านหิน

อุบลลัษณ์ รัตนศักดิ์<sup>1</sup> วิเชียร ชาลี<sup>2</sup>

มหาวิทยาลัยบูรพา อ.เมือง จ.ชลบุรี 20131

และ ปริญญา จินดาประเสริฐ<sup>3</sup>

มหาวิทยาลัยขอนแก่น อ.เมือง จ.ขอนแก่น 40002

### บทคัดย่อ

งานวิจัยนี้ได้ศึกษาการชะของซิลิกา ( $\text{SiO}_2$ ) และอะลูมินา ( $\text{Al}_2\text{O}_3$ ) จากถ่้าถ่านหินลิกไนต์ด้วยสารละลายโซเดียมไฮดรอกไซด์ ( $\text{NaOH}$ ) และผลที่มีต่อกำลังอัดของวัสดุจีโอโพลิเมอร์ โดยทำตัวอย่างถ่้าถ่านหินให้เป็นสารแขวนลอยด้วยสารละลายโซเดียมไฮดรอกไซด์ที่ความเข้มข้นต่างกัน และนำสารละลายที่ระยะเวลาการชะต่างกันไปวิเคราะห์หาปริมาณซิลิกาและอะลูมินา นอกจากนี้ได้ทำการทดสอบกำลังอัดของวัสดุจีโอโพลิเมอร์ ผลการทดลองแสดงให้เห็นว่าการชะละลายของถ่้าถ่านหินขึ้นอยู่กับความเข้มข้นของสารละลายโซเดียมไฮดรอกไซด์และระยะเวลาการชะ สารละลายโซเดียมไฮดรอกไซด์ที่มีความเข้มข้นปานกลางคือ 10 โมลาร์ และเวลาในการชะ 10 นาทีให้กำลังอัดที่สูง สามารถทำวัสดุจีโอโพลิเมอร์ให้ค่ากำลังอัดสูงถึง 65 เมกะปาสกาล ซึ่งเทียบได้กับมอร์ต้าร์หรือคอนกรีตกำลังสูงที่ผลิตจากปูนซีเมนต์ปอร์ตแลนด์แลนด้ประเภทที่ 1

**คำสำคัญ :** จีโอโพลิเมอร์ / ถ่้าถ่านหิน / การชะ / การละลาย / โซเดียมไฮดรอกไซด์ / กำลังอัด

<sup>1</sup>อาจารย์, ภาควิชาเคมี คณะวิทยาศาสตร์

<sup>2</sup>อาจารย์, ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์

<sup>3</sup>รองศาสตราจารย์, ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์

## Study of Leaching of Lignite Fly Ash and Strength of Fly Ash Based-Geopolymer

**Uboluk Rattanasak<sup>1</sup>, Wichian Chalee<sup>2</sup>,**  
Burapha University, Muang, Chonburi 20131  
**and Prinya Chindapasirt<sup>3</sup>**  
Khon Kaen University, Muang, Khon Kaen 40002

### Abstract

A study was conducted on the leaching of the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  of lignite fly ash in NaOH solution and its effect on the strength of geopolymer. The fly ash samples were suspended in the different NaOH concentration solution. The leachates with different leaching time intervals, were analysed in term of silica and alumina leached. In addition, the strength of the geopolymer was also tested. The results revealed that the solubility of the fly ash depended on the concentration of NaOH and the leaching time. High compressive strength was obtained with a moderate concentration of NaOH (10M) and a selected leaching time of 10 minutes. A geopolymer with relatively high strength of up to 65 MPa is obtained and is comparable to the high strength mortar and concrete made from ordinary Portland cement type I.

**Keywords** : Geopolymer / Fly Ash / Leaching / Solubility / Sodium Hydroxide / Compressive Strength

---

<sup>1</sup>Lecturer, Department of Chemistry.

<sup>2</sup>Lecturer, Department of Civil Engineering.

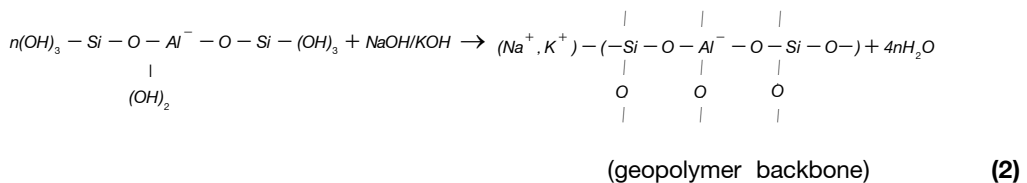
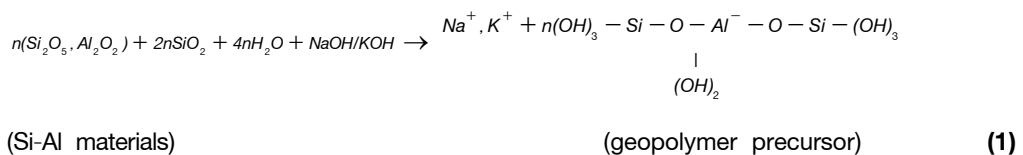
<sup>3</sup>Associate Professor, Department of Civil Engineering.

## 1. Introduction

Fly ash is an industrial waste normally used as partial replacement of Portland cement for making of concrete owing to its availability. However, it can not totally replace Portland cement since SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in fly ash still need Ca(OH)<sub>2</sub> from cement hydration for its pozzolanic reaction to produce calcium silicate hydrate and calcium aluminate hydrate, which possess cementitious properties. Recently, it was found that fly ash could be activated with alkaline solution at room temperature to produce a cementitious binder called geopolymer [1-2].

The formation of geopolymer can be synthesised at low temperature and follows the same route as that for most zeolites providing the useful properties, for example, high compressive strength and stability at temperature up to 1300-1400°C [3]. Geopolymerisation can be carried out with alumino-silica material, i.e. fly ash that partly dissolved in high alkali solution (at a high pH) in the presence of soluble alkali metal silicates, and is therefore, a source of geopolymeric precursors. The alkali solution will dissolve alumina and silica precursors, and also hydrolyses the particle surface leading this surface to highly react with the dissolved silicate species [4]. Therefore, the alkali base concentration is significant factor to control the alumina and silica leached out from the particles, and consequent geopolymer formation and properties.

The exact mechanism by which geopolymer setting and hardening occur is not fully understood. Most proposed mechanisms consist of dissolution, transportation or orientation, as well as a reprecipitation (polycondensation) step. Hua and Van Deventer [5] presented the mechanism as follows:



The present work investigates the alumina and silica (in the form of Al<sup>3+</sup> and Si<sup>4+</sup>, respectively) leached out from the fly ash particles at different alkali concentration and leaching time before forming the geopolymer matrix with alkali-silicate solution. The optimum alkali concentration and leaching time are selected to prepare the geopolymer matrix, and subsequently the strength of geopolymer is provided.

It is believed that this geopolymer product will be more used in concrete industries in the future. The knowledge of the leaching of alumina and silica would help understanding the reaction and the strength development of geopolymer.

## 2. Experimental Program

### 2.1 Materials

Sodium hydroxide pellet (AR grade) was dissolved in deionised water to obtain NaOH solution at concentrations of 5, 10, and 15M. Sodium silicate solution (weight ratio  $\text{SiO}_2:\text{Na}_2\text{O} = 3.2$ ) was supplied by Eastern Silicate Company. Fly ash was alumino-silicate source obtained from Mae Moh Power Plant, Thailand, with mean particle size of 19  $\mu\text{m}$ . The major chemical composition of the fly ash is presented in Table 1. Deionised water and polyethylene containers were used throughout the experiment to avoid silica contamination. River sand passed a sieve no. 16 (1.18 mm sieve opening) and retained on a sieve no. 100 (150 sieve opening) with a fineness modulus of 2.8, a specific gravity of 2.65 and a water absorption of 1.0% was used for making mortar specimen.

**Table 1** Composition of lignite fly ash.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{TiO}_2$	MgO	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	LOI
Fly ash	38.7	20.8	16.6	15.3	1.2	0.4	1.5	2.7	0.1	2.6	0.1

### 2.2 Methods

*Leaching test:* Three NaOH concentrations of 5M, 10M, and 15M were used to dissolve alumina and silica from fly ash particles with fly ash/NaOH ratio of 3:1 by weight. These tests were carried out with the leaching time of 5, 10, 20, and 30 minutes. Longer period of time (more than 30 minutes) was not performed as the suspension became thick with the gel formations of  $\text{Si}(\text{OH})_4$  and  $\text{Al}(\text{OH})_3$  resulting in difficulty of mixing and for practical purpose. After that, the filtrate was collected through membrane filter and analysed for Si and Al. Concentrations of these metals were determined by forming complex compound with suitable chemicals followed by spectronic measurement of the resulting colored complex. Colored Si and Al complexes were measured at the wavelength of 810 nm and 550 nm, respectively.

*Synthesis:* Fly ash was mixed with NaOH at optimal concentration and mixing time obtained from leaching test. Sodium silicate solution was sequentially added to the mixture in order to enhance the formation of geopolymer precursors upon contact between a mineral and the solution. For preparing mortar for strength testing, sand was also added to the mixture at sand/fly ash ratio of 2 by weight. The molar ratio of geopolymer matrix was varied in the range as followed:

$\text{Na}_2\text{O}/\text{SiO}_2 = 0.2-0.48$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.3-4.5$ ,  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10-25$  and  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.8-1.2$  [6]. The mix proportions are showed in Table 2, in the form of molar ratio of metal oxide.

The viscose mixture was then placed into 5 cm cubic mold covering with clingfilm to keep avoid moisture rapidly evaporated during heating cure. Geopolymeric mixture was cured in oven at  $65^\circ\text{C}$  for 48 hours to complete the geopolymeric reaction.

*Testing:* Geopolymeric pastes were microscopically examined with optical microscope and Scanning Electron Microscope (SEM). The strength test of mortars was also tested after samples were demolded and cooled to room temperature.

**Table 2** Compositions of the fly ash-based geopolymer matrices ( $\text{Na}_2\text{O}.\text{SiO}_2 = \text{Sodium silicate solution}$ ).

Samples	weight ratio	mole ratio			
	10M NaOH/ $\text{Na}_2\text{O}.\text{SiO}_2$	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$
FA-A	0.5	0.17	4.8	14.3	0.82
FA-B	0.6	0.18	4.7	13.7	0.86
FA-C	1.0	0.22	4.5	12.1	0.99
FA-D	1.5	0.25	4.3	11.2	1.09
FA-E	2.0	0.28	4.2	10.6	1.16

### 3. Results and discussion

#### 3.1 Leaching test

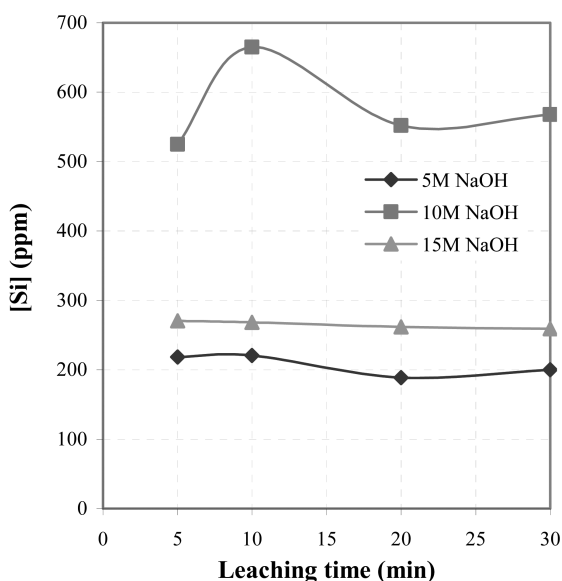
It is known that alkali solution concentration and leaching time affirmatively influence the geopolymer formation. When aluminosilicate materials come into contact with alkali solution, leaching of both Al and Si species starts. These species then diffuse into the gel phase leading to reduction in the concentration of Al and Si species at the particle surface, and therefore stimulates further leaching of Al and Si. Fig. 1 shows the Si concentration (in ppm) leached from fly ash particles with 5M, 10M, and 15M NaOH at different leaching periods. The result of the Al leachate is presented in Fig. 2.

From Fig. 1, the average Si concentration of close to 600 ppm was obtained with the 10M NaOH. For the 5 and 15M NaOH, the concentration was much less. This could be caused by an increase in the viscosity and density of solution. At high viscosity and low flowability, lower pore surface-solution interaction is expected.

The results also suggested that the leaching time of 5-10 minutes was sufficient as an increase in the leaching time to 20 and 30 minutes did not seem to increase the concentration of Si. In addition, the gel formation of  $\text{Si(OH)}_4$  (geopolymeric precursor) could occur at longer leaching time resulting in the difficulties for the solution to pass through membrane filter. This created a risk of obtaining a lower measured Si in the liquid phase.

From Fig. 2, the concentration of the Al was much lower than that of the Si. The concentration of Al was around 130 ppm at 10 minutes of leaching for 10 M NaOH, and, at 30 minutes, it decreased to around 30 ppm for all NaOH concentrations. With the longer leaching time,  $\text{Al(OH)}_3$  gel formed and could not pass through member filter resulted in lower Al ion in the solution. It had been reported that Al concentration in leachate was quite low comparing with Si owing partly to the higher content of Si than Al in the fly ash particles, and also to the high intrinsic extent of dissolution of Si than Al [8]. At low leaching time of 5 minutes, the Al concentration was relatively low, approximately 30 ppm. It was found that the Al concentration increased to 100-130 ppm with 10 and 15M NaOH. It was also observed that, for the high NaOH concentration, after 10 minutes of leaching time, the Al concentration decreased dramatically at high rate. This was associated with the formation of  $\text{Al(OH)}_3$  gel in the suspension.

With the constant leaching rate of Si and reducing in Al after 10 minutes, 10M NaOH with 10 minutes of leaching period was thought to be sufficient for the synthesis of geopolymer considering economy and time consumed in the preparation.



**Fig. 1** Si leaching concentration (ppm) with weight ratio fly ash/NaOH = 3:1 in 5M, 10M, and 15M NaOH at different leaching time.

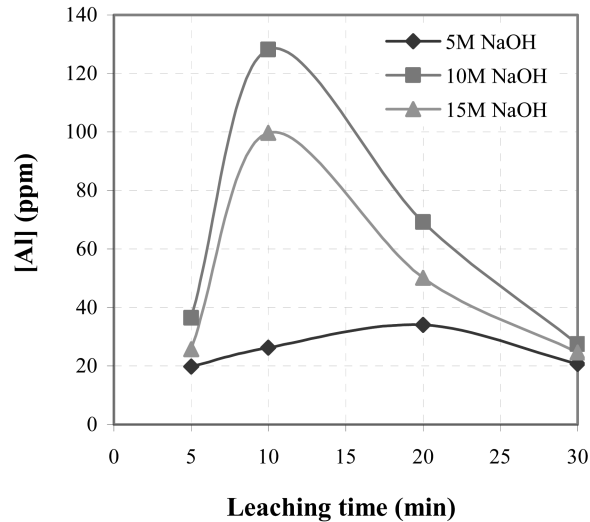


Fig. 2 Al leaching concentration (ppm) with the same condition as Fig. 1.

### 3.2 Microstructure

Optical microscope and SEM were used to characterise the hardened geopolymer paste. As shown in Fig. 3, typical optical microscopy of the sample exhibited the gel formation (white spots) around fly ash particles (dark color). In addition, there were unreacted and/or partially reacted grains of fly ash as displayed in Fig. 4. This resulted in a lower gel formation and hence a possible lower compressive strength. The cracks and pores were also found in the matrix which again limited the improvement in the compressive strength.

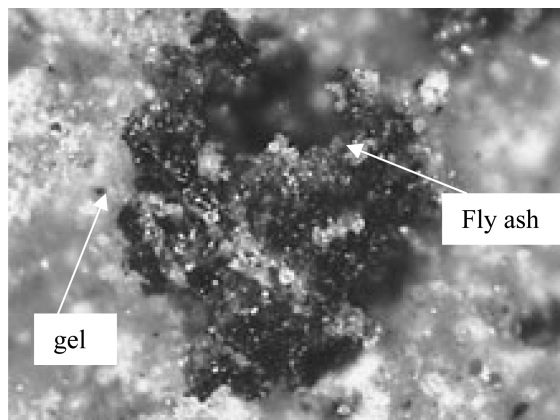


Fig. 3 Optical micrograph of geopolymer

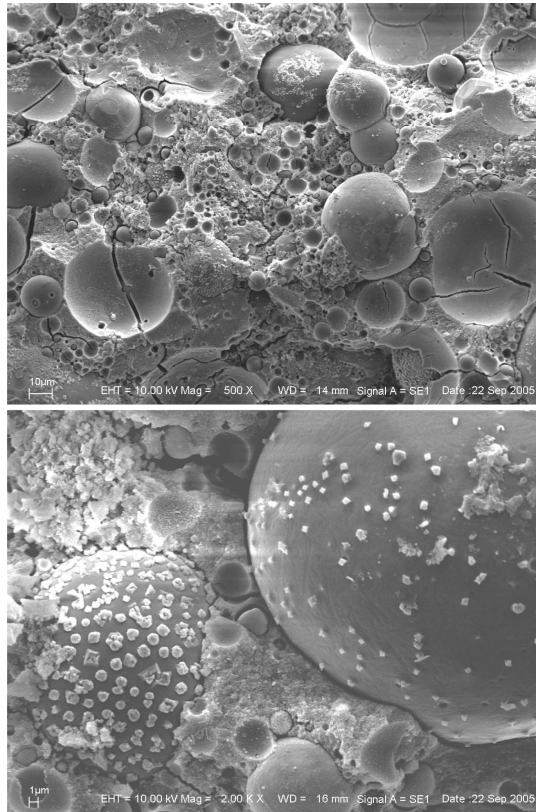


Fig. 4 SEM micrograph of geopolymer.

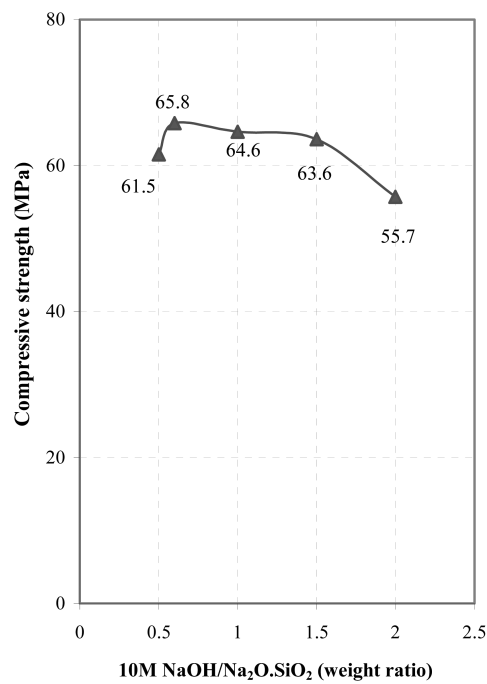


Fig. 5 Relationship between NaOH-to-Na<sub>2</sub>O.SiO<sub>2</sub> and strength.



**Table 3** Compressive strength of the fly ash-based geopolymer mortars at 48 hours of curing.

Samples	weight ratio 10M NaOH/Na <sub>2</sub> O.SiO <sub>2</sub>	mole ratio				Strength (MPa)
		Na <sub>2</sub> O/SiO <sub>2</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Na <sub>2</sub> O	Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	
FA-A	0.5	0.17	4.8	14.3	0.82	61.5
FA-B	0.6	0.18	4.7	13.7	0.86	65.8
FA-C	1.0	0.22	4.5	12.1	0.99	64.6
FA-D	1.5	0.25	4.3	11.2	1.09	63.6
FA-E	2.0	0.28	4.2	10.6	1.16	55.7

### 3.3 Compressive strength

The compressive strength of fly ash-based geopolymer mortars is shown in Table 3 and Fig. 5. The results indicated that the selected geopolymer mortars with 10M NaOH and varying NaOH/Na<sub>2</sub>O.SiO ratios reached quite high compressive strength at 48 hours of curing. The obtained strength was 55-65 MPa, which is comparable to that of the conventional high strength cement mortar.

The amount of NaOH has some effects on the strength of geopolymer as shown in Fig. 5. The NaOH/Na<sub>2</sub>O.SiO<sub>2</sub> ratios between 0.5 and 1.5 produced geopolymer with strength higher than 60 MPa. NaOH/Na<sub>2</sub>O.SiO<sub>2</sub> ratio of 2, however, reduced strength to about 55 MPa which probably caused by an insufficient sodium silicate solution for geopolymeric precursors to form the gel matrix.

## 4. Conclusions

From the test it can be concluded that the leaching of the Si and Al depends on the mole of NaOH and the leaching time. The leaching time has little effect of the Si concentration but large effect on the Al concentration. Although, longer leaching period increases the Al dissolution, 10M NaOH and 10 minutes of leaching period were considered sufficient for the synthesis of geopolymer considering economy and time.

Optical microscope and SEM studies suggested that the geopolymerisation resulted in gel formation and the strength of the geopolymer was limited by unreacted fly ash particles and the formation of voids and cracks in the matrix.

With the use of 10M NaOH and various NaOH/Na<sub>2</sub>O.SiO ratios, geopolymer mortars with relatively high strength of up to 65 MPa was obtained and is comparable to the high strength mortar made with ordinary Portland cement.

## 5. References

1. Davidovits, J., 1991, "Geopolymer: Inorganic Polymeric New Materials", *Journal of Thermal Analysis*, Vol. 37, pp. 1633-1659.
2. Davidovits, J., 1994, "Properties of Geopolymer Cements", *Proceedings of the 1<sup>st</sup> International Conference on Alkaline Cements and Concretes*, Ukraine, pp. 131-149.
3. Hussain, M., Varley, R.J., Cheng, Y.B., Mathys, Z., and Simon, G.P., 2005, "Synthesis and Thermal Behavior of Inorganic-Organic Hybrid Geopolymer Composites", *Journal of Applied Polymer Science*, Vol. 96, pp. 112-121.
4. Van Jaarsveld, JGS and Van Deventer, JSL, 1999, "Effect of the Alkali Metal Activator on the Properties of Fly Ash-based Geopolymer", *Industrial and Engineering Chemistry Research*, Vol. 88, pp. 3932-3941.
5. Hua, X. and Van Deventer, JSJ, 1999, "The Geopolymerisation of Natural Alumino-Silicates", *Proceedings of the 2<sup>nd</sup> International Conference on Geopolymer'99*, pp. 43-63.
6. Davidovits, J., 1994, "Process for Obtaining a Geopolymeric Alumino-Silicate and Products thus Obtained", *US Patent no. 5,342,595*.
7. Li, Z., Ding, Z., and Zhang, Y., 2004, "Development of Sustainable Cementitious Materials", *Proceedings of the International Workshop on Sustainable Development and Concrete Technology*, Beijing, pp. 55-76.
8. Xu, H. and Van Deventer, JSL, 2000, "The Geopolymerisation of Alumino-Silicate Minerals", *International Journal of Mineral Processing*, Vol. 59, pp. 247-266.