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Influence of NaOH solution on the synthesis of fly ash geopolymer

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ABSTRACT

A study was conducted on leaching of fly ash mixed with NaOH solution and on mixing procedure for preparing geopolymer. Leaching of SiO_2 and Al_2O_3 was investigated by mixing fly ash with NaOH solution for different time intervals and leachates were analyzed in terms of silica and alumina contents. To make geopolymer paste, separate mixing and normal mixing were used. For separate mixing, NaOH solution was mixed with fly ash for the first 10 min; subsequently sodium silicate solution was added into the mixture. For normal mixing, fly ash, sodium hydroxide and sodium silicate solution were incorporated and mixed at the same time. Geopolymers were cured at 65 °C for 48 h. Microstructure of paste and compressive strength of mortar were investigated. Results revealed that solubility of fly ash depended on concentration of NaOH and duration of mixing with NaOH. For mixing procedure, separate mixing gave slightly better strength mortar than normal mixing. High strength geopolymer mortar up to 70.0 MPa was obtained when the mixture was formulated with 10 M NaOH and sodium silicate to NaOH ratio of 1.0, and the separate mixing sequence was used.

1. Introduction

Fly ash is an industrial waste normally used to replace Portland cement for making concrete. However, it can only partially replace Portland cement since SiO_2 and Al_2O_3 in fly ash still need $Ca(OH)_2$ from Portland cement hydration for its pozzolanic reaction to produce calcium silicate hydrate and calcium aluminate hydrate. Recently, another form of cementitious materials called geopolymer has been developed (Davidovits, 1991). This geopolymer is usually made of fly ash activated with alkaline solution at low temperature and it is sometimes called alkali-activated fly ash.

Geopolymer with good mechanical properties viz., high compressive strength and stability at temperature up to 1300–1400 °C can be synthesized at low temperature using similar technique to that of zeolites (Hussain et al., 2005). Geopolymerization is based on alumino-silica chain. Fly ash contains high percentage of amorphous silica and alumina, hence is suitable as a source material for making geopolymer. Fly ash is usually mixed with alkali solution to obtain alumina and silica precursors. When it comes into contact with alkali solution, dissolution of silicate species starts (Comrie and Kriven, 2003). The type and concentration of alkali solution affect the dissolution of fly ash. Leaching of Al^{3+} and Si^{4+} ions are generally high with sodium hydroxide solution compared to potassium hydroxide solution (Van Jaarsveld and Van Deventer, 1999; Xu and Van Deventer; 1999). Therefore, alkali concentration is a significant factor in controlling the leaching of alumina and silica from fly ash particles, subsequent geopolymerization and mechanical properties of hardened geopolymer.

The present work investigates alumina and silica in the form of Al^{3+} and Si^{4+} ions leached out from fly ash particles after mixing with sodium hydroxide at different alkali concentrations and leaching times before forming geopolymer with silicate solution. The mixing procedures were also investigated. The knowledge would help to understand the reaction and strength development of geopolymer and to better utilize it in the future.

2. Materials and methods

2.1. Materials

Fly ash from Mae Moh power plant in the north of Thailand with a mean particle size of 19 μm, NaOH and sodium silicate solution (water glass) with SiO_2:Na_2O weight ratio of 3.2 were used. Sodium hydroxide pellet (AR grade) was dissolved in deionised water to obtain NaOH solution at concentrations of 5, 10, and 15 M. The viscosities of 5, 10, and 15 M NaOH solutions were 3.9, 9.3, and 14.3 cps (centipoises), respectively. The viscosity of sodium silicate solution was higher at 60.6 cps. Major chemical composition of the fly ash is shown in Table 1. Deionised water and polyethylene containers were used throughout the experiment to avoid silica contamination. River sand passed No. 16 sieve (1.18 mm opening) and retained on No. 100 sieve (150 μm opening) with fineness modulus of 2.8 and specific gravity of 2.65 was used for making mortar specimen.

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Table 1
Chemical composition (%) of high calcium lignite fly ash.

SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	TiO_2	MgO	K_2O	P_2O_5	SO_3	LOI
39.5	19.5	17.3	14.1	1.3	0.5	1.3	2.9	0.2	2.6	0.8

2.2. Leaching test of fly ash

Three NaOH concentrations of 5, 10, and 15 M with fly ash/NaOH ratio of 3:1 by weight were used to dissolve silica and alumina from fly ash particles. Fly ash was mixed with NaOH solution in a mixer at 120 rpm for 5, 10, 20, and 30 min. Longer period of time (more than 30 min) was not performed since the mixture would become very sticky with formations of $Si(OH)_4$ and $Al(OH)_3$ gel. After mixing, the filtrates were collected through membrane filter and analyzed for Si and Al ions. Concentrations of these products were determined by forming complex compound with suitable chemicals followed by UV spectronic measurement. Color Si and Al complexes were measured at wavelengths of 810 nm and 550 nm (Bartram and Balance, 1996; Roelofs and Vogelsberger, 2006).

2.3. Geopolymer paste

For separate mixing (S), fly ash was mixed with NaOH for 10 min to allow leaching of ions. Sodium silicate solution was then added to the mixture and mixed for 1 min. Only short mixing time was required here since the mixes were relatively fluid. For normal mixing (N), fly ash, sodium silicate solution, and 10 M NaOH were mixed together for 1 min as this corresponds to the time of exposure to sodium silicate solution for separate mixing. The mix proportions are shown in Table 2. Oxide molar ratios of geopolymer matrix were varied in the following ranges: $Na_2O/SiO_2 = 0.2–0.48$, $SiO_2/Al_2O_3 = 3.3–4.5$, $H_2O/Na_2O = 10–25$ and $Na_2O/Al_2O_3 = 0.8–1.2$. After mixing, paste specimens were molded in 25 mm diameter × 25 mm height plastic containers. They were wrapped with clingfilm and cured at 65 °C for 48 h. XRD and IR analyses were performed on the hardened sample. In addition, samples were microscopically examined with optical microscope and scanning electron microscope (SEM).

2.4. Geopolymer mortar

To make mortar, sand was added to paste mixture at sand to fly ash ratio by weight of 2.75 and mixed for one more minute. The mixture was cast into 50 mm cubic mould and wrapped with clingfilm to avoid moisture evaporation during heat curing. Samples were then cured in oven at 65 °C for 48 h to complete geopolymerization reaction. The temperature and curing time were selected because they gave high strength geopolymer mortars (Chindaprasirt et al., 2007, 2009). Specimens were cooled down to room temperature and tested for strength in accordance with ASTM C109. Results are reported as an average of three samples.

Table 2
Mix proportion of paste.

Mix	Method of mixing	Water glass/10 M NaOH (G/N)
S-0.5	S	0.5
S-1.0	S	1.0
S-1.5	S	1.5
S-2.0	S	2.0
N-0.5	N	0.5
N-1.0	N	1.0
N-1.5	N	1.5
N-2.0	N	2.0

Note: fly ash-to-liquid ratio = 1.5.

3. Results and discussion

3.1. Leaching test

Results of measuring of Si^{4+} and Al^{3+} ions are shown in Figs. 1 and 2. From Fig. 1, an average Si^{4+} ion concentration close to 600 ppm was obtained with 10 M NaOH. For 5 M and 15 M NaOH, the concentrations were much less at approximately 200 and 260 ppm. At 5 M NaOH, the dissolution was low due to relatively low base condition. For 10 M NaOH, the base condition was higher and the dissolution was, therefore, increased. For the 15 M NaOH, the dissolution was again reduced owing primarily to an increase in coagulation of silica (Bergna and Roberts, 2006).

From Fig. 2, the concentration of Al^{3+} ion was much lower than that of Si^{4+} ion. This was expected since alumina content in fly ash was approximately half of silica. Si^{4+} ion possessed higher intrinsic

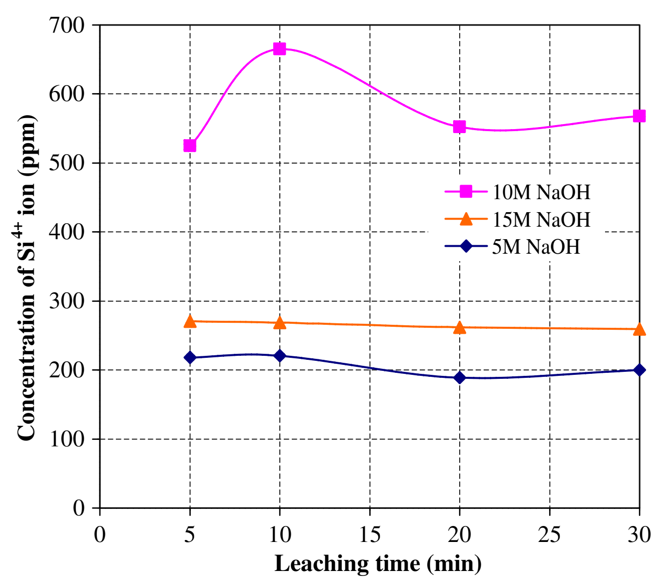

Fig. 1. Si^{4+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH.

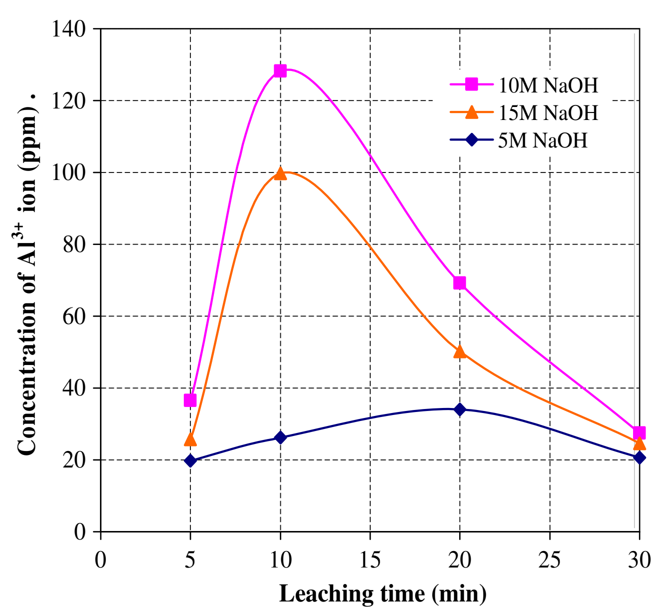

Fig. 2. Al^{3+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH.