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Investigation of alkali solution and NaOH concentration on the setting and hardening of high calcium fly ash geopolymer pastes

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ABSTRACT

The effects of alkali solution and sodium hydroxide (NaOH) concentration on the setting and hardening of high calcium fly ash geopolymer pastes were investigated. The setting time and compressive strength with liquid alkaline to ash (L/A) ratios of 0.4, 0.5, 0.6 and NaOH concentrations of 8, 10 and 15 molar were studied. The results showed that the liquid alkaline ratio and NaOH concentration had affected to the properties of geopolymer pastes. The L/A ratio of 0.4 and variables of NaOH concentration were selected to study by XRD, SEM and FTIR techniques due to higher strength. It is revealed that the high NaOH concentration results in the increases in the CSH co-existed with geopolymer gel. Thus, it showed dense matrix and less unreacted fly ash in the geopolymer matrix.

Keywords: alkaline solution, NaOH concentration, setting time, compressive strength, microstructure.

INTRODUCTION

Fly ash is an industrial by-product generated during the combustion of coal for energy productions. Currently, the annual production of coal ash worldwide is estimated about 600 million tons, with fly ash constituting about 500 million tons at 75–80% of the total ash produced (Ahmaruzzaman, 2010). In Thailand, the annual output of lignite fly ash from Mae Moh power station is about 3.0 million tons. Approximately 1.8 million tons are used as pozzolanic material in cement and concrete industry. However, about 1.2 million tons are still left over and discarded at landfill site (Chindaprasirt et al., 2009) which poses a serious environmental problem. This lignite fly ash contains a reasonable amount of silica and alumina...
which can be used as a source material for making geopolymer (Chindaprasirt et al., 2007). The geopolymer materials have recently received considerable attention owing to their excellent fire resistance, excellent thermal properties and environmentally friendly nature (Barbosa and MacKenzie, 2003).

Aluminosilicate inorganic polymers, also called geopolymers, were firstly described by Davidovits as materials formed under high alkali condition from aluminosilicate solid and alkali silicate solutions (Khale and Chaudhary, 2007). The geopolymer is a type of cross-linked long chain inorganic polymer material between tetrahedral AlO$_4$ and SiO$_4$ units built in three dimensional structures. The linkages of AlO$_4$ and SiO$_4$ units require charge balancing from alkali ions such as Li$^+$, Na$^+$ and K$^+$. The parameters as type of materials, liquid alkali to ash ratio, sodium silicate to alkali hydroxide ratio, alkali hydroxide concentration, curing time and curing temperature also affected to properties of geopolymer materials (Albakri et al., 2011; Chindaprasert et al., 2007; Rattanasak and Chindaprasirt, 2009).

This research aims to study the effects of liquid alkaline solution and NaOH concentration on properties of high calcium fly ash geopolymer pastes. The knowledge would be beneficial to the understanding of this material.

**MATERIALS AND METHODS**

**Raw Material**

Lignite high calcium fly ash from Mae Moh power plant in Thailand was used for this study. The percentage retained on sieve no. 325 was 40%. The chemical compositions were 35.21% SiO$_2$, 16.57% Al$_2$O$_3$, 25.52% CaO, 13.66% Fe$_2$O$_3$, 2.73% Na$_2$O, 6.31% other, and 0.37% LOI. Sodium silicate (Na$_2$SiO$_3$) with 32.39% SiO$_2$, 13.44% Na$_2$O and 54.17% H$_2$O by weight and sodium hydroxide solutions (NaOH) were used as alkali solutions.

**Mix proportion and testing procedures**

The compositions of fly ash geopolymer pastes representing as SiO$_2$/Al$_2$O$_3$, Na$_2$O/SiO$_2$, Na$_2$O/Al$_2$O$_3$, and H$_2$O/Na$_2$O ratios are shown in Table 1. A constant of the Na$_2$SiO$_3$/NaOH ratio of 0.67 was used in all mixtures. The effects of the L/A ratios and the NaOH concentrations were also studied. The mixing procedure started with mixing fly ash (FA) and NaOH solution for 5 minutes. Sodium silicate solution was added and mixed for another 5 minutes.

After mixing, the setting time of geopolymer pastes were tested in accordance with ASTM C191 (2008). The geopolymer paste was casted in 50x50x50 mm cube moulds in accordance with the ASTM C 109 (2002) for the compressive strength test. The cast samples were left standing in the 25°C for 1 h. It was then covered by cling film to avoid the loss of water and put to cure in an electric oven at 40°C for 24 h. After curing, the specimens were kept in the 25 °C controlled room. The compressive strength was measured at the ages of 7 days. The reported results were the average of three samples. In addition, the x-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) of hardened pastes were investigated.
Table 1 Molar ratios of chemical compositions of pastes

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Molar compositions</th>
<th>SiO₂/Al₂O₃</th>
<th>Na₂O/SiO₂</th>
<th>Na₂O/Al₂O₃</th>
<th>H₂O/Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4LA8M</td>
<td>Na₂O. 1.47Al₂O₃, 6.06SiO₂, 13.98H₂O</td>
<td>4.13</td>
<td>0.17</td>
<td>0.68</td>
<td>13.98</td>
</tr>
<tr>
<td>0.4LA10M</td>
<td>Na₂O. 1.30Al₂O₃, 5.36SiO₂, 11.96H₂O</td>
<td>4.13</td>
<td>0.19</td>
<td>0.77</td>
<td>11.96</td>
</tr>
<tr>
<td>0.4LA15M</td>
<td>Na₂O. 1.00Al₂O₃, 4.14SiO₂, 8.47H₂O</td>
<td>4.13</td>
<td>0.24</td>
<td>1.00</td>
<td>8.47</td>
</tr>
<tr>
<td>0.5LA8M</td>
<td>Na₂O. 1.17Al₂O₃, 5.00SiO₂, 13.98H₂O</td>
<td>4.26</td>
<td>0.20</td>
<td>0.85</td>
<td>13.98</td>
</tr>
<tr>
<td>0.5LA10M</td>
<td>Na₂O. 1.04Al₂O₃, 4.42SiO₂, 11.96H₂O</td>
<td>4.26</td>
<td>0.23</td>
<td>0.96</td>
<td>11.96</td>
</tr>
<tr>
<td>0.5LA15M</td>
<td>Na₂O. 0.80Al₂O₃, 3.42SiO₂, 8.48H₂O</td>
<td>4.26</td>
<td>0.29</td>
<td>1.25</td>
<td>8.48</td>
</tr>
<tr>
<td>0.6LA8M</td>
<td>Na₂O. 0.98Al₂O₃, 4.30SiO₂, 13.98H₂O</td>
<td>4.39</td>
<td>0.23</td>
<td>1.02</td>
<td>13.98</td>
</tr>
<tr>
<td>0.6LA10M</td>
<td>Na₂O. 0.86Al₂O₃, 3.80SiO₂, 11.96H₂O</td>
<td>4.39</td>
<td>0.26</td>
<td>1.16</td>
<td>11.96</td>
</tr>
<tr>
<td>0.6LA15M</td>
<td>Na₂O. 0.67Al₂O₃, 2.94SiO₂, 8.48H₂O</td>
<td>4.39</td>
<td>0.34</td>
<td>1.49</td>
<td>8.48</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Setting time

The setting time results of fly ash geopolymer pastes are shown in Fig. 1. The initial and final setting times were increased with increase of NaOH concentration and L/A ratio. The final setting times were 100, 100 and 139 min for the 0.4LA8M, 0.4LA10M and 0.4LA15M, respectively. The final sets were 100, 290 and 340 min for the 0.4LA8M, 0.5LA8M and 0.6LA8M, respectively. At low NaOH concentration, the leaching out of silica and alumina was low (Rattanasak and Chindaprasirt, 2009). The leaching out of Ca²⁺ to the solution was not interrupted and the solution was thus filled with calcium. The amount of calcium was sufficient for the precipitation and reacted to form calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH). This resulted in the setting of paste and the setting time was thus short (Alonso and Palomo, 2001; Chindaprasirt et al., 2012). The setting time of geopolymer paste was thus related to the amount of the available calcium (Rattanasak et al., 2011). In contrast, at high NaOH concentration, the leaching of silica and alumina were much better in this case. The leaching out of Ca²⁺ was hindered and the amount of calcium in the solution was limited, thus the setting time was increased.
Compressive strength

The compressive strength results of fly ash geopolymer pastes are shown in Fig. 2. The compressive strength was increased with increase in the NaOH concentration. The compressive strengths were 43.31, 46.68 and 54.12 MPa for the 0.4LA8M, 0.4LA10M, and 0.4LA15M, respectively. The high NaOH concentrations, the dissolution of Si$^{4+}$ and Al$^{3+}$ ions from fly ash increased and the additional formation of sodium alumino-silicate resulted in the increase of strength (Guo et al., 2010; Rattanasak and Chindaprasirt, 2009). The compressive strength decreased with increase the L/A ratio. The workability of the mixes increased with increase the liquid alkali solution (Sinsiri et al., 2012). However, the excess of OH$^-$ concentration of the mixture (Hardjito et al., 2004) could disrupt the geopolymerization process.

Solid phase development by XRD
The XRD patterns of as-received fly ash and fly ash geopolymer paste at L/A ratio of 0.4 and various NaOH concentrations are shown in Figs. 3 (a-d). The fly ash consists of an amorphous phase as indicated by the broad hump around 20°-38° and crystalline phase as indicated by the sharp peaks of quartz (SiO₂), hematite (Fe₂O₃), anhydrite (CaSO₄), magnesioferrite (MgFe₂O₄) and calcium oxide (CaO). The glassy component of fly ash was the first to dissolve and formed a new phase of alkaline aluminosilicate gel with apparent shift of broad hump around 25°-38° (Guo et al., 2010; Rattanasak and Chindaprasirt, 2009). The quartz and magnesioferrite were still present from remain of the unreacted fly ash with the disappearance of anhydrite. The new phases were found of portlandite (Ca(OH)₂), sodium sulfate (Na₂SO₄) and hydrosodalite (Na₄Al₃Si₃O₁₂(OH)). The presence of Ca(OH)₂ affected to the setting time of pastes due to the formation of CSH gel (Chindaprasirt et al., 2009; Guo et al., 2010). At high NaOH concentrations, it had positive effect to dissolve fly ash particles resulted in the increase peaks of hydrosodalite and CSH, the results correspond well with the strength behavior.

Fig. 3 XRD patterns of fly ash and fly ash geopolymer with various NaOH concentrations

(a) As-receive fly ash (b) 0.4LA8M (c) 0.4LA10M (d) 0.4LA15M

SEM analysis

Figs. 4 (a)-(c) show the SEM of fly ash geopolymer paste at L/A ratio of 0.4 and various NaOH concentrations. The unreacted and/or partially reacted of fly ash and a continuous mass of aluminosilicate were easily detected. With increasing NaOH concentration, the unreacted fly ash particles were less and dense (Albakri et al., 2011). This probably due to the leaching of the silica and alumina from the fly ash particles increased (Rattanasak and Chindaprasirt, 2009).
Fourier Transform Infrared Spectroscopy (FTIR)

Figs. 5 (a)-(d) show the FTIR spectrum of as-received fly ash and fly ash geopolymer paste at L/A ratio of 0.4 and various NaOH concentrations. The IR spectrums of fly ash geopolymer were appeared at the same pattern and a bit change of wave number with increase NaOH concentration. The as-received fly ash was observed at 3450 cm$^{-1}$ and 1650 cm$^{-1}$ for O-H stretching and O-H bending (spectra of water molecule). The band at 670 cm$^{-1}$ was ascribed to S-O indicated that the anhydrite phase in matrix. The band at 455 cm$^{-1}$ was ascribed to O-Si-O bending indicated that remaining of quartz. The FTIR spectra of geopolymer were slightly different from the as-received fly ash. After activated fly ash, the significant broad bands were observed at approximately 3450 cm$^{-1}$ and 1650-1600 cm$^{-1}$ for O-H stretching and O-H bending. This probably due to higher water molecule in geopolymer structure (Panias et al., 2007). In addition, the Si-O-Si stretching was detected at wave number range 1200-950 cm$^{-1}$ which related to the ability of geopolymerization (Rattanasak and Chindaprasirt, 2009).

Fig. 5 FTIR spectrums of fly ash geopolymer with various NaOH concentrations
(a) As-receive fly ash (b) 0.4LA8M (c) 0.4LA10M (d) 0.4LA15M

CONCLUSIONS

1. The initial and final setting times were increased with increase of NaOH concentration and L/A ratio.
2. The high NaOH concentrations result in the increase of compressive strength due to the additional formation of sodium alumino-silicate and CSH.
3. The compressive strength decreased with increase of L/A ratio due to the excess of OH- concentration of the mixture, which disrupt the geopolymerization process.
4. The dense and strong pastes are obtained at the high NaOH concentrations.

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