Fly Ash-based Geopolymer: Clean Production, Properties and Applications

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Graphic abstract
Fly Ash-based Geopolymer: Clean Production, Properties and Applications

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ABSTRACT

Fly ash is the fine solid particulate residue driven out of the boiler with the flue gases in coal-fired power plants. Now it can be used for making geopolymer which acts as a cement-like product. The geopolymer technology provides an alternative good solution to the utilization of fly ash with little negative impact on environment. This review summarizes and examines the scientific advances in the preparation, properties and applications of fly ash-based geopolymer. The production of fly ash-based geopolymer is mainly based on alkali activated geopolymerization which can occur under mild conditions and is considered as a cleaner process due to much lower CO₂ emission than that from the production of cement. The geopolymerization can trap and fix the trace toxic metal elements from fly ash or external sources. The Si/Al ratios, the type and the amount of the alkali solution, the temperature, the curing conditions, and the additives are critical factors in a geopolymerization process. The
mechanical performances of the fly ash-based geopolymer, including compressive strength, flexural and splitting tensile strength, and durability such as the resistance to chloride, sulfuric, acid, thermal, freeze-thaw and efflorescence, are the primary concerns. These properties of fly ash-based geopolymer are inherently dependent upon the chemical composition and chemical bonding and the porosity. The mechanical properties and durability can be improved by fine tuning Si/Al ratios, alkali solutions, curing conditions, and adding slag, fiber, rice husk-bark ash and red mud. Fly ash-based geopolymer is expected to be used as a kind of novel green cement. Fly ash-based geopolymer can be used as a class of materials to adsorb and immobilize toxic or radioactive metals. The factors affecting the performances of fly ash-based geopolymer concrete, in particular aggregate, are discussed. For future studies on fly ash-based geopolymer, further enhancing mechanical performance, scaling up production and exploring new applications are suggested.

Key words: Fly ash; Alkali activation; Geopolymer; Waste utilization; Cement, Concrete

1. Introduction

Fly ash is one of the solid residues composed of the fine particles that are driven out of the boiler with flue gases in coal-fired power plants. It is generally captured from flue gases by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys (Ahmaruzzaman, 2010; Gorai et al., 2006). Depending upon the source of the coal being burned, the components of fly ash vary considerably. In general, the components of fly ash typically include SiO$_2$, Al$_2$O$_3$, CaO and Fe$_2$O$_3$, which exists in the form of amorphous and crystalline oxides or various minerals. According to the American Society for Testing and Materials standard C 618 (ASTM C618-12a; 2012), fly ash can be classified as Class C and Class F types based on their calcium oxide contents. Class C fly ash has a high calcium content, and is mainly generated from the burning of lignite coal sources. Class C fly ash has a total SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ content between 50 wt.% and 70 wt. % and CaO content more than 20 wt.%. Class F fly ash has a low calcium content, and is generated from burning anthracite or bituminous coal. Class F fly ash has a total SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ content over 70 wt% and CaO content less than 10% (Bankowski et al., 2004, Antiohos and Tsimas, 2007). In
addition to Si, Al, Fe, and Ca, usually fly ash also contains many other trace metal elements, such as Ti, V, Cr, Mn, Co, As, Sr, Mo, Pb and Hg. The concentrations of the toxic trace elements in fly ash could be 4-10 times higher than those in coal (Neupane and Donahoe, 2013; Nyale et al., 2014; Yao et al., 2015). It may also include small concentrations of dioxins and polycyclic aromatic hydrocarbon compounds (Shibayama et al., 2005; Nomura et al., 2010). Thus, fly ash is considered as a hazardous material, and the improper disposal of fly ash will not only increase the occupation of land but also deteriorate the environment and ecology. In last few decades, increasing efforts have been made towards the utilization of fly ash, especially in an efficient and green fashion.

**Fig. 1** a) The generation of fly ash from 2008-2013 in the USA. b) The utilization fields of fly ash in 2013 in the USA (Data from American Coal Ash Association).

Due to the cost and availability of oil and natural gas, coal-fired power plants will be still run for a long period, especially in the coal-rich countries, for example, China, the USA, India and Australia (Lior, 2010). Under such a circumstance, the generation of fly ash remain significant and thus its economic and green utilization technology of fly ash are desired (**Fig. 1a**). Fly ash can be used for soil amendment (Ukwattage et al., 2013) and nutrients (Kováčik et al., 2011). It can also be used to make a low-cost adsorbent for waste removal (Rubel et al., 2005; Yildiz, 2004). Besides, it can act as silica and alumina sources for zeolite production (Chang and Shih, 2000; Izidoro et al., 2012) (**Fig. 1b**). More recently, fly ash has been used as an alternative source to make geopolymer, a new binder or cement roughly comparable to hydrated cement in appearance, reactivity and properties. In principle, geopolymer is a product of alkali activation of any aluminosilicate materials. It has a three-dimensional
aluminosilicate network structure with an empirical formula of $M_n[\{(SiO_2)_{z}AlO_2\}_{n}wH_2O$, where $z$ is the Si/Al molar ratio, $M$ is an alkali cation, such as Na$^+$ or K$^+$, $n$ is the polymerization degree, and $w$ is the water content (Palomo et al., 1999a). Importantly, such a geopolymer has the similar bind performances to those of ordinary Portland cement (OPC). The alkali activation is conducted by adding NaOH, KOH, Na$_2$SiO$_3$ or K$_2$SiO$_3$ into fly ash together or individually. The so-called geopolymerization can occur at room temperature or slightly elevated temperatures (usually<100°C), and much importantly, with little CO$_2$ emission (Davidovits, 1991; Verdolotti et al., 2008; Zhang et al., 2016).

The geopolymer technology provides a new good and green solution to the utilization of fly ash, avoiding its negative impact on environment and ecology. The alumina and silica in fly ash can be activated with alkali to form geopolymer. Moreover, the toxic trace metal elements can be trapped and fixed in the geopolymer structure (Li et al., 2013a). Remarkably, the process of the production of fly ash-based geopolymer has lower CO$_2$ emission compared with that of OPC during which much limestone (CaCO$_3$) is calcined and decomposed at high temperatures (Davidovits, 1994; McLellan et al., 2011). Approximately 0.8 ton of CO$_2$ is produced when one ton of OPC is produced (Rashad and Zeedan, 2011; Yang, 2009). Fly ash-based geopolymer usually show mechanical strength and durability nearly comparable to hydrated Portland cement and can used as a class of green cement with natural resource efficiency (Nasvi and Gamage, 2012).

In particular, recent years have witnessed many scientific advances in the preparation technology, and the insights into the performances of the fly ash-based geopolymer. The fast-growing knowledge in turn results in many modification methods to significantly improve the production and the performances of the fly ash-based geopolymer. Meanwhile, there are increasing pilot and commercial process. The large-scale use of fly ash-based geopolymer in construction industry seems to come true. In this review article, the state-of-the-art preparation of fly ash-based geopolymer is examined. Attention will therein be paid to understanding how the Si/Al ratios, the type and the amount of the alkali solution, the temperature, the curing conditions, and the additives are controllably used to reinforce properties of fly ash–based geopolymer. Discussed are the critical properties, including compressive, flexural and splitting tensile strength, and the durability such as chloride, sulfate, acid, thermal, freeze-thaw and efflorescence resistance. Then, the applications of fly ash–based geopolymer are surveyed. They involve cement-based construction, adsorption and immobilization of toxic metals materials. The existing challenges and future work are finally analyzed and proposed.
2. Preparation and formation

The basic and simplified principle of the formation of fly ash-based geopolymer is the alkali-facilitated decomposition of aluminosilicate in the fly ash and then polycondensation. The reactions can proceed under mild temperatures so the production is considered to be energy and source efficient, namely much cleaner. However, the real reactions occurred in the process are very complicated and remain elusive. Apparently, there are reactions between fly ash and alkali and condensation between the resultant Si$^{4+}$ and Al$^{3+}$ species, followed by other complicated nucleation, oligomerization, and polymerization, which finally lead to a new aluminosilicate-based polymer with new amorphous three-dimensional network structure. In tests or uses, the as-prepared fly ash-based geopolymer paste is further cast into a mould and placed into an oven at a required temperature or left at room temperature to be cured for a specific time to form construction (Fig. 2.).
oligomers consists of SiO$_4$ and AlO$_4$ tetrahedra. The chains in aluminosilicate oligomers can be in the form of polysialate -Al-O-Si- chain, polysialate siloxo -Al-O-Si-Si- chain, and polysialate disiloxo -Al-O-Si-Si-Si- chain, depending upon the Si/Al ratio (Fig. 3). In aluminosilicate monomers, Si$^{4+}$ is partially substituted by Al$^{3+}$, and the resultant negative charge in the aluminosilicate chains is balanced by alkali cations such as Na$^+$ or K$^+$ (Davidovits, 2002; Dimas et al., 2009) (Fig. 2). In the context, the Si/Al ratio significantly determines the final structure of the resulted geopolymer materials (He et al., 2012). For example, it have been found that the Si/Al ratio in the fly ash reactant has a remarkable effect on the porosity (size and amount) of amorphous geopolymer which is one of important parameters to govern the mechanical strength of geopolymer products (Kriven et al., 2003; Duxson et al., 2005b).

![Dependent upon the different Si/Al molar ratio, different aluminosilicate chains is formed in the aluminosilicate oligomers which then further to form geopolymer (Davidovits, 2002) (Reprinted and adapted by courtesy of Geopolymer Institute).](image)

**Fig. 3.** Dependent upon the different Si/Al molar ratio, different aluminosilicate chains is formed in the aluminosilicate oligomers which then further to form geopolymer (Davidovits, 2002) (Reprinted and adapted by courtesy of Geopolymer Institute).

In addition to the Si/Al ratio, the microstructure of the formed fly ash-based geopolymer is strongly affected by the alkaline solution. When fly ash contacts with alkaline (e.g. NaOH, KOH), Si$^{4+}$, Al$^{3+}$ and other ions start to be released and to transfer. For instance, the amount of released Si$^{4+}$ and Al$^{3+}$ is influenced by the concentration of NaOH solution. NaOH solution of high concentration (10 mol/L) is beneficial for decomposing aluminosilicate in the fly ash and then release Si$^{4+}$ and Al$^{3+}$ (Table 1). For example, the solubility of Al$^{3+}$ and Si$^{4+}$ in NaOH solution is higher than that in KOH solution with the same concentration (Xu and Van Deventer, 1999). Moreover, the transfer of Al$^{3+}$ and
Si$^{4+}$ species and the polycondensation of aluminosilicate oligomers can also be accelerated by an alkaline solution of high concentration (Lizcano et al., 2011). Furthermore, different alkaline cations have different sizes and charge density, and they hydrate differently. These will then have a certain effect on the nucleation of aluminosilicate chain, the growth of the chain, the charge density on the chain, the rate, and the extent of polymerization (Duxson et al., 2005a). For instance, the K$^+$ cation (1.33 Å) is larger than the Na$^+$ cation (0.97 Å) and the K$^+$ cation lead to a lower surface charge density and a higher degree of polymerization of geopolymer matrix (van Jaarsveld and van Deventer, 1999). In addition, alkaline cations can even serve as a structure-directing agent in the geopolymerization. In brief, the leaching rate of Si$^{4+}$ and Al$^{3+}$ decide the real available Si/Al ratio in a series of reactions to form geopolymer and subsequently play a pivotal role in the structure of fly ash-based geopolymer. Interestingly, a recent study revealed that the addition of Na$_2$SiO$_3$ to alkali solution can increase such a Si/Al ratio, resulting in a lower porosity and a finer pore system of geopolymer matrix (Ma et al., 2013).

The setting time of fly ash-based geopolymer is usually considered for the workability of final fly ash-based geopolymer products. In general, the final setting can be achieved within 1–2 h at room temperature while Class C fly ash with high CaO content and calcium-content additives, such as CaCl$_2$, were found to shorten the setting time of fly ash-based geopolymer paste (Rattanasak et al., 2011). In geopolymerization, Si$^{4+}$ or Al$^{3+}$ species react with Ca$^{2+}$, either in the fly ash or from an external calcium-content additives, to form calcium silicate hydrate gel (C-S-H), calcium aluminate hydrate gel (C-A-H) or calcium aluminum silicate gel (C-A-S-H) (C = CaO, S = SiO$_2$, A = Al$_2$O$_3$, H = H$_2$O) in the presence of water (Diaz et al., 2010; Chindaprasirt et al., 2011). Ca$^{2+}$ is beneficial for accelerating the nuclei formation and agglomeration of C-A-S-H gel and C-S-H gel (Geetha and Ramamurthy, 2013). The rapid formation of amorphous C-A-S-H gel and C-S-H gel leads to a shorter setting time of the final products and decreases the porosity, while the rapid setting time has a negative on the formation of more geopolymer gel (N-A-S-H). The high NaOH concentration can prolong the setting time by limiting the leaching of calcium and allows normal geopolymerization process to control the setting of geopolymer paste (Hanjitsuwan et al., 2014).

At room temperature, however, the dissolution of fly ash is not completed (Chen et al., 2011; Xu et al., 2010). In addition, the low reactivity of fly ash increases the setting time of fly ash-based geopolymer. As a result, curing is a necessary step, namely, geopolymer paste needs to be kept within a
reasonable range of temperature and moisture and the extended curing time promotes the formation of a more cross-linked binding and denser microstructure. It is found that when the curing temperature increases from 30 to 50°C, the reactivity of fly ash becomes higher and the geopolymerization is almost more complete when the curing temperature lies between 60 and 90°C (Hardjito et al., 2004).

To improve the reactivity of fly ash and the performances of geopolymer, slag, chitosan, fiber, rice husk-bark ash (RHBA) and red mud have been added into fly ash to synthesize geopolymer (Table 1). Interestingly, the addition of slag, which is the waste from iron extraction process from raw ore, can enhance the reactivity of fly ash during geopolymerization (Li and Liu, 2007). Blast furnace slag (BFS) is the by-product of iron production industry and it contains more than 70% of SiO$_2$ and CaO (Manz, 1999). Idawati et al. (2014) investigated the fly ash/ground blast furnace slag (GBFS)-based geopolymer with different fly ash/slag ratios and they found the geopolymerization of slag-based geopolymer was dominated by C–A–S–H type gel, while fly ash-based geopolymer was dominated by sodium aluminosilicate (N–A–S–H) gel. Kumar et al. (2010) substituted fly ash by 5 - 50% GBFS to synthesize geopolymer at 27°C and found that the reaction was dominated by dissolution and precipitation of C-S-H gel. Moreover, Yang et al. (2012) found that the initial setting time of fly ash/GBFS-based geopolymer increased and the degree of polymerization of the geopolymer decreased due to the high content of calcium in GBFS. RHBA is a solid waste generated from rice husk and eucalyptus bark by biomass power plants. RHBA contains about 75% SiO$_2$ and the addition of RHBA enriched the silica content of the geopolymer matrix and increased the amount of -Si-O-Si- bonds in the geopolymer gel (N-A-S-H gel). Red mud is the major residue of Bayer process with highly alkaline of alumina refining from bauxite ores (Zhang et al., 2010a). The annual generation of red mud is estimated to be about 70 million tons in the world (Klauber et al., 2011). Due to the use of a highly concentrated NaOH solution in the bauxite processing, red mud is a highly alkaline material. Red mud essentially consists of oxides and hydroxides of Fe, Al and Si, as well as minor quantities of CaO and TiO$_2$. Addition of red mud can adjust the Si/Al ratio and reduce the consumption of alkali activator (Piga and Stoppa, 1993). The addition of chitosan and fiber can increase the hydrogen bonds, bridge the micro cracks and delay the development of micro cracks (Li et al., 2013b).

Table 1. Preparation and compressive strength of fly ash-based geopolymer with additives
<table>
<thead>
<tr>
<th>Material/Alkaline activators</th>
<th>Mix</th>
<th>Curing time</th>
<th>Compressive strength (MPa)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>T</td>
<td>/Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash</td>
<td>48 h/65</td>
<td>26.9-32.2</td>
<td>Rattanasak et al., 2011</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$ +NaOH (10 mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl$_2$, CaSO$_4$, Na$_2$SO$_4$, sucrose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash</td>
<td>-</td>
<td>&lt;25.5</td>
<td>Somna et al., 2011</td>
<td></td>
</tr>
<tr>
<td>NaOH (4.5, 7.0, 9.5, 12.0, 14.0, 16.5 mol/L)</td>
<td>25-28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash+RHBA/</td>
<td>25</td>
<td>14.8-55.6</td>
<td>Bohlooli et al., 2012</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$ +NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4.8,12 mol/L) 2/5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash+RHBA/</td>
<td>25</td>
<td>12.6-35.1</td>
<td>Riahi et al., 2012</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$ or water glass+NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5-12 mol/L) 2/5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash+</td>
<td>91 days</td>
<td>31.2-60.6</td>
<td>Yan et al., 2012</td>
<td></td>
</tr>
<tr>
<td>wastepaper sludge/</td>
<td>23-60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$+NaOH</td>
<td>1/5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulverized coal combustion</td>
<td>Fly n.a.</td>
<td>25.5-55.5</td>
<td>Boonserm et al., 2012</td>
<td></td>
</tr>
<tr>
<td>ash+</td>
<td>48 h/40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCC Bottom ash+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fly gas desulfurization gypsum/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$+NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash+</td>
<td>AT</td>
<td>42.0-58.0</td>
<td>Joseph and Mathew, 2012</td>
<td></td>
</tr>
<tr>
<td>Crushed granite rock+</td>
<td>6-72 h/60-120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>natural river sand/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$+NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FFA+ N-carboxymethyl chitosan</td>
<td>AT</td>
<td>&lt;30.0</td>
<td>Li et al., 2013b</td>
<td></td>
</tr>
<tr>
<td>NaOH (10 mol/L)</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash+ RHBA/</td>
<td>7,28 days/ RT</td>
<td>&lt;58.9</td>
<td>Nazari et al., 2013</td>
<td></td>
</tr>
<tr>
<td>water glass+NaOH</td>
<td>36h/40–90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FFA+crushed granite stone+</td>
<td>48 h;</td>
<td>40.85-53.08</td>
<td>Demie et al., 2013</td>
<td></td>
</tr>
<tr>
<td>Superplasticizer/</td>
<td>1,3 days/70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$+NaOH 5/2</td>
<td></td>
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</tbody>
</table>
Using waste materials, fly ash and additives like slag, RHBA, red mud and fibers, to produce a construction material geopolymer can help reduce the consumption of mineral reserves such as limestone and the emission of greenhouse gases. Without proper utilization, fly ash is a solid waste. Improper disposal of fly ash brings the danger of the release of toxic elements. By contrast, fly ash-based geopolymer can solidify and immobilize the trace of heavy metal elements. Furthermore, the simple alkaline activation of fly ash to produce geopolymer completely bypasses the high-temperature calcination process in OPC production. All these would justify the thought that the production of fly ash-based polymer is a cleaner process with improved natural resource efficiency.

3. Properties

3.1 Compressive strength

The improvement of mechanical properties of fly ash-based geopolymer is major concerns because its main uses are in construction materials as cement and concrete. The compressive strength of fly ash-based geopolymer is dependent on alkali solutions, Si/Al ratios, calcium content, curing conditions (temperature and time) and the various additives.

<table>
<thead>
<tr>
<th>System</th>
<th>Alkali Solution</th>
<th>Curing Condition</th>
<th>7 Days</th>
<th>28 Days</th>
<th>28 Days</th>
<th>AT</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFA+BFS</td>
<td>K$_2$SiO$_3$/Al (85 g/L) + NaOH (30g/L)</td>
<td>RT</td>
<td>7 days</td>
<td>1.38-9.93</td>
<td>Ogundiran et al., 2013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FFA/NaOH 3/5</td>
<td>25</td>
<td>7 day/</td>
<td>1.38-9.93</td>
<td>Jun and Oh, 2014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash+Palm oil fuel ash/Na$_2$SiO$_3$+NaOH</td>
<td>24h</td>
<td>&lt;38</td>
<td>Ranjbar et al., 2014</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGBF+Palm oil fuel ash+Fly ash+ Manufactured-sand/Na$_2$SiO$_3$+NaOH</td>
<td>24h</td>
<td>9-66</td>
<td>Islam et al., 2014</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FFA+Red mud (50wt.%) + sodium trisilicate (2 mol/L)</td>
<td>28 days</td>
<td>11.3-21.3</td>
<td>Zhang et al., 2014a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*T: temperature, RT: room temperature, AT: ambient temperature, BFS: Blast furnace slag, FFA: Class F fly ash, RHBA: Rice husk-bark ash, GGBF: Ground granulated blast furnace slag
The type and the concentration of the alkaline solution influence the release of Si$^{4+}$ and Al$^{3+}$ from fly ash during geopolymerization. Alkaline solution of a high concentration is generally beneficial for obtaining high compressive strength but there is an optimal range (de Vargas et al., 2011). Görhan and Kürklü (2014) prepared fly ash-based geopolymer with different NaOH concentrations (3 mol/L, 6 mol/L and 9 mol/L). A highest compressive strength of 22 MPa was achieved when the fly ash-based geopolymer paste was activated in 6 mol/L NaOH and cured at 85°C for 24 h.

Na$_2$SiO$_3$ solution is usually used with NaOH to increase compressive strength (Criado et al., 2005). This is because of Na$_2$SiO$_3$ with high viscosity can help the formation of geopolymer gels and a compact final fly ash-based geopolymer microstructure is achieved. Moreover, the activation procedure also influences the compressive strength of fly ash-based geopolymer. For example, Rattanasak and Chindaprasirt (2009) first added NaOH solution to fly ash to leach the Si$^{4+}$ and Al$^{3+}$ species for 10 min, followed by using Na$_2$SiO$_3$ to help form a uniform geopolymer paste for another 1 min. Such separate activation gave a higher strength for the fly ash-based geopolymer. When fly ash was separately mixed and activated with NaOH (10 mol/L) and Na$_2$SiO$_3$ with the NaOH/Na$_2$SiO$_3$ molar ratio of 1.0 and cured at 65°C for 48 h, the compressive strength of fly ash-based geopolymer was 60-70.0 MPa.

As discussed in previous section, the Si/Al ratios are determined by the source materials and alkali solution (Na$_2$SiO$_3$ is used). High Si/Al ratios increase the amount of -Si-O-Si- bonds to get a higher compressive strength of fully condensed structural matrix of geopolymer, since the -Si-O-Si- bonds are stronger than -Si-O-Al- and -Al-O-Al- bonds. The addition of slag, RHBA, and red mud can alter the Si/Al ratios (Table 1). For example, Yang et al. (2014a) prepared geopolymer fly ash and high magnesium nickel slag (HMNS) activated by Na$_2$SiO$_3$ solution. It was discovered that the major phase in fly ash/HMNS geopolymer was a type of sodium magnesium aluminosilicate gel. The addition of HMNS increased the silica content. In addition, HMNS particles worked as microaggregates and decreased the total volume of pores in the geopolymer pastes. As a result, the geopolymer possessed a high compressive strength of above 60 MPa when 20% HMNS was used for the preparation. Though the higher content of slag increased the compressive strength of fly ash/HMNS-based geopolymer, it caused rapid setting and crack due to autogenous shrinkage of slag (slag/binder>70%) (Jang et al., 2014). Wang et al. (2015) prepared fly ash/slag-based geopolymer with different fly ash/slag ratios (0 wt.%, 20 wt.%, 40 wt.%, and 60 wt.%) and various NaOH solutions (0.5%, 1% and 1.5%), and then cured for 1, 3, 7 and 28 days. The increasing portion of slag increased the compressive strength of
geopolymer and the optimal compressive strength was 93.06 MPa. Deb et al. (2014) activated Class F fly ash/GBFS-based geopolymer (GBFS/Class F fly ash ratio=0%, 10% and 20%) in NaOH and Na$_2$SiO$_3$ solution, respectively. High compressive strength increased with the increase of the GBFS/Class F fly ash ratio. When the geopolymer concrete synthesized by 20% slag and 80% fly ash with 40% NaOH and Na$_2$SiO$_3$ solution and cured at 20°C, it had the highest compressive strength of 51 MPa. Xu et al. (2014) used GBFS of grade 80, 100 and 120 and fly ash to synthesize geopolymer with an activating solution prepared from concentrated Hanford secondary waste (HSW) stimulant (5 mol/L NaOH mixed with solid binders). The highest compressive strength was 52.5 MPa when the fly ash/GBFS mass ratio was 5/3.

The addition of RHBA enriched the silica content of the geopolymer matrix, increased the amount of -Si-O-Si- bonds in the geopolymer gel (N-A-S-H gel) and the compressive strength (Sata et al., 2007; Tangchirapat et al., 2008). Nazari et al. (2011) added RHBA into fly ash to synthesize geopolymer paste and cured it in oven at 80°C for 28 days. They found the geopolymer had the compressive strength of about 60 MPa. Songpiriyakij et al. (2010) prepared fly ash-based geopolymer using the reactants of fly ash, RHBA and NaOH and curing at 27°C first for 24h and then curing at 60°C for 24h. It was found that the optimal SiO$_2$/Al$_2$O$_3$ ratio to obtain the highest compressive strength (73 MPa) was 15.9. Red mud of highly alkalinity is the major residue of Bayer process of alumina refining from bauxite ores. Zhang et al. (2014a) prepared geopolymer using fly ash and red mud at 23°C. They found compressive strengths ranging from 11.3 to 21.3 MPa and the highest compressive strength was obtained when the Si/Al molar ratio was 2.

Calcium is proved to interfere with the gelation of silica and alumina in geopolymerization process and alter the microstructures of fly ash-based geopolymer and thus alter the compressive strength (Schmucker and Mackenzie, 2005). The coexistence of C-S-H gel and the N-A-S-H gel usually improves the compressive strength of final products. One of reasons is that the amorphous C-S-H gel decreases the porosity (Temuujin and van Riessen, 2009).

Curing time and temperature also affect the compressive strength of fly ash-based geopolymer. Longer curing time, in the range of 6 hours to 28 days, produced fly ash-based geopolymer with a higher compressive strength (Table 1). Curing at high temperatures increases the compressive strength by removing the water from the fresh geopolymer, causing the collapse of the capillary pores with a denser structure (Leung and Pheerapha, 1995). Fly ash-based geopolymer can be cured at room
temperature, but the compressive strength develops slowly and always needs prolonged curing time (Somna et al., 2011). Nasvi et al. (2012; 2014) found that the crack closure and crack initiation thresholds of fly ash-based geopolymer cured at elevated temperatures (60-80°C) was higher (30-60% peak stress) compared to those (15-30% of peak stress) cured at ambient temperature (23°C and 40°C). However, prolonged curing at higher temperatures breaks down the granular structure of geopolymer, resulting in the dehydration and the excessive shrinkage, and finally decreasing the compressive strength (Palomo et al., 1999b).

Steam curing is the conventional heating technique, relying on the conduction of heat from the exterior to the interior of fly ash-based geopolymer paste by steam. The heating is non-uniform and required a long heating period to attain the required temperature. Microwave heating is based on internal energy dissipation associated with the excitation of molecular dipoles in electromagnetic fields, and it delivers faster and more uniform heating (Kim et al., 2015). Chindaprasirt et al., (2013b) prepared fly ash-based geopolymer pastes with 10 mol/L NaOH and Na$_2$SiO$_3$ solution and cured them under the 90-W microwave radiation for 5 min followed by additional heating at 65°C for 6 h. The compressive strength was comparable to that of the fly ash-based geopolymer cured at 65°C for 24 h. The microwave radiation quickened the dissolution of fly ash in the alkaline solution and formed a denser microstructure. Accordingly, the microwave radiation shortened the required curing time and enhanced the geopolymerization.

To put together, increasing the Si/Al ratios usually enhance the compressive strength of fly ash-based geopolymer. Though the increase of the Si/Al ratios can be realized by adding the external slag, RHBA and red mud, the inherent reasons are complicated. Advances in the preparation indicated that one of major reasons can be ascribed to the increased amount of -Si-O-Si- bonds rather than -Si-O-Al- and -Al-O-Al- bonds. To this end, the use of Na$_2$SiO$_3$ or K$_2$SiO$_3$ with NaOH for the activation of fly ash can increase the Si/Al ratios, thereby leading to a more compact structure with higher compressive strength (Fig. 3). In addition, the presence of calcium in fly ash or used as additive is beneficial for forming the amorphous C-S-H gel and C-A-S-H gel and decreases the porosity and obtain geopolymer with a higher compressive strength. Curing had a significant effect on the compressive strength of fly ash-based geopolymer by changing the porosity and density of the product.

3.2 Flexural and splitting tensile strength
Fly ash-based geopolymer would suffer from brittle failure with low tensile strength and fracture toughness. A typical method is to incorporate chitosan or fibers into the fly ash-based geopolymer matrix because this hybridization can improve the bond strength and reinforcing bending behaviors in strain hardening and multiple cracking procedure. In this way, the flexural and splitting tensile strength can be enhanced. The fibers for reinforcing fly ash-based geopolymer composites include steel (ST) fiber (Shaikh, 2013), polyvinyl alcohol (PVA) fiber (Nematollahi, 2015; Zhang et al., 2006; Zhang et al., 2008b; Sun and Wu, 2008), sweet sorghum fiber (Chen et al., 2014), and cotton (Alomayri et al., 2014a; 2014b).

In order to obtain higher flexural strength, Shaikh (2013) added 2 v/v% steel fiber, 2 v/v% PVA fiber and a hybrid combination of 1 v/v% ST + 1 v/v% PVA fiber and investigated the deflection hardening behavior of hybrid fiber reinforced fly ash-based geopolymer. They found a higher bond strength and flexural strength between the PVA fiber and geopolymer matrix than with cement matrix. The alkalinity of geopolymer matrix did not affect the degradation of PVA and steel fiber as seen in SEM (Fig.4). Alomayri et al. (2014a) added cotton fabric layers in fly ash-based geopolymer structure to improve flexural strength. The flexural strength of the fly ash-based geopolymer increased from 8.2 MPa to 31.7 MPa when the cotton fiber content was increased from 0 to 8.3 wt%. Moreover, the orientation of cotton fabric layers had effects on the flexural strength of fly ash-based geopolymer. The higher flexural strength of the fly ash-based geopolymer reinforced with horizontally laid cotton fabric could be attributed to the better uniformity in load distribution among the consecutive layers of cotton fabric, while the geopolymer with vertical fabric orientation suffered from detachments and delamination between the cotton fabric and geopolymer matrix, and had a lower flexural strength (Alomayri et al., 2014b).
Fig. 4. SEM image of steel fiber in fly ash-based geopolymer matrix (left). SEM image of PVA fiber in fly ash-based geopolymer matrix (right) (Reprinted from Shaikh (2013), Copyright (2013), with permission from Elsevier).

Splitting tensile strength can be increased by using N-carboxymethyl chitosan, and the fibers, such as PVA fiber and sweet sorghum fiber as additives in fly ash-based geopolymer (Table 1). Nematollahi et al., (2015) prepared geopolymer with short PVA fibers (2% v/v), Class F fly ash activated in 8.0 mol/L NaOH (28.6% w/w) and Na$_2$SiO$_3$ (71.4% w/w) solution. The bond strength of the geopolymer increased more than the cracking strength, resulting in a high fiber-bridging strength. The splitting tensile strength of PVA reinforced Class F fly ash-based geopolymer was 4.7 MPa.

Chitosan with stable crystalline structure from strong hydrogen bonds suffers poor solubility at higher pH required for geopolymer. N-carboxymethyl chitosan, a chitosan derivative, can avoid this problem and realize the better coordination with geopolymer gel (Mourya et al., 2010; Pillai et al., 2009). Li et al., (2013b) mixed NaOH solution (10 mol/L), N-carboxymethyl chitosan uniform solution with fly ash under stirring under ambient conditions for 20 min. Then, the specimens were aged at room temperature for 24 h and placed in an oven for curing at 60°C for 6 days. N-carboxymethyl chitosan biopolymer coated on fly ash particles and N-carboxymethyl chitosan were well incorporated into geopolymer matrix. In particular, there were additional hydrogen bonds formed between N-carboxymethyl chitosan macromolecules and fly ash-based geopolymer, in addition to the hydrogen bonds within the N-carboxymethyl chitosan macromolecules (Fig. 5). All these interactions led to a more condensed network structure in geopolymer. Thus the fly ash-based geopolymer reinforced by N-carboxymethyl chitosan exhibit enhanced the mechanical behavior of the fly ash-based geopolymer. The N-carboxymethyl chitosan reinforced fly ash-based geopolymer had a substantial increase of the tensile strength from 7 MPa to 8 MPa when the N-carboxymethyl chitosan content increased to 0.1 wt.%.
Chen et al., (2014) used alkali-pretreated sweet sorghum fiber with fly ash to prepare geopolymer. The sweet sorghum fiber was obtained from the bagasse waste after juice being extracted from sweet sorghum stalks for ethanol production. When 2% sweet sorghum fibers were used, an increase about 36% of the splitting tensile strength of the geopolymer was obtained. But further increase of the fiber content decreased tensile strength. The flexural strength of the fiber-reinforced geopolymer showed a similar trend. The addition of 2% fiber effectively carried higher tensile load and thus delayed the growth of microcracks and increased the flexural strength. However, further increase of the fiber content induced fiber agglomeration, resulting in an increase of air bubbles entrapped in the composite and nonuniform fiber dispersion. As consequence, flexural strength decreased. The addition of cotton to fly ash-based geopolymer showed the similar trend in flexural strength.

According the studies mentioned above, the increase of splitting tensile strength and flexural strength in chitosan-reinforced and fiber-reinforced fly ash-based geopolymer was primarily because the micro- and macro-fibers can increase the hydrogen bonds, bridge the micro cracks, transfer the load, and delay the development of micro cracks (Dias and Thaumaturgo, 2005).
3.3 Durability

The durability of fly ash-based geopolymer and geopolymer concrete includes resistance to chloride, sulfate, acid, freeze-thaw cycles, heat, fire and efflorescence. Durability is closely related to the microstructure and the migration behavior of ions from fly ash-based geopolymer. These in turn can be adjusted by the alkali solution, curing and addition of calcium and silica fume composite during the preparation of fly ash-based geopolymer.

3.3.1 Chloride resistance

Resistance to chloride is one of the main areas in durability of cement and concrete. Chloride penetration promotes the corrosion of the embedded steel bars when steel bars are used as reinforcements for geopolymer concrete. Chloride penetrates into fly ash-based geopolymer through capillary absorption, hydrostatic pressure and diffusion of ions.

The relatively high concentration of NaOH enabled the leaching of more Si and Al from fly ash and produced a better degree of polycondensation and resulted in a decrease the porosity of fly ash-based geopolymer. The porosity of the material affects the chloride penetration. For example, Chindaprasirt and Chalee (2014) prepared fly ash-based geopolymer using a Na$_2$SiO$_3$/NaOH mixture solution as the activator. The concentrations of NaOH were 8, 10, 12, 14, 16 and 18 mol/L with a constant SiO$_2$/Al$_2$O$_3$ molar ratio. The chloride penetration decreased with the increase of NaOH concentration used in geopolymerization process owing to the refinement of the pore structures as a result of polycondensation reaction.

Ismail et al. (2013) examined the permeability of chlorides in Class F fly ash/slag-based geopolymer, slag-based geopolymer, and OPC by the chloride accelerated method (NordTest NT Build 492) and the ponding method (ASTM C1543). AgNO$_3$ was used to reveal chloride penetration depths. The result showed that a little formation of silver chloride for the slag-based geopolymer (Fig. 6A), and fly ash/slag-based geopolymer (Fig. 6B, Fig. 6C), while OPC-based concrete (Fig. 6D) had the deepest chloride penetration depth. They found the slag promote the formation of denser C–A–S–H gel contributing to a higher mechanical strength, and durability under chloride exposure and fly ash promote the formation of more porous N–A–S–H gels, reducing the resistance to chloride transport.
Although a higher porosity was observed in the geopolymer compared to the OPC specimens, geopolymer still showed a higher chloride resistance.

![Image](image_url)

**Fig. 6.** Boundary of chloride penetration in 28-day cured concretes at the end of the Nord Test procedure, as a function of slag/fly ash ratio: (A) 100 wt.% slag, (B) 75 wt.% slag/25 wt.% fly ash, (C) 50 wt.% slag/50 wt.% fly ash, (D) OPC (Reprinted from Ismail et al. (2013), Copyright (2013), with permission from Elsevier).

Yang et al., (2014b) prepared fly ash/slag-based geopolymer (Slag/Fly ash ratio= 0, 0.25 and 0.50) and exposed the materials to a 3% NaCl solution for 72 h. The C-A-S-H gel formed in the fly ash/slag-based geopolymer resulted in lower chloride diffusion compared with the N–A–S–H gel. In addition, the incorporation of slag in fly ash-based geopolymers led to the refinement of the pore structure.

### 3.3.2 Sulfate resistance

The migration of Na⁺ from fly ash-based geopolymer into the sulfate solution results in vertical cracks and causes the deterioration of strength. In addition, the sulfate solution usually caused the breaking of -Si-O-Si- bonds in geopolymer gel and the leaching of silicon (Baščarević et al., 2015).

Bakharev (2005a) prepared fly ash-based geopolymer using NaOH, KOH, or Na₂SiO₃ as activator and investigated the durability after exposed them to sulfate environments (5% MgSO₄ solution, 5% Na₂SO₄ solution and a solution of 5% MgSO₄ +5% Na₂SO₄) for 5 months. After immersion, the fly ash-based geopolymer samples changed little. The geopolymer activated by NaOH had the best sulfate
resistance owing to a more stable cross-linked structure.

Sukmak et al., (2015) used a mixture of silty clay and fly ash as the source materials to prepare geopolymer and examined the resistance of the geopolymer in 5 wt% Na$_2$SO$_4$ and 5 wt% MgSO$_4$ solutions. The decrease in the compressive strength of the clay/fly ash-based geopolymer after 240 days of exposure was 10.8% in Na$_2$SO$_4$ solution and 21.6% in MgSO$_4$ solution. Ettringite, gypsum and brucite, were detected after the exposure to sulfate environment. The C-S-H phase disappeared due to its reaction with sulfates and forming ettringite phase.

3.3.3 Acid resistance

The lifetime of cement and concrete can be severely shortened in the acidic environment. For fly ash-based geopolymer, the acid attack is associated with the depolymerization of aluminosilicate network structure and the liberation of silicic acid (Si(OH)$_4$). When immersed in a strong acid solution, Na$^+$ and K$^+$ from fly ash-based geopolymer could be substituted by H$^+$ or H$_3$O$^+$, breaking -Si-O-Al- bond and -Si-O-Si- bond, and releasing silicic acid (Breck, 1974).

Different alkali solutions (NaOH, KOH and Na$_2$SiO$_3$) have been used by Bakharev (2005b) to prepare fly ash-based geopolymer followed by immersing the geopolymers in 5% CH$_3$COOH and H$_2$SO$_4$ solutions for 5 months. The fly ash-based geopolymer activated by 8% NaOH had more stable structure and showed high resistance to both acid solutions, while the fly ash-based geopolymer activated by KOH showed an increase in the average pore diameter and the number of active sites in the geopolymer gels on the surface, leading to a lower durability.

The effect of calcium and silica fume on the acid resistance of fly ash-based geopolymer is also noteworthy. Lloyd et al. (2012) investigated the corrosion rates of Class C fly ash-based and slag-based geopolymer in HNO$_3$ and H$_2$SO$_4$ acids (pH=1.0-3.0). It was found that the calcium content introduced from the Class C fly ash or slag reduced the mass transport rates by forming fine and tortuous pore networks in geopolymer. In addition, as the increase of alkali content (Na$_2$O), the nature of the corroded layer became harder, more brittle and more prone to the development of cracks (Fig. 7.). The high content of alkali is beneficial for releasing more calcium and aluminium and for forming geopolymer gels while when removed upon exposure to acid, the geopolymer structure was more vulnerable under acidic conditions. Chindaprasirt et al. (2014) added silica fume (1.5%, 3.75% and 5.0%) to fly ash to prepare geopolymer composite mortars. The acid resistance of composite mortars
was tested in 3 vol% \( \text{H}_2\text{SO}_4 \) acid. The optimum silica fume addition of 3.75% increased the strength of fly ash-based geopolymer and showed the best acid durability owing to the increase of C-S-H gels and a more dense structure.

![Fig.7. The appearance of the corroded layers on the fly ash-based geopolymer samples, containing 7% Na\(_2\)O (left) and 15% Na\(_2\)O (right) after 28 days exposure to pH 1.0 sulphuric acid (Reprint from Lloyd et al. (2012), with permission from Springer).](image)

Curing at a high temperature is beneficial to the resistance of geopolymer to acid. Nguyen et al. (2013) cured the fly ash-based geopolymer at 80°C for 10 h, and then immersed the geopolymer in HCl solution (1 mol/L, 2 mol/L, and 4 mol/L). It was found that the fly ash-based geopolymer still maintained a compressive strength of about 20 MPa which was much higher than OPC in HCl solution (1 mol/L, 2 mol/L, and 4 mol/L). In addition, Chindaprasirt et al. (2013a) cured fly ash-based geopolymer with 90 W microwaves for 5 min. They found the microwave radiation accelerated the geopolymerization and gave enhanced densification comparable to the conventional curing. The microwave cured fly ash-based geopolymer was immersed in 3 vol% of \( \text{H}_2\text{SO}_4 \) and found that it only had a small loss of strength under the acid attack.

### 3.3.4 Thermal resistance

When fly ash-based geopolymer is exposed to elevated temperatures, shrinkage of geopolymer occurs in proportion to the amount of water being vaporized from the structure (Rickard et al., 2011). Some of the fly ash-based geopolymers exhibit a strength increase after exposure to high temperature,
and have been used as concrete, thermal barriers, refractories and fire resistant structures. Heat travelled faster in geopolymer concrete than in OPC concrete when exposed to fire, resulted in less temperature gradient inside geopolymer concrete (Sarker et al., 2014). OPC concrete showed an average residual strength of 90%, 52% and 11-16% respectively after exposed to fire at 400°C, 650°C and 800-1,000°C, whereas the average residual strengths of geopolymer concretes were 93%, 82%, and 21-29% after the same treatments. Moreover, the OPC concrete suffered severe spalling and extensive surface cracking after exposure at 800-1,000°C, while there was no spalling and only minor surface crackings in the geopolymer concrete. Guerrieri and Sanjayan (2010) exposed fly ash/slag-based geopolymer (fly ash/slag ratio=100, 65/35, 50/50, 35/65) to 800°C. They found the geopolymer specimens with very low initial strengths (< 7.6MPa) experienced an increase in residual strength up to 90% gain after exposure to 800°C while specimens with initial strengths of 28 MPa and specimens with initial strengths of 83 MPa had residual strength losses of approximately 70% and 90% after exposure to 800°C, respectively. The different residual strengths of fly ash/slag-based geopolymer after exposure to 800°C were caused by the further hydration and sintering of the unreacted fly ash or slag. Geopolymer with higher initial strengths have a smaller capacity to allow for thermal incompatibilities between the inner and outer parts of the specimen due to uneven temperatures arising during heating.

Rickard et al. (2010) investigated the thermal characteristics of Class F fly ash-based geopolymer at the temperature >500°C. The maximum shrinkage was approximately 3% when the geopolymer was heated to 900°C. The iron oxides (15 wt.%) in fly ash directly affected the thermal properties of the geopolymer by influencing the thermal expansion, altering the phase composition and changing the morphology after heating.

The pore structure and density of fly ash-based geopolymer facilitates the escape of moisture and help avoid damaging during heating. Kong et al., (2007) prepared fly ash-based geopolymer and exposed it to 800°C. They found a small amount of moisture escaped from fly ash matrix and the pore spaces provided escape routes for moisture in the matrix thereby decreasing the likelihood of the damage to the matrix at elevated temperatures. Bakharev (2006) compared the effects of heating at 800-1200°C on the geopolymer made form Class F fly ash activated by NaOH and KOH, respectively. The geopolymer activated by NaOH had a rapid strength deterioration and a high shrinkage at 800°C due to a dramatic increase of average pore size, while the other activated by KOH showed a significant increase of compressive strength upon heating and the strength deterioration only started at 1000°C.
The addition of foaming agent of a low concentration led to a low density with cellular structure. Rickard and van Riessen (2014) prepared foamed Class F fly ash-based geopolymer with a Si/Al ratio of 2.5 ($\rho \approx 0.9$ g/cm$^3$, $k \approx 0.3$ W/m$\cdot$K). Under a simulated fire for 60 to 90 min, the foamed geopolymer lost its strength significantly. Foaming significantly reduced the strength of Class F fly ash-based geopolymer, while the thermal insulating property improved as their thermal conductivities were reduced by approximately half.

Using Ca(OH)$_2$ as additive to synthesize fly ash-based geopolymer formed the C–S–H gel and helped the different mineral formation and transformation processes at elevated temperatures. Dombrowski et al. (2007) prepared fly ash-based geopolymer and investigated the influence of the calcium content on thermal resistance. When the geopolymer exposed to temperatures higher than 600°C, sodalite and amorphous aluminosilicates were formed and then they were transformed into nepheline, resulted in a denser structure. As the temperature was further increased, the nepheline was converted into albite. The fly ash-based geopolymer with 8% Ca(OH)$_2$ addition for the preparation had the highest strength and the lowest shrinkage with the highest amount of nepheline at 800°C and of feldspar at 1,000°C.

Geopolymer exposed to fire has the tendency to shrinkage and cracking as well. According to the International Standards Organization standard (ISO 834), Sarker et al. (2014) test the fire resistance of the fly ash-based geopolymer and OPC by exposing the samples to fire heating at 400°C, 650°C, 800°C and 1000°C. When exposed to fire at 1,000°C, fly ash-based geopolymer had only minor surface cracking and the average mass loss of only 4.8%, while OPC had the average mass loss of 90%.

### 3.3.5 Freeze-thaw resistance

Freeze-thaw attack usually causes cement and concrete expansion, internal cracking, and scaling mass loss (Hobbs, 2001). It is a major attack to cement and concrete second to chloride attack. Fly ash based-geopolymer has been reported to show no sign of damage even after 150 freezing cycles. Temuujin et al. (2014) prepared geopolymer from Class F fly ash activated by a NaOH/Na$_2$SiO$_3$ solution and cured it at 70°C for 22 h. The freeze-thaw cycles of geopolymer were higher than 40. The addition of Na$_2$SiO$_3$ solution did not improve the freeze-thaw durability of fly ash-based geopolymer. The presence of crystalline, anhydrite and amorphous calcium compounds (such as lime) in fly ash negatively influenced the freeze-thaw resistance. Na$_2$SiO$_3$ reacted with calcium compounds
(CaO, CaSO\textsubscript{4} and amorphous calcium aluminosilicate) in the fly ash source and formed C–A–S–H gel or Ca(OH)\textsubscript{2}. The formation of Ca(OH)\textsubscript{2} weakened internal structure and increased water permeability and had a negative effect on the freeze-thaw resistance.

Air entrainment has been proved as an effective method to increase freeze-thaw resistance of OPC (Mindess and Young, 1981). Sun and Wu (2013) compared fly ash-based geopolymer and OPC with or without air entrainment for 300 freeze-thaw cycles according to ASTM C666. OPC without air entrainment deteriorated most seriously, showing a strength loss of about 20\% after 300 cycles, while OPC with air entrainment lost only 5\%. Fly ash-based geopolymer without air entrainment had a final loss of 8.4\% after 300 cycle. With the air entrainment, fly ash-based geopolymer showed a strength loss of 6.8\%. Clearly, the air entrainment had no much positive influence on fly ash-based geopolymer.

Brooks et al. (2010) studies the effects of air entrainment on the scaling rate of fly ash-based geopolymer. Air-entrained fly ash-based geopolymer showed slight scaling after 40 freeze-thaw cycles while non-air entrained fly ash-based geopolymer showed no scaling. Air entrainment significantly reduced the compressive strength of fly ash-based geopolymer 10-30\% than the non-air entrained fly ash-based geopolymer and the uniform and stable pore structure believed to increase freeze-thaw durability was not formed in non-air entrained fly ash-based geopolymer.

### 3.3.6 Efflorescence resistance

Geopolymer, especially with a high alkali content and a low calcium content, tends to have a porous and open microstructure. The aqueous solution remains entrapped in the pores or bonded to the network when the three-dimensional geopolymer structure has finally formed (Davidovits, 2008). Within the pore network, the excess sodium oxide is mobile, and is prone to form white crystal (i.e. efflorescence) when in contact with atmospheric CO\textsubscript{2} and results in the degradation of geopolymer (Najafi and Allahverdi, 2009; Pacheco-Torgal and Jalali, 2010).

The efflorescence behavior of fly ash-based geopolymers is strongly dependent on the alkali activator solution type, curing temperature and calcium content. Using KOH instead of NaOH as activator reduces the efflorescence of geopolymer (Duxson et al., 2006). The high alkali concentration in the pore solution and the weak binding of Na\textsuperscript{+} in the geopolymer structure are the reasons for more mobile Na\textsuperscript{+} in pore solution and cause the severe efflorescence of geopolymer (Bortnovsky et al., 2008). K\textsuperscript{+} is more strongly bound to the aluminosilicate gel framework, and also potassium carbonate crystals
are usually less visually evident than their sodium counterparts (Szklorzová and Bílek, 2008; Škvára et al., 2008). Zhang et al., (2014b) activated fly ash by NaOH to synthesize geopolymer and cured (23°C, 80°C). They found geopolymer at high temperature exhibiting much lower efflorescence than those synthesized at low temperature. The curing was beneficial for reorganization and crystallization of N-A-S-H gels and decreasing the efflorescence rate.

The presence of calcium helps formed C–S–H in fly ash-based geopolymer and a smaller pore size with low-permeability, which prevents alkali diffusion (Lloyd et al., 2010). Conversely, for foamed fly ash-based geopolymer, the foaming caused large pore size and high porosity of geopolymer and it led to fast alkali leaching and caused fast efflorescence consequently (Zhang et al., 2014b).

4. Fly ash-based geopolymer for adsorption and immobilization of toxic metals

Geopolymerization offers an alternative technique to immobilize soluble heavy metals from fly ash, slag or other industrial and residential wastes (Malviya and Chaudhary, 2006; Ojovan and Lee, 2005; Li and Wang, 2005). The hazardous elements, such as Ba, Cd, Co, Cr, Cu, Nb, Ni, Pb, Sn, and U can be tightly fixed in the three-dimension structure of fly ash-based geopolymer matrix. The main mechanisms of metal immobilization in fly ash-based geopolymer are physical encapsulation and chemical stabilization. The high pH values enhance the oxyanionic mobility, such as As, B, Mo, Se, V and W (Izquierdo et al., 2009). Temuujin et al. (2014) prepare geopolymer from high-calcium Mongolian fly ash (CaO =14–30 wt.%) with a high radioactivity (314–343 Bq/kg) and used NaOH solution or mixtures of NaOH and Na₂SiO₃ as activator and cured it at 70°C for 22 h. The radioactivity of the radioactive high-calcium Mongolian fly ash-based geopolymer product was then became 130–152 Bq/kg, within the standard safe limits for construction of dwellings.

Fly ash-based geopolymer showed higher immobilization of metal ions than OPC and fly ash itself. Li et al., (2013a) compared the immobilization of $^{133}$Cs⁺ in fly ash-based geopolymer and OPC. Leaching tests was carried out in deionized water, sulfuric acid and magnesium sulfate solutions, respectively. It was revealed that neither the microstructure nor the geopolymeric phases of fly ash-based geopolymer were significantly affected by the incorporation of $^{133}$Cs⁺. The cumulative fraction leaching concentration (CFLC) of fly ash-based geopolymer in deionized water was only 5.4 % of that of OPC for 25°C, and 6.1 % for 70°C. The leaching of $^{133}$Cs⁺ from the geopolymer in 5% (w/w)
magnesium sulfate solution was only 9.1% that from OPC. The difference of leaching of $^{133}$Cs$^+$ between the geopolymer and OPC in sulfate acid solution was small. Al-Zboon et al., (2011) used fly ash-based geopolymer as an adsorbent for lead Pb(II) removal from wastewater. They found the lead removal efficiency of fly ash-based geopolymer was 90.6%, which was much higher than that of raw fly ash (39.87%) ($pH = 5$; $C_0 = 100$ ppm; contact time $= 120$ min). The removal efficiency was 95% when the dose of fly ash-based geopolymer was 0.07 g at 40°C, pH=5, and 120 min contact time in 1,000 ppm standard lead (Pb) solution.

The fly ash-based geopolymer showed different metal immobilization behaviors in acid and sulfate solutions. Zhang et al., (2008a) prepared geopolymer with fly ash, sand and some heavy metal additives, such as Cr(VI), Cd(II) and Pb(II), to investigate the immobilization effect of heavy metal ions and the leaching behavior in $H_2SO_4$ and $Na_2SO_4$ solutions. The low level of heavy metal salts had little effect on the compressive strength of the geopolymer. The immobilization of these species was based on the chemical binding into the geopolymer gel or into aluminosilicate phases in geopolymer. They found Pb was immobilized effectively by a chemical binding mechanism in geopolymer, Cr(VI) was ineffectively immobilized, and Cd immobilization was depended on the solubility of a hydroxide phase with effectively at high pH but poor at low pH.

5. Fly ash-based geopolymer for concrete

The growing environmental awareness and the demand for high efficiency of natural resource encourage the construction industry to look for alternative materials (McKelvey et al., 2002; Schneider et al., 2011). Fly ash has already been used as supplementary cementitious material in concrete industry for over 50 years in the world (Uysal and Akyuncu, 2012). In the hydration of traditional cement, fly ash with a high content of $Al_2O_3$ and $SiO_2$ can be activated by $Ca(OH)_2$ and thus produce more C-S-H gel, C-A-H gel and C-A-S-H gel to fill the capillary of concrete effectively, thereby increasing concrete strength (Sahmaran and Li, 2009). Fly ash can reduce the hydration heat and thermal cracking of concrete at early stage, and improve the mechanical and durability properties.

Fly ash-based geopolymer concrete completely moves away from OPC and the high CO$_2$ emission associated with OPC production (Cakir and Akoz, 2008; Aldea et al., 2000; Habert et al., 2011). Fly ash-based geopolymer itself is a good binder that can be used as cement to mix with aggregates to
produce the geopolymer concrete. Fly ash-based geopolymer cement has shown a better performance than OPC in some areas aspects or conditions. For example, fly ash-based geopolymer concrete has a denser microstructure with lower chloride diffusion and lower porosity compared with OPC concrete. Reddy et al. (2013) used Class F fly ash as source material and NaOH and Na$_2$SiO$_3$ solution as activator to synthesize geopolymer cement. They found that the geopolymer concrete had excellent resistance to chloride attack and less corrosion cracking when exposed to simulated seawater and induced current.

Alkali silica reaction (ASR) is a common chemical reaction between the OH$^-$ in the pores within the concrete matrix and the reactive aggregate compounds in concrete (Swamy and Al-Asali, 1988; Diamond, 1975). ASR causes the strength loss, cracking, and expansion of the concrete structure. Fly ash-based geopolymer concrete is significantly less vulnerable to ASR than OPC concrete. Kupwade-Patil and Allouche (2013) prepared steel reinforced fly ash-based geopolymer concrete with quartz, sandstone and siliceous limestone as aggregates, and compared the chloride diffusion in a cyclic wet-dry chloride environment over a period of 12 months with OPC concrete. It was found that fly ash-based geopolymer concrete specimens did not exceed the ASTM threshold for expansion while OPC concrete exceeded the permissible threshold. In addition, the leaching and visual cracks were observed in the OPC concrete but not in the fly ash-based geopolymer concrete.

In concrete, aggregate takes up as high as 85% of the material. Interactions among aluminosilicate framework, alkali cations, additives and aggregate in fly ash-based geopolymer concrete are important factors that influence the overall mechanical performance. The strong interfacial interactions between the aggregate and the fly ash-based geopolymer matrix in a large zone contributes to the high splitting tensile strengths between geopolymer and steel reinforcements (Topark-Ngarm et al., 2015).

The size of the aggregates affects the fly ash-based geopolymer concrete performance. Kong and Sanjayan (2010) studied the effect of aggregate size on the compressive strength at high temperatures of the fly ash-based geopolymer concrete containing crushed old basalt aggregates, river sand and slag aggregates. It was found the thermal incompatibility between the geopolymer matrix and the aggregates caused the strength loss of geopolymer concrete specimens at elevated temperatures. Large aggregates (> 10 mm) resulted in good strength performances at both ambient and elevated temperatures while smaller sized aggregates (< 10 mm) promoted spalling and extensive cracking at elevated temperature.

Recycled coarse aggregate has been used with fly ash geopolymer to synthesize concrete with
acceptable properties. Sata et al., (2013) used crushed structural concrete beams and crushed clay bricks as recycled coarse aggregates for making fly ash-based geopolymer concrete. The geopolymer concrete with recycled aggregate showed lower compressive strengths (2.9–10.3 MPa) than those containing natural aggregate, however, it was within the typical strength distribution reported (American Concrete Institute (ACI) committee 522, 2010). In addition, the total void ratio of the geopolymer concrete with recycled aggregate (21.7-26.9%) was similar to those with natural aggregate (24.2-27.4%), and the water permeability was 0.71-1.47 cm/s versus 1.18-1.71 cm/s. Nuaklong et al., (2016) used recycled aggregates from old concrete with compressive strength of 30-40 MPa and high calcium fly ash to make fly ash-based geopolymer. They found fly ash-based geopolymer with recycled aggregate showed compressive strengths of 30.6-38.4 MPa, which were slightly lower than those of fly ash-based geopolymer concretes with crushed limestone.

Different superplasticizers (naphthalene (N) and polycarboxylates (PC)) as the water reduction admixture have been used to improve the workability of the geopolymer concrete by Nematollahi and Sanjayan (2014). PC superplasticizer with a dosage of 3.3 wt.% caused significant reduction (54%) in strength with reference to concrete without superplasticizer. By contrast, N superplasticizer with a dosage of 1.19% caused a 22% reduction in strength. The use of superplasticizers was not beneficial to geopolymer concrete used at elevated temperatures.

Injecting and storing CO\textsubscript{2} into underground has been proposed as one of the long-term strategies for handling greenhouse gases (Laudet et al., 2011; Bachu and Bennion, 2009). OPC-based sealant has been used in injection wells and it has been found experiencing cement degradation under CO\textsubscript{2}-rich down-hole conditions. The low permeability of fly ash-based geopolymer can effectively prevent CO\textsubscript{2} leakage. Nasvi et al. (2013) found that the apparent CO\textsubscript{2} permeability of fly ash-based geopolymer cement is in the range of 2×10\textsuperscript{-21} - 6×10\textsuperscript{-20} m\textsuperscript{2}, which is lower than the typical oil well cements (10\textsuperscript{-20} - 10\textsuperscript{-11} m\textsuperscript{2}). Moreover, Nasvi et al. (2014) prepared fly ash-based geopolymer cement from fly ash activated by a mixed Na\textsubscript{2}SiO\textsubscript{3}/NaOH solution and tested the CO\textsubscript{2} permeability under three conditions: (1) temperatures of 23–70°C; (2) CO\textsubscript{2} injection pressures of 6–17 MPa; and (3) confining pressures of 12–20 MPa. The results showed that the apparent CO\textsubscript{2} permeability of geopolymer increased with curing temperature and the increasing rates were as high as 200–1,000 %. The maximum permeability (0.04 ID) value obtained was approximately 5,000 times lower than the permeability value (200 ID) recommended by the American petroleum industry (API) for a typical well sealant. The findings
6. Conclusions and future work

Geopolymer technology offers a facile approach for fly ash utilization. In principle, the geopolymerization includes the dissolution of alumina, silica, aluminosilicate in the fly ash feedstock by alkali, the recombination of Al\textsuperscript{3+} and Si\textsuperscript{4+} species and the generation of three-dimensional amorphous aluminosilicate polymers. The preparation and formation, and properties of the fly ash-based geopolymer products depend heavily upon the chemical and physical characteristics of fly ash, alkali activators, curing conditions and the addition of slag, fiber and red mud.

NaOH and Na\textsubscript{2}SiO\textsubscript{3} are used as alkali activators; CaCl\textsubscript{2} is used as chemical additives to form C-A-S-H gel, C-A-H gel and C-S-H gel and change the setting time; and slag, fiber, RHBA and red mud are used as additives to change the Si/Al ratios and introduce the hydrogen bonds between geopolymer gel (N-A-S-H gel) and the additive molecules.

For the practical applications of fly ash-based geopolymer, mechanical properties (such as compressive strength, splitting tensile strength and flexural strength) and durability (chloride, sulfate, acid, thermal, freeze-thaw cycles and efflorescence resistances) should be comprehensively considered. The Si/Al ratios of reactants, alkali solutions, curing conditions, and the addition of slag, fibers, RHBA, red mud and calcium can be fine tuned to improve those properties. The changes of Si/Al ratios, alkali solutions, and adding slag, RHBA, red mud and calcium can lead to the different gels, including N-A-S-H gel, C-A-S-H gel, C-A-H gel and C-S-H gel. The gels influence the final structure of geopolymer and control the ionic transport. Alkali solutions influence the hydrolyzation of fly ash and the porosity of geopolymer structure. The porosity influences the migration of alkali from fly ash-based geopolymer into the ion solutions, the moisture and then has an effect on the mechanical strength and durability. Fly ash-based geopolymer with compact and denser structure shows high mechanical strength and good resistance to chloride, sulfate and acid solutions and good efflorescence.

Fly ash-based geopolymer can be used as cement to mix with aggregates to form concrete. In this context, considering the low cost, low CO\textsubscript{2} emission and low energy usage in the production of fly ash-based geopolymer, fly ash-based geopolymer cement and concrete are regarded as possible alternative green materials to OPC. Fly ash-based geopolymer has also been used to adsorb and
immobilize toxic metals and it shows better adsorption and immobilization performance than those of OPC. Besides, fly ash-based geopolymer cement has been used as a well sealant to store CO$_2$ in the underground. However, the CO$_2$ permeability value of fly ash-based geopolymer is still lower than the permeability value for a typical well sealant recommended by the API.

Though last decades or so have witness remarkable advance in the science and technology of fly ash-based geopolymer as discussed above, there exists several issues and some issues are proposed below for future work.

(1) Inherently, to control the production and to improve the performances of fly ash-based geopolymer, the reaction mechanisms in each step should be uncovered in details. To this end, involved are many aspects such as thermodynamics, kinetics, identifications of intermediates and insights into their structures, and the degrees to which the -Si-O-Al- are oligomerized and polymerized. All these will become more sophisticated once the additional elements or additives are included. But further studies must be made in order to ensure that the correlation of production-structure-performances is clear-out.

(2) Most of fly ash-based geopolymer concretes are brittle and sensitive to cracking. Such behavior not only imposes constraints in applications, but also affects the long-term durability of geopolymer concretes (Zhao et al., 2007; Zhang et al., 2010b; Pernica et al., 2010). Therefore, innovation in the preparation to create improved fly ash-based geopolymer composites is still needed.

(3) At present, in most cases, fly ash-based geopolymer are merely produced at laboratory scale with empirical formulations. It could be exciting to see a report by Wagners (Wagners Earth Friendly Concrete product) that the production of fly ash-based geopolymer concrete is being realized on a large-scale. To put producing and using fly ash-based geopolymer on a large-scale are encouraging and need further input and endeavor.

(4) As for the uses of fly ash-based geopolymer for toxic metals adsorption and immobilization and sealing CO$_2$, the performances are still unsatisfactory. Changing of the recipes for preparation is worth for further investigation.

(5) Instead of using fly ash-based geopolymer as alternative cement, it is also possible to endow fly ash-based geopolymer with more functionalities or unique properties. Consequently, new applications of fly ash-based geopolymer are worth exploring and can be found. For instance, fly ash-based geopolymer with biomass can be developed as a class of novel lightweight fireproof
materials.

**Abbreviations**

ACI: American Concrete Institute  
API: American Petroleum Industry  
ASR: Alkali silica reaction  
ASTM: American Society for Testing and Materials  
BFS: Blast furnace slag  
C-A-H gel: Calcium aluminate hydrate gel  
C-A-S-H gel: Calcium aluminum silicate gel  
CCS: Carbon capture and storage  
C-S-H gel: Calcium silicate hydrate gel  
CFA: Class C fly ash  
CFLC: Cumulative fraction leaching concentration  
FFA: Class F fly ash  
GGBF: Ground granulated blast furnace slag  
HHW: Harford secondary waste  
HMNS: High magnesium nickel slag  
ISO: International Standards Organization  
N-A-S-H gel: Sodium aluminosilicate gel  
OPC: ordinary Portland cement  
PC: Polycarboxylates  
PVA: Polyvinyl alcohol  
RHBA: Rice husk-bark ash

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Highlights

- Fly ash is activated by alkali to form geopolymer and such a process is cleaner.
- Slag, rice husk-bark ash, fiber and red mud are added to improve the performance of fly ash-based geopolymer.
- Mechanical properties and durability of fly ash-based geopolymer are main concerns.
- Fly ash-based geopolymer is used as cement and as fixation materials for toxic metals.
- Improving performance, scaling-up production and finding new applications are proposed for future.