Acid Resistance and Curing Properties for Green Fly Ash-geopolymer Concrete

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Abstract

Global warming has recently become a topical issue throughout the world, and the cement industry is widely seen as one of the prominent factors responsible for it. Therefore, the development of new binders with enhanced environment and durability performance is needed. In this regard, geopolymer technology is a breakthrough development as an alternative to Portland cement. In this study, such properties of geopolymer concrete as curing temperature, curing time, rest period before curing, and acid resistance are emphasized. Geopolymerization needs energy and time to occur, and higher curing temperatures result in larger compressive strength, while longer curing times result in higher compressive strength. For geopolymer concrete, the time for hardening can be extended up to 5 days. Geopolymer concrete shows good acid resistance. As products of geopolymerization have no sulfate, acid or salt attack mechanism, geopolymer concrete can be a good substitute for traditional building materials, and finding renewable materials to satisfy the increasing demand for building structures will eventually be a major issue.

Keywords: geopolymer concrete; curing time; curing temperature; rest period; acid resistance

1. Introduction

Concrete is an essential building material for societal infrastructures throughout the world. In fact, concrete usage around the world is second only to water⁵. Portland cement is a main component of concrete, however, it is not an environmentally friendly material. The production of Portland cement not only depletes a significant amount of natural resources but also emits a huge quantity of carbon dioxide (CO₂) and other greenhouse gases into the atmosphere as a result of decarbonation of limestone and the combustion of fossil fuels. Global warming is caused by the emission of greenhouse gases, such as CO₂ into the atmosphere by human activities. Among greenhouse gases, CO₂ contributes about 65% of global warming⁶. The cement industry is responsible for about 6% of all CO₂ emissions because the production of one ton of Portland cement emits approximately one ton of CO₂ into the atmosphere⁷. Due to the production of Portland cement, it is estimated that by the year 2020, CO₂ emissions will rise by about 50% from current levels⁸. Therefore, to preserve the global environment from the impact of cement production, it is imperative to search for and explore new possibilities to develop a concrete material that is more environmentally friendly and yet remain an efficient construction material to replace conventional Portland cement concrete⁹. Enormous efforts have been made throughout the world to reduce the use of Portland cement in order to address global warming issues. These include the utilization of waste by-products and the development of alternative binders to Portland cement⁶. In this regard, geopolymer concrete is a revolutionary development related to novel materials resulting in low-cost and environmentally friendly material as an alternative to Portland cement⁰.

In recent years, geopolymers have received significant attention because they show environmental benefits such as a reduction in the consumption of natural resources and a decrease in the net production of CO₂. The production of one ton of kaolin based–geopolymeric cement generates 0.180 tons of CO₂, from combustion carbon-fuel compared with one ton of CO₂ for Portland cement, which is six times less. Fly ash based-geopolymeric cement has attracted intensive research worldwide because it emits up to nine times less CO₂ than Portland cement.

The object of this study is to evaluate such properties of fly ash-geopolymer concrete as the effect of curing time, curing temperature on compressive strength, the rest period before curing and acid resistance.

2. Materials and Test Methods

2.1 Materials

The materials used for making fly ash-based geopolymer concrete specimens are low-calcium dry
fly ash as the source material, aggregates, alkaline liquids and water.  

2.1.1 Fly ash  
Fly ash used in this study was low-calcium (ASTM class F) dry fly ash from the F power station as shown in Fig.1. The chemical composition of fly ash is presented in Table 1. The specific gravity of this type of fly ash is 2500 kg/m³.

![Fig.1. Fly Ash Type F](image)

2.1.2 Alkaline liquid  
The alkaline liquid used was a combination of sodium silicates solution (water glass liquid) and sodium hydroxide solution. The sodium silicate solution included Na₂O and SiO₂ about 36 to 38% by mass.  

2.1.3 Aggregates  
Aggregates comprising 20 mm and 10 mm coarse aggregates and fine aggregates in the saturated surface dry condition, were used. The ratio between coarse and fine aggregates was 40% (20 mm), 30% (10 mm) and 30% (fine aggregate). The specific gravity of coarse aggregates is 2700 kg/m³ and 2650 kg/m³ for fine aggregates, respectively.  

2.2 Test Methods  
The specimens of this study were made by mixing aggregates and fly ash, and then adding the alkali solution to the mixture. Finally, the fresh concrete was cast and compacted to the molds, after which, they were sent to the oven and cured.  

2.2.1 Compressive strength  
The compressive strength of geopolymer concrete specimens was measured by testing a cylinder 100 mm in diameter and 200 mm in height with the ASTM C39/C39M-99.  

2.2.2 Acid resistance  
Acid resistance was decided by the compressive strength test with specimens 100 mm in diameter and 200 mm in height. After curing the specimens for 10 hours at 80°C they were immersed in acid water, hydrochloric acid, 1 mol/l (1M), 2M, 4M. After the first and second months, the specimens were taken out and evaluated by compressive strength.  
The mix proportions per cubic meter for concrete are given in Table 2.

In three mixture proportions, the concentration of sodium hydroxide solution was 8 Molars (M). The ratio between water glass and sodium hydroxide is 0.4, 1.2 and 2.5. And the ratio between alkali solutions (including water glass and sodium hydroxide) and fly ash is 0.34 and 0.44.

3. Test Results and Investigations  
In this section, the test results are presented and discussed. The test results cover the effect of the curing temperature, curing time, rest period before curing and resistance to hydrochloric acid.  
Test specimens were made using geopolymer concrete as GF1, GF2 and GF3. The details of these mixtures are given above.  

3.1 Influence of curing temperature  
Table 3. and Fig.2. show the effect of the curing temperature on the compressive strength for GF1, GF2 and GF3 after curing the specimens in an oven for 10 hours.

When the temperature was increased from 40 to 100°C, all of the specimens had a greater compressive strength value. However, the speed increasing
The compressive strength of three mix proportions was different. The compressive strength of GF1 increased the fastest and that of GF3 the slowest. For example, from 40 to 100°C the compressive strength of GF1 increased 17 MPa, while that for GF3 increased to 4.5 MPa.

From 40 to 60°C, the compressive strengths of GF1, GF2 and GF3 increased faster than from 60 to 100°C. For GF1, the value cured at 60°C is 40% higher than that cured at 40°C. However, this value increased 20.3% when the temperature changed from 60 to 100°C.

Higher curing temperatures resulted in larger compressive strengths, although an increase in the curing temperature beyond 60°C did not increase the compressive strength significantly.

According to the geopolymerization, this process has three steps:
- Dissolution of Si and Al atoms from the alumino-silicate source material in the strongly alkaline solution through the action of hydroxide ions.
- Diffusion or transportation or orientation or condensation of precursor ions into monomers.
- Setting or polycondensation/polymerization of monomers into solid inorganic polymeric structures.

All three steps need energy to occur. This energy is known as thermodynamic, and it has three roles in geopolymerization. First, it provides the kinetic energy for Si and Al atoms to dissolve from the alumino-silicate source material. In order to do that, the kinetic energy has to be greater than the chemical bond energy. Then, this energy provides the energy for molecules to diffuse, transport, orient or condense into monomers. Finally, it plays a significant role on the polycondensation of monomers into solid inorganic polymeric structures. If this energy is great enough, a great deal of polymer is produced. These polymers connect together to become a long chain that creates the compressive strength for geopolymer concrete. As a result, the more polymers are created, the higher the compressive strength of the geopolymer concrete.

In terms of application, we can increase the compressive strength of geopolymer concrete based on this property, which is in complete contrast to Portland cement concrete.

### 3.2 Influence of curing time

Table 4. and Fig.3. show the effect of curing time on the compressive strength for GF1, GF2 and GF3 after curing the specimens in an oven at 80°C at 4, 8 and 12 hours, respectively.

According to Fig.3., the compressive strength of geopolymer concrete increased when the curing time was longer. For GF1, the compressive strength increased to 68.8% when the curing time increased from 4 to 12 hours, while that of GF2 and GF3 increased 63.0%, and 53.7%, respectively.

From 4 to 8 hours, the compressive strength values of geopolymer concrete increased faster than those from 8 to 12 hours. For example, the compressive strength of specimens GF1 cured for 8 hours increased 43.7% in comparison to that of specimens cured for 4 hours. However, this tendency increased only 17.4% for those cured for 12 hours. This trend was the same for GF2 (34.4% and 2.3%) and GF3 (30.9% and 17.4%).

At the same curing temperature, longer curing time resulted in a higher compressive strength because the longer curing time extends the chemical reaction. As a result, many productions of polymerization are created and these productions will connect together if the curing time is long enough. Eventually the final result increases the compressive strength of geopolymer concrete. By comparison, geopolymer concrete and ordinary Portland cement concrete have increased compressive strength according to the curing time.

### 3.3 Influence of rest period before curing

The term "rest period" means the time taken from the completion of casting of test specimens to the start of curing.

Table 4. Relationship between Curing Time and Compressive Strength

| Curing time | GF1 | GF2 | GF3 |
|-------------|-----|-----|-----|
| 4 hrs.      | 22.2| 14.6| 8.1 |
| 8 hrs.      | 31.9| 19.6| 10.6|
| 12 hrs.     | 37.5| 23.8| 12.4|

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of curing at an elevated temperature. This may be important in certain practical applications. Especially, when geopolymer concrete is used in precast concrete products, there must be sufficient time available between the casting of products and sending them to the curing oven. In order to study the effects of rest period, mixtures of GF1, GF2 and GF3 were made. The specimens are cured for about 10 hours at 80°C.

Table 5. Relationship between Rest Period and Compressive Strength

| Rest period (days) | GF1 | GF2 | GF3 |
|-------------------|-----|-----|-----|
| 0                 | 30.9| 14.9| 11.4|
| 1                 | 34.6| 18.3| 12.6|
| 2                 | 35.1| 18.5| 13.3|
| 3                 | 34.8| 18.1| 13.3|
| 4                 | 36.0| 19.2| 11.5|
| 5                 | 35.7| 18.6| 12.5|

Fig.4. Effect of Rest Period on Compressive Strength

In Fig.4., the "rest period" of zero day means that the test cylinders were cured immediately after mixing, whereas the rest period of 5 days indicates that the fresh concrete was mixed and placed in the moulds for 5 days. According to Table 5. and Fig.4., the compressive strength of concretes shows little change, and is insignificant.

This result shows a significant difference between normal concrete and geopolymer concrete. As we know, normal concretes are supposed to take about 1 hour to harden, however, we can extend this time up to 5 days. Because the geopolymerization or hardening process of geopolymer concrete needs heat to occur, if heat is not provided, the geopolymerization does not have the energy for this to properly occur. It also means that for precast concrete products a lot of flexibility and control of the curing time is available.

3.4 Acid resistance

A series of tests were performed to study the acid resistance of fly ash-based geopolymer concrete. The test specimens were soaked in 1M, 2M and 4M of hydrochloric acid. The acid resistance was evaluated based on the change in compressive strength. All specimens were heat-cured at 80°C for 10 hours. Table 6. and Fig.5. show the results of the test for mixture proportion GF2.

Table 6. Relationship between Concentrations of HCl and Compressive Strength

| HCl | Exposure time (week) | 1M | 2M | 4M |
|-----|----------------------|----|----|----|
|     |                      |    |    |    |
| 0   | 19.6                 | 19.6| 19.6| 19.6|
| 4   | 19.1                 | 18.8| 18.8| 18.8|
| 8   | 19.3                 | 18.9| 19.4| 19.4|

Fig.5. Effect of the Concentrations of HCl on Compressive Strength

According to Fig.5., the compressive strength of specimens decreased slightly less than 4% from 0 to 4 weeks. However, this trend changed when the exposure time changed from 4 to 8 weeks, but the increase was also small. For example, in 4M HCl, the compressive strength increased just 3%, the increase for 2M HCl was 0.5% and the increase for 1M HCl was 1%. In general, for geopolymer concrete, the compressive strength of specimens does not change significantly when the exposure time is increased.

The process of acid resistance follows these steps:

Step 1: Attachment of the acid proton to the lone electron pair of the siloxane oxygen:

\[
\text{Cleavage} \quad \text{Si-O-Si}^+ \rightarrow \text{Si-O-Si}^0 + \text{H}^+ \quad (4.1)
\]

Cleavage is ruled by the relative susceptibility of the siloxo oxygen Si-O-Si against proton attack, not by the cleavage of the silicate bond Si-O-Al, due to its protection by the metallic cations (Na, K). The oxygen of the Si-O-Al sialate bond is attacked only after leaching of the protecting cation has occurred.

Step 2: Subsequent reactions leading to the scission and re-formation of siloxane/siloxo bonds,
decomposition of the oxonium complex with the formation of a silanol unit Si-OH and formation of a silicon-anion Si-X bond (X is chloride):

\[
\begin{align*}
\text{Si} - \overset{\ominus}{\text{O}} - \text{Si}^{-} + \overset{\ominus}{\text{X}} & \rightarrow \text{Si-OH} + \overset{\ominus}{\text{Si}} - \text{X} \\
& \text{(4.2)}
\end{align*}
\]

The destruction of geopolymeric backbone is limited to the effective amount of anion chloride present in the solution\(^9\).

Furthermore, the visual appearances of test specimens that prove the acid resistance are shown in Fig.6.

In Fig.6., the 3 red circles indicate the dark color, which is the part that absorbed the HCl solution. This also means that the geopolymer structure makes the endosmosis happen slowly.

It can be explained that one of the components for creating concrete plays a prevention role with regards to the penetration of acid. This component could be water glass or sodium silicate. At the Fukushima Daiichi nuclear power plant in Japan in April 2011, it was used as a chemical injected into the ground in order to harden it and thereby prevent leakage of highly radioactive water\(^9\). As a result, the geopolymer concrete has a good acid resistance.

On the other hand, SEM photos are used for investigation. Figs.7.a and b are photos taken from the outside of the specimens, and Figs.7.c and d are photos taken from inside the concrete. In these photos, Figs.7.a and b show a significant difference with Figs.7.c and d. There are a significant number of sticks in Figs.7.a and b, however there are no sticks in Figs.7.c and d, just a sphere. These sticks are sodium chlorides (NaCl), resulting from the chemical reaction:

\[
\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} \quad \text{(4.3)}
\]

NaOH is remainder from geopolymerization.

4. Conclusion

The properties of geopolymer concrete depend on geopolymerization which needs energy to occur. This energy is known as thermodynamic, which is provided by heat from an oven. If the energy is great enough, the properties or compressive strength of concrete are increased. Thus, higher curing temperatures and longer curing times produce a greater compressive strength. For applications, a higher compressive strength is attainable with increases in the curing time and temperature. Notably, if energy is not provided, geopolymerization is delayed. This delay is up to about 5 days. This result shows a significant difference between geopolymer concrete and normal concrete. This is also an advantage when applied to producing precast concrete articles, as the curing time can be arranged flexibly.

The acid resistance of heat-cured geopolymer concrete is significantly better than that of Portland cement concrete\(^{10}\), because the geopolymer concrete structure makes endosmosis happen slowly. On the other hand, sodium silicate or water glass prevents the penetration of acid.
Acknowledgement
This research was supported by the MSIP (Ministry of Science, ICT & Future Planning), Korea, under the C-ITRC (Convergence Information Technology Research Center) support program (NIPA-2013-H0401-13-1003) supervised by the NIPA (National IT Industry Promotion Agency) and a grant (code# 2010-0019373 and 2011-0010300) from the National Research Foundation of Korea (NRF) funded by the Korea government.

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