

BRIEF REVIEW OF DEVELOPMENT OF GEOPOLYMER CONCRETE

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Synopsis: Geopolymer or inorganic alumino-silicates polymer is synthesised from predominantly silicon and aluminium materials of geological origin or by product materials, such as fly ash. The chemical composition of geopolymer is similar to that of zeolite, but amorphous in microstructure. Fly ash-based geopolymer binders show excellent short and long-term mechanical characteristics. The development of geopolymer concrete described in this paper includes the chemical reaction, the source materials, and the manufacturing process. The workability and the setting time of fresh concrete as well as the compressive strength and the long-term characteristics of hardened geopolymer concrete are discussed.

Keywords: Alumino silicate polymer, concrete, long-term properties, strength, workability.

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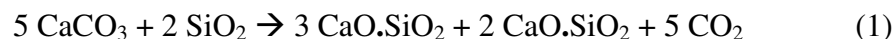
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INTRODUCTION

The search for environmentally friendly construction materials is imperative, as the world is facing serious problems due to environmental degradation. There is a significant expectation on the industry to reduce carbon dioxide (CO₂) emissions to the atmosphere.

In view of this, one of the efforts to produce environmentally friendly concrete is to reduce the use of Portland cement by using by-product materials, such as fly ash. It is known that production of one ton of Portland cement accounts for about one ton of carbon dioxide released to the atmosphere, as the result of de-carbonation of limestone in the kiln during manufacturing of cement, i.e.:

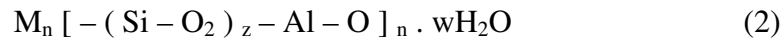


A significant advance in the usage of fly ash in concrete is the development of high volume fly ash (HVFA) concrete, which partially replaces the use of Portland cement in concrete (up to 60%), while maintaining excellent mechanical properties with enhanced durability performance. Another development is geopolymer, i.e. inorganic alumino-silicates polymer synthesised from minerals of geological origin or by-products materials, such as fly ash, rice husk ash etc., that are rich in silicon (Si) and aluminium (Al). Fly ash is abundantly available world wide, and efforts to utilise it in concrete production is of significant interest to the concrete technologists and industry.

This paper gives a brief review of the development of geopolymer concrete. The factors that affect the production of geopolymer concrete such as source minerals, workability, curing time, and curing temperature are discussed in the paper. The potential use of geopolymer concrete and the future challenges are also mentioned.

GEOPOLYMER MATERIAL

The term geopolymer was introduced by Davidovits to represent the mineral polymers resulting from geochemistry. The polymerisation process involves a chemical reaction under highly alkaline conditions on Al-Si minerals, yielding polymeric Si-O-Al-O bonds, as described by ¹:



where M is the alkaline element, the symbol – indicates the presence of a bond, z is 1, 2, or 3, and n is the degree of polymerisation.

The chemical composition of geopolymers is similar to zeolites, but shows an amorphous microstructure ². The structural model of geopolymer material is still under investigation; hence the exact mechanism by which geopolymer setting and hardening occur is not yet clear ^{1, 3}. The mechanism of geopolymerisation may consist of dissolution, transportation or orientation, and polycondensation ², and takes place through an exothermic process ^{1, 4}.

Palomo et al. ⁴ described the difference between the alkali-activated and the aluminosilicate polymer or geopolymer materials. Although both of these materials are the result of alkali activation, the starting situations are different. In the case of alkali-activated materials, the source material is activated by a mild alkaline solution, and the main reaction product is a C-S-H gel. The composition of the source material essentially contains high silicon (Si) and calcium (Ca). On the other hand, the source material for geopolymers contains high silicon (Si) and aluminium (Al), and is activated by a high alkaline liquid. The end product of this process is an amorphous polymeric material.

The strength of geopolymer depends on the nature of source materials. Geopolymers made from calcined source materials, such as metakaolin (calcined kaolin), fly ash, slag etc., yield higher compressive strength when compared to those synthesised from non-calcined materials, such as kaolin clay. The source material used for geopolymerisation can be a single material or a combination of several types of materials ⁵. A combination of sodium silicate and sodium or potassium hydroxide has been widely used as the alkaline activator ^{2-4, 6}, with the activator liquid-to-source material ratio by mass in the range of 0.25-0.30 ^{4, 6}.

Because heat is a reaction accelerator, curing of fresh geopolymer is carried out mostly at an elevated temperature ⁴. When curing at elevated temperatures, care must be taken to minimize the loss of water. However, curing at room temperature has successfully been carried out by using calcined source material of pure geological origin, such as metakaolin ^{1, 7}.

The geopolymer material can be used in various applications, such as fire and heat resistant fibre composites, sealants, concretes, ceramics, etc., depending on the chemical composition of the source materials and the activators. Davidovits¹ suggested that the atomic ratio of Si-to-Al of 2 for making cement and concrete. Geopolymer can also be used as waste encapsulation to immobilise toxic metals ⁸.

GEOPOLYMER CONCRETE

In the authors' experimental work, geopolymer is used as the binder, instead of cement paste, to produce concrete. The manufacture of geopolymer concrete is carried out using the usual concrete technology methods.

In the laboratory experiments, low calcium (class F) fly ash from Western Australia was used as the source material. The chemical composition of the fly ash, as determined by X-Ray Fluorescence (XRF) analysis, is given in Table 1. A combination of sodium silicate ($\text{Na}_2\text{O}=14.7\%$, $\text{SiO}_2=29.4\%$, and water=55.9% by mass) solution and sodium hydroxide solution was used as the alkaline activator. A combination of four types of locally available aggregates, with a fineness modulus of 5.0, was used.

The fresh concrete mixture was then cast in 100x200 mm cylinder steel moulds in three layers. Each concrete layer was given 60 manual strokes by a rod and then vibrated for 10 seconds. After covering the samples using a film to protect the loss of water, the concrete specimens were cured in an oven at a specified temperature for a period of time. The details of the authors' research have been reported elsewhere⁹⁻¹².

FRESH GEOPOLYMER CONCRETE

Workability

Fresh geopolymer concrete has been reported to be highly viscous and cohesive with low workability^{12, 13}. Using calcined kaolin as the source material, Teixeira-Pinto et al.¹³ reported that the fresh geopolymer concrete became stiff in a short time, thus implying a short initial setting time.

These findings are different to those observed in the experimental work conducted by the authors. Numerous trial mixtures have been made and tested in order to identify the salient parameters affecting the properties of fresh and hardened geopolymer concrete⁹⁻¹². These extensive test results show that the water content in the mixture plays an important role with regard to workability of fresh geopolymer concrete. By keeping the molar H_2O -to- Na_2O ratio of the mixture constant, the water content may be adjusted to produce the desired workability for a specified compressive strength of hardened concrete¹⁰.

Recently, the authors have successfully manufactured 175x175x1500 mm reinforced concrete test columns (Fig. 1). The fresh geopolymer concrete used in manufacture of these columns had a slump of 240 mm (Fig. 2); the 7th day compressive strength of this hardened concrete was 40 MPa.

Although the slump was high, there was no sign of any segregation. The details of this geopolymer concrete mixture are given in Table 2.

Setting time

Using granulated blast furnace slag as the source material with the addition of metakaolinite, Cheng and Chiu¹⁴ found that the setting time of geopolymer paste was affected by the curing temperature, type of alkaline activator, and the composition of the source material. They found that the setting time of geopolymer paste was between 15 to 45 minutes at 60° C.

The authors believe that measuring setting time at elevated temperatures may not be appropriate. Instead, the time available between the end of mixing and the start of casting of fresh geopolymer concrete may be more relevant in practical applications. The laboratory experiments showed that the fresh geopolymer concrete could be handled at least up to 120 minutes after mixing, without any sign of setting, and without any degradation in compressive strength⁹.

One of the reasons for the difference between the authors observation and that of Cheng and Chiu¹⁴ may be due to the difference in the calcium oxide (CaO) content in the source materials. The CaO content in the granulated blast furnace slag used by Cheng and Chiu¹⁴ was 41.67% by mass, while the CaO content of the fly ash used in authors study was only 1.34% by mass (Table 1).

The presence of compounds other than Al_2O_3 and SiO_2 in the source material may also delay the setting. In materials of pure geological origin (say calcined kaolin), the dominant chemical contents are only Al_2O_3 and SiO_2 , whereas by-product materials such as fly ash may contain other compounds, e.g. Fe_2O_3 (Table 1). It appears that pure geological materials may be more reactive to the alkaline activators, and hence a reduction in initial setting time.

HARDENED GEOPOLYMER

Compressive strength

There are many different views regarding the main parameters affecting the compressive strength and other mechanical properties of hardened geopolymer materials. Palomo et al.⁴ stated that the significant factors affecting the compressive strength are the curing temperature, curing time, and the type of alkaline activator. Other researchers have reported that the important parameters for satisfactory polymerisation are water content, the relative amounts of Si, Al and Na, the type of alkaline activator, the extent of dissolution of Si and the molar Si-to-Al ratio in solution, the ratio of fly ash-to-kaolinite, and curing temperature^{2, 7, 15}. Van Jaarsveld et al.³ found that curing at elevated temperature for long periods of time may weaken the structure of hardened material.

The authors' research on geopolymer concrete confirmed that curing temperature and curing time significantly influenced the compressive strength. Longer curing time and higher curing temperature increased the compressive strength, although the increase in strength may not be significant for curing at

more than 60°C and curing for periods longer than 48 hours. The compressive strength of fly ash-based geopolymer concrete cured at 60° C for 24 hours did not vary with the age and remained constant at approximately 60 MPa, due to the fast polymerisation reaction ^{9, 12}.

The authors' experimental results show that the H₂O-to-Na₂O molar ratio in the mixture composition is a significant parameter affecting the compressive strength of fly ash-based geopolymer concrete, whereas the influence of the Na₂O-to-SiO₂ molar ratio is insignificant. As the H₂O-to-Na₂O molar ratio increased the compressive strength of geopolymer concrete decreased. Also, the compressive strength decreased when the water-to-geopolymer solids ratio by mass increased. Note that the total mass of water in the mixture is the sum of water contained in the sodium silicate solution, the mass of water in the sodium hydroxide solution, and the mass of extra water, if any, added to the mixture. The mass of geopolymer solids in the mixture is the sum of the mass of fly ash, the mass of sodium hydroxide flakes, and the mass of solids in sodium silicate solution ¹⁰.

Long term performance

The test results showed that the drying shrinkage strains of fly ash-based geopolymer concretes were found to be insignificant. The ratio of creep strain-to-elastic strain (called creep factor) reached a value of 0.30 in approximately 6 weeks after loading on the 7th day with a sustained stress of 40% of the compressive strength. Beyond this time, the creep factor increased only marginally ⁹.

A series of tests were performed on the resistance of fly ash-based geopolymer concrete to sulfate attack. After soaking the specimens in a 5% sodium sulfate (Na₂SO₄) solution for 12 weeks, there were no significant changes in the compressive strength, the mass, and the length of the test specimens ¹¹. These series of tests on the long-term behaviour of the fly ash based geopolymer concrete are continuing for a period of one year. The effect of the sulphuric acid on fly ash-based geopolymer concrete is currently being investigated by the authors. Davidovits¹ has reported earlier that geopolymer cement is acid resistant. He also reported that geopolymer materials do not generate any dangerous alkali-aggregate reaction, even in the presence of high alkali content. In addition, Palomo et al. ¹⁶ reported that metakaolin-based geopolymer mortars remained stable and showed negligible deterioration in microstructure and strength after being soaked in ASTM sea water, sodium sulfate solution (4.4% by mass), and sulfuric acid solution (0.001 M) for 9 months.

CONCLUDING REMARKS

Geopolymer concrete shows significant potential to be a material for the future, because it is not only environmentally friendly but also possesses excellent mechanical properties, both in short term and long term, and

durability. Significant information is already available in the literature to utilise geopolymer concrete technology in practical applications such as precast concrete products and waste encapsulation.

However, further research is needed to understand the science behind geopolymer technology, i.e:

- Reactivity and reaction mechanism of the geopolymer material.
- The rheology of the fresh geopolymer concrete or paste.

In addition, a large data base of various characteristics of geopolymer concrete should be collected in order to prepare design tools and codes/standards for this new material.

DEDICATION

This paper is dedicated to Dr. George Hoff in respect of his long innovative service and contributions to concrete technology and the industry.

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Table 1: Composition of fly ash as determined by XRF (mass %)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	TiO ₂	MgO	P ₂ O ₅	SO ₃	LOI ^{*)}
53.36	26.49	10.86	1.34	0.37	0.80	1.47	0.77	1.43	1.70	1.39

^{*)} LOI = Loss on ignition

Table 2: Mixture proportion of geopolymer concrete used in the manufacture of test columns

Material	Mass (kg/m ³)
Coarse and fine aggregates (Fineness Modulus = 5.0)	1848.0
Fly ash (Table 1)	408.0
Sodium hydroxide (16M) solution	41.0
Sodium silicate solution (Na ₂ O=14.7%, SiO ₂ =29.4%, water=55.9% by mass)	103.0
Added water	26.5



Figure 1: Manufacture of geopolymer reinforced concrete column



Figure 2: Workability of fresh geopolymer concrete (240 mm slump)