

Fly ash-based geopolymer concrete *

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SUMMARY: *In recent years, attempts to increase the utilisation of fly ash to partially replace the use of Portland cement in concrete are gathering momentum. Geopolymer concrete is a 'new' material that does not need the presence of Portland cement as a binder. Instead, activating the source materials such as fly ash that are rich in Silicon (Si) and Aluminium (Al) using high alkaline liquids produces the binder required to manufacture the concrete. Hence, concrete with no cement.*

This paper presents information on fly ash-based geopolymer concrete. The paper covers the material and the mixture proportions, the manufacturing process, and the influence of various parameters on the properties of fresh and hardened concrete.

1 INTRODUCTION

The demand for concrete as a material of construction will increase as the demand for infrastructure development increases, especially in countries such as China and India. In order to meet this demand, the production of Portland cement must increase. However, the contribution of green house gas emission from the Portland cement production is about 1.35 billion tons annually or about 7% of the total greenhouse gas emissions to the earth's atmosphere.¹ Furthermore, Portland cement is also among the most energy-intensive construction materials, after aluminium and steel.

On the other hand, fly ash, "the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gases from the combustion zone to the particle removal system",² is available abundantly worldwide. In 2001, the fly ash production in the USA was in the order of 68 million tons, but only 32 percent was

used in various applications, such as in concrete, structural fills, waste stabilisation/solidification, etc.³ Worldwide, the estimated production of coal ash in 1998 was more than 390 million tons. The main contributors for this amount were China and India. Only about 14 percent of this fly ash was utilized, while the rest was disposed in landfills.⁴ By the year 2010, the amount of fly ash produced worldwide is estimated to be about 780 million tons annually.⁵ There are benefits in using fly ash as a substitute for Portland cement, especially to meet the increase in demand for concrete needed for infrastructure developments. With silicon and aluminium as the main constituents, fly ash has great potential as a cement replacement material in concrete.

To totally replace the use of Portland cement as concrete binder, fly ash needs to be activated, usually using alkaline solutions. Palomo et al⁶ described two different models of activation of fly ash or other similar materials. In the first model, the material containing essentially silicon and calcium is activated by low to mild concentration of alkaline solution. The main product of the reaction is calcium silicate hydrate (C-S-H). On the contrary, the

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material used in the second model contains mostly silicon and aluminium, and is activated using highly alkaline solution. The chemical process in this case is polymerisation.

Investigations on the first model have a long history in the former Soviet Union, Scandinavian and Eastern Europe countries.⁷ A very well known example is the activation of blast furnace slag. On the other hand, only limited research has been carried out on the second model.⁶ Therefore many aspects of the material characteristics, reaction mechanisms and so on for the second model are still not clear. For the binders produced using the second model, also known as inorganic alumino-silicate polymers, Davidovits⁸ coined the term Geopolymer in 1978 to describe the alkali-activated material from geological origin or by-product materials such as fly ash and rice husk ash. Davidovits⁹ also stated that often information on geopolymer material is tied to patent-oriented literature. Only from the end of 1990s, scientific data are becoming available and published; however most of the data deal with small size specimens made of geopolymer paste or mortar.

This paper presents information on fly ash-based geopolymer concrete. The paper covers the material and the mixture proportions, the manufacturing process, and the influence of various parameters on the properties of fresh and hardened concrete.

2 PAST RESEARCH ON GEOPOLYMER MATERIAL

In geopolymers, 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 Davidovits.⁸ The chemical composition of geopolymers is similar to zeolites, but shows an amorphous microstructure.¹⁰ 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.^{8, 11} The mechanism of geopolymerisation may consist of dissolution, transportation or orientation, and polycondensation,¹⁰ and takes place through an exothermic process.^{6, 8}

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.¹² A combination of sodium or potassium

silicate and sodium or potassium hydroxide has been widely used as the alkaline activator,^{6, 10, 11, 13} with the activator liquid-to-source material ratio by mass in the range of 0.25-0.30.^{6, 13}

Because heat is a reaction accelerator, curing of fresh geopolymer is carried out mostly at an elevated temperature.⁶ 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.^{8, 14}

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. Davidovits⁸ suggested that the atomic ratio of Si-to-Al of about 2 for making cement and concrete. Geopolymer can also be used as waste encapsulation to immobilise toxic metals.¹⁵

3 GEOPOLYMER CONCRETE

In the authors' experimental work, geopolymer is used as the binder, instead of cement paste, to produce concrete. The geopolymer paste binds the loose coarse aggregates, fine aggregates and other un-reacted materials together to form the geopolymer concrete. The manufacture of geopolymer concrete is carried out using the usual concrete technology methods.

As in the Portland cement concrete, the aggregates occupy the largest volume, i.e. about 75-80 % by mass, in geopolymer concrete. The silicon and the aluminium in the fly ash are activated by a combination of sodium hydroxide and sodium silicate solutions to form the geopolymer paste that binds the aggregates and other un-reacted materials.

4 MATERIALS, MIXTURE COMPOSITIONS, AND TEST SPECIMENS

In the authors' experimental work, two batches of low calcium (class F) dry fly ash obtained from the silos at a local power station were used as the base material.¹⁶ The specific surface area of the fly ash from Batch I was 1.29 m²/cc, with 80% of the particles size of fly ash smaller than 55 µm. For fly ash from Batch II, the specific surface area was 1.94 m²/cc and 80% of the size of the particles less than 38 µm. The chemical compositions of the fly ash from Batch I and Batch II, as determined by X-Ray Fluorescence (XRF) analysis, are given in Table 1.

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

Oxides	Batch I	Batch II
SiO ₂	53.36	47.80
Al ₂ O ₃	26.49	24.40
Fe ₂ O ₃	10.86	17.40
CaO	1.34	2.42
Na ₂ O	0.37	0.31
K ₂ O	0.80	0.55
TiO ₂	1.47	1.328
MgO	0.77	1.19
P ₂ O ₅	1.43	2.00
SO ₃	0.20	0.29
Cr	0	0.01
MnO	0	0.12
LOI ⁾	1.39	1.10

⁾ LOI = Loss on Ignition

The fly ash from Batch I was used in Mixtures 6 to 10, while other Mixtures utilised the fly ash from Batch II (Table 2).

Analytical grade sodium hydroxide (NaOH with 98% purity) and sodium silicate solutions (Na₂O=14.7%, SiO₂=29.4% and water=55.9% by mass) were used as the alkaline activators. In order to avoid the effect of unknown contaminants in the mixing water, the sodium hydroxide flakes were dissolved in distilled water. The activator solution was prepared at least one day prior to its use. To improve the workability of fresh concrete, a commercially available naphthalene based super plasticiser was used. A combination of locally available aggregates, i.e. granite type coarse aggregate and fine sand, in saturated surface dry condition, were mixed together. The grading of this combined aggregate had a fineness modulus of 4.5.

The aggregates and the fly ash were mixed dry in a pan mixer for 3 minutes. The alkaline solutions and the super plasticiser were mixed together, then added to the solid particles and mixed for another 3 to 5 minutes. The fresh concrete had a stiff consistency and was glossy in appearance. The fresh concrete mixture was then cast in 100x200 mm cylinder steel moulds in three layers. Each layer received 60 manual strokes and vibrated for 10 seconds on a vibrating table. Five cylinders were prepared for each test variable.

Table 2
Details of the mixtures

Mixture No.	Aggregates	Fly Ash	Sodium Silicate solution	Sodium Hydroxide solution	Super-Plasticiser	Added Water	Curing
1	1848	408	103	41 (8M)	6	-	60°C Oven
2	1848	408	103	41 (10M)	6	7.5	60°C Oven
3	1848	408	103	41 (12M)	6	14.4	60°C Oven
4	1848	408	103	41 (14M)	6	20.7	60°C Oven
5	1848	408	103	41 (16M)	6	26.5	60°C Oven
6	1848	408	103	41 (14)	8	-	Varied Oven
7	1848	408	103	41 (14)	8	10.6	Varied Oven
8	1848	408	103	41 (14M)	8	21.3	Varied Oven
9	1756	476	120	48 (8M)	-	-	60°C Oven
10	1756	476	120	48 (14M)	-	-	60°C Oven
11	1848	408	103	41 (14M)	8	-	90°C Oven
12	1848	408	103	41 (8M)	6	-	90°C Oven
13	1848	408	103	55.4 (8M)	6	-	60°C Oven
14	1848	408	103	55.4 (8M)	6	-	60°C Steam

Immediately after casting, the samples were covered by a film to avoid the loss of water due to evaporation during curing at an elevated temperature. The specimens were cured in an oven or steamed chamber at a specified temperature for a period of time in accordance with the test variables selected. The details of authors' research have been reported elsewhere.¹⁶⁻¹⁸

At the end of the curing period, the 100x200 mm test cylinders were removed from the curing chamber, and were left in the moulds for six hours in order to avoid a drastic change of the environmental conditions. The specimens were then removed from the moulds, and left to air dry at room temperature until loaded in compression at the specified age in a universal test machine. Before testing, the specimens were weighed to determine the density of the material. The loading rate and other test procedures used were in accordance with the details specified in the relevant Australian Standard for testing Portland cement concrete.¹⁹ Each of the compressive strength test data points plotted in various Figures or stated in Table 3 corresponds to the mean value of the compressive strengths of five test cylinders in a series. The standard deviations are plotted on the test data points as the error bar.

5 PARAMETERS AFFECTING FRESH AND HARDENED CONCRETE

The fresh fly ash-based geopolymer concrete has a stiff consistency and is glossy in appearance.

As in the case of Portland cement concrete, water content of the mixture influences the workability of geopolymer concrete, as measured by the conventional slump test. This is demonstrated in Figure 1.

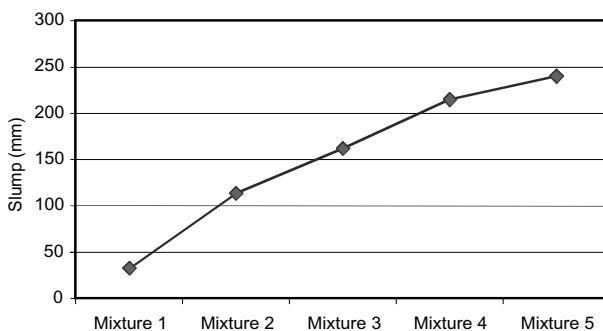


Figure 1: Slump values for mixtures 1 to 5.

In Figure 1, the slumps of various mixtures are plotted. In order to maintain the compressive strength approximately constant, the concentration (in terms of Molar) of sodium hydroxide (NaOH) solution was increased in the mixtures that were added with extra water. The net effect is that higher the water content of the mixture higher is also the Na_2O -to- SiO_2 molar ratio. It is interesting to note that an increase in the Na_2O -to- SiO_2 ratio has insignificant effect on the compressive strength of hardened concrete (Figure 2).

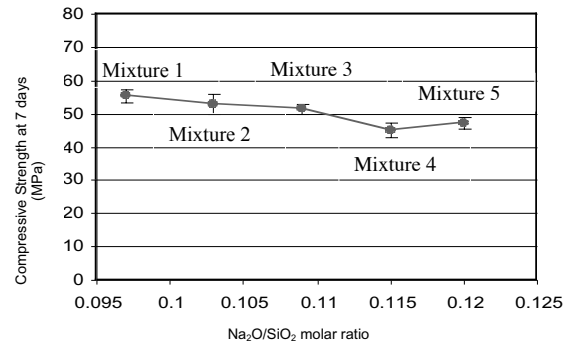


Figure 2: Effect of molar Na_2O -to- SiO_2 ratio on compressive strength.

Another important characteristic of fresh concrete state is the setting time. Our laboratory experiments showed that fresh fly ash-based geopolymer concrete could be handled at least up to 120 minutes after mixing, without any sign of setting, and without any degradation in compressive strength.¹⁷

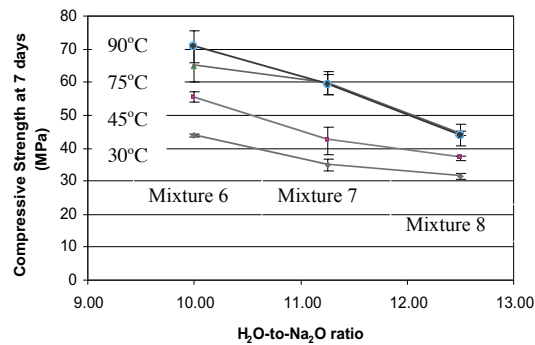


Figure 3: Effect of the H_2O -to- Na_2O molar ratio on compressive strength.

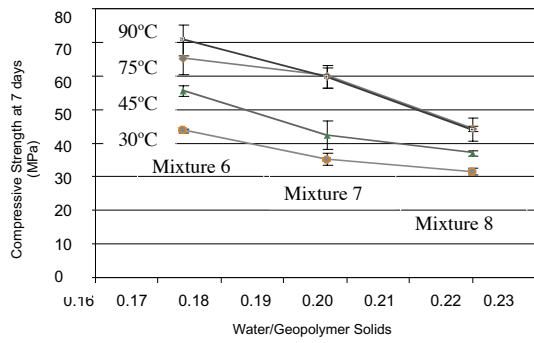


Figure 4: Effect of Water-to-Geopolymer Solids ratio by mass on compressive strength.

With regard to hardened concrete, the molar ratio of H_2O -to- Na_2O significantly influences the compressive strength of fly ash-based geopolymer concrete. An increase in this ratio decreases the compressive strength (Figure 3). The test results plotted in Figure 3 are recast in Figure 4 in terms of geopolymer solids-to-water ratio by mass versus compressive strength. For a given geopolymer concrete, the total mass of water in the mixture is taken as the sum of the mass of water 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 is the sum of the mass of fly ash, the mass of sodium hydroxide flakes, and the mass of sodium silicate solids (i.e. the mass of Na_2O and SiO_2 in sodium silicate solution). Again, this relation is similar to the relationship between the water-to-cement ratio and the compressive strength of Portland cement concrete.

Other important factors that influence the properties of hardened fly ash-based geopolymer concrete are the curing temperature and the curing time. Higher the curing temperature higher is the compressive strength (Figure 5).

On the influence of curing time, fly ash-based geopolymer concrete cured for longer periods of time, shows an increase in its compressive strength, at least up to 48 hours (Figure 6).

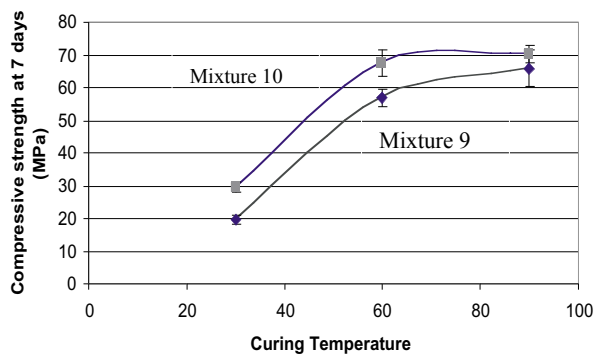


Figure 5: Effect of curing temperature on compressive strength.

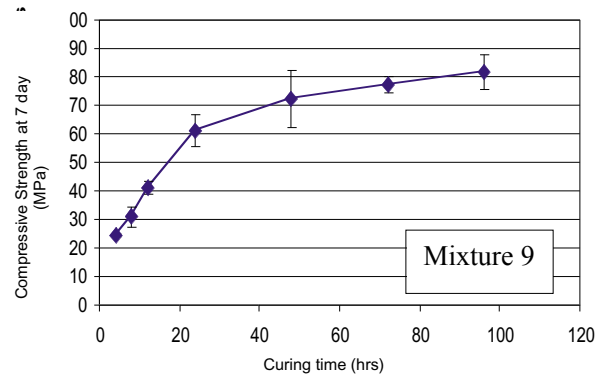


Figure 6: Influence of curing time on compressive strength.

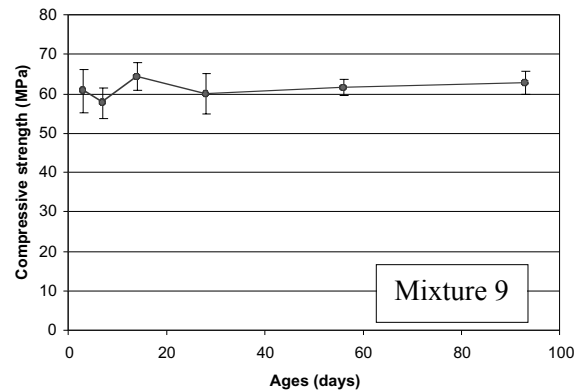


Figure 7: Compressive strength at different ages.

In geopolymers, the curing temperature and the curing time play significant roles not only as accelerators of chemical reaction, but also determine the extent of that reaction.^{8,9} Therefore, we found that geopolymer concrete samples cured at 60°C for a period of 24 hours showed very little strength gain after curing (Figure 7).

6 ELASTIC CONSTANTS

To measure the elastic constants of fly ash-based geopolymer concrete, four different mixtures were prepared to obtain four different compressive strengths in the range of 40 to 90 MPa.²⁰ The elastic properties, Young’s modulus and Poisson’s ratio, were measured in accordance with the Australian Standard AS 1012.17-1997.²¹ The Young’s modulus was determined as the secant modulus, measured at a stress level equal to 40 percent of the compressive strength of concrete.

Table 3
Young's Modulus (E_c) and Poisson's Ratio (ν)
of fly ash-based geopolymer concrete.

Mixture No.	f_{cm} (MPa)	E_c (GPa)	ν
11	89	30.84	0.16
12	68	27.29	0.12
13	55	26.05	0.14
14	44	22.95	0.13

The values of Young's modulus of fly ash-based geopolymer concrete are given in Table 3. Aitcin and Mehta²² reported that using granite type of coarse aggregate, the Young's modulus of Portland cement concrete with $f_{cm}=84.8$ MPa was 31.7 GPa, while for concrete with $f_{cm}=88.6$ MPa, $E_c=33.8$ GPa. The values reported in Table 3 are at the lower end of those calculated using the empirical expression given in the Australian Concrete Structures Standard, AS3600.

The Poisson's ratio falls between 0.12 and 0.16, and is within the range observed for Portland cement concrete.

7 LONG-TERM PROPERTIES AND DURABILITY

On the long-term properties, our laboratory experiments have shown that the fly ash-based geopolymer concrete undergoes low creep and very little drying shrinkage.²³ The specimens for these tests and the test procedure used for creep strain measurements were in accordance with the relevant Australian Standards. Shrinkage strain measurements commenced on the same day when the creep specimens were loaded. Some typical results for the specimens manufactured using Mixture 1 (Table 2) and cured for 24 hours are shown in Figures 8 and 9. After 24 weeks under sustained load of 40 % of the compressive strength, the drying shrinkage strain measured varied from 66 to 104 $\times 10^{-6}$ (Figure 8), and the creep factor (the ratio of creep strain to elastic strain) was found to vary between

0.28 and 0.39 (Figure 9).

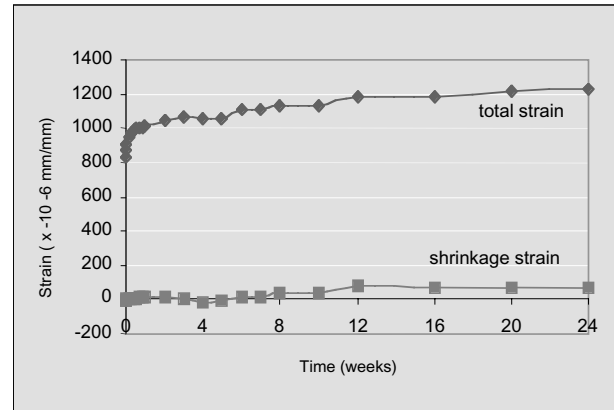


Figure 8: Total and shrinkage strains.

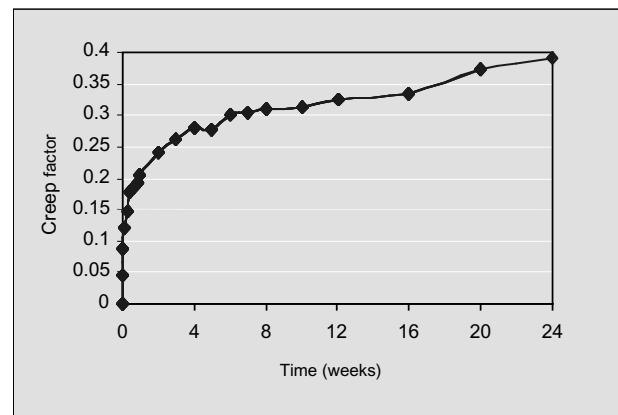


Figure 9: Creep factor.

In order to study the effect of sulfate attack, specimens of fly ash-based geopolymer concrete were soaked in 5% concentration of sodium sulfate solution (Na_2SO_4). The variations in the compressive strength, the unit mass, the length change, as well as the physical appearance, were observed.²⁴ Some typical results are presented in Figure 10 for the specimens manufactured using Mixture 1 (Table 2) and cured for 24 hours. It was found that geopolymer concrete did not show any sign of sulfate attack or degradation in properties.

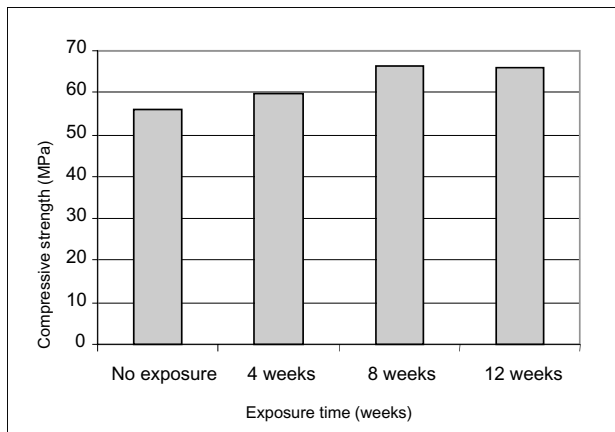


Figure 10: Compressive strength after sodium sulfate exposure.

8 CONCLUDING REMARKS

This paper presented information on the development of fly ash-based geopolymer concrete. Fly ash-based geopolymer concrete has excellent compressive strength and is suitable for structural applications. The effects of various salient parameters that influence the properties of fresh and hardened concrete have been illustrated.

The fly ash-based geopolymer concrete also shows excellent resistance to sulfate attack, undergoes low creep, and suffers very little drying shrinkage. Further research on the material and structural applications is continuing, and will be reported in the future.²⁵

9 ACKNOWLEDGEMENTS

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