Geopolymer concrete for environmental protection

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Extensive studies conducted on fly ash-based geopolymer concrete are presented. Salient factors that influence the properties of the geopolymer concrete in the fresh and hardened states are identified. Test data of various short-term and long-term properties of the geopolymer concrete are then presented. The paper describes the results of the tests conducted on large-scale reinforced geopolymer concrete members and illustrates the application of the geopolymer concrete in the construction industry. Some recent applications of geopolymer concrete in the precast construction and the economic merits of the geopolymer concrete are also included.

Keywords: *Geopolymer concrete; fly ash; blast-furnace slag; precast concrete; structural concrete.*

1. INTRODUCTION

The global use of concrete is second only to water. As the demand for concrete as a construction material increases, so also the demand for Portland cement. It is estimated that the production of cement will increase from about from 1.5 billion tons in 1995 to 2.2 billion tons in 2010 [1].

On the other hand, the climate change due to global warming and environmental protection has become major concerns. The global warming is caused by the emission of greenhouse gases, such as carbon dioxide (CO_2), to the atmosphere by human activities. Among the greenhouse gases, CO_2 contributes about 65% of global warming [2]. The cement industry is held responsible for some of the CO_2 emissions, because the production of one ton of Portland cement emits approximately one ton of CO_2 into the atmosphere [2, 3]. The environment must be protected by preventing dumping of waste/by-product materials in un-controlled manners.

Several efforts are in progress to address these issues. These include the utilization of supplementary cementing materials such as fly ash, silica fume, granulated blast furnace slag, rice-husk ash and metakaolin, and the development of alternative binders to Portland cement.

In this respect, the geopolymer concrete with a much lower environmental footprint shows considerable promise for application in the concrete industry [4]. In terms of global warming, the geopolymer technology could significantly reduce the CO_2 emission to the atmosphere caused by the cement industries as shown by the detailed analyses by Gartner [5].

2. GEOPOLYMERS

Davidovits [3, 6] proposed that an alkaline liquid could be used to react with the silicon (Si) and the aluminum (Al) in a source material of geological origin or in by-product materials such as fly ash, blast furnace slag, and rice husk ash to produce binders. Because the chemical reaction that takes place in this case is a polymerization process, he coined the term 'Geopolymer' to represent these binders.

Water, expelled from the geopolymer matrix during the curing and further drying periods, leaves behind

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The Indian Concrete Journal, April 2014, Vol. 88, Issue 4, pp. 41-48, 50-59.

nano-pores in the matrix, which provide benefits to the performance of geopolymers. The water in a low-calcium fly ash-based geopolymer mixture, therefore, plays no direct role in the chemical reaction that takes place; it merely provides the workability to the mixture during handling. This is in contrast to the chemical reaction of water in a Portland cement concrete mixture during the hydration process. However, a small proportion of calcium-rich source materials such as slag may be included in the source material in order to accelerate the setting time and to alter the curing regime adopted for the geopolymer mixture. In that situation, the water released during the geopolymerisation reacts with the calcium present to produce hydration products.

There are two main constituents of geopolymers, namely the source materials and the alkaline liquids. The source materials for geopolymers based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, etc. Alternatively, by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud, etc could be used as source materials. The choice of the source materials for making geopolymers depends on factors such as availability, cost, type of application, and specific demand of the end users.

The alkaline liquids are from soluble alkali metals that are usually Sodium or Potassium based. The most common alkaline liquid used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate.

According to Davidovits [3], geopolymeric materials have a wide range of applications in the field of industries such as in the automobile and aerospace, non-ferrous foundries and metallurgy, civil engineering and plastic industries. The type of application of geopolymeric materials is determined by the chemical structure in terms of the atomic ratio Si: Al in the polysialate. Davidovits [3] classified the type of application according to the Si:Al ratio as presented in Table 1. A low ratio of Si: Al of 1, 2, or 3 initiates a 3D-Network that is very rigid, while Si: Al ratio higher than 15 provides a polymeric character to the geopolymeric material. For many applications in the civil engineering field, a low Si: Al ratio is suitable (Table 1).

Table 1. Applications of geopolymeric materials based on silica-to-alumina atomic ratio [3]

Si:Al ratio	Applications
1	- Bricks - Ceramics - Fire protection
2	- Low CO_2 cements and concretes - Radioactive and toxic waste encapsulation
3	- Fire protection fibre glass composite - Foundry equipments - Heat resistant composites, 200°C to 1000°C - Tooling for aeronautics titanium process
>3	- Sealants for industry, 200°C to 600°C - Tooling for aeronautics SPF aluminium
20 - 35	- Fire resistant and heat resistant fibre composites

This paper is deals primarily with low-calcium fly ash-based geopolymer concrete. Low-calcium (ASTM Class F) fly ash is preferred as a source material than high-calcium (ASTM Class C) fly ash. The presence of calcium in high amounts may interfere with the polymerization process and alter the microstructure [7,8], and hence compromise some of the benefits offered by geopolymer concrete.

3. CONSTITUENTS OF GEOPOLYMER CONCRETE

Geopolymer concrete can be manufactured by using the low-calcium (ASTM Class F) fly ash obtained from coal-burning power stations. Most of the fly ash available globally is low-calcium fly ash formed as a by-product of burning anthracite or bituminous coal. Although coal burning power plants are considered to be environmentally unfriendly, the extent of power generated by these plants is on the increase due to the huge reserves of good quality coal available worldwide and the low cost of power produced from these sources. The energy returned-to-energy invested ratio of coal burning power plants is high, and second only to the hydro-power generation plants as given as follows [9]:

Energy returned/Energy invested ratio

Hydro = 100
Coal = 80
Oil = 35
Wind = 18
Solar = 6 to 20
Nuclear = 15
Biofuels = 3

Therefore, huge quantities of fly ash will be available for many years in the future (10). The chemical composition and the particle size distribution of the fly ash must be established prior to use. An X-Ray Fluorescence (XRF) analysis may be used to determine the chemical composition of the fly ash.

Low-calcium fly ash has been successfully used to manufacture geopolymer concrete when the silicon and aluminum oxides constituted about 80% by mass, with the Si-to-Al ratio of about 2. The content of the iron oxide usually ranged from 10 to 20% by mass, whereas the calcium oxide content was less than 5% by mass. The carbon content of the fly ash, as indicated by the loss on ignition by mass, was as low as less than 2%. The particle size distribution tests revealed that 80% of the fly ash particles were smaller than 50 µm [7, 8, 11-18]. The reactivity of low-calcium fly ash in geopolymer matrix has been studied by Fernandez-Jimenez, et al [19].

Coarse and fine aggregates used by the concrete industry are suitable to manufacture geopolymer concrete. The aggregate grading curves currently used in concrete practice are applicable in the case of geopolymer concrete [7, 8, 11-15].

A combination of sodium silicate solution and sodium hydroxide (NaOH) solution can be used as the alkaline liquid. It is recommended that the alkaline liquid is prepared at least 24 hours prior to use.

The sodium silicate solution is commercially available in different grades. The sodium silicate solution A53 with SiO_2-to-Na_2O ratio by mass of approximately 2, i.e., SiO_2 = 29.4%, Na_2O = 14.7%, and water = 55.9% by mass, is generally used.

The sodium hydroxide with 97-98% purity, in flake or pellet form, is commercially available. The solids must be dissolved in water to make a solution with the required concentration. The concentration of sodium hydroxide solution can vary in the range between 8 Molar and 16 Molar; however, 8 Molar solution is adequate for most applications. The mass of NaOH solids in a solution varies depending on the concentration of the solution. For instance, NaOH solution with a concentration of 8 Molar consists of 8x40 = 320 grams of NaOH solids per litre of the solution, where 40 is the molecular weight of NaOH. Note that the mass of water is the major component in both the alkaline solutions.

In order to accelerate the setting time of fresh geopolymer concrete and to facilitate room-temperature curing, a small proportion of calcium-rich source material such as blast furnace slag may be added to the mixture. Extra water and a high range water reducer super plasticizer may be added to the mixture to improve the workability.

4. MIXTURE PROPORTIONS OF GEOPOLYMER CONCRETE

The primary difference between geopolymer concrete and Portland cement concrete is the binder. The silicon and aluminum oxides in the low-calcium fly ash reacts with the alkaline liquid to form the geopolymer paste that binds the loose coarse aggregates, fine aggregates, and other un-reacted materials together to form the geopolymer concrete.

As in the case of Portland cement concrete, the coarse and fine aggregates occupy about 75 to 80% of the mass of geopolymer concrete. This component of geopolymer concrete mixtures can be designed using the tools currently available for Portland cement concrete.

The compressive strength and the workability of geopolymer concrete are influenced by the proportions and properties of the constituent materials that make the geopolymer paste. Experimental results [11] have shown the following:

- Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of geopolymer concrete.

- Higher the ratio of sodium silicate solution-to-sodium hydroxide solution ratio by mass, higher is the compressive strength of geopolymer concrete.

- The addition of naphthalene sulphonate-based super plasticizer, up to approximately 4% of fly ash by mass, improves the workability of the fresh geopolymer concrete; however, there is a slight degradation in the compressive strength of hardened concrete when the super plasticizer dosage is greater than 2%.

- The slump value of the fresh geopolymer concrete increases when the water content of the mixture increases.

- As the H_2O-to-Na_2O molar ratio increases, the compressive strength of geopolymer concrete decreases.

As can be seen from the above, the interaction of various parameters on the compressive strength and the workability of geopolymer concrete is complex. In order to assist the design of low-calcium fly ash-based geopolymer concrete mixtures, a single parameter called **'water-to-geopolymer solids ratio'** by mass was devised [11]. In this parameter, the total mass of water is the sum of the mass of water contained in the sodium silicate solution, the mass of water used in the making of the sodium hydroxide solution, and the mass of extra water, if any, present in the mixture. The mass of geopolymer solids is the sum of the mass of fly ash, the mass of sodium hydroxide solids used to make the sodium hydroxide solution, and the mass of solids in the sodium silicate solution (i.e. the mass of Na_2O and SiO_2).

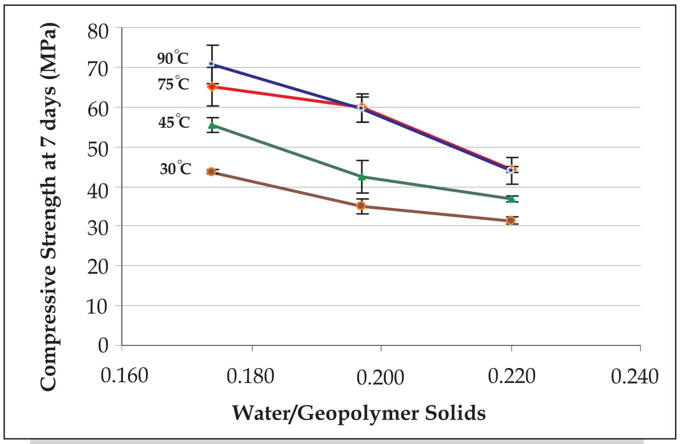


Figure 1. Effect of Water-to-Geopolymer Solids Ratio by Mass on Compressive Strength of Geopolymer Concrete [11]

Tests were performed to establish the effect of water-to-geopolymer solids ratio by mass on the compressive strength and the workability of geopolymer concrete. The test specimens were 100x200 mm cylinders, heat-cured in an oven at various temperatures for 24 hours. The results of these tests, plotted in Figure 1, show that the compressive strength of geopolymer concrete decreases as the water-to-geopolymer solids ratio by mass increases [11]. This test trend is analogous to the well-known effect of water-to-cement ratio on the compressive strength of Portland cement concrete. Obviously, as the water-to-geopolymer solids ratio increased, the workability increased as the mixtures contained more water.

Table 2. Geopolymer concrete mixture proportions [12]

Materials		**Mass (kg/m^3)**	
		Mixture-1	**Mixture-2**
Coarse aggregates:	20 mm	277	277
	14 mm	370	370
	7 mm	647	647
Fine sand		554	554
Fly ash (low-calcium ASTM Class F)		408	408
Sodium silicate solution ($SiO_2/Na_2O=2$)		103	103
Sodium hydroxide solution		41 (8 Molar)	41 (14 Molar)
Super plasticizer		6	6
Extra water		None	22.5

The test trend shown in Figure 1 is also observed by Siddiqui [16] in the studies conducted on steam-cured reinforced geopolymer concrete culverts.

The proportions of two different geopolymer concrete mixtures used in laboratory studies are given in Table 2 [12]. The details of numerous other mixtures are reported elsewhere [11-13, 17, 18, 20].

5. MIXING, CASTING, AND COMPACTION OF GEOPOLYMER CONCRETE

Geopolymer concrete can be manufactured by adopting the conventional techniques used in the manufacture of Portland cement concrete. In the laboratory, the fly ash and the aggregates were first mixed together dry in a pan mixer for about three minutes. The aggregates were prepared in saturated-surface-dry (SSD) condition.

The alkaline liquid was mixed with the super plasticiser and the extra water, if any. The liquid component of the mixture was then added to the dry materials and the mixing continued usually for another four minutes. The fresh concrete could be handled up to 120 minutes without any sign of setting and without any degradation in the compressive strength. The fresh concrete was cast and compacted by the usual methods used in the case of Portland cement concrete [11-13]. Fresh fly ash-based geopolymer concrete was usually cohesive. The workability of the fresh concrete was measured by means of the conventional slump test.

The compressive strength of geopolymer concrete is influenced by the wet-mixing time. Test results show that the compressive strength increased as the wet-mixing time increased [11].

6. CURING OF GEOPOLYMER CONCRETE

Heat-curing substantially assists the chemical reaction that occurs in the geopolymer paste. Both curing time and curing temperature influence the compressive strength of geopolymer concrete. The effect of curing time is illustrated in Figure 2 [11]. The test specimens were 100x200 mm cylinders heat-cured at 60°C in an oven. The curing time varied from 4 hours to 96 hours (4 days). Longer curing time improved the polymerization process resulting in higher compressive strength. The rate of increase in strength was rapid up to 24 hours of curing time; beyond 24 hours, the gain in strength is only moderate. Therefore, heat-curing time need not be more than 24 hours in practical applications.

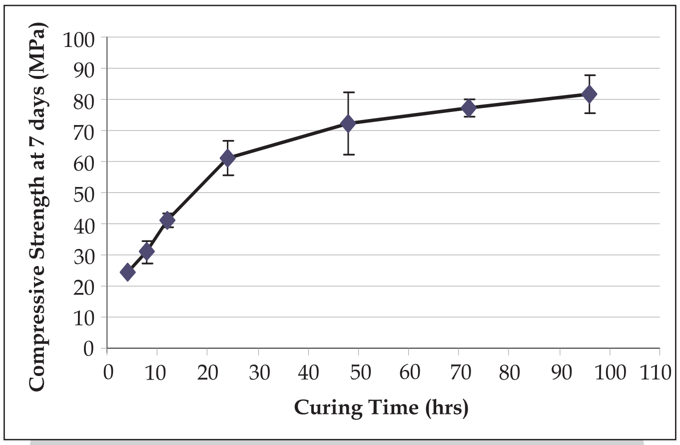


Figure 2. Effect of Curing Time on Compressive Strength of Geopolymer Concrete [11]

Figure 1 shows the effect of curing temperature on the compressive strength of geopolymer concrete [11]. Higher curing temperature resulted in larger compressive strength.

Heat-curing can be achieved by either steam-curing or dry-curing. Test data show that the compressive strength of dry-cured geopolymer concrete is approximately 15% larger than that of steam-cured geopolymer concrete [11].

The required heat-curing regime can be manipulated to fit the needs of practical applications. In laboratory trials [11], precast products were manufactured using geopolymer concrete; the design specifications required steam-curing at 60°C for 24 hours. In order to optimize the usage of formwork, the products were cast and steam-cured initially for about 4 hours. The steam-curing was then stopped for some time to allow the release of the products from the formwork. The steam-curing of the products then continued for another 21 hours. This two-stage steam-curing regime did not produce any degradation in the strength of the products.

A two-stage steam-curing regime was also used by Siddiqui [18] in the manufacture of prototype reinforced geopolymer concrete box culverts. It was found that steam curing at 80 ˚C for a period of 4 hours provided enough strength for de-moulding of the culverts; this was then followed by steam curing further for another 20 hours at 80 ˚C to attain the required design compressive strength.

Also, the start of heat-curing of geopolymer concrete can be delayed for several days. Tests have shown that a delay in the start of heat-curing up to five days did not produce any degradation in the compressive strength. In fact, such a delay in the start of heat-curing substantially increased the compressive strength of geopolymer concrete [11]. This may be due to the geopolymerisation that occurs prior to the start of heat-curing.

The temperature required for heat-curing can be as low as 30 degrees C (Figure 1). In tropical climates, this range of temperature can be provided by the ambient conditions, as illustrated by two recent studies. Nuruddin, et al at Universiti Teknologi Petronas, Malaysia studied the geopolymer concrete mixture as given below [21]:

Coarse aggregates (max. 20 mm) : 1200 kg/m^3
Fine sand : 645 kg/m^3
Fly ash (Class F) : 350 kg/m^3
Sodium silicate solution (A53) : 103 kg/m^3
Sodium hydroxide solution (8 Molar) : 41 kg/m^3
Extra water : 35 kg/m^3
Table sugar (to delay setting) : 10.5 kg/m^3

The workability of the fresh concrete as measured by the standard slump test was 230 mm. The test specimens (100 mm cubes) were removed from the moulds 24 hours after casting, and cured in ambient conditions in shade as well as in direct sun-light. The compressive strength test performed on test cubes yielded the following results:

Age (days)	Compressive strength (MPa)	
	Shade	Sun-light
3	10	35
7	14	42
28	20	49
56	22	50
90	24	51

In another study, Barber [22] at Curtin University manufactured and tested the properties of the following geopolymer concrete mixture developed by the author:

20 mm Coarse aggregates : 700 kg/m^3
10 mm Coarse aggregates : 350 kg/m^3
Fine sand : 800 kg/m^3
Fly ash (Class F) : 380 kg/m^3
Sodium silicate solution (A53) : 110 kg/m^3
Sodium hydroxide solution (8 Molar) : 40 kg/m^3

The workability of the fresh concrete as measured by the standard slump test was 210 mm. The test specimens (100x200 mm cylinders) were removed from the moulds two days after casting and cured at 30 degrees C in an oven. The results of the compressive strength test performed on the test cylinders are as follows:

Age (days)	Compressive strength (MPa)
3	8
7	18
14	23
28	24
56	32

The above flexibilities in the curing regime of geopolymer concrete can be exploited in practical applications.

7. DESIGN OF GEOPOLYMER CONCRETE MIXTURES

Concrete mixture design process is vast and generally based on performance criteria. Based on the information given in Sections 3 to 6 above, some simple guidelines for the design of low-calcium fly ash-based geopolymer concrete have been proposed [14, 15].

The role and the influence of aggregates are considered to be the same as in the case of Portland cement concrete. The mass of combined aggregates may be taken to be between 75% and 80% of the mass of geopolymer concrete.

The performance criteria of a geopolymer concrete mixture depend on the application. For simplicity, the compressive strength of hardened concrete and the workability of fresh concrete may be selected as the performance criteria. In order to meet these performance criteria, the alkaline liquid-to-fly ash ratio by mass, **water-to-geopolymer solids ratio** (*see Section 4 for definition*) by mass, the wet-mixing time, the heat-curing temperature, and the heat-curing time are selected as parameters.

As a good practice, the aggregates should in saturated-surface-dry (SSD) condition. In other words, the coarse and fine aggregates in a geopolymer concrete mixture must neither be too dry to absorb the liquid from the mixture nor too wet to add water to the mixture. In practical applications, aggregates may contain water over and above the SSD condition. Therefore, the extra water in the aggregates above the SSD condition must be estimated and included in the calculation of water-to-geopolymer solids ratio. When the aggregates are too dry, the aggregates must be brought to SSD condition by pre-mixing them with water before the commencement of the mixing process for geopolymer concrete.

With regard to alkaline liquid-to-fly ash ratio by mass, values in the range of 0.30 and 0.45 are recommended. The data given in Figures 1 and 2 may be used as guides to choose curing temperature and curing time. For instance, when the geopolymer concrete is cured in ambient conditions and the temperature is about 30 degrees C, the design compressive strength is expected to be in the range of 50 to 60% of the values cured at 60 degree C.

Sodium silicate solution is cheaper than sodium hydroxide solids. Laboratory experience suggests that the ratio of sodium silicate solution-to-sodium hydroxide solution by mass may be taken approximately as 2.5 [11].

Geopolymer concrete can be manufactured by using only sodium (or potassium) silicate solution. The following can be used as a base trial mixture; the mass of constituents are given for one cubic metre of geopolymer concrete: Low-calcium Fly Ash = 385 kg; Blast-furnace slag = 85 kg; Sodium silicate solution = 110 kg; Water = 45 kg; Coarse Aggregates: 20 mm = 280 kg, 14 mm = 370 kg, 7 mm = 650 kg; Fine sand = 550 kg. The geopolymer concrete can be cured at room temperature (21 degree C) or at ambient temperature in tropical climate (30-40 degree C). The expected 28-day compressive strength may be in the range of 30 to 40 MPa. This base trial mixture is rich and stiff, and can be modified to suit the required design requirements and the local materials.

8. SHORT-TERM PROPERTIES OF GEOPOLYMER CONCRETE

8.1. Behavior in compression

The behavior and failure mode of fly ash-based geopolymer concrete in compression is similar to that of Portland cement concrete. Test data show that the strain at peak stress is in the range of 0.0024 to 0.0026. As expected, the modulus of elasticity increased as the compressive strength of geopolymer concrete increased [11].

Experimental studies have shown that the aggregate-binder interfaces are stronger in geopolymers than in the case of Portland cement [23]. This may lead to superior mechanical properties and long-term durability of geopolymer concretes [24].

The Poisson's ratio of fly ash-based geopolymer concrete with compressive strength in the range of 40 to 90 MPa falls between 0.12 and 0.16. These values are similar to those of Portland cement concrete.

8.2. Indirect tensile strength

Test results show that the tensile splitting strength of geopolymer concrete is only a fraction of the compressive strength, as in the case of Portland cement concrete [11]. Sofi et al [17] also performed indirect tensile tests on geopolymer mortar and concrete specimens made using three different sources of low-calcium fly ash. The test trends observed in that study also confirm the above trend. Similar results are reported by Anuradha, et al [20].

8.3. Unit-weight

The unit-weight of concrete primarily depends on the unit mass of aggregates used in the mixture. Tests show that the unit-weight of the low-calcium fly ash-based geopolymer concrete is similar to that of Portland cement concrete. When granite-type coarse aggregates were used, the unit-weight varied between 2330 and 2430 kg/m^3 [11]. It is possible to produce geopolymer light-weight concrete and geopolymer foamed concrete by following the processes used in the case of Portland cement concrete.

9. LONG-TERM PROPERTIES OF GEOPOLYMER CONCRETE

9.1. Compressive strength

Two geopolymer concrete mixture proportions used in laboratory studies are given in Table 2 [12]. Numerous batches of these mixtures were manufactured during a period of four years. For each batch of geopolymer concrete made, 100x200 mm cylinders specimens were prepared. At least three of these cylinders were tested for compressive strength at an age of seven days after casting. The unit-weight of specimens was also determined at the same time. For these numerous specimens made from Mixture-1 and Mixture-2 and heat-cured at 60°C for 24 hours after casting, the average results are presented in Table 3 [12].

In order to observe the effect of age on compressive strength of heat-cured geopolymer concrete, 100x200 mm cylinders were made from several batches of Mixture-1 given in Table 2. The specimens were heat-cured in the oven for 24 hours at 60°C. Test data show that the compressive strength increased with age in the order of 10 to 20 percent when compared to the 7th day compressive strength [12].

In order to study the effect of age on the compressive strength of fly ash-based geopolymer concrete cured in laboratory ambient conditions, three batches of geopolymer concrete were made using Mixture-1 given in Table 2. The test specimens were 100x200 mm cylinders. The first batch was cast in the month of May 2005, while the second batch was cast in the month of July 2005 and the third batch in September 2005. The ambient temperature in May 2005 during the first week after casting the concrete ranged from about 18 to 25°C, while this temperature was around 8 to 18°C in July 2005 and 12 to 22°C in September 2005. The average humidity in the laboratory during those months was between 40% and 60%. The test cylinders were removed from the moulds one day after casting and left in laboratory ambient conditions until the day of test.

Table 3. Mean compressive strength and unit-weight of geopolymer concrete [12]

Mixture	Curing type	7th Day compressive strength (heat-curing at 60°C for 24 hours), (MPa)		Unit-weight, (kg/m^3)	
		Mean	Standard deviation	Mean	Standard deviation
Mixture-1	Dry curing (oven)	58	6	2379	17
	Steam curing	56	3	2388	15
Mixture-2	Dry curing (oven)	45	7	2302	52
	Steam curing	36	8	2302	49

Test result show that the compressive strength of ambient-cured geopolymer concrete significantly increased with the age [12]. This test trend is in contrast to the effect of age on the compressive strength of heat-cured geopolymer concrete.

9.2. Creep and drying shrinkage

The creep and drying shrinkage behavior of heat-cured low-calcium fly ash-based geopolymer concrete was studied for a period of one year [12]. The geopolymer concrete mixture proportions used in that study were Mixture-1 and Mixture-2, as given in Table 2. The test specimens were 150x300 mm cylinders, heat-cured at 60°C for 24 hours. The creep tests commenced on the 7th day after casting the test specimens and the sustained stress was 40% of the compressive strength on that day. The trend of test results obtained were similar for both Mixture-1 and Mixture-2, heat-cured either in an oven or steam-cured.

Test results showed that heat-cured fly ash-based geopolymer concrete undergoes very little drying shrinkage in the order of about 100 micro strains after one year. This value is significantly smaller than the range of values of 500 to 800 micro strains experienced by Portland cement concrete.

The creep coefficient, defined as the ratio of creep strain-to-elastic strain, after one year of loading for heat-cured geopolymer concrete with compressive strength of 40, 47 and 57 MPa is between 0.6 and 0.7, while for geopolymer concrete with compressive strength of 67 MPa this value is between 0.4 and 0.5. The specific creep, defined as the creep strain per unit of sustained stress, data are shown in Figure 3 [12]. These values are about 50% of the values recommended by the Australian Standard AS 3600 for Portland cement concrete.

The low drying shrinkage and the low creep of heat-cured geopolymer concrete offer benefits to the long-term performance of geopolymer concrete members.

The drying shrinkage strains of geopolymer concrete cured in ambient conditions are many folds larger than those experienced by the heat-cured specimens (Figure 4). As mentioned earlier, water is released during the chemical reaction process of geopolymers. In the specimens cured in ambient conditions, this water may evaporate over a period of time causing significantly large drying shrinkage strains especially in first two weeks as can be seen in Figure 4 [12].

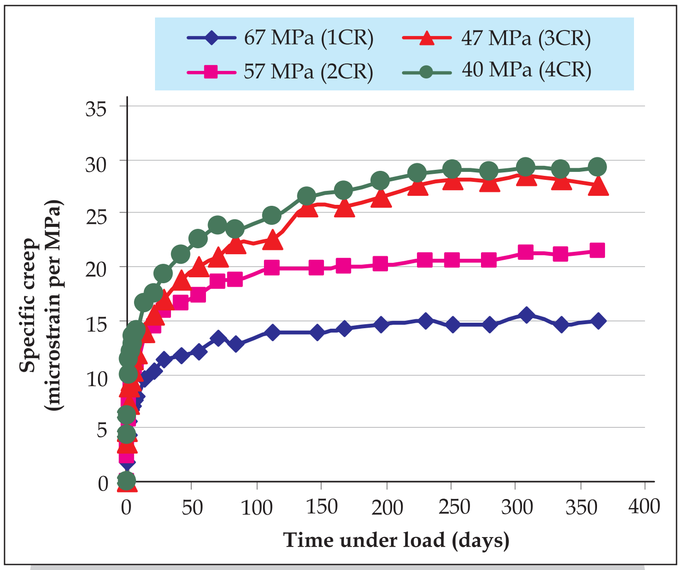


Figure 3. Effect of Compressive Strength on Creep of Heat-Cured Geopolymer Concrete [12]

9.3. Sulfate resistance

Tests were performed to study the sulfate resistance of heat-cured low-calcium fly ash-based geopolymer concrete. The test specimens were made using Mixture-1 (Table 2) and heat-cured at 60°C for 24 hours after casting; they were immersed in 5% sodium sulfate solution for various periods of exposure up to one year. The sulfate resistance was evaluated based on the change in mass, change in length, and change in compressive strength of the specimens after sulfate exposure. The test specimens were 100x200 mm cylinders for change in mass and change in compressive strength tests and 75x75x285 mm prisms for change in length test [12].

Test results showed that heat-cured low-calcium fly ash-based geopolymer concrete has an excellent resistance to sulfate attack. There was no damage to the surface of test specimens after exposure to sodium sulfate solution up to one year. The visual appearances of the test specimens after soaking in sodium sulfate solution up to one year revealed that there was no change in the appearance of the specimens compared to the condition before they were exposed (Figure 5). There was no sign of surface erosion, cracking or spalling on the specimens. The specimens soaked in tap water also showed no change in the visual appearance. There were no significant changes in the mass and the compressive strength of test specimens after various periods of exposure up to one year. The change in length was extremely small and less than 0.015% [12].

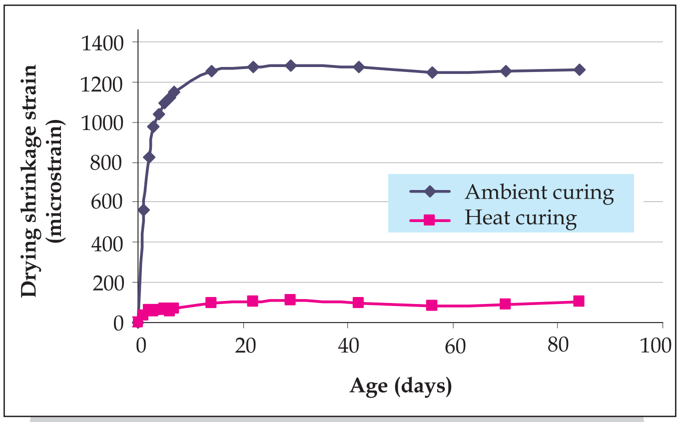


Figure 4. Drying Shrinkage of Heat-cured and Ambient-cured Geopolymer Concrete [12]

The deterioration of Portland cement concrete due to sulfate attack is attributed to the formation of expansive gypsum and ettringite which causes expansion, cracking, and spalling in the concrete. Low-calcium fly ash-based geopolymer concrete undergoes a different mechanism to that of Portland cement concrete and the geopolymerisation products are also different from hydration products. The main product of geopolymerisation is not susceptible to sulfate attack like the hydration products. Because there is generally no gypsum or ettringite formation in the main products of geopolymerisation, there is no mechanism of sulfate attack in heat-cured low-calcium fly ash-based geopolymer concrete. However, presence of high calcium either in the fly ash or in the aggregates could cause the formation of gypsum and ettringite in geopolymer concrete.

9.4. Sulfuric acid resistance

Tests were performed to study the sulfuric acid resistance of heat-cured low-calcium fly ash-based geopolymer concrete. The concentration of sulfuric acid solution was 2%, 1% and 0.5%. The sulfuric acid resistance of geopolymer concrete was evaluated based on the mass loss and the residual compressive strength of the test specimens after acid exposure up to one year. The test specimens, 100x200 mm cylinders, were made using Mixture-1 (Table 2) and heat-cured at 60°C for 24 hours after casting [12].

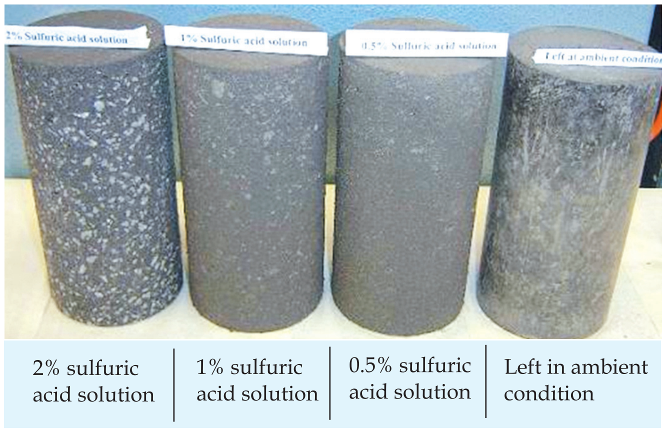
The visual appearance of specimens after exposure to sulfuric acid solution showed that acid attack slightly damaged the surface of the specimens. The damage to the surface of the specimens increased as the concentration of the acid solution increased (Figure 6).

The maximum mass loss of test specimens of about 3% after one year of exposure is relatively small compared to that for Portland cement concrete as reported in other studies. As shown in Figure 7, exposure to sulfuric acid caused degradation in the compressive strength; the extent of degradation depended on the concentration of the acid solution and the period of exposure [12].

The acid resistance of geopolymer concrete must be considered in relation to the performance of Portland cement concrete in a similar environment. Past research data have shown that geopolymeric materials performed significantly better in acid resistance compared to Portland cement [3, 8]. The superior performance of geopolymeric

Soaked in 5% sodium sulfate solution | Soaked in water | Left in ambient condition

Figure 5. Visual Appearance of Heat-cured Geopolymer Concrete Specimens after One Year of Exposure [12]



2% sulfuric acid solution | 1% sulfuric acid solution | 0.5% sulfuric acid solution | Left in ambient condition

Figure 6. Visual Appearance of Heat-cured Geopolymer Concrete after One Year of Exposure in Sulfuric Acid Solution [12]

materials in acidic environment, attributed to the lower calcium content of the source material, can be utilized in applications such as sewer pipes.

10. REINFORCED GEOPOLYMER CONCRETE COLUMNS AND BEAMS

In order to demonstrate the application of heat-cured low-calcium fly ash-based geopolymer concrete, twelve reinforced columns and twelve reinforced beams were manufactured and tested [13].

In the column test program, the primary parameters were longitudinal reinforcement ratio, load eccentricity, and compressive strength of geopolymer concrete. The longitudinal reinforcement ratio was 1.47% and 2.95%. The column cross-section was 175 mm square. The average yield strength of longitudinal steel was 519 MPa. Closed ties made of 6mm diameter hard-drawn wires at 100 mm spacing were used as lateral reinforcement. The concrete cover was 15 mm. The columns were subjected to eccentric compression and bent in single curvature bending. The columns were pin-ended with an effective length of 1684 mm.

The mixture proportions of geopolymer concrete used in the manufacture column specimens are given in Table 4. The average slump of fresh concrete varied between 210 mm and 240 mm. The nominal compressive strength of geopolymer concrete was 40 MPa and 60 MPa. These target compressive strengths were achieved by using the mixtures given in Table 4 and by exploiting the flexibilities of heat-curing regime of geopolymer concrete. Accordingly, in the case of columns with 40 MPa compressive strength (GCI and GCII), the test specimens were steam-cured at a temperature of 60°C for 24 hours after casting; on the other hand, the specimens of 60 MPa compressive strength series (GCIII and GCIV) were kept in laboratory ambient conditions for three days and then steam-cured at a temperature of 60°C for 24 hours.

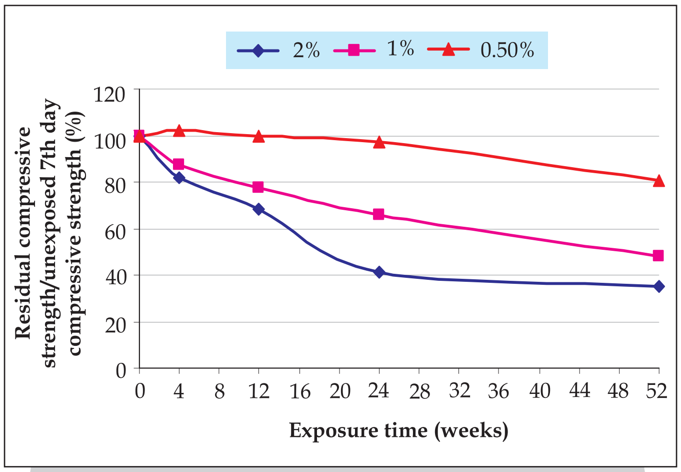


Figure 7. Acid Resistance of Heat-cured Geopolymer Concrete [12]

The mixture proportions of geopolymer concrete used in the manufacture of beam specimens are also given in Table 4. The average slump of the fresh concrete varied from 175 mm for GBIII series to 255 mm for GBI series. The target compressive strength of geopolymer concrete was 40 MPa for GBI series, 50 MPa for GBII series, and 70 MPa for GBIII series. The specimens were kept in laboratory ambient conditions for three days after casting, and then steam-cured at 60°C for 24 hours to achieve the target strengths.

The beam cross-section was 200mm wide by 300mm deep, and 3300mm in length. The test parameters were concrete compressive strength and longitudinal tensile

Table 4. Geopolymer concrete mixture proportions for reinforced columns and beams [13]

Materials	Columns		Beams
	Mass (kg/m^3)		
10mm aggregates	555	550	550
7mm aggregates	647	640	640
Fine sand	647	640	640
Fly ash	408	404	404
Sodium hydroxide solution	41 (16Molar)	41 (14Molar)	41 (14 Molar)
Sodium silicate solution	103	102	102
Super plasticizer	6	6	6
Extra added water	26 (GCI and GCII)	16.5 (GCIII and GCIV)	25.5 (GBI) 17.0 (GBII) 13.5(GBIII)

Figure 8. Failure Mode of Reinforced Geopolymer Concrete Columns [13]

reinforcement ratio. All beams contained two 12mm diameter deformed bars as compression reinforcement, and two-legged vertical stirrups made of 12 mm diameter deformed bars at 150 mm spacing as shear reinforcement. The longitudinal tensile reinforcement ratios were 0.64, 1.18, 1.84, and 2.69%. The average yield strength of tensile steel bars varied between 550 and 560 MPa. The concrete cover was 25 mm. The beams were simply supported over a span of 3000mm, and subjected to two concentrated loads placed symmetrically on the span. The distance between the loads was 1000mm.

The behavior and failure modes of reinforced geopolymer concrete columns were similar to those observed in the case of reinforced Portland cement concrete columns (Figure 8). As expected, the load capacity of columns was influenced by the load-eccentricity, the concrete compressive strength, and the longitudinal reinforcement ratio. When the load eccentricity decreased, the load capacity of columns increased. The load capacity also increased when the compressive strength of concrete and the longitudinal reinforcement ratio increased.

The load-carrying capacity of reinforced geopolymer concrete columns was calculated using both a simplified stability analysis proposed by Rangan [25] and the moment-magnifier method incorporated in the Australian Standard for Concrete Structures AS 3600 and the American Concrete Institute Building Code ACI 318. The calculated failure loads correlated well with the test values. These results demonstrate that the methods of calculations used in the case of reinforced Portland cement concrete columns are applicable for reinforced geopolymer concrete columns.

The behavior and failure mode of reinforced geopolymer concrete beams were similar to those observed in the case of reinforced Portland cement concrete beams (Figure 9). The flexural capacity of beams was influenced by the concrete compressive strength and the tensile reinforcement ratio. The flexural strength of reinforced geopolymer concrete beams was calculated using the conventional flexural strength theory of reinforced concrete beams as described in standards and building codes such as the Australian Standard, AS 3600 and the ACI Building Code, ACI 318 [13] For beams with tensile reinforcement ratio of 1.18%, 1.84%, and 2.69%, the test and calculated values agreed well. In the case of beams with tensile steel ratio of 0.64%, as expected, the calculated values were conservative due to the neglect of the effect of strain hardening of tensile steel bars on the ultimate bending moment.

Mid-span deflection at service load of reinforced geopolymer concrete beams was calculated using the elastic bending theory and the serviceability design provisions given in the Australian Standard, AS 3600. According to AS 3600, the calculation of short-term deflection of reinforced concrete beams should include the effects of cracking, tension stiffening, and shrinkage properties of the concrete. In these calculations, the service load was taken as the test failure load divided by 1.5; measured values of modulus of elasticity and drying shrinkage strain of geopolymer concrete were used. Good correlation of test and calculated deflections at service load was obtained [13].

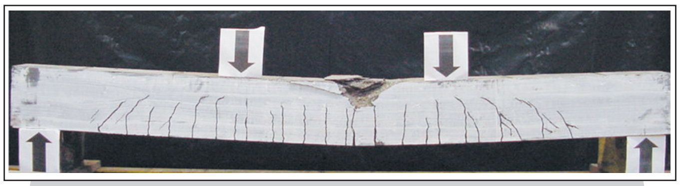


Figure 9. Crack Pattern and Failure Mode of Reinforced Geopolymer Concrete Beam [13]

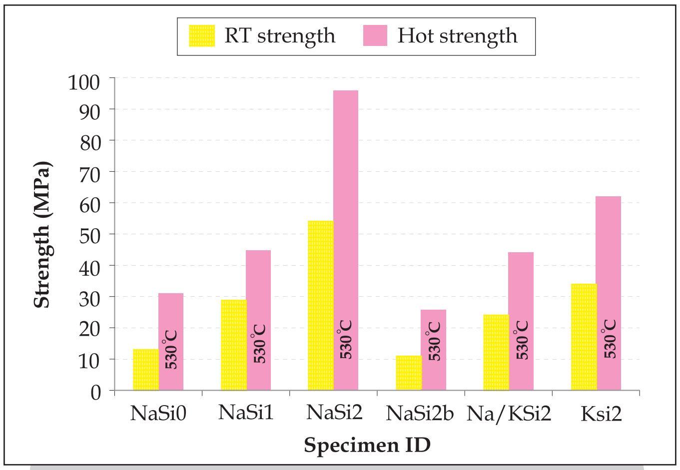


Figure 10. Geopolymer Paste at High Temperature [27]

Chang et al [26] studied the shear and bond strength of reinforced geopolymer concrete beams. The failure modes and crack patterns observed for reinforced geopolymer concrete beams were similar to those reported in the literature for reinforced Portland cement concrete beams. The design provisions contained in the Australian Standard for Concrete Structures AS 3600 and American Concrete Institute Building Code ACI318 are found to give conservative predictions for the shear strength and bond strength of reinforced geopolymer concrete beams; these design provisions are, therefore, applicable to design of reinforced geopolymer concrete beams.

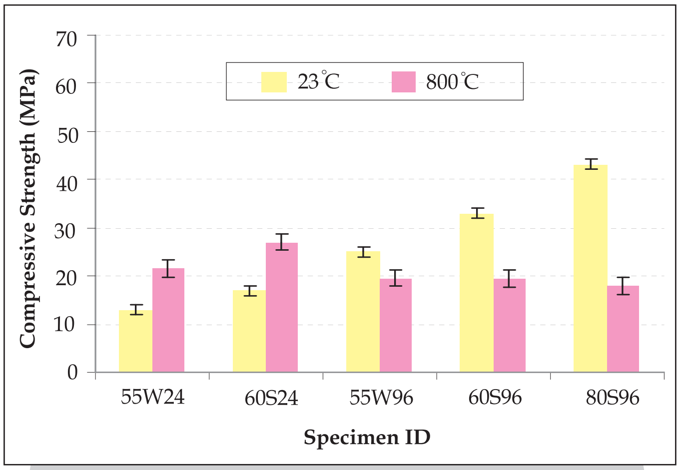


Figure 11. Geopolymer Mortar at High Temperature [27]

In all, the above results demonstrated that reinforced low-calcium (ASTM Class F) fly ash-based geopolymer concrete structural members can be designed using the design provisions currently used in the case of reinforced Portland cement concrete members.

The fire resistance of fly ash-based geopolymers has been studied by Zhu et al [27]. Some test results are shown in Figures 10 and 11. It can be seen that geopolymer paste (i.e. no aggregates) gains strength after exposure to high temperature (Figure 10). Geopolymer mortars (geopolymer + sand) sometimes increase in strength and other times decrease in strength after exposure to elevated temperature of 800 degrees C (Figure 11). The behaviour of the geopolymer mortar appears to be related to two opposing processes in action at high temperature exposures. That is, sintering and/or further geopolymarisation process at high temperature increases the strength, whereas the thermal incompatibility may cause a decrease in strength. In the case of geopolymer mortars with low strength, the loss in strength due to thermal incompatibility may be minimal with the result that there is a gain in strength. On the other hand, in the case of high strength geopolymer mortars, the loss of strength due to thermal incompatibility is larger than the strength gained by the other process, and hence there is an overall strength loss (Figure 11).

Figure 12. Geopolymer Concrete 1500 mm Sewer Pipes [8]

The studies carried out by Sarker, et al [28, 29], and Sofi, et al [30] also demonstrate the application of fly ash-based geopolymer concrete.

11. GEOPOLYMER PRECAST CONCRETE PRODUCTS

High-early strength gain is a characteristic of geopolymer concrete when dry-heat or steam cured, although ambient temperature curing is possible for geopolymer concrete. It has been used to produce precast railway sleepers, sewer pipes, and other prestressed concrete building components. The early-age strength gain is a characteristic that can best be exploited in the precast industry where steam curing or heated bed curing is common practice and is used to maximise the rate of production of elements.

Geopolymer concrete has excellent resistance to chemical attack and shows promise in the use of aggressive environments where the durability of Portland cement concrete may be of concern. This is particularly applicable in aggressive marine environments, environments with high carbon dioxide or sulphate rich soils. Similarly in highly acidic conditions, geopolymer concrete has shown to have superior acid resistance and may be suitable for applications such as mining, some manufacturing industries and sewer systems.

Figure 13. Precast Geopolymer Box Culverts [18,31]

Gourley and Johnson [8] have reported the details of geopolymer precast concrete products on a commercial scale. The products included sewer pipes, railway sleepers, and wall panels. Reinforced geopolymer concrete sewer pipes with diameters in the range from 375 mm to 1800 mm have been manufactured using the facilities currently available to make similar pipes using Portland cement concrete (Figure 12). Tests performed in a simulated aggressive sewer environment have shown that geopolymer concrete sewer pipes outperformed comparable Portland cement concrete pipes by many folds. Gourley and Johnson [8] also reported the good performance of reinforced geopolymer concrete railway sleepers in mainline tracks and excellent resistance of geopolymer mortar wall panels exposed to fire.

Siddiqui [18] and Cheema et al [31] demonstrated the manufacture of reinforced geopolymer concrete culverts on a commercial scale. Reinforced geopolymer concrete box culverts of 1200 mm (length) x600 mm (depth) x1200 mm (width) and compressive cylinders were manufactured in a commercial precast concrete plant located in Perth, Western Australia (Figure 13). The dry materials were mixed for about 3 minutes. The liquid component of the mixture was then added, and the mixing continued for another 4 minutes. The geopolymer concrete was transferred by a kibble into the culvert moulds (one mould for two box culverts). The culverts were compacted on a vibrating table and using a hand -held vibrator. The cylinders were cast in 2 layers with each layer compacted on a vibrating table for 15 seconds. The slump of every batch of fresh geopolymer concrete was also measured in order to observe the consistency of the mixtures.

After casting, the cylinders were covered with plastic bags and placed under the culvert moulds. A plastic cover was placed over the culvert mould and the steam tube was inserted inside the cover. The culverts and the cylinders were steam-cured for 24 hours. Initially, the specimens were steam-cured for about 4 hours; the strength at that stage was adequate for the specimens to be released from the moulds. The culverts and the remaining cylinders were steam-cured for another 20 hours. The operation of the precast plant was such that the 20 hours of steam-curing has to be split into two parts. That is, the steam-curing was shut down at 11 p.m. and restarted at 6 a.m. next day. In all, the total time taken for steam-curing was 24 hours.

Figure 14. Precast Geopolymer Floor Beams [32]

The box culvert made of geopolymer concrete was tested for load bearing strength in a load testing machine which had a capacity of 370 kN and operated to Australian Standards, AS 1597.1-1974. The culvert was positioned with the legs firmly inside the channel supports. Load was then applied and increased continuously so that the proof load of 125 kN was reached in 5 minutes. After the application of the proof load, the culvert was examined for cracks using a crack-measuring gauge. The measured width of cracks did not exceed 0.08 mm. The load was then increased to 220 kN and a crack of width 0.15 mm appeared underside the crown. As the load increased to about 300 kN, a crack of 0.4 mm width appeared in the leg of the culvert. The load was then released to examine to see whether all cracks had closed. No crack was observed after the removal of the load.

According to Australian Standard AS 1597, a reinforced concrete culvert should carry the proof load without developing a crack greater than 0.15 mm and on removal of the load; no crack should be greater than 0.08 mm. The tests demonstrated that geopolymer concrete box culvert met these requirements.

Thirty-three reinforced geopolymer concrete precast beams (Figure 14) have been used in the construction of The University of Queensland's Global Change

Institute building in Australia. The details are reported in References 32 and 33. The geopolymer concrete mixture comprised both fly ash and ground blast furnace slag as the source materials. The geopolymer floor panels experienced low shrinkage, low heat of reaction which avoids the possibility of thermal cracking, 30 per cent higher flexural tensile strength, and higher durability than similar Portland cement concrete. The proprietary geopolymer concrete used in the building proved to fully compliant with the structural performance parameters specified in the current Australian Standard for Concrete Structures. Geopolymer concrete is also being used in a new regional airport in southeast Queensland, Australia [34]. The airport's concrete pavements have a flexural strength specification of 4.8 MPa and typical depths will be 400-450 mm.

Andrews-Phaedonos and Ahmad Shayan [35,36] presented several trial applications of geopolymer concrete by VicRoads Australia; these include geoplymer precast footway panels and in-situ geopolymer concrete landscape retaining walls. Other applications and use of geopolymer concrete are contained in the Recommended Practice Note on Geopolymer Concrete published by the Concrete Institute of Australia [37]. Recently, Berndt et al [38] commented that geopolymer concrete is ready for applications in precast industry.

12. ECONOMIC BENEFITS OF GEOPOLYMER CONCRETE

Geopolymer concrete offers several economic benefits over Portland cement concrete. The cost of one ton of fly ash or blast furnace slag is only a small fraction of the cost of one ton of Portland cement. Therefore, after allowing for the cost of alkaline liquids needed to the make the geopolymer concrete, geopolymer concrete is cost effective against Portland cement concrete that ned to be of a similar performance level.

In addition, geopolymer concrete is a low-carbon alternative to Portland cement concrete. For instance, the appropriate usage of one ton of fly ash earns approximately one carbon-credit that has a redemption value. Based on the information given in this paper, one ton low-calcium fly ash can be utilized to manufacture approximately three cubic meters of high quality fly ash-based geopolymer concrete, and hence earn monetary benefits through carbon-credit trade.

Furthermore, the low drying shrinkage, the low creep, the excellent resistance to sulfate attack, good acid resistance, and excellent fire resistance offered by geopolymer concrete may yield additional economic benefits when it is utilized in infrastructure applications.

13. CONCLUDING REMARKS

Geopolymer concrete offers environmental protection by means of upcycling low-calcium fly ash and blast furnace slag, waste/by-products from the industries, into a high-value construction material needed for infrastructure developments. The paper presented information on fly ash-based geopolymer concrete. Low-calcium fly ash (ASTM Class F) is used as the source material, instead of the Portland cement, to make concrete.

Geopolymer concrete has excellent compressive strength and is suitable for structural applications. The salient factors that influence the properties of the fresh concrete and the hardened concrete have been identified. Simple guidelines for the design of mixture proportions are included.

The elastic properties of hardened geopolymer concrete and the behavior and strength of reinforced geopolymer concrete structural members are similar to those observed in the case of Portland cement concrete. Therefore, the design provisions contained in the current standards and codes can be used to design reinforced geopolymer concrete structural members.

Heat-cured low-calcium fly ash-based geopolymer concrete also shows excellent resistance to sulfate attack and fire, good acid resistance, undergoes low creep, and suffers very little drying shrinkage. Some applications of geopolymers have also been included. The paper has identified several economic benefits of using geopolymer concrete.

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