

Upcycling Fly Ash into Geopolymer Concrete Products

B. VIJAYA RANGAN

Department of Civil Engineering, Curtin University, Perth, Australia
Email: V.Rangan@curtin.edu.au

Abstract: Recycling is turning a by-product source material to a low-cost usable material. On the other hand, the term *upcycling* refers to a process of using a low-cost by-product source material (such as low-calcium fly ash) to produce a material (geopolymer concrete) that is of higher value than the source material. Extensive studies have been conducted on fly ash-based geopolymer concrete; the results of these studies have been reported in the literature. This paper focuses on some recent applications of geopolymer concrete in the precast construction.

Keywords: Fly Ash, Geopolymer, Concrete, Upcycling

Introduction:

Davidovits (1, 2) 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 low-calcium fly 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.

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 aluminum (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 and combination 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.

Water is released during the chemical reaction that occurs in the formation of geopolymers. This water, expelled from the geopolymer matrix during the curing and further drying periods, leaves behind nanopores in the matrix, which provide benefits to the performance of geopolymers. When a small proportion of calcium-rich source material such as slag is included in the source material in order to accelerate the setting time and to alter the curing regime adopted for the geopolymer mixture, the water released during the geopolymerisation reacts with the calcium present to produce hydration products. According to Davidovits (1), 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 (1) 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).

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. 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 fly ash.

Table 1: Applications of Geopolymeric Materials Based on Silica-to-Alumina Atomic Ratio (1)

S. No	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 aluminum
20 - 35	- Fire resistant and heat resistant fiber composites

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 particle size distribution tests revealed that 80% of the fly ash particles were smaller than 50 μm (3-10).

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 (3-10).

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 by mixing both the solutions together at least 24 hours prior to use. The sodium silicate solution is commercially available in different grades. 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 solutions are adequate for most applications. 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 slag may be added to the mixture. When required, a high range water reducer super plasticizer and extra water may also be added to the mixture.

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 aggregates must be prepared to be in saturated-surface-dry (SSD) condition, a state in which the aggregates will not absorb any further moisture but no surface water is present. In geopolymer concrete, the necessity for SSD is to eliminate the absorption of the alkaline solution by the aggregates thus reducing the polymerization of the fly ash. Conversely the presence of excessive water may compromise the properties of the geopolymer concrete.

Design of Geopolymer Concrete

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. In order to meet the performance criteria, the alkaline liquid-to-fly ash ratio by mass, the wet-mixing time, the heat-curing temperature, and the heat-curing time may be selected as parameters.

With regard to alkaline liquid-to-fly ash ratio by mass, values in the range of 0.30 and 0.45 are recommended. Sodium silicate solution is cheaper than sodium hydroxide solids. Geopolymer concrete mixtures can be designed using the data given in the literature (3-17).

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. This base trial mixture is rich and stiff, and can be modified to suit the required design requirements and the local materials. The expected 28-day compressive strength may be in the range of 30 to 40 MPa.

The geopolymer concrete can be cured at room temperature (21 degree C) or at ambient temperature in tropical climate (30-40 degree C). For precast concrete products, heat-curing at 60-80 degree C is suitable.

Prior to use, both the short-term and the long-term properties of geopolymer concrete must be established in order to meet the design requirements. Extensive information is available in the literature (3-17). It has been demonstrated that the behavior and the strength of reinforced geopolymer concrete structural members are similar to those of reinforced Portland cement concrete, and that the geopolymer concrete members can be designed using the design methods currently used in practice (7-17).

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 maximize 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.

Gourley and Johnson (3, 4) 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 (Fig 1). 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 (3, 4) 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 (12) and Cheema et al (18) 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 (Fig 2). 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.



Figure 1: Geopolymer Concrete 1500 mm Sewer Pipes (3, 4)

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.

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.



Figure 2: Precast Geopolymer Box Culverts (12, 18)

Thirty-three reinforced geopolymer concrete precast beams (Fig 3) have been used in the construction of The University of Queensland's Global Change Institute building in Australia. The details are reported in References 19 and 20. 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 (21). The airport's concrete pavements have a flexural strength specification of 4.8 MPa and typical depths will be 400-450 mm.



Figure 3: Precast Geopolymer Floor Beams (19, 20)

Andrews-Phaedonos and Ahmad Shayan (22, 23) presented several trial applications of geopolymer concrete by VicRoads Australia; these include geopolymer 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 (24). Recently, Berndt et al (25) commented that geopolymer concrete is ready for applications in precast industry.

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 make the geopolymer concrete, geopolymer concrete is cost effective against Portland cement concrete that need 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.

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.

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, and guidelines for the design of mixture proportions are available.

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 geopolymer concrete are given. The paper has identified several economic benefits of using geopolymer concrete.

References:

- [1] Davidovits, J, "High-Alkali Cements for 21st Century Concretes. in Concrete Technology, Past, Present and Future", Proceedings of V. Mohan Malhotra Symposium, Editor: P. Kumar Metha, ACI SP- 144, 1994, pp.383-397.
- [2] Davidovits, J, "Soft Mineralogy and Geopolymers", Proceedings of the of Geopolymer 88 International Conference, the Université de Technologie, Compiègne, France, 1988.
- [3] Gourley, J. T., "Geopolymers; Opportunities for Environmentally Friendly Construction Materials", Paper presented at the Materials 2003 Conference: Adaptive Materials for a Modern Society, Sydney, 2003.
- [4] Gourley, J. T., & Johnson, G. B., "Developments in Geopolymer Precast Concrete", Paper

- presented at the International Workshop on Geopolymers and Geopolymer Concrete, Perth, Australia, 2005.
- [5] Hardjito, D. and Rangan, B. V., Development and Properties of Low-Calcium Fly Ash-based Geopolymer Concrete, Research Report GC1, Faculty of Engineering, Curtin University of Technology, Perth, 2005 available at espace@curtin or www.geopolymer.org.
- [6] Wallah, S.E. and Rangan, B.V., Low-Calcium Fly Ash-Based Geopolymer Concrete: Long-Term Properties, Research Report GC2, Faculty of Engineering, Curtin University of Technology, Perth, 2006, available at espace@curtin or www.geopolymer.org.
- [7] Sumajouw, M.D.J. and Rangan, B.V. , Low-Calcium Fly Ash-Based Geopolymer Concrete: Reinforced Beams and Columns, Research Report GC3, Faculty of Engineering, Curtin University of Technology, Perth, 2006, available at espace@curtin or www.geopolymer.org.
- [8] Rangan, B.V. “Low-Calcium Fly Ash-based Geopolymer Concrete”, Chapter 26 in Concrete Construction Engineering Handbook, Editor-in-Chief: E.G. Nawy, Second Edition, CRC Press, New York, 2008.
- [9] Rangan, B.V., “Engineering Properties of Geopolymer Concrete”, Chapter 11 in Geopolymers: Structures, Processing, Properties, and Applications, Editors: J.Provis and J. van Deventer, Woodhead Publishing Limited, London, 2009.
- [10] Rangan, B.V., “Geopolymer Concrete for Environmental Protection”, The Indian Concrete Journal, Vol.88, No.4, April 2014.
- [11] Sofi M, van Deventer J S J, Mendis P A and Lukey G C , “Engineering Properties of Inorganic Polymer Concretes (IPCs)”, Cement and Concrete Research, 37(2), 2007, pp.251-257.
- [12] Siddiqui, K.S.,”Strength and Durability of Low-Calcium Fly Ash-based Geopolymer Concrete”, Final Year Honours Dissertation, The University of Western Australia, Perth, 2007.
- [13] Anuradha, R., Sreevidya, V., Venkatasubramai, R., and Rangan, B. V.,“Relationship between compressive and splitting tensile strength of geopolymer concrete”, The Indian Concrete Journal, 85(11), November 2011, pp. 18- 24.
- [14] Lee W K W and van Deventer J S J, “The Interface between Natural Siliceous Aggregates and Geopolymers”, Cement and Concrete Research, 34(2), 2004, pp. 195-206.
- [15] Chang, E. H. , Sarker, P, Lloyd, N and Rangan, B.V., “Shear behaviour of reinforced fly ash-based geopolymer concrete beams”, Proceedings of the 23rd Biennial Conference of the Concrete Institute of Australia, Adelaide, Australia, 2007, pp 679 – 688.
- [16] Sarker P.K., and deMeillon T, “Residual Strength of Geopolymer Concrete After Exposure to High Temperature”, Proceedings of Recent Developments in Structural Engineering, Mechanics and Computation, CD ROM, Editor: A. Zingoni, Millpress, the Netherlands, 2007, pp.1566-1571.
- [17] Sofi M, van Deventer J S J, Mendis P A and Lukey G C , “Bond Performance of Reinforcing Bars in Inorganic Polymer Concrete (IPC)”, Journal of Materials Science, 42(9), 2007, pp.3007-3016.
- [18] Cheema, D.S., Lloyd, N.A., Rangan, B.V., “Durability of Geopolymer Concrete Box Culverts- A Green Alternative”, Proceedings of the 34th Conference on Our World in Concrete and Structures, Singapore, 2009.
- [19] Concrete in Australia, “Geopolymer Concrete for Construction”, News, Vol 39, Issue No 4, December, 2013, pp 4-5.
- [20] Bligh R and Glasby T, “Development of Geopolymer Precast Floor Panels for the Global Institute at the University of Queensland”, Concrete in Australia, Vol 40, Issue 1, March 2014, pp. 39-43.
- [21] Concrete in Australia, “World First Earth-friendly Concrete Airport”, News, Vol 40, Issue 1, March 2014, pp.7-8.
- [22] Andrews-Phaedonos, F., “Reducing the carbon footprint- VicRoads experience” Concrete in Australia, 38(1), March 2012 , pp. 40-48.
- [23] Ahmad Shayan, Amin Xu, Andrews-Phaedonos, F., “Field applications of geopolymer concrete: a measure towards reducing carbon dioxide emission “Concrete in Australia, Vol.39, No.3, 2013, pp.34-44.
- [24] Concrete Institute of Australia, “Geopolymer Recommended Practice Note” CIA Z16-2011, 37 pp.
- [25] Berndt, Marita L., Sanjayan, Jay, Foster, Stephen, Sagoe-Crentsil, Kwesi, and Heidrich, Craig, “Overcoming barriers to implementation of geopolymer concrete” Concrete in Australia, Vol.39, No.3, 2013, pp.27-33.