Geopolymer Concrete—Sustainable Cementless Concrete

by N. Lloyd and V. Rangan

Synopsis: Geopolymer is a specialized material resulting from the reaction of a source material that is rich in silica and alumina with alkaline solution. It is essentially portland cement free concrete. This material is being studied extensively and shows promise as a greener alternative to normal portland cement concrete. It has been found that geopolymer concrete has good engineering properties with a reduced carbon footprint resulting from the total replacement of normal portland cement.

The research undertaken at Curtin University of Technology has included studies on geopolymer concrete mixture proportions, structural behavior, and durability. This paper presents the results on mixture proportions development to enhance workability and strength of geopolymer concrete. The influence of factors such as: curing temperature and régime, aggregate shape, strength, moisture content, preparation and grading, and the addition of superplasticizers, on workability and strength are presented.

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INTRODUCTION

Use of concrete and environment impact

Utilization of concrete as a major construction material is a worldwide phenomenon and the concrete industry is the largest user of natural resources in the world.[1] This use of concrete is driving the massive global production of cement, estimated at over 2.8 billion tonnes according to recent industry data.[2] Associated with this is the inevitable carbon dioxide emissions estimated to be responsible for 5 to 7% of the total global production of carbon dioxide.[3] Significant increases in cement production have been observed and were anticipated to increase due to the massive increase in infrastructure and industrialization in India, China, and South America.[4] A recent report to the United Nations Industrial Development Organization highlighted that as of 2005, 60% of China's cement production was from Vertical Shaft Kilns (VSKs); characterized by low production efficiency, high energy consumption and heavy environmental pollution.[5] The VSKs generally produced low quality cement unsuitable for large structures, infrastructure, or export. It was estimated that the Chinese cement industry emitted more than 13.2 million tonnes (14.6 million tons) of dust, about 27% of all emissions from the nations industry, about 22% of all CO_2 emissions, and about 4.85% of all SO_2 emissions in 2003.

The emission of carbon dioxide in the production of cement is due to clinker production, combustion of fuels in the cement kilns, and the use of energy for grinding raw material and clinker. Recent German emissions data indicate that the carbon dioxide emission due to German cement production are of the order 600 kg of carbon dioxide per tonne (1343 pounds per ton) of cement of which around 400 kg per tonne (896 pounds per ton) of cement is originated from the raw material induced carbon dioxide emission caused by the calcination of limestone.[6] Further, the initiatives which can be exploited to reduce green house gas emissions by the cement industry are: substitution of clinker by secondary materials, substitution of fossil fuels by secondary fuels, and improved kiln efficiency. The most effective strategy appears to be the substitution of clinker and substitution of fossil fuels. The use of secondary fuels has increased dramatically to a level of over 50% use in kilns in 2007 and the clinker factor for German portland cement is already below 75%. The option of reduction of carbon dioxide emission through

improved kiln efficiency is limited as 92% of cement production is a result of kilns with cyclone pre-heaters, which means the energy consumption of kilns is already close to the theoretical limit.[6]

The worldwide concern and governance on carbon dioxide emissions has prompted research into the partial replacement of cement with supplementary cementitious materials such as fly ash and slag. Abundant research has been conducted on the fresh and hardened properties of concrete with partial replacement of cement by these materials and their use has been adopted in many construction solutions as they provide viable means of reducing the carbon footprint of concrete.[7] The use of greener concrete by the partial replacement of cement is increasing. A recent post-tensioned structure had concrete with 50% replacement of cement by slag for the slabs, columns, and walls; and 70% replacement in the mat foundation, resulting in an estimated reduction on carbon dioxide emissions for the project of 4500 tonnes (4400 tons).[8]

The research into the mechanical properties of concrete with partial replacement of cement by fly ash and slag is extensive. Researchers have examined the durability and mechanical properties of concrete with partial replacement of cement by fly ash.[9, 10] High volume replacement of cement with fly ash has been shown to produce high strength and high durability concrete.[11]

In the final stages of development, a sustainability rating scheme for infrastructure is likely to be finalized in 2010 in Australia and a scheme for the evaluation of industrial operations is being developed. The infrastructure rating scheme will complement the present Green Star environmental rating scheme for building which was launched in 2003 and is operated by the Green Building Council of Australia. The Australian Governments' Carbon Pollution Reduction Scheme issued in December 2008 outlines the final design of the carbon pollution reduction scheme and the medium-term target range for reducing carbon pollution. The scheme will place a price on carbon and employs a cap and trade emission trading mechanism to limit carbon pollution. The impact for the cement industry may be somewhat mitigated by eligibility for assistance at 90% rate for the clinker industry which is identified as an emissions-intensive trade-exposed industry. In Australia, a relative minor producer in terms of global standards, cement production was responsible for approximately 3.5 million tonnes (3.4 million tons) of carbon dioxide emissions in 2001 and over 5.6 million tonnes (5.5 million tons) in 2005.[12]

Geopolymer concrete development

Geopolymer concrete is concrete which does not utilize any portland cement in its production. Rather, the binder is an alkali activated alumino-silicate. Geopolymers were developed as a result of research into heat resistant materials after a series of catastrophic fires.[13] The research yielded non-flammable and non-combustible geopolymer resins and binders.

Geopolymer is a material resulting from the reaction of a source material that is rich in silica and alumina with alkaline solution. It is essentially portland cement free concrete. This material is being studied extensively and shows promise as a greener alternative to normal portland cement concrete. Research is shifting from the chemistry domain to engineering applications and commercial production of geopolymer. It has

been found that geopolymer concrete has good engineering properties with a reduced carbon footprint resulting from the total replacement of portland cement.[14]

The use of fly ash has additional environment advantages. The annual production of fly ash in Australia in 2007 was approximately 14.5 million tonnes (14 million tons) of which only 2.3 million tonnes (2.2 million tones) were utilized in beneficial ways; principally for the partial replacement of portland cement.[15] Development of geopolymer technology and applications would see a further increase in the beneficial use as ash, similar to what has been observed in the last 14 years with the use of fly ash in concrete and other building materials.

Geopolymer concrete properties

High-early strength gain is a characteristic of geopolymer concrete when heat or steam cured, although ambient temperature curing is possible for geopolymer concrete.[16] It has been used to produce precast railway sleepers and other prestressed 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. Recently geopolymer concrete has been tried in the production of precast box culverts with successful production in a commercial precast yard with steam curing.

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. Commercial geopolymer sewer pipes are in use today. Current research at Curtin University of Technology examines the durability of precast box culverts manufactured from geopolymer concrete which are exposed to a highly aggressive environment with wet-dry cycling in sulphate rich soils.

The bond characteristics of reinforcing bar in geopolymer concrete have been researched and determined to be comparable or superior to normal portland cement concrete.[17,18]

The mechanical properties offered by geopolymer suggest its use in structural applications is beneficial from an enhanced durability and fire resistance perspective. Its high strength gain at elevated curing temperatures lends geopolymer concrete to precast structural applications and the possibility of prestressed application is one which is being explored with the development of suitable mixture proportions and curing regimes. This paper outlines a series of trial mixtures which were prepared with the view to develop prestressed geopolymer beams. Although the outcome of the pre-stressing trials was not all positive, the trials yielded valuable information of the fresh and hardened properties of geopolymer concrete and mixture proportions issues which require addressing.

TEST PROGRAM MATERIALS

Fly ash

The fly ash used in the production of geopolymer concrete at Curtin University is

Class F fly ash sourced from the coal fired power station approximately 200 km (124 miles) south of Perth, Western Australia. The results of X-ray fluorescence testing (XRF) are shown in Table 1 for the fly ash used in the research program. The Class F fly ash is characterized by high silicon and aluminum contents and low calcium content, and a loss on ignition of 0.46.

Alkaline liquids

Sodium based alkaline liquids were used to activate the fly ash polymerization. Sodium-silicate solution type A53 was used for the concrete production. The chemical composition is shown in Table 2. Sodium hydroxide solution was prepared by dissolving sodium hydroxide pellets in water. The pellets are commercial grade with 97% purity; thus 14 molar solutions were made by dissolving 404 grams (14 ounces) of sodium hydroxide pellets in 596 grams (21 ounces) of water.

The sodium hydroxide pellets were prepared one to two days prior to the concrete batching to allow the exothermically heated liquid to cool to room temperature. The sodium silicate and sodium hydroxide were mixed just prior to the concrete batching. This was a different process than had been employed previously at Curtin University where the two alkaline liquids were mixed 24 hour prior to casting. A number of alkaline liquids when combined were observed to harden upon mixing making them unusable. Subsequently, the two alkaline liquids were mixed together only on the day of casting and stored in a sealed container until required.

Basic mixture proportions

The basic mixture proportions used for the majority of the trial mixtures was based upon previous research on the geopolymer mixture proportions and is detailed in Table 3.[19] These mixture proportions are characterized by an alkaline liquid to fly ash by mass of 0.35 and aggregate to total mass proportion of approximately 75% with the nominal strengths, as shown in Table 3, for curing with three rest days and elevated temperature curing at 60°C (140°F) for 24 hours . Modifications to the basic mixture proportions were used to assess the impact of different variables, especially aggregate grading and type, and superplasticizer as detailed in later sections of this article.

Aggregates

Coarse aggregates with nominal sizes of 7, 10 and 20 mm (approximately 1/4, 3/8, and 3/4 in.) granite and dolerite, were sourced from two local quarries. The aggregates had a particle density of 2.6 tonnes/cubic metre (162 lb/ft³) for the granite and 2.63 tonnes/ cubic metre (164 lb/ft³) for the dolerite. The dolerite aggregate was used in one series of trial mixtures to assess the impact of aggregate type on workability and strength gain of the geopolymer concrete. Fine sand was sourced from a local supplier. The sand has a low clay content (less than 4%) and fineness modulus of 1.99. The grading curves were within the limits of BS 882:92 (and AS 2758.1) as shown in Fig. 1. While the grading curves were changed to assess the impact of grading on workability, the majority of the mixture proportions used a maximum aggregate sixe of 20 mm (3/4 in.) and grading curve as shown in Fig. 1.

Previous geopolymer research had been performed with aggregates being prepared to surface saturated dry (SSD) condition, a state of aggregate saturation in which the

aggregate will not absorb any further moisture but no surface water is present (Australian Standards AS 1141.5-2000 and AS 1141.6-2000). In geopolymer concrete the necessity for SSD was due 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 compressive strength of the geopolymer concrete. The preparation of aggregate to surface saturated dry condition is achieved by soaking the aggregate in water for 24 hours, draining, and air drying on trays to remove surface moisture. Preparation of significant quantities of aggregate is time consuming (4 to 7 days) and inconsistent with commercial production techniques.

The actual moisture content of aggregates prepared to SSD condition was tested with the view to replacing SSD aggregates with aggregates sourced from stock piles with variable moisture contents. The results of moisture content determination on aggregates prepared to surface saturated dry condition are shown in Table 4. The total quantity of free water was adjusted in the mixture by the addition or reduction of added water to the mixture; in winter when the aggregate stockpiles were typically saturated, the aggregates were left to dry in the laboratory for up to three days prior to casting. This technique was used for most of the trial mixtures described in this paper, unless otherwise noted.

Superplasticizers

Seven different superplasticizers which were readily available commercially were used at two different dosages: the manufacturers' recommended dose and twice the recommended dose (apart from the RH superplasticizer which was added at the typical dose used in previous geopolymer research as per Table 3). The superplasticizers were added to the mixture after the addition of the alkali liquids and mixed for at least three minutes to obtain full dispersion throughout the concrete. The superplasticizers used were:

RH: Based on sodium naphthalene formaldehyde sulphonate. Used for previous geopolymer research.

SN: High-range water reducer, based on sodium naphthalene formaldehyde sulphonate.

VC10: High-range water reducer/retarder utilizing modified polycarboxylates.

VC16: High-range water reducer based on modified polycarboxylates.

VC305: Polycarboxylates polymer admixture.

G27:   Polycarboxylic ether hyper plasticizer.

GA30: Superplasticizer, based on polycarboxylic ether polymers.

DISCUSSION OF RESULTS

Fresh concrete tests

The slump test was used to assess workability of the geopolymer mixtures as described in AS 1012.3-1988. In addition, some mixtures were assessed using the compacting factor test AS 1012.3-1988.

Hardened concrete tests

Hardened properties of the geopolymer concrete that were assessed were the compressive strength using 100 mm (3.9 in.) diameter by 200 mm (7.9 in.) high

cylinders consistent with AS 1012.9-1999, and indirect tensile strength using 150 mm diameter (5.9 in.) by 300 mm (11.8 in.) cylinders for the Brazilian or splitting tensile test consistent with AS 1012.10-2000.

Aggregate tests

Tests were performed on some of the aggregates. These were the aggregate crushing value AS 1141.21-1997, flakiness index AS 1141.5 – 1999, particle size distribution and moisture content. The results of the aggregate testing are shown in Table 5.

Curing temperature: Steam room and specimen temperature

Thermocouples were placed in three different sized samples during one of the geopolymer concrete trials to measure the actual temperatures reached inside the concrete samples; a small compression cylinder, a large tension cylinder, and a compaction beam; a small beam 350 mm long by 85 mm square (13.8 in. long by 3.4 in. square). Thermocouples to control the steam were located 200 mm (7.9 in.) above the steam room floor within the enclosed steam tent consistent with earlier research.[14,16,19] The steam curing regime was notionally 80°C (176°F) for 24 hours. Figure 2 shows the results of the Nicolet data logger readings taken at 10 second intervals in these samples over the curing period.

The ambient temperature in the concrete lab was recorded as a control, indicating temperatures outside the steam room were about 17 to 20°C (62 to 68°F). The thermo-couple readings inside the compression, tensile, and compaction beam samples in the steam tent were around 50 to 70°C (122 to 158°F). The variations in temperature correspond to the to the boiler system cutting in and out to achieve an approximately constant temperature in the steam tent of 80°C (176°F).

As can be seen from the Fig. 2, although the steam tent thermocouple was set at 80°C (176°F), the average temperature in the samples was only around 60°C (140°F). This is the same as the minimum steam room temperature found to be optimum for steam curing of geopolymer concrete.[16]

Comparing the different sample sizes; the compression sample reached the highest temperature, at a maximum of 71°C (160°F) and varied around an average of 64°C (147°F). This was followed by the compaction beam around 60°C (140°F), and finally the tensile sample around 53°C (127°F).

In another phase of the research, a thermocouple was placed into a 250 x 100 x 3600 mm (9.8 x 3.9 x 142 in.) pre-stressed beam specimen and monitored. The temperature in the beam was recorded at 68.7 °C (156 °F), 1.5 hours after commencing curing, to 70.5°C (159°F) just prior to turning off the boiler. This rate of increase was faster than both the tensile cylinder and compaction beam, while the final temperature was higher than any of the smaller specimens. The temperature data refutes a previous suggestion that the additional thermal mass of the pre-stressing frame may reduce curing temperatures inside the prestressed beams resulting in lower strength compared to the standard cylinders.

Effect of rest period on compressive strength gain

A trial mixture of geopolymer concrete using the mixture proportions shown in

Table 6 was produced to examine the impact of delayed steam curing (rest period) on the strength gain of the geopolymer concrete. The trial mixtures had 75% aggregate by mass consisting of 20 and 7 mm (3/4 and 1/4 in.) coarse aggregate and fine sand, and varying quantities of added water as shown in Table 7 consistent with the nominal mixture proportions of previous research shown in Table 3, however , using a larger maximum aggregate size. All mixtures were cured at 80 °C (176 °F) for 24 hours with or without a 24 hour delay or rest day before curing.

The compressive strength data at 28 days is shown in Fig. 3. It can be seen that the inclusion of a 24 hour period before curing, or rest day, increased the compressive strength of all the mixtures. The compressive strength for Mixture 1 with no rest day was 37.5 MPa (5400 psi), while 1 rest day increased this value to 46.4 MPa (6700 psi). Mixtures 2 and 3 achieved compressive strengths of 55.8 MPa (8100 psi) and 63.1 MPa (9200 psi) with 1 rest day. Mixture 3 had the least amount of air voids and superior compaction, due to the high slump and increased workability, as shown in Fig. 4 which shows images of the split cylinder tests for each mixture.

Effect of aggregate grading and type on strength and workability
Four trial mixtures were used to asses the influence of the proportion of fines on the plastic and hardened properties of the geopolymer concrete. The mixtures used a maximum aggregate size of either 10 mm (3/8 in.) granite or 20 mm (3/4 in.) dolerite as shown in Table 7, the basic mixture was derived from the nominal 40 MPa (6000 psi) mixture shown in Table 3, all mixtures were cured at 60 °C (140 °F) for 24 hours.

Comparison of the three mixtures cast with granite with a maximum aggregate size of 10 mm (3/8 in.) found that the decrease in fines from 35% (1:granite:10) to 27% (3:granite:10) of the total aggregate mass resulted in an increase of slump of less than 10% and an increase in the compaction factor of less than 5% (from 0.93 to 0.97). No segregation of the mixture was evident with the low fines percentage however there was a reduction in the compressive strength.

The impact of the angularity of the aggregate on workability was assessed by comparing the four trial mixtures in Table 7. Normal portland cement concrete exhibits a less workable and less compactable mixture with an increase in the angularity of the aggregates. Mixture 1: granite: 10 and 2: granite: 10 contain the same proportion of 7 mm (1/4 in.) aggregate, whilst the two mixtures 3: granite: 10 and 8: dolerite: 20 contain progressively less of the 7 mm (1/4 in.) aggregate. The mixtures displayed increasing slump and compaction factor with decreased 7 mm (1/4 in.) angular aggregate content consistent with normal portland cement concrete.

Density
The geopolymer mixtures tried with different aggregate types and grading were used to assess density at 28 days for mixtures which were cured for 24 hours at 60°C (140°F). The density of the geopolymer concrete was 2360±60 kg/m³ (147±4 lb/ft³).

Strength gain with age
From the compressive strength tests of 13 geopolymer mixtures data was obtained on compressive strength gain with age by testing compressive strength at ages of

1 day, 3 days, 7 days, 14 days and 28 days for mixtures which were cured for 24 hours at 60 °C (140 °F) (in one instance for 36 hours). Compressive strength values at 28 days ranged from 20 MPa to 50 MPa (3000 to 7300 psi). A variety of aggregate types and were used. The mixtures were based on the mixture proportions of Table 3. The ratio of compressive strength at different ages to the compressive strength at 28 days was

$$f_{cm.1\,day} = 0.82 \pm 0.07\, f_{cm.28\,days}$$
$$f_{cm.3\,days} = 0.87 \pm 0.05\, f_{cm.28\,days}$$
$$f_{cm.7\,days} = 0.92 \pm 0.03\, f_{cm.28\,days}$$
$$f_{cm.14\,days} = 0.97 \pm 0.04\, f_{cm.28\,days}$$

The strength gain with age was relatively consistent for all thirteen mixtures; three typical strength gains with age curves are shown in Fig. 5 for mixtures described in Table 7.

Relationship between tensile and compressive strength

From the data bank of compressive, tensile and elastic modulus tests from 2007-2008 undergraduate students a total for 41 values for compressive strength and tensile strength were obtained. Compressive strength values ranged from 19 to 63 MPa (2800 to 9000 psi). A variety of aggregate types and grading were used. The mixtures were based on the mixture proportions of Table 3, curing regimes varied with no rest day or one rest day and temperature was 60 or 80 °C (140 to 176 °F) in the steam room. The relationship between the compressive strength and tensile strength was

$$f_{ct} = 0.6 \pm 0.1\sqrt{f_{cm}}$$

Influence of superplasticizers on workability

The influence of superplasticizer addition into the geopolymer mixture was conducted using seven different superplasticizers most with 2 different dose rates (only one superplasticizer, RH, which had been used for all previous geopolymer research was used at the usual dosage rate). Hence, 13 different mixtures were cast and slump and 2 day compressive strength determined for each. Each mixture had the same aggregates, grading curve and curing regime of 24 hour as 80 °C (176 °F) after one rest day base upon the mixture proportions of Mixture 2 as shown in Table 6.

Unfortunately, the added water content was not adjusted to account for the addition of extra liquid of the superplasticizer thus the water plus superplasticizer volume to fly ash mass ratio was not constant for the 13 mixtures. However, comparison can be made by normalizing the slump values with respect to water (water plus superplasticizer volume) to fly ash mass ratio. Then, assessment was made of the compressive strength with respect to water (water plus superplasticizer volume) to fly ash mass ratio. In this way a ranking system of the superplasticizer types and dosage rates was applied to the different concrete mixtures; the superplasticizer which resulted in the best (largest) slump with respect to water to fly ash ratio was given a rank of 1, in this case Mixture 10. The superplasticizer which resulted in the best (highest) strength divided by water to fly ash ratio was given a rank of 1, in this case Mixture 17. The mixture rankings are shown

in Table 8.

The most effective superplasticizers and dosages were, when considering the combined rankings of both high slump and high compressive strength, with respect to water plus superplasticizer to fly ash ratio, were all superplasticizers dosed at the manufacturers recommended dose rates. The best performers were superplasticizers; GA30:1 (Mixture 10) and VC16-1 (Mixture 17) then the next two best were G27-1 (Mixture 8) and VC10-1 (Mixture 15). Both Mixture 10 and Mixture 17 exhibited well compacted geopolymer concrete, in contrast to Mixture 11 for instance, which was one of the lower ranking mixtures in terms of workability and compressive strength.

Phenomenon of flash setting

During 2006-2007 inclusive the phenomenon of flash setting was observed for a number of geopolymer mixtures. Hardening of the mixture occurred within minutes of mixing the alkaline liquids with the fly ash and aggregates making the mixture unworkable; an image of one such mixture with flash setting whilst in the concrete pan mixer is shown in Fig. 6. This is in contrast to previous experiences with geopolymer mixtures which showed handling times of 120 minutes were achievable without loss of workability. The process of polymerization expels water from the binder indicating the workability should not decrease rapidly suggesting the hardening process was not a result of polymerization.

Investigations into the chemical composition of the sodium silicate solution were undertaken as the solution had become cloudy and grey where as previously was clear. New sodium silicate solution was obtained from a different chemical supplier to compare with samples taken from the existing stock of sodium silicate. The new sodium silicate solution was clear and glassy in appearance. The chemical analysis was undertaken in the Nanochemistry Department of Curtin University of Technology and the results are shown in Table 9. Although there was a high proportion of colloidal material in the existing stock sodium silicate solutions, there would appear to be no significant variance in chemical composition to the new solution.

The existing stock of sodium silicate solutions (A and B) were used to manufacture a series of geopolymer mortars with varying water contents as indicated in Table 10. It was found that all of the mortars exhibited rapid setting to different degrees. The degree of flash setting in the mortars appeared related to water content and temperature; the mortar with higher water content could maintain workability for up to one hour and the hardening rate of the mortars was faster with decreasing temperature.

Both existing and new sodium silicate solutions, from the new chemical supplier, were used to cast two trial mixtures of geopolymer concrete with mixture proportions as shown in Table 11 to assess if the new supply of sodium silicate resulted in flash setting. Both mixtures exhibited flash setting within minutes of mixing the alkaline solution to the fly ash and aggregates. The geopolymer mixtures, as indicated in Table 11, were virtually zero slump, were un-compactable and had lower than anticipated compressive strengths after curing [around 80% of the anticipated compressive strength based on previously successful geopolymer production using the same mixture proportions which yield one day strengths of 45 MPa (6500 psi)].

Another possible cause of flash setting was the contamination of the fly ash with

cement. The contamination of the fly ash with cement had been communicated by a commercial producer, of concrete and geopolymer concrete, to have been the cause of flash setting observed by them. Their batching plant had in place procedures to ensure non contamination of the fly ash during storage, handling or batching. A trial was undertaken to cast two mixtures of geopolymer concrete using fly ash sourced from the same power station as the Curtin fly ash but stored at the commercial concrete facility. Two trial mixtures were prepared using the new fly ash with one of the mixtures deliberately contaminated with 5% cement (by mass of fly ash) as shown in Table 12. The mixtures were steam cured at 60 ºC (140 ºF) for 17 hours. The strength gain of the mixture with the portland cement contamination was found to be greater than that of the mixture with no portland cement suggesting the possibility that some polymerization occurred in addition to hydration of the cement. The cement used to contaminate the fly ash had 64.2% calcium oxide. The high calcium content deliberately introduced into the fly ash did initiate flash setting and is consistent with the finding that the presence of calcium interferers with the polymerization reaction. It is possible the fly ash was contaminated by Class C bottom ash which has high calcium content. The stock of fly ash has subsequently been replenished and no further instances of flash setting have been observed.

CONCLUDING REMARKS

Basic mixture proportions characterized by 75% aggregate to total mass, alkaline liquid to fly ash of 0.35 (analogous to water to cement ratio) and elevated temperature curing results in a high strength geopolymer concrete. Ambient curing of geopolymer has been trialed and further mixture trials with ambient curing are presently being researched.

Temperature specification for curing should be correlated to actual specimen temperature for high and very high-strength geopolymer concretes, monitoring temperature may be warranted if strength is critical and when steam curing, placement of the steam vents or hoses and control thermocouples as well as specimens is important. In the curing regime adopted at Curtin University a nominal curing temperature of 80 ºC (176 ºF) was found to correlate to a specimen temperature of 10 to 20 ºC (50-68 ºF) less.

The introduction of a rest day, that is ambient curing for 24 hours prior to team curing, resulted in elevated compressive strengths of the order of 20%. As with normal portland cement concrete, strength was increased and workability and ease of compaction decreased with a reduction in added water. Strength gain at 1 day is approximately 80% of the 28 day strength when cured for 24 hours.

As with normal portland cement concrete, the aggregate moisture content can be accommodated by adjusting the total water added to a geopolymer concrete mixture without sacrificing strength or workability. Additionally, the impact of aggregate particle shape and grading is similar to the impact with normal portland cement concrete. An increase in angularity decreases workability and compaction factor (the degree of compact ability) for geopolymer concrete as it would do for normal portland cement concrete. Superplasticizers which best enhance the workability of geopolymer are polycarboxilic superplasticizers.

Density of geopolymer concrete is comparable to normal portland cement concrete with equivalent aggregates. Tensile strength of geopolymer concrete is greater than

that of equivalent strength normal portland cement concrete.

The phenomenon of flash setting may be attributed to high calcium content either via cement contamination or bottom ash contamination.

RECOMMENDATIONS

Geopolymer concrete offers an opportunity to explore concrete sustainability options with the full replacement of portland cement as a binder constituent. High strength geopolymer concrete can be achieved with steam curing, low calcium fly ash, and alkaline liquid; there is considerable scope to research lower strength geopolymer concretes with ambient temperature activation of polymerization.

The use of alternative alkaline liquids warrants investigation as they may provide a more stable alkaline solution. Conventional mixture proportions theory and knowledge can readily be transferred to the design of geopolymer mixtures with similar outcomes in terms of workability and strength for aggregate grading, strength, and angularity. Further advances in mixture proportions development and the use of superplasticizers to enhance workability and compatibility are recommended.

Tensile strength of geopolymer concrete has been shown to be superior and current research into shear strength of geopolymer concrete in beam applications is recommended and is presently being explored to fully exploit this characteristic of geopolymer concrete.

ACKNOWLEDGEMENTS

REFERENCES

1. Mehta, P.K., "Greening of the Concrete Industry for Sustainable Development," *Concrete International*, V. 24, No. 7, July, 2002, pp. 23-28.

2. Cembureau, "Cement in Cembureau Countries Statistics 2005- 2007" available at: http://www.cembureau.be/Documents/KeyFacts/STATISTICS/Cement%20in%20CEMB%20countries.pdf.

3. Mehta, P.K., "Reducing the Environmental Impact of Concrete," *Concrete International*, V. 23, No. 10, Oct., 2001, pp. 61-66.

4. Portland Cement Association, "World Cement Consumption Growth Expected to Continue," Portland Cement Association *Executive Report*, 2006, available at: http://www.cement.org/exec/10-23-06.htm.

5. Karstensen, K.H., "Cement Production in Vertical Shaft Kilns in China –Status and Opportunities for Investment," UNIDO Contract RB-308-D40-8213110-2005, 2006.

6. Lieblang, P., "Green Europe: Emission Trading on a Large-Scale and Individual Green Concrete Housing on a Small-Scale," *Proceedings of International Concrete Conference and Exhibition ICCX Oceania—Concrete Solutions for Oceania*, ed. Katutz, H., Sydney, Australia, 2009, pp. 26-26.

7. Mehta, P.K., "High-Performance, High-Volume Fly Ash Concrete for Sustainable Development," *Proceedings of International Workshop on Sustainable Development and Concrete Technology*, Beijing, China, 2004, pp. 3-14.

8. Stevenson, M., and Panian, L., "Sustainability through Strength," *Concrete International*, V. 31, No. 3, Mar. 2009, pp. 34-39.

9. Poon, C.S.; Lam, L.; and Wong, Y.L., "A Study on High Strength Concrete Prepared with Large Volumes of Low-Calcium Fly Ash," *Cement and Concrete Research*, V. 30, No. 3, 2000, pp. 447-455.

10. Papadikis, V.G., 1999, "Effect of Fly Ash on Portland Cement Systems, Part I: Low-Calcium Fly Ash," *Cement and Concrete Research*, V. 29, No. 11, Nov. 1999, pp. 1727-1736.

11. Malhotra, V.M., "High-Performance High-Volume Fly Concrete," *Concrete International*, V. 24, No. 7, July 2002, pp. 30-34.

12. Austrailian Department of Environment and Water, "Industrial Process Sector Greenhouse Gas Emissions Projections 2007," 2007. (http://www.climatechange.gov.au/projections/pubs/industrial2007.pdf)

13. Davidovits, J., "Geopolymers: Inorganic Geopolymeric New Materials," *Journal of Thermal Analysis*, V. 37, 1991, pp. 1633-1656.

14. Rangan, B.V., and Sumajouw, M.D.J., "Low-Calcium Fly Ash-Based Geopolymer Concrete: Reinforced Beams and Columns," Research Report GC3, Faculty of Engineering, Curtin University of Technology, 2006. (http://espace.library.curtin.edu.au/R/?func=dbin-jump-full&object_id=19466&local_base=GEN01)

15. Ash Development Association of Australia, "Total Ash Production and Beneficial Usage." (http://www.adaa.asn.au/statistics.htm)

16. Rangan, B.V. and Wallah, S.E., "Low Calcium Fly Ash Based Geopolymer Concrete: Long–Term Properties," *Research Report* GC2, Faculty of Engineering, Curtin University of Technology, 2006. (http://espace.library.curtin.edu.au/R/?func=dbin-jump-full&object_id=19464&local_base=GEN01)

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*, V. 42, No. 9, Sept. 2007, pp. 3107-3116.

18. Sarker, P.K.; Grigg, A.; and Chang, E.H., "Bond Strength of Geopolymer Concrete with Reinforcing Steel," *Proceedings of Recent Development in Structural Engineering*, A. Zingoni, ed., Mechanics and Computation, The Netherlands, 2007, pp. 1315-1320.

19. 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, 2005. (http://espace.library.curtin.edu.au/R?func=dbin-jump-full&object_id=19327&local_base=gen01-era02)

Table 1—Chemical composition Class F fly ash

Oxides	Quantity (%)
SiO_2	50.18
Al_2O_3	26.31
Fe_2O_3	13.68
CaO	2.63
MgO	1.29
SO_3	0.02
Na_2O	0.32
K_2O	0.53
TiO	1.66
SrO	0.30
P_2O_5	1.55
Mn_2O_3	0.09

Table 2—Chemical composition sodium silicate solution

Compound	Percentage by mass (%)
Na_2O	14.7
SiO_2	29.4
H_2O	55.9

Table 3—Mixture proportions of geopolymer concrete

Material	Nominal 40 MPa Mixture 1 Mass kg/m³ (lb/ft³)	Nominal 60 MPa Mixture 2 Mass kg/m³ (lb/ft³)	Nominal 75 MPa Mixture 3 Mass kg/m³ (lb/ft³)
20 mm (3/4 in.) aggregate	640.5 (40)	640.5 (40)	640.5 (40)
7 mm (1/4 in.) aggregate	640.5 (40)	640.5 (40)	640.5 (40)
Sand	549 (34)	549 (34)	549 (34)
Fly ash	404 (25)	404 (25)	404 (25)
Sodium hydroxide solution 14M	41 (2.7)	41 (2.7)	41 (2.7)
Sodium silicate solution	102 (6.4)	102 (6.4)	102 (6.4)
Superplasticizer (sulphonated-napthalene)	6 (0.4)	6 (0.4)	6 (0.4)
Added water	25.5 (1.6)	17.0 (1.06)	13.5 (0.8)

Table 4—Moisture content of aggregates prepared to SSD condition

Aggregate	Moisture content (%)
20 mm (3/4 in.)	0.4
10 mm (3/8 in.)	0.3
7 mm (1/4 in.)	0.5
Sand	0.7

Table 5—Aggregate properties

Material	Aggregate crushing value (%)	Flakiness index (%)		
		20 mm (3/4 in.)	10 mm (3/8 in.)	7 mm (1/4 in.)
Granite	27.3	10.2	14.0	19.7
Dolerite	20.8	7.7	11.1	19.3

Table 6—Mixture proportions, slump, and compressive strength of geopolymer concrete trial mixtures

Constituent	Mixture 1		Mixture 2		Mixture 3	
	kg/m³ (lb/ft³)		kg/m³ (lb/ft³)		kg/m³ (lb/ft³)	
Aggregate 20 mm (3/4 in.)	570 (35)		570 (35)		570 (35)	
Aggregate 7 mm (1/4 in.)	570 (35)		570 (35)		570 (35)	
Aggregate sand	485 (30)		485 (30)		485 (30)	
Fly ash	360 (22)		360 (22)		360 (22)	
14 M sodium hydroxide solution	30.5 (1.9)		30.5 (1.9)		30.5 (1.9)	
Sodium hydroxide solution	90 (5.6)		90 (5.6)		90 (5.6)	
Superplasticizer	7 (0.5)		7 (0.5)		7 (0.5)	
Added water	15 (0.9)		12 (0.7)		9 (0.6)	
Added water to fly ash ratio	0.042		0.033		0.025	
Properties						
Slump	130 mm (5 in.)		200 mm (8 in.)		235 mm (9 in.)	
Rest period	No rest	One day	No rest	One day	No rest	One day
Mean strength @ 28 days (MPa)	37.5 ± 1.3	46.4 ± 0.2	45.4 ± 4.1	55.8 ± 3.4	53.9 ± 7.4	63.1 ± 3.6
Indirect Tensile @ 28 days (MPa)	3.5 ± 0.5	3.7 ± 0.1	3.9 ± 0.5	4.9 ± 0.1	4.7 ± 0.9	5.5 ± 1.0

Table 6—Mixture proportions, slump, and compressive strength of geopolymer concrete trial mixtures (cont.)

Constituent	Mixture 1		Mixture 2		Mixture 3	
	kg/m³ (lb/ft³)		kg/m³ (lb/ft³)		kg/m³ (lb/ft³)	
Mean strength @ 28 days (psi)	5400 ± 200	6700 ± 30	6600 ± 600	8100 ± 500	7800 ± 1000	9200 ± 500
Indirect tensile @ 28 days (psi)	510 ± 70	540 ± 15	560 ± 70	710 ± 15	680 ± 130	800 ± 145

Table 7—Mixture proportions and properties of geopolymer concrete for varying aggregate grading

Material Mass kg/m³ (lb/ft³)	Trial Mixture Identifier			
	1:granite:10	2:granite:10	3:granite:10	8:dolerite:20
20 mm (3/4 in.) aggregate	0	0	0	646.8
10 mm (3/8 in.) aggregate	541.5 (34)	631.8 (39)	722.0 (45)	646.8
7 mm (1/4 in.) aggregate	631.8 (39)	631.8 (39)	595.7 (37)	0
Sand	631.8 (39)	541.5 (34)	487.4 (30)	554.4 (35)
Fly ash	423.3 (26)	423.3 (26)	423.3 (26)	392.8 (24)
NaOH solution 14 M	43.0 (2.7)	43.0 (2.7)	43.0 (2.7)	39.9 (2.5)
Sodium silicate solution	106.9 (6.7)	106.9 (6.7)	106.9 (6.7)	99.2 (6.2)
Added water	21.5 (1.3)	21.5 (1.3)	21.5 (1.3)	20.0 (1.2)
Properties				
Slump mm (in)	230 (9.1)	230 (9.1)	245 (9.6)	270 (10.6)
Compacting Factor	0.93	0.94	0.97	1.0
Density kg/m³ (lb/ft³)	2396 (150)	2399 (150)	2388 (149)	2400 (150)
Indirect tensile strength 28 days MPa (psi)	3.6 (500)	3.6 (500)	3.1 (450)	2.4 (350)
Compressive strength 1 day MPa (psi)	40 (6000)	37 (5370)	32 (4640)	27 (3920)
Compressive strength 7 days MPa (psi)	41 (5950)	40 (6000)	36 (5220)	29 (4200)
Compressive strength 28 days MPa (psi)	44 (6380)	47 (6820)	39 (5660)	32 (4640)

Table 8—Superplasticizer geopolymer mixture ranking

Superplasticizer type and dose rate	Mixture	Water plus superplasticizer to fly ash ratio (L/kg)	Compressive strength at 2 days MPa (psi)	Slump mm (in.)	Slump rank	Strength rank	Overall rank
RH	7	0.079	46.7 (6800)	230 (9.1)	6	9	15
G27:1	8	0.069	48.4 (7100)	220 (8.7)	3	6	9
G27:2	9	0.079	42.1 (6100)	240 (9.4)	4	12	16
GA30:1	10	0.068	48.1 (7000)	240 (9.4)	1	4	5
GA30:2	11	0.076	48.3 (7000)	215 (8.5)	10	8	18
SN:1	12	0.069	39.8 (5800)	245 (9.6)	2	11	13
SN:2	13	0.079	35.2 (5100)	225 (8.9)	9	13	22
VC10:1	15	0.069	54.2 (7900)	200 (7.9)	7	3	10
VC10:2	16	0.079	55.6 (8100)	210 (8.3)	12	5	17
VC16:1	17	0.068	54.8 (7900)	200 (7.9)	5	1	6
VC16:2	18	0.076	51.8 (7500)	210 (8.3)	11	7	18
VC305:1	19	0.069	54.8 (7900)	180 (7.1)	13	2	15
VC305:2	20	0.079	46.1 (6700)	225 (8.9)	8	10	18

Table 9—Properties of sodium silicate solutions

Parameter	Existing sample A	Existing sample B	New sample C
Na_2O (% by mass)	14.49	14.58	14.64
SiO_2 (% by mass)	29.4	29.39	29.46
Solids (% by mass)	43.89	43.97	44.10
SiO_2 / Na_2O ratio	2.03	2.02	2.01
Viscosity at 20 °C (68 °F)(cps)	347	358	345

Table 10—Mortar mixture proportions

Material	Mass kg/m³ (lb/ft³)	
Fly ash	396 (24.7)	
Sodium silicate solutions A or B	100 (6.2)	
Sodium hydroxide solution 14 M	40 (2.5)	
Added water	Mortar 1	16.5 (1.0)
	Mortar 2	20.7 (1.3)
	Mortar 3	25.8 (1.6)
	Mortar 4	30.1 (1.9)
	Mortar 5	38.7 (2.4)

Table 11—Trial mixture proportions and properties of geopolymer concrete-different sodium silicates

Material	Mass kg/m³ (lb/ft³)	
20 mm (3/4 in.) aggregate	640 (40)	
7 mm (1/4 in.) aggregate	640 (40)	
sand	550 (34)	
Fly ash	403 (25)	
NaOH solution 14 M	41 (2.6)	
Added water	41 (2.6)	
Sodium silicate solution	102 (Curtin sample A)	102 (New sample C)
Ambient temperature	19 °C (66 °F)	17 °C (63 °F)
Properties		
Slump mm (in.)	10 (0.4)	15 (0.6)
Compacting factor	0.68	0.74
Density kg/m³ (lb/ft³)	2338 (145)	2392 (139)
Compressive strength @ 1 day MPa (psi)	38 (5500)	36 (5200)

Table 12—Trial mixture proportions and properties of geopolymer concrete-cement contamination

Material	Mass kg/m³ (lb/ft³)	
10 mm (3/8 in.) aggregate	542 (34)	
7 mm (1/4 in.) aggregate	632 (39)	
Sand	632 (39)	
NaOH solution 14 M	43 (2.7)	
Added water	21.5 (1.3)	
Sodium silicate solution	107 (6.7)	
Fly ash	402 (25)	423 (26)
Portland cement	21 (1.3)	nil
Properties		
Slump mm (in)	250 (9.8)	260 (10.2)
Setting time	15 minutes	More than 45 minutes
Curing	17 hours @ 60 ºC (140 ºF)	17 hours @ 60 ºC (140 ºF)
Compressive strength @ 1 day MPa (psi)	18 (2600)	14 (2000)
Compressive strength @ 6 days MPa (psi)	29 (4200)	17 (2500)
Compressive strength @ 14 days MPa (psi)	32 (4640)	24 (3500)
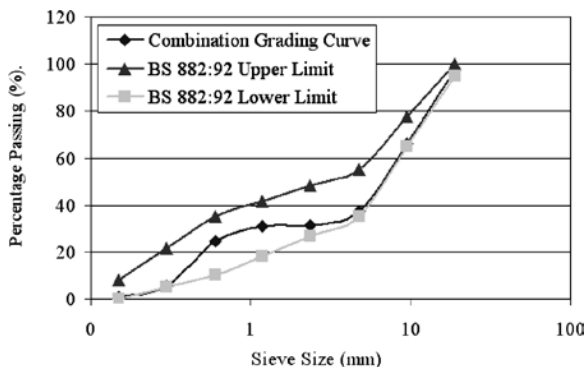
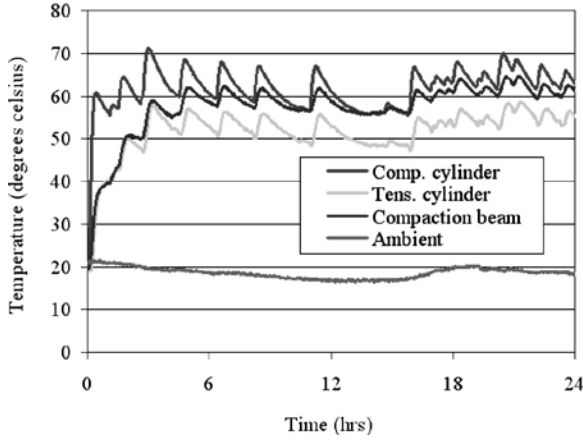Fig. 1—Typical grading curve (combination grading curve) for geopolymer mixtures.

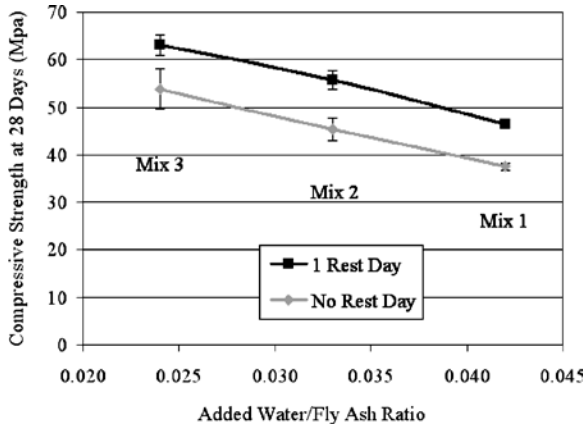Fig. 2—Specimen and ambient temperatures time relationship.

Fig. 3—Compressive strength at 28 days variation with added water-to-fly ash ratio and rest day.
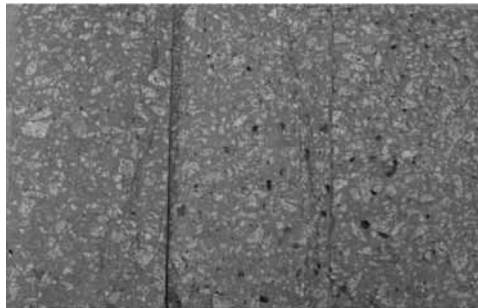

Fig. 4—Compaction as evidenced by split tensile test for Mixture 3 (left), Mixture 2 (center), and Mixture 1 (right).
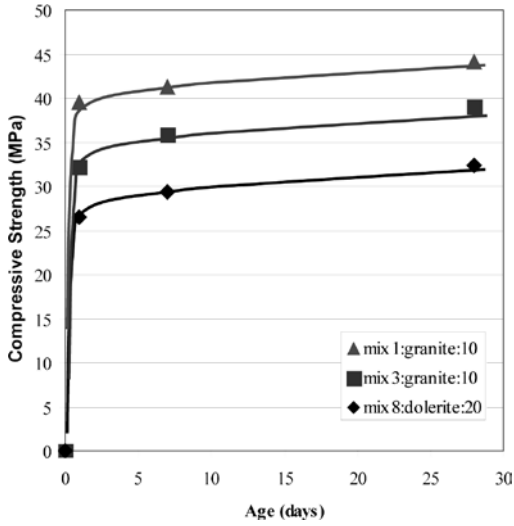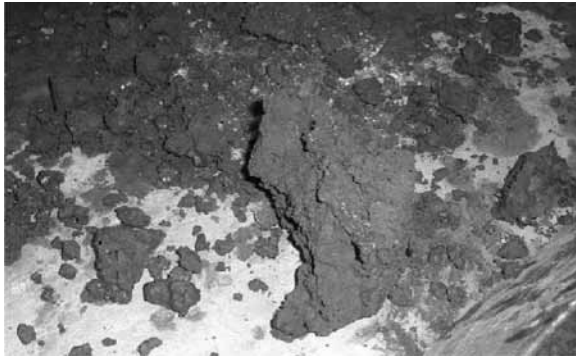
Fig. 5—Typical strength gain with age relationship.

Fig. 6—Geopolymer mixture exhibiting flash setting in mixer.