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Fire Resistance of Fly Ash-Based Geopolymer Concrete Blended with Calcium Aluminate Cement

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Abstract

Geopolymer has been known as an eco-friendly alternative to Portland cement-based concrete. Geopolymer concrete usually uses alkali-activated fly ash as the binder, and develops desirable strength within 8 hours when a heat-curing regime is used. Due to its ceramic-like properties, geopolymer concrete is believed to have high fire resistance. When heat-cured geopolymer concrete is exposed to high temperatures, a strength gain is often reported. However, the heat-curing procedure limits the future of geopolymers for on-site applications. To solve this issue, suitable additives (e.g., ground granulated blast-furnace slag and calcium aluminate cement) can be used in the binder which can develop the desirable strength of geopolymer concrete. It is important to understand the high-temperature performance of ambient-cured geopolymer concretes which have received little attention. This paper presents a study on the high-temperature performance of fly ash-based geopolymer concrete cured at ambient temperature. Compression tests were carried out on geopolymer mortars at temperatures of 23, 600 and 800 °C. As an outcome from this work, the authors have proposed a geopolymer concrete mixing design based on the parameter analysis, and the fire performance of the geopolymer concrete are compared with that of the reference OPC concrete at different temperatures.

Keywords: CAC, Fire resistance, Geopolymer, Concrete.

1. INTRODUCTION

Concrete has been known as a fire-resistant material. Conventional concrete contains ordinary Portland cement (OPC) as a binder material. However, the binder of conventional concrete suffers severe damage under fire conditions. Due to increasing population, high rise buildings have become prevalent in megacities. Extremely high residential density has increased the probability of fire hazard as well as the severity of consequence. The threat of fire has raised the interest into studies on fire-resistant binders as such geopolymer has been considered as a promising alternative to OPC in construction applications.

At 100–200 °C, the free water evaporation causes the mass loss of OPC binder. For the OPC binder, the strength loss starts to fleet after approximately 400 °C. The dehydration and decomposition of C-S-H gel and other hydrates under high temperatures are probably responsible for failure of OPC binders (Seleem, Rashad & Elsokary 2011). The hydrated OPC contains a considerable amount of $Ca(OH)_2$ which releases water after 400 °C, and this water-release reaction causes the volume to expand which is responsible for the spalling phenomenon of OPC concrete at high temperatures from 350 to 450 °C (Guerrieri & Sanjayan 2010). The thermal response of OPC is evaluated by performance-based fire engineering method which

has been widely adopted among the world (Wang et al. 2012), and the strength reduction of normal weight concrete is supposed to be 85% after 800 °C exposure in the performance-based design method.
Ceramic-like properties of alkali aluminosilicate materials are the reason why some geopolymer binders exhibited better fire performance than OPC. The properties of geopolymers are dependent on compositions of raw material. Regarding compositions, Al_2O_3, SiO_2, and the calcium content have an important role in determining the mechanical properties and fire performance. In Australia, the majority of fly ash produced is low calcium (class F) fly ash. The low calcium content leads to slow strength development at ambient temperature. Thus, elevated temperature curing regime was used to improve the mechanical properties of geopolymer in former researches (Mendes, Sanjayan & Collins 2008), (Pan, Sanjayan & Rangan 2009). The heat curing procedure inhibits the application of geopolymer in the construction industry. Some researchers have found the addition of calcium aluminate cement (CAC) (Cao et al. 2016), OPC (Nath & Sarker 2015) or ground granulated blast-furnace slag (GGBFS) was able to improve the mechanical properties at ambient temperature (Khan et al. 2016). These three additions are considered as a solution for curing geopolymers at ambient temperature. However, the addition of OPC introduced the hazard of spalling into geopolymer under high temperature, while the GGBFS blended geopolymer was reported to have strength decrease when exposure to temperatures of 50 °C and above (Jambunathan et al. 2013). In contrast, CAC is known for its high early strength and fire performance. The mechanical properties of geopolymer blended with CAC at ambient temperature have been studied by the authors in the former paper (Cao et al. 2016). The study of using geopolymer blended with CAC in fire-resistance application will be conducted in this paper.

To the Authors' best knowledge there has been no reported literature on the fire resistance of fly ash-based geopolymer blended with CAC. In order to investigate fire performance of geopolymer, the hot strength of geopolymer mortar tested at 600 and 800 °C are reported in this paper. The crack patterns of geopolymer under fire are compared to typical failure pattern proposed by ASTM, C (1996). Influence of three different factors including activator concentration, CAC replacement ratio and activator to binder ratio on the hot strength of geopolymer is analysed. Based on results obtained in mortars, one optimised mix has been selected for casting concrete. The fire performance of this geopolymer concrete mix is compared with OPC concrete at 23, 200, 400, 600 and 800 °C.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

The raw materials used in mortar mixing were divided into three parts (activator, binder and sand). Activator was uniform solution composing of sodium hydroxide, tap water and sodium silicate. The majority of the binder was low calcium fly ash from a power plant in Victoria, and 5-20% of fly ash by mass was replaced by CAC. Locally available river sand which fits the grading curve was used by ASTM (2003). Nine (No. 1 to No. 9) mixing designs were made based on three different factors at three levels. The mixture design was shown in Table 1. The mixture No. 10 was concrete mixing design which used lime stone as coarse aggregate, and the maximum nominal size was 20 mm which fits the grading curve suggested in the ASTM (2003).

The binder materials include fly ash, CAC and OPC (ASTM type I cement) of which chemical compositions are shown in Table 2. The SiO_2 content of fly ash was the major, followed by Al_2O_3. The sum of the oxides Al_2O_3+SiO_2+Fe_2O_3 was more than 70% while the content of CaO was only 2.8%. The CAC used in geopolymer has an alumina content of around 68.5%. The alumina and calcium contents of fly ash were improved by replacing fly ash with 5% to 20% CAC. Geopolymers made with fly ash blended with CAC does not require heat curing for strength development.

Table 1. Mixture proportions (kg/m^3).

Mixture No.	Activator			Binder		Sand	Lime stone	Extra water
	NaOH pellet	Water	Sodium silicate	Fly ash	Calcium aluminate cement			
1	40.7	89.0	324.3	1232.4	64.9	648.6	-	-
2	45.3	99.0	360.9	1136.8	126.3	631.6	-	-
3	49.7	108.6	395.6	984.6	246.2	615.4	-	-
4	52.1	92.2	360.9	1200.0	63.2	631.6	-	-
5	57.1	101.1	395.6	1107.7	123.1	615.4	-	-
6	46.8	82.9	324.3	1037.8	259.5	648.6	-	-
7	63.9	94.3	395.6	1169.2	61.5	615.4	-	-
8	52.4	77.3	324.3	1167.6	129.7	648.6	-	-
9	58.3	86.0	360.9	1010.5	252.6	631.6	-	-
10	21.1	31.1	130.3	467.9	52.1	586.3	1080.2	31.1

Table 2. Chemical compositions by X-Ray Fluorescence of binder materials.

Constituent (%)	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	SO_3	K_2O+ Na_2O
Fly ash	30.5	48.3	12.1	2.8	1.2	0.3	0.6
CAC	68.5	0.8	0.4	31	0.5	0.3	0.5
OPC	4.7	19.9	3.4	63.9	1.3	2.6	0.7

2.2 Specimen preparation

Three factors (activator concentration, CAC replacement ratio and activator to binder ratio) at three levels were investigated with nine mixture designs. These three factors were designed from the knowledge of preliminary experiments. The sodium silicate to sodium hydroxide ratio was kept constantly at 2.5 which was an optimised value concluded in the former research (Cao et al. 2016). The key factors of the nine mixture designs are shown in Table 3.

Table 3. Experimental factors.

Level	**Experimental factors**		
	Activator concentration	CAC replacement ratio	Activator to binder ratio
1	10 M	5%	35%
2	12 M	10%	40%
3	14 M	20%	45%

The alkali activators were prepared 24 hours before the geopolymer mortar mixing. The sodium hydroxide pellets were dissolved into tap water to form uniform solution. After the sodium hydroxide solutions cooled down to room temperature, the sodium silicate, known as grade D water glass, was added into the sodium hydroxide solutions and mixed and stored in corrosive chemical cabinet 24 hours before the casting of geopolymer.

The binders and sand were dry-mixed in a mixer for 3 minutes before the alkali activator was added into the mixer. The mixing proceeded for 6 minutes until the mixture formed homogenous slurry. The fresh mortar was casted into 60 × 180 mm cylinder moulds in three layers. A vibrating table was working all the process of casting fresh mortar into moulds. Each layer was kept vibrating for 15 seconds to 30 seconds to chase the bubbles out. The specimens were demoulded after one day and then they were cured at room temperature constantly. A CIVILAB core facing grinder was employed to grinder both ends of each cylinder to get smooth and flat surfaces.

2.3 Testing method

After 28 days of curing, compression tests and fire performance tests were conducted. The concrete cylinders were tested with an INSTRON 8036 universal testing machine in accordance with the requirement in ASTM, C (1996). The loading rate was 0.25 ± 0.05 MPa/s. The testing was conducted in Structural Research and Testing Laboratory at Western Sydney University in which the temperature was constantly around 23 °C. The cross-sectional area of each cylinder was measured to calculate the stress.

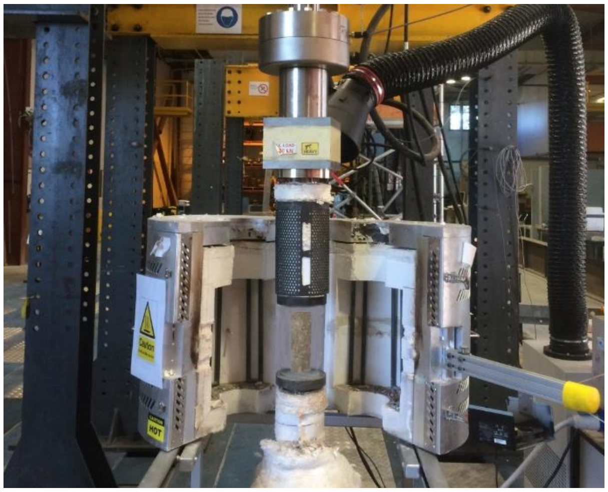


Figure 1. Vertical tube furnace

A vertical electric tube furnace, as shown in Figure 1, was employed to heat the specimens. A hydraulic loading jack which had 1000 kN capacity was located at the top of the vertical tube furnace. The upper and lower holders were cast by 253MA high temperature stainless steel. The steel casing was installed after the cylinder sample was steadily put on the lower holder. Then, the furnace temperature was increased to the target temperature of 600 or 800 °C with a heating rate of 5 °C/min. To investigate the ultimate strength of geopolymer mortars in hot status, the hydraulic jack started loading when the furnace had held the target temperature for 2 hours. Two specimens were conducted in the same condition to get an average compressive strength. The furnace was cooled naturally to ambient temperature to avoid thermal shock.

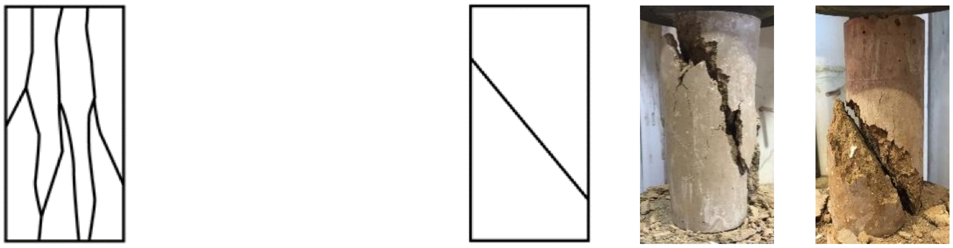
3. RESULTS AND DISCUSSION

3.1 Visual appearance

The geopolymer specimen was dark grey in appearance after 28 days curing. After heating at 600 °C for 2 hours and cooled down, the colour had turned light grey, whereas at 800 °C the sample turned yellow ochre.

(a) Type 1

(b) Type 2



(c) Type 3

(d) Type 4

(e) Type 5

(f) Type 6

Figure 2. Typical fracture patterns of specimens subjected to elevated temperature exposure

The crack patterns of the specimens after compressive strength testing for high temperature exposure are presented in Figure 2. The crack patterns are compared with typical fracture patterns defined in ASTM, C (1996). Type 1 (reasonably well-formed cones on both ends, less than 25 mm cracking through caps) was found very common in geopolymer mortars. Type 2 (well-formed cone on one end, no well-defined cone on the other end, vertical cracks running through caps) was least common among the three fracture patterns appeared. Type 4 (Diagonal fracture with no cracking through ends; tap with hammer to distinguish from type 1) was the most common fracture pattern in geopolymer mortar specimens exposed to high temperature. No type 3 fracture pattern (columnar vertical cracking through both ends, no well-formed cones) was observed among all the specimens recorded. Neither type 5 nor type 6 fracture pattern was observed because the compression was conducted with bonded caps.

In conclusion, the fracture patterns of geopolymer mortar were easier to form cones or diagonal fracture. Vertical cracks were fewer than shear failure cracks to be observed.

3.2 Compressive strength

The results were calculated based on at least two samples after 28 days curing. A third specimen was tested if the deviation exceeded 5%. Table 4 shows the compression testing results of different geopolymer mortar mixes at 23, 600 and 800 °C. The average strength at ambient temperature was 79.4 MPa, while the strength tested at 600 and 800 °C were 33.0 MPa and 48.1 MPa, respectively. The compressive strength of geopolymer blended with CAC tested at high temperature was lower than its ambient temperature strength.

Geopolymer mortar exhibited ideal mechanical properties and fire resistance in general. After exposed to 600 °C for two hours, the strength of mortar specimens decreased by 58.4% on average, while geopolymer subjected to 800 °C decreased only 39.4% of ambient compressive strength. In temperature range of 600 to 800 °C, the geopolymer samples regained their strength, indicating a phase transformation taking place in this temperature range. Further research is required to provide evidence for such transformation.

At ambient temperature, the highest compressive strength achieved was 118.9 MPa in mix 8 which was two times more than the weakest mixture, mix 3. At 600 °C, the highest compressive strength was 49.5 MPa (mix 6), while the highest strength retain ratio was 87.3% (mix 9). The highest strength of specimens tested at 800 °C was 67.7 MPa (mix 8), and the best strength retain ratio was 91.5% (mix 4).

Table 4. Compressive strengths of geopolymer mortars at different temperatures

Mixture No.	**Mixture factors**			**Compressive strength (MPa)**		
	Activator concentration	CAC replacement ratio	Activator/binder ratio	23 °C	600 °C	800 °C
1	10 M	5%	35%	62.5	26.4	52.9
2	10 M	10%	40%	107.6	25.8	58.5
3	10 M	20%	45%	50.4	40.9	23.1
4	12 M	5%	40%	63.5	23.1	58.1
5	12 M	10%	45%	101.1	26.2	41.1
6	12 M	20%	35%	80.0	49.5	38.5
7	14 M	5%	45%	75.1	25.6	55.4
8	14 M	10%	35%	118.9	31.2	67.7
9	14 M	20%	40%	55.7	48.6	38.0

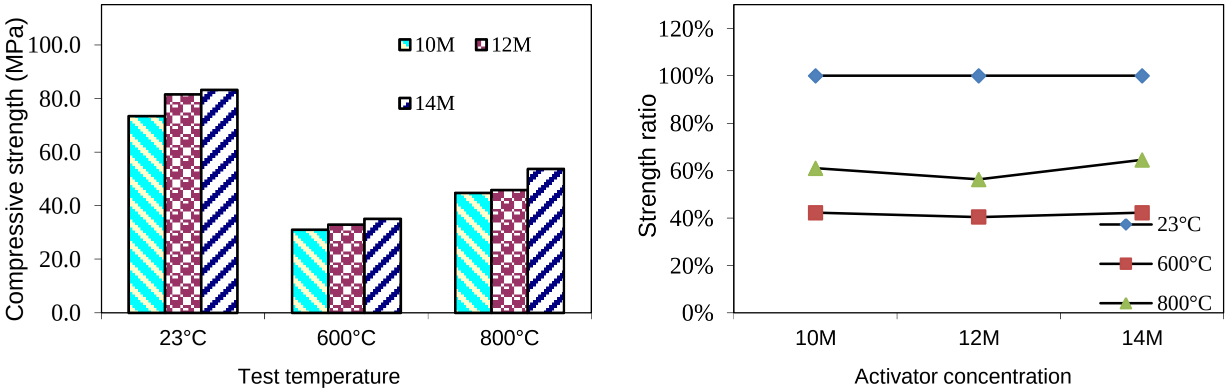
3.3 Parameter analysis on high temperature performance of geopolymer mortars

The variations of compression results regarding to the three key factors are shown in Figures 3–5. Most of the samples exhibit lower strength at 600 °C than that at 800 °C. However, geopolymers with 5% CAC at 600 °C had higher strength than 800 °C. In the following, parameter analysis is conducted by changing one factor while keeping other two factors consistent, where the compressive strength of heated geopolymer is referred to its ambient temperature strength. The test result of one level is the averaged compressive strength of 3 results, and three levels of other two parameters all appear once. For example, the compressive strength result of 12 M is calculated from mixing design Nos. 4, 5 and 6, while 14 M parameter is the averaged value of mixing design Nos. 7, 8 and 9.

3.3.1 Activator concentration

As shown in Figure 3 (a), the compressive strength of geopolymer mortar increased as the alkali activator concentration increased before fire exposure. Geopolymer specimens with 14 M concentration had higher compressive strength than others. At 800 °C, the strength increase of 14 M geopolymer was as high as 18.6% compared with 10 M and 12 M geopolymers.

Strength ratios of different geopolymer samples at specific temperatures were almost the same. The results in Figure 3 (b) show the strength of geopolymer decreased by 60% when heated to 600 °C, while the strength decrease was only about 40% for geopolymers heated at 800 °C.



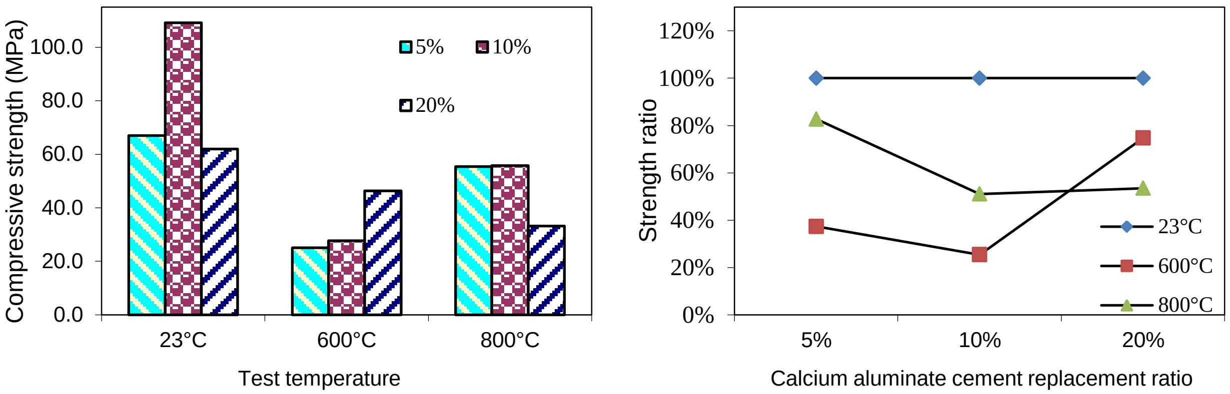
(a) Compressive strength vs. activator concentration

(b) Strength ratio vs. activator concentration

Figure 3. Influence of activator concentration

3.3.2 CAC replacement ratio

CAC replacement ratio is the most important parameter on the fire performance of geopolymer mortar, shown in Figure 4(a). The geopolymer mortar with 10% CAC exhibited highest compressive strength at ambient temperature. Geopolymer with 5% CAC had the lowest compressive strength under fire condition which was 25 MPa. The compressive strength of geopolymer at 800 °C was higher than strength at 600 °C when the CAC addition was 5%.



(a) Compressive strength vs. CAC replacement ratio

(b) Strength ratio vs. CAC replacement ratio

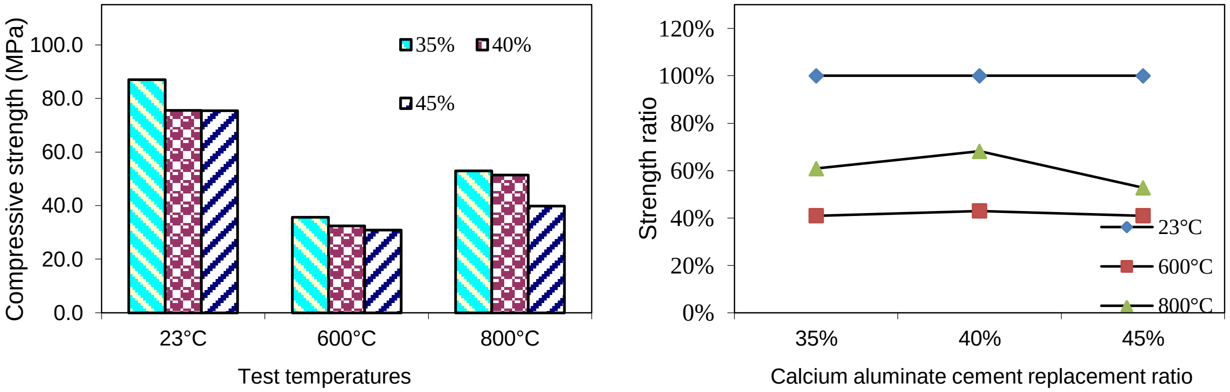
Figure 4. Influence of CAC replacement ratio

As can be seen from the results in Figure 4 (b), geopolymer with 20% CAC only decreased 15.3% in compressive strength at 600 °C, while 46.5% of strength was lost at 800 °C. The addition of 5% CAC improved the fire performance of geopolymer at 800°C which remained 82.7% compressive strength compared to the strength results tested at room temperature.

3.3.3 Activator to binder ratio

The increasing of liquid in geopolymer mortar caused the decreasing of strength at all temperatures. For specimens tested at 23 and 600 °C, the average strengths dropped 15.4% and 15.5% respectively when the activator content was increased from 35% to 45%. When the activator increased from 35% to 45%, the strength loss increased 33.0% for geopolymer exposed to 800 °C, as shown in Figure 5 (a).

Changing activator to binder ratio had negligible influence on strength ratio of geopolymers at 600 °C which was around 41% of that at ambient temperature, as shown in Figure 5(b). At 800 °C, the relative changes of strength for geopolymers with activator contents ranging from 35% to 45% were 60.7%, 68.2% and 52.8%, respectively.



(a) Compressive strength vs. activator to binder ratio

(b) Strength ratio vs. activator to binder ratio

Figure 5. Influence of activator to binder ratio

3.4 Fire performance of concrete

Performance-based fire engineering design method requires a full analysis of structures. In order for geopolymer to be applied in construction, the material properties at elevated temperatures should be understood. However, many researchers reported only residual strength of small geopolymer samples (Hussin et al. 2015). In this section, the investigation of geopolymer concrete at temperatures ranging from 23 to 800 °C is conducted. Reference OPC concrete samples with similar strength have also been tested at the same conditions.

The key factors of geopolymer concrete mixing design are alkali concentration, CAC replacement ratio and activator to binder ratio. The 14 M alkali solution and 35% activator to binder ratio were chosen because high concentration geopolymer binder exhibited best fire performance and ambient performance. The CAC was added into geopolymer concrete with the ratio of 10%. Although the performance of this mix at 600 °C is not the best, the ambient strength is extremely high and the performance at 800 °C is reasonable. Extra water was added into geopolymer concrete mixing to improve the workability of fresh concrete.

As shown in Figure 6, CAC geopolymer concrete exhibited higher fire performance than the OPC concrete at all temperatures. The strength reduction of concrete was calculated by dividing the strength at the elevated temperature to the initial strength (at ambient temperature). By comparing the relative changes of strength, it is found that geopolymer had much higher strength over OPC at the temperatures of 200 and 800 °C. The strength decreasing at 200 °C was accounted for an increase in porosity caused by evaporation. The geopolymer also had a mild drop of strength at 400 °C which was possibly caused by the evaporation. At the temperature of 800 °C, the strength of geopolymer dropped slowly because of the ceramic-like property of matrix. Some researchers even reported strength gain of geopolymers at high temperature (Pan, Sanjayan & Rangan 2009). However, OPC concrete exposed to 800 °C suffered a severe decrease in the mechanical properties which was accounted for the chemical decomposition of its matrix.

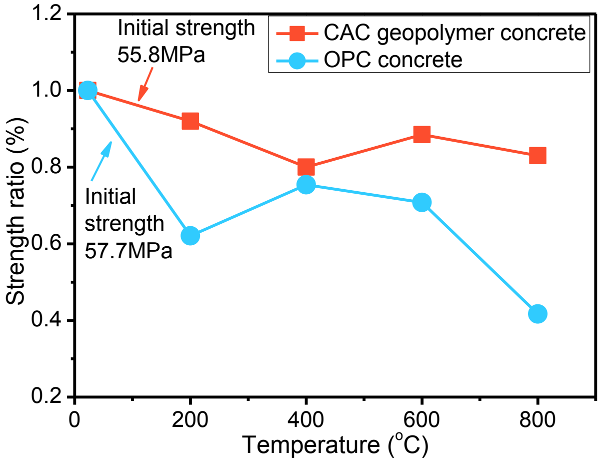


Figure 6. Fire performance of concrete

In conclusion, geopolymer concrete exhibited better fire performance than OPC concrete among the whole range of temperatures. This was accounted for the matrix of geopolymer which was much more stable and durable than OPC.

4. CONCLUSIONS

This research investigated the feasibility of using geopolymer to improve the fire performance of concrete. Nine mortar mixing designs were tested to conduct a parameter analysis of geopolymers at three different temperatures. Three parameters (activator concentration, CAC replacement ratio and activator to binder ratio) were analysed at three levels respectively.

1. The failure patterns of geopolymer mortars were investigated. The results showed geopolymer mortar mainly formed cones or diagonal fracture, while vertical cracks were seldom observed.

2. The influence of three parameters on the compressive strength of geopolymer mortar at elevated temperatures was studied. Geopolymer with the addition of CAC could achieve very high strength (118.9 MPa) before heating. This mix still had 67.7 MPa residual strength at 800 °C. CAC addition among all three factors is the most important factor on the fire performance of geopolymer.

3. The fire performance of geopolymer concrete was studied by comparison with OPC concrete with the same aggregates except for the binder. Geopolymer concrete blended with CAC exhibited better fire endurance than OPC concrete at all tested temperatures. This is due to the fact that the matrix of geopolymer concrete was much stable and endurable than the matrix of OPC concrete.

5. ACKNOWLEDGEMENTS

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