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Factors influencing softening temperature and hot-strength of geopolymers

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ABSTRACT

This paper presents the effects of cation type, silicate concentration, compositions of low-calcium fly ash and test load on softening temperature and hot-strength (loaded while at high temperature) of fly ash-based geopolymers. It was found that softening temperature (T_s) of sodium (Na) based-geopolymer remained the same (610 °C ± 20 °C) regardless of the silicate concentration, fly ash composition, and test load. However, when the cation was changed from sodium to potassium (K), the T_s increased to 800 °C. Further, when Na/K is mixed, the T_s dropped to 570 °C.

Significant increases in hot-strengths (at 530 °C and 730 °C) were found in all geopolymers. This increase in strength was observed to be in conjunction with heat release, indicating an exothermic reaction. Since the reaction between fly ash and activators is exothermic, this reaction is believed to be the reason for the strength gain at high temperatures.

1. Introduction

During the last couple of decades the worldwide interest in alkali-activated binders increased remarkably for both economical and environmental reasons as alkali activation was found to be useful to make cementitious materials from industrial by-products, such as slag or fly ash [1]. Another motivation for driving extensive research into this area was the good potential of alkali-activated aluminosilicates for high-temperature applications. In terms of raw materials, alkali-activated aluminosilicates can be categorised into alkali-activated slag or alkali-activated fly ash. High-temperature performance of alkali-activated slag has been studied to some extent [1–3], but this issue for alkali-activated fly ash has received less attention.

Davidovits [4] first introduced the term geopolymer, which is popularly used for the alkali activated fly ash. Geopolymers have a great potential to be used as building materials because of their comparable, and superior in some cases, engineering properties to Portland cement binder [5,6].

Due to their ceramic-like properties, geopolymers are believed to possess a good capacity of resistance against high temperatures [4,7]. Therefore, in the near future, they may be put into a competitive position against Portland cement in the construction of high fire risk infrastructures such as tunnels and high-rise buildings. When structural members are exposed to fire, their behaviour is dependent partly on the mechanical properties of the material of which the member is composed. Thus, to predict the fire endurance of structural members, the mechanical properties of materials at elevated temperatures must be understood.

At elevated temperatures, our early work [8] found an increase in compressive strength of the geopolymer as opposed to the performance of Portland cement binder. The latter, at temperatures above 300 °C, significantly decreased in strength due to the dehydration and rehydration of CaO [9]. However, abrupt softening of the geopolymer, accompanied by large deformation, was observed at around 600 °C [8].

It is believed that geopolymers could be tailored by correct mix and processing design in order to optimise properties for a given application [10]. The effects of synthesising parameters on the mechanical properties of geopolymers at high temperatures have not been reported in literature. The purpose of this paper is to report the effects of the synthesising parameters such as cation type, silicate concentration, and compositions of low-calcium fly ash on the softening temperature and strength of fly ash-based geopolymers at high temperatures. Since the materials in a structure are in a stressed state, the effect of heating the specimen whilst under different load was also investigated.

2. Experimental work

Fly ashes (ASTM class F) used in the synthesis of geopolymer are from coal-fired power stations with chemical compositions as shown in Table 1. Sodium hydroxide, potassium hydroxide, sodium silicate (14.7% Na_2O, 29.4% SiO_2) and potassium silicate (13.5% K_2O,

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

Element as oxide	Al_2O_3	SiO_2	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	Loss on ignition
Fly ash a	30.5	48.3	2.8	12.1	0.4	1.2	0.2	0.3	1.7
Fly ash b	23.2	72.2	0.2	0.6	0.4	0.1	0.1	0.1	1.4

27% SiO_2) were used as alkaline liquids. The alkali cation and silicate concentration are known to affect microstructural development [5] which plays a significant role in determining the mechanical properties of geopolymers. Therefore, the mixture was selected by considering the variation of cation type and silicate concentration. To achieve these variations in the composition of the geopolymers, the alkaline solution was manipulated to introduce different cation type and varying silicate concentrations. The variation in silicate concentration of geopolymers was further achieved by using fly ashes with different silicate content. Ash b presents a much higher SiO_2 content (72.2%) compared to Ash a (48.3%). It is also noted that Si/Al ratio of Ash b is 2.64 while this ratio of Ash a is 1.35. Fernandez-Jimenez et al. [11] suggested that fly ashes having best performance under alkaline activation are ashes with Si/Al ratios below 2. The reason for this is attributed to fact that a certain amount of Al is always necessary to favour the formation of aluminosilicate gels. Therefore, most of mixes were prepared by using Ash a. The mix compositions of the geopolymers produced are given in Table 2. The materials were proportioned by mass and the mixing was conducted in a mechanical mixer of 20 l of capacity at 80 rpm for 5 min. Cylindrical specimens were made for testing by using moulds of diameter 24 mm and length 48 mm. All the moulds were filled and compacted in layers by using vibration, and were sealed with plastic sheets. The covered moulds were cured in an oven at 60 °C for 18 h. After curing, specimens were de-moulded and kept in the laboratory under ambient conditions until testing. In order to obtain smoother ends, the specimens were polished with a rock-grinder machine before testing.

All the tests were carried out on a closed-loop servo-control (500 kN) hydraulic pump actuator with a loading frame and an electric furnace. Details of the design for the test equipment have been reported in our previous work [8]. Two cylinders from each mix were instrumented with type K thermocouples, placed at the center and surface. The instrumented cylinders were used to develop the heating regimens required to attain the desired target temperatures and steady-state condition.

To estimate the influence of elevated temperatures on the deformation and strength of geopolymers, two types of tests were conducted as follows:

Test I: This test was performed to study the deformation of heated geopolymers under constant load. The specimens were first loaded in compression to a particular pre-determined load and then heated to the required temperatures at 5 °C/min. Tests were performed at stress levels of 0.05 σ_r and 0.55 σ_r, where σ_r is the reference strength at room temperature before heating. The deformation of heated geopolymers was measured until it reached 83% of specimens' initial length. The abrupt change in slope of deformation–temperature curve was observed in previous work [8], which is a characteristic indication of softening of geopolymers.

Test II: This test was conducted to determine the compressive strength of geopolymers at elevated temperatures. Specimens without being subjected to load were heated to the target temperatures which were 50 °C below the softening temperatures measured in Test I. After a further heating period of 1 h at the target temperatures, which was found to be sufficient for reaching a steady-state condition, the specimens were loaded at the rate of 20 MPa/min up to failure.

3. Results and discussion

3.1. Deformation (softening behaviour)

Typical deformation–temperature curves of geopolymers are shown in Figs. 1 and 2. These Figures show sudden softening of geopolymers associated with large deformations at temperatures in the range of 570–800 °C. The phenomenon of sudden softening at high temperature has been found to occur for all geopolymers tested in this study regardless of the type of fly ash, silicate concentration and cation type.

The softening temperature (T_s) of each deformation versus temperature curve is determined by the intersection of the extended lines following the two slopes before and after the transition as illustrated in Fig. 1 for the curve NaSi2. The softening temperatures determined according to this method for NaSi2 for two load levels of 0.05 σ_r and 0.55 σ_r are 590 °C and 610 °C respectively, where σ_r is the compressive strength of the corresponding geopolymer prior to exposure to high temperature. This shows that the softening temperatures are not significantly affected by the load levels.

The softening temperatures (T_s) for NaSi2 and NaSi2b, which had the same mixture proportions but with different fly ash types a and b, are determined to be 590 °C and 610 °C, respectively. Again the differences in T_s are insignificant, indicating that the dif-

Table 2
Composition of geopolymer mixes investigated.

Material Fly ash (type)	NaSi0 a	NaSi1 a	NaSi2 a	NaSi2b b	Na/KSi2 a	KSi2 a
Fly ash mass (kg/m^3)	2100	2100	2100	2100	2100	2100
Sodium hydroxide solution mass (kg/m^3)	945	573	270	270	–	–
Sodium silicate solution mass (kg/m^3)	–	372	675	675	630	–
Potassium hydroxide solution mass (kg/m^3)	–	–	–	–	315	540
Potassium silicate solution mass (kg/m^3)	–	–	–	–	–	405
Component[a]						
H_2O/M_2O (M represents alkali cation, Na, Na + K and K) (molar ratio)	12.9	13.0	13.0	13.0	14.1	15.4
SiO_2/M_2O (M represents alkali cation, Na, Na + K and K) (molar ratio)	0 (SiO_2/Na_2O)	0.65 (SiO_2/Na_2O)	1.3 (SiO_2/Na_2O)	1.3 (SiO_2/Na_2O)	1.3 ($SiO_2/Na_2O + K_2O$)	1.3 (SiO_2/K_2O)

[a] Only ions in solution were considered in these ratios.

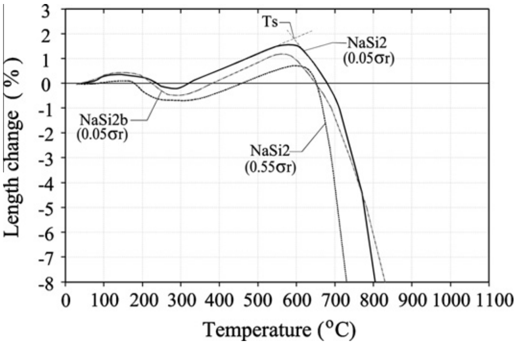

Fig. 1. Deformation–temperature curves of geopolymers prepared by using different fly ashes, under different loading.

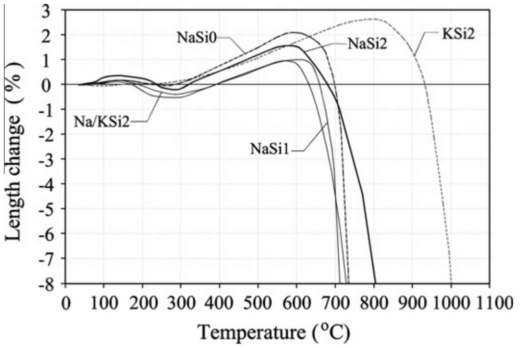

Fig. 2. Deformation–temperature curves of geopolymers with various compositions, Load = 0.05 σ_r.

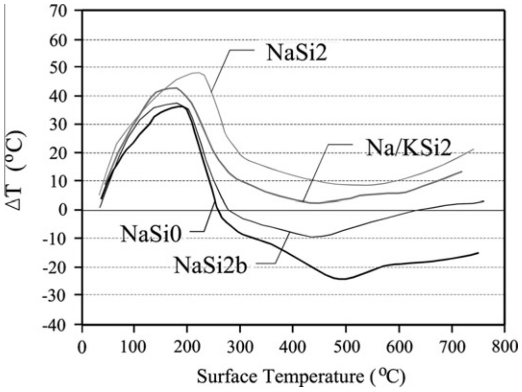

Fig. 3. ΔT (T_{surface}–T_{center}) curves of geopolymers in the transient state.

ferent compositions of low-calcium fly ash may not be a major factor.

The mixtures NaSi0, NaSi1 and NaSi2 were all made with the same fly ash type (type a) and cation type (Na), but increasing levels of silicate concentrations in alkali solutions. The T_s of NaSi0, NaSi1 and NaSi2 are determined to be 630 °C, 610 °C and 590 °C respectively. The differences in T_s are again relatively small indicating that silicate concentrations have little influence on T_s.

The major difference in T_s is observed to occur when the cation type is changed. The T_s of KSi2 (K based alkaline liquid) and NaSi2 (Na based alkaline liquid) are determined to be 800 °C and 590 °C, respectively. The substitution of Na^+ for K^+ is widely known to reduce the softening temperature of aluminosilicate glasses [14]. Both Na^+ and K^+ are called modifiers since when added to the glass they modify the Si–O network. Modifiers disrupt the network and therefore induce a decrease in T_s in glasses. Further, the Na–O bonds are shorter than K–O bonds. The closeness of Na to the bridging oxygen leads to a greater inductive effect of Na relative to K resulting in a greater weakening of T–O–T linkages (T is Al or Si) in glass [12]. It seems that this mechanism is also applicable to geopolymers tested in this study.

In the case of mixed cation type geopolymer, Na/KSi2, where the alkali cation consisted of Na^+ and K^+ in approximately equal content, the T_s is determined to be 570 °C. This value of T_s is lower than that of both NaSi2 (T_s = 590 °C) and KSi2 (T_s = 800 °C). This is known as mixed alkali cation effect in glasses [13] where it has been observed that substation of second alkali cation reduces the T_s from the single cation type.

3.2. Characteristics of ΔT (temperature difference between the surface and center)

Fig. 3 shows the temperature difference (ΔT) between the surface and center of geopolymers specimens. The specimens were heated at a constant rate of 5 °C/min up to about 800 °C. Initially, the center temperature lagged the surface temperature, which is expected since the heat flow is from the surface to the center. However, this lag peaked at the furnace temperature of about 200 °C, and starts to decrease, and even became negatives in two of the four cases tested. The negative ΔT indicates that the center temperature is larger than surface temperature. This can only occur if heat is released from the inside of the specimen. Hence, the decrease in ΔT is believed to be a result of the exothermic process occurring between 200 and 290 °C.

3.3. Compressive strength

Fig. 4 presents results of strength prior to exposure to high temperature (RT, abbreviation for Room Temperature) and strength of geopolymers at high temperature. It can be seen in Fig. 4 that all the synthesis parameters (the presence of different alkali cation, fly ash type and silicate concentration in solution) investigated have major influence on the strength (RT) of geopolymer prior to exposure to high temperature. These results agree with those reported by other researchers [15,16], where the effect of different alkali cation [15] and fly ashes [16] and silicate concentration in solution [16] on compressive strength have been investigated.

When the geopolymers were exposed to elevated temperatures (heating), a significant increase in strength was observed in all geopolymers, as shown in Fig. 4. In earlier work [8], we identified the effect of temperatures on strength of geopolymers made using Mix NaSi2 when exposed to 100, 200, 290, 380, 520, 575 and 680 °C. Test results showed that a major increase in compressive strength occurred between 200 and 290 °C. The strength increased by 61% in this interval, with a further 14% increase between 290 to 575 °C. By comparing with Fig. 3, it can be seen that there was a

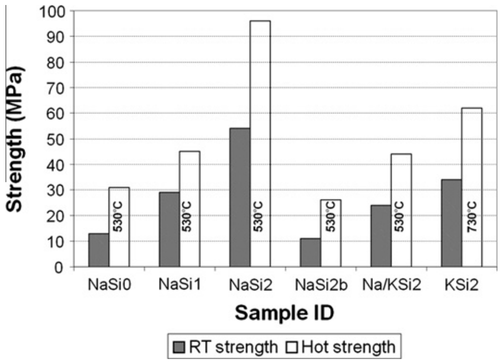

Fig. 4. RT strength (after initial heat-curing) and hot-strength (at temperatures in the vicinity of T_s).

heat release at the same time as strength increase in the range of 200–290 °C. The heat release must be associated with some exothermic reaction occurring inside the specimen.

Exothermic reaction has been observed in the calorimetry analysis of geopolymer reactions, where all stages of the reaction were observed to be exothermic [17,18]. Therefore, the strength increase can be inferred to be due to some stages of geopolymer reactions occurring at this temperature range. This hypothesis is further evidenced by exploring the relationship between the degree of strength increase and the degree of heat release in the current investigation. By comparing strength and ΔT results obtained in NaSi0 with those obtained in NaSi2, it can be seen that a high degree of strength increase is associated with a high degree of heat release.

Fig. 4 shows a correlation between the Room Temperature (RT) strength and the percentage strength gain. NaSi0 and NaSi2b had quite low RT strength (10–12 MPa), but had significantly improved strength at high temperatures (20–27 MPa). The reason for this is hypothesised to be the following mechanism. The geopolymers with low RT strength may retain more unreacted starting materials compared to the geopolymers with high RT strength. At high temperatures, these unreacted starting materials may be transformed into reaction products by geopolymer reactions. The higher content of unreacted starting materials the higher strength increase, which is due to high extent of geopolymer reactions. This hypothesis is consistent with the higher amount of heat released from the geopolymer with lower RT strength.

4. Conclusions

Heat-cured low-calcium fly ash-based geopolymer specimens were subjected to loads at high temperatures. It was found that geopolymers demonstrate a softening behaviour at high temperatures. This softening temperature (T_s) has been found to be independent of the compositions of fly ash, silicate concentration, and test load.

The only parameter found to affect the T_s is the alkali cation type. In this study, three types of cations were studied, namely, sodium (Na), potassium (K) and mix of Na and K. The T_s was found to be in the range of 610 °C (±20 °C) for the four types of Na based geopolymer tested. When the cation was changed to K, the T_s increased to 800 °C. Further, when mixed cation type (Na/K) was used, the T_s dropped to 570 °C.

All geopolymers, regardless of the synthesising parameters, showed remarkable hot strength increases at high temperatures. Geopolymers released heat in the temperature range of 200–290 °C, indicating the occurrence of an exothermic reaction. This reaction at high temperatures is believed to be the reason for the strength gain at high temperatures.

Although all geopolymers showed an increase in hot strength, the extent of strength increase is different. The geopolymers with low Room Temperature (RT) strength exhibited a higher strength increase compared to the geopolymers with high RT strength.

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