COMPARATIVE STUDY OF SODIUM AND POTASSIUM BASED FLY ASH GEOPOLYMER AT ELEVATED TEMPERATURES

Anwar Hosan[1,*], SharanyHaque[1] and Faiz Shaikh[1]
[1*]Email: anwarhosan@yahoo.com
[1]Department of Civil Engineering, Curtin University, Perth, Western Australia.

ABSTRACT

This paper presents the effects of sodium and potassium based activators on compressive strengths and physical changes of class F fly ash geopolymer exposed to elevated temperatures. Samples were heated at 200^{0}C, 400^{0}C, 600^{0}C and 800^{0}C to evaluate the residual compressive strength after 28 days of curing. The fly ash geopolymer were synthesized with combined sodium silicate and sodium hydroxide solutions and potassium silicate and potassium hydroxide solutions by varying mass ratios of Na_2SiO_3/NaOH and K_2SiO_3/KOH of 2, 2.5 and 3. Results show that in the cases of Na_2SiO_3/NaOH ratios of 2 and 2.5, the compressive strengths of geopolymers are decreased at 400, 600 and 800^{o}C, with exception at 200^{o}C. The reduction is significantly high from 32-61% at 800^{o}C compared to ambient temperature strength. However, significant improvement is noticed in the case of Na_2SiO_3/NaOH ratio of 3, where the residual compressive strengths are increased upto 600^{o}C. Better results on the geopolymer synthesized with potassium based activators are obtained where the residual compressive strength up to 600^{o}C are much higher than their sodium based counterparts. The geopolymer containing K_2SiO_3/KOH ratio of 3 even gained about 5% strength at 800^{o}C. It is also found that the fly ash geopolymer synthesized with potassium based activators is more stable at elevated temperatures than its sodium based counterparts in terms of higher residual compressive strengths, lower mass loss, lower volumetric shrinkage and lower cracking damage.

KEYWORDS

Geopolymer, fly ash, elevated temperatures, sodium silicate, sodium hydroxide, potassium silicate, potassium hydroxide.

INTRODUCTION

Geopolymeris a new construction material which gained its popularity in recent years due to its environment friendliness and excellent mechanical and durability properties in severe environment. Geopolymer is first introduced by Davidovits (1991) and is generally made by reacting aluminate and silicate bearing source materials with alkali activator. Excellent fire resistance of geopolymer is its most significant advantage over cement based binder due to its ceramic like property.

Extensive researches have been conducted to study various mechanical and durability properties of geopolymer. Significant efforts have also been made by many researchers to study the effect of elevated temperatures on mechanical properties of geopolymer. However, most of the studies were on different geopolymers which consisted of various types of source materials and alkali activators, e.g. fly ash activated by sodium based alkali activators (Rickard et al., 2012, Abdulkareem et al., 2014, Ranjbar et al.,2014, Shaikh and Vimonsatit, 2015), fly ash activated by combined sodium and potassium based activators (Kong and Sanjayan, 2008 and 2010, Bakharev, 2006), combined fly ash and slag activated by sodium based activator (Guerrier and Sanjayan, 2010), metakaolin activated by combined sodium and potassium based activators (Kong et al., 2007), etc.. Among all above source materials the class F fly ash is rich in silica and alumina and low in calcium oxide, which enables its higher stability in fire than others. Moreover, it is cheaper, easily and widely available than other source materials.

This paper presents the effects of sodium and potassium based activators on the compressive strength of fly ash geopolymer at various elevated temperatures of 200, 400, 600 and 800^{o}C. The effects of silicate to hydroxide ratios for both sodium and potassium based activators on the compressive strengths and physical changes like the mass loss, volumetric shrinkage, damage cracking at above elevated temperatures are also evaluated.

EXPERIMENTALPROGRAM

The experimental program is consisted of two parts. The first part is geopolymer paste containing sodium based activators combinations, where three different sodium silicate to sodium hydroxide ratios of 2, 2.5 and 3 are considered and for each ratio the geopolymers are heated at 200, 400, 600 and 800ºC temperatures as well as at ambient temperature. Thus fifteen series of pastes are cast and tested at elevated temperatures in the first part. The second part is similar to the first part in every aspect except the alkali activators where potassium silicate and potassium hydroxide are used. For each series, in both parts, six 50 mm cube specimens are cast and tested and the average value is shown in the results. Detail experimental program and mix proportions can be seen in Table 1. In all pastes a constant activators/fly ash ratio of 0.35 is considered.

Table 1 Experimental program and mix proportions

Part 1				Part 2			
Sample ID	Na_2SiO_3/ NaOH	Activators/ fly ash	Kiln Temperature	Sample ID	K_2SiO_3 /KOH	Activators/ fly ash	Kiln Temperature
Na-2-28	2	0.35	Ambient	K-2-28	2	0.35	Ambient
Na-2-200	2	0.35	200	K-2-200	2	0.35	200
Na-2-400	2	0.35	400	K-2-400	2	0.35	400
Na-2-600	2	0.35	600	K-2-600	2	0.35	600
Na-2-800	2	0.35	800	K-2-800	2	0.35	800
Na-2.5-28	2.5	0.35	Ambient	K-2.5-28	2.5	0.35	Ambient
Na-2.5-200	2.5	0.35	200	K-2.5-200	2.5	0.35	200
Na-2.5-400	2.5	0.35	400	K-2.5-400	2.5	0.35	400
Na-2.5-600	2.5	0.35	600	K-2.5-600	2.5	0.35	600
Na-2.5-800	2.5	0.35	800	K-2.5-800	2.5	0.35	800
Na-3-28	3	0.35	Ambient	K-3-28	3	0.35	Ambient
Na-3-200	3	0.35	200	K-3-200	3	0.35	200
Na-3-400	3	0.35	400	K-3-400	3	0.35	400
Na-3-600	3	0.35	600	K-3-600	3	0.35	600
Na-3-800	3	0.35	800	K-3-800	3	0.35	800

MATERIALS AND MIXING

Class F fly ash supplied by Gladstone power station of Queensland was used as source material to prepare the geopolymer pastes. Table 2 shows the chemical compositions of the fly ash. The activating alkali liquids consisted of Na_2SiO_3 and NaOH solutions as well as K_2SiO_3 and KOH solutions. The Na-based activator was composed of 8.0 M sodium hydroxide (NaOH) and D Grade sodium silicate (Na_2SiO_3) solutions. NaOH solution was prepared with a concentration of 8.0 M using NaOH beads of 97% purity and tap water. The D Grade Na2SiO3 solution was supplied by PQ Australia with a specific gravity of 1.51 and a modulus ratio (Ms) equal to 2.0 (where Ms = SiO_2/ Na_2O, Na_2O = 14.7% and SiO2 = 29.4%). The NaOH and Na_2SiO_3 solutions were mixed together with Na_2SiO_3/NaOH mass ratio of 2, 2.5 and 3 to prepare the Na-based activators. The K-based activator was composed of 8.0 M potassium hydroxide (KOH) and potassium silicate (K_2SiO_3) solutions. KOH solution was prepared with a concentration of 8.0 M using KOH flakes of 90% purity supplied by Perth Scientific, Australia and tap water. The K_2SiO_3 (KASIL 2236 Grade) solution was supplied by PQ Australia with a specific gravity of 1.32 and a modulus ratio (Ms) equal to 2.23 (where Ms = SiO_2/K_2O, K_2O = 11.2% and SiO_2 = 24.8%). KOH and K_2SiO_3 solutions were mixed together with K_2SiO_3/KOH mass ratio of 2, 2.5 and 3 to prepare the K-based activators.

Table 2 Chemical Composition of Fly Ash (mass %)

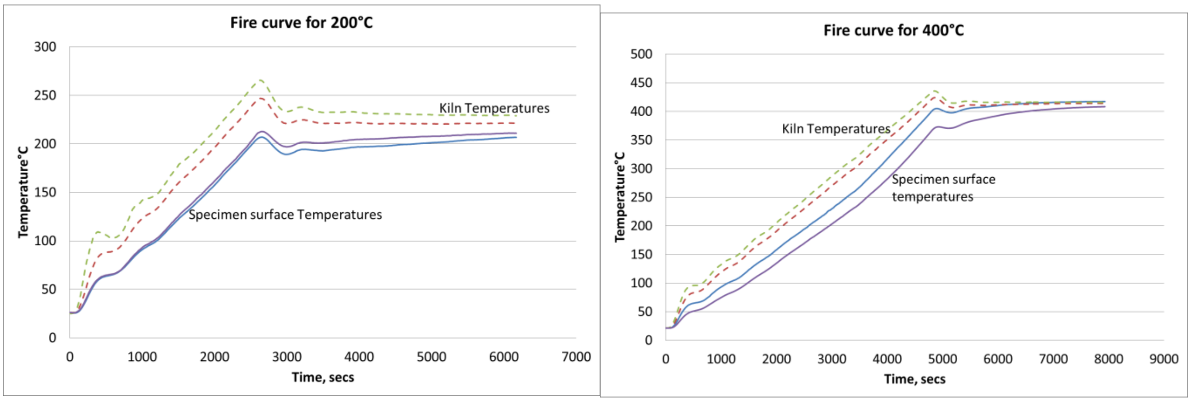
Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	MgO	P_2O_5	SO_3	TiO_2	MnO	LOI
Fly ash	51.11	25.56	12.48	4.3	0.77	0.7	1.57	1.45	0.885	0.24	1.32	0.15	0.57

All pastes were prepared in a Hobart mixer. To prepare the Na- and K-based geopolymer paste the alkaline activators in the form of solution were added to the fly ash and mixed for about 4 min. The fresh geopolymer pastes were cast into standard 50 mm plastic cube moulds and compacted using a vibrating table. The specimens were subjected to heat curing. In this regard, all moulds were sealed to minimize moisture loss and placed in an oven at 70°C for 24 h. At the end of heat curing period, the specimens were removed from the oven and kept undisturbed until being cool and then removed from the moulds and left in the laboratory at ambient temperature until the day of testing. Compressive strength of all specimens was measured according to AS 1012.9:2014. For each mix, at least six specimens were tested in order to check the variability of performance under compression. The volume stability or in other words the volumetric shrinkage of pastes was determined by measuring the length of three sides of the cubes before and after heating at respective elevated temperatures. The difference in volume changes indicates the shrinkage and six specimens were used to measure the shrinkage for each series. Similar method was used to determine the mass loss of geopolymer pastes after exposed to respective elevated temperatures.

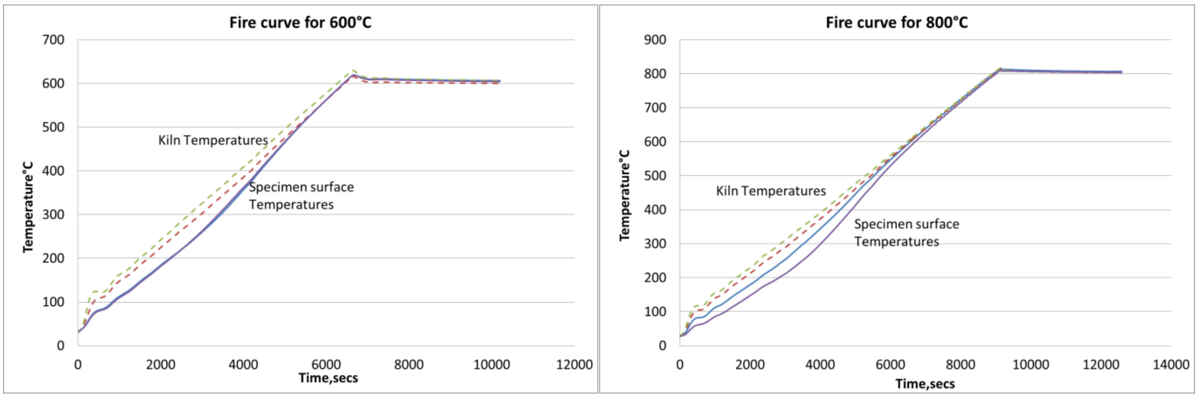
ELEVATED TEMPERATURE EXPOSURE:

A locally manufactured kiln was used to heat the geopolymer specimens, where the specimens were heated up to 800°C. The specimens were positioned inside the kiln where two thermocouples were touched the specimens, and two more thermocouples were also inserted into the kiln in order to monitor the kiln air temperature. The thermocouples were connected to the data logger and were used to monitor the temperature inside the concrete and the kiln air as shown in Figure 1. A heating rate of 500°C per hour was selected. During heating process the temperatures of four thermocouples were monitored. Once the specimen's surface reached the target temperature, the temperature inside the kiln was hold for one hour. The rate of temperature increase in the kiln and in the specimen is shown in Figure 2.

Figure 1 Geopolymer specimens inside the kiln.



(a) (b)



(c)

(d)

Figure 2 Fire curves for different elevated temperatures in the kiln during heating.

RESULTS AND DISCUSSIONS

The measured compressive strengths of geopolymer pastes containing different $Na_2SiO_3/NaOH$ ratios of 2, 2.5 and 3 after exposing to 200, 400, 600 and 800°C temperatures are shown in Figure 3. It can be seen that the residual compressive strengths of geopolymer paste containing $Na_2SiO_3/NaOH$ ratio of 2 and 2.5 are increased by about 9-11% at 200°C compared to ambient temperature strength. However, with further heating at 400, 600 and 800°C temperatures the residual compressive strengths of above geopolymer pastes are decreased below the ambient condition (see Figure 4). On the other hand, the same geopolymer paste containing $Na_2SiO_3/NaOH$ ratio of 3 showed significant increase in residual compressive strength by about 25-35% up to 600°C with exception at 800°C, where the residual compressive strength is decreased by more than 30% (See Figure 4).

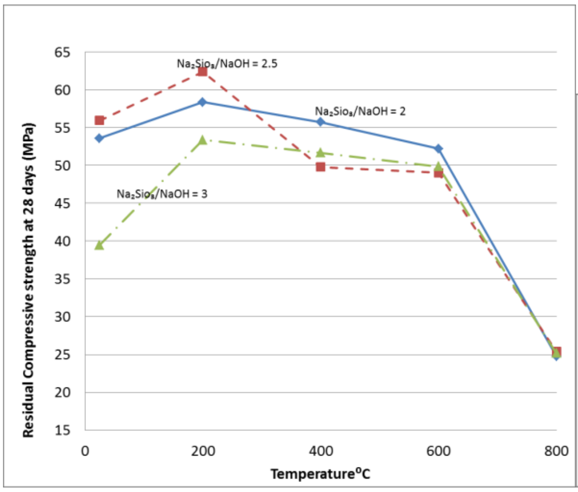


Figure 3 Residual compressive strength of geopolymer pastes containing Na-based activators at various elevated temperatures

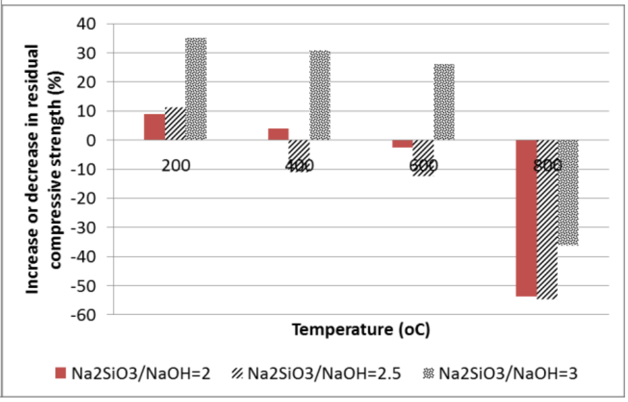


Figure 4 Relative increase or decrease in residual compressive strength of geopolymer pastes containing Na-based activators at various elevated temperatures compared to ambient temperature.

The effect of K-based activators on the compressive strength of geopolymer paste at elevated temperatures is also evaluated in this study and is shown in Figures 5-6. Figure 5 shows the measured compressive strengths of geopolymer pastes containing different K_2SiO_3/KOH ratios of 2, 2.5 and 3 after exposing to 200, 400, 600 and 800°C temperatures. It can be seen in the figure that for all three K_2SiO_3/KOH ratios the residual compressive strengths of geopolymer pastes are much higher than the ambient temperature strength and the residual compressive strengths are increased with increase in elevated temperatures until 600°C. It is also interesting to see that at 400 and 600°C the geopolymer paste containing K_2SiO_3/KOH ratios of 2 and 2.5 show about 40-55% increase in compressive strength compared to ambient condition. Although the increase in compressive strength of paste containing K_2SiO_3/KOH ratios of 3 is slightly lower (about 22-26%) at those temperatures, the compressive strength is increased by about 5% at 800°C temperature, which is not observed in the case of K_2SiO_3/KOH ratios of 2 and 2.5 (see Figure 6).

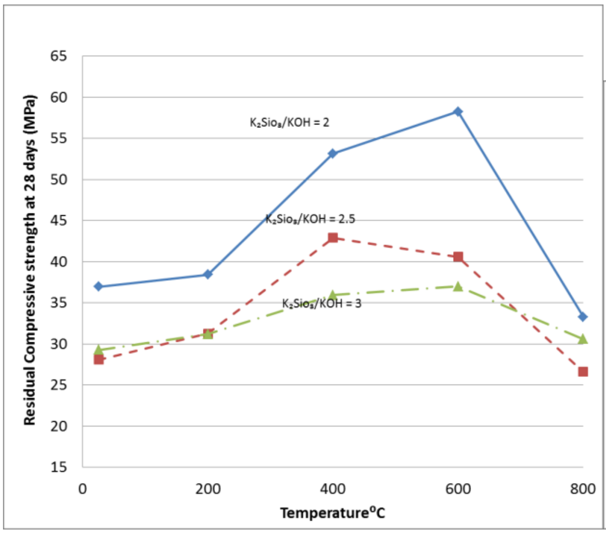


Figure 5 Residual compressive strength of geopolymer pastes containing K-based activators at various elevated temperatures

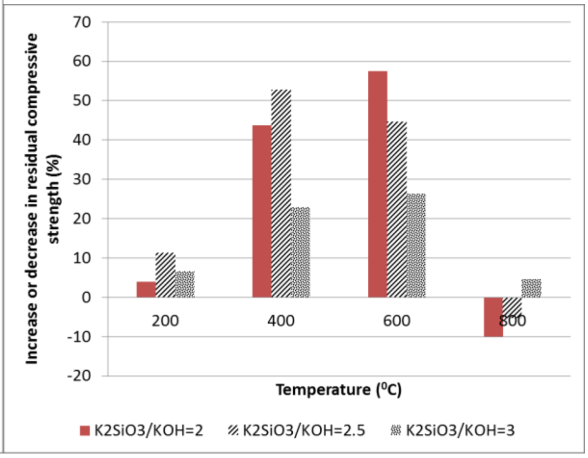


Figure 6 Relative increase or decrease in residual compressive strength of geopolymer pastes containing K-based activators at various elevated temperatures compared to ambient temperature.

By comparing both Na and K based geopolymer series in Figure 7 it can be clearly seen that the K-based activators show higher compressive strength retention capacity for geopolymer pastes than its counterpart Na-based series compared to ambient temperature strength. It can also be seen that in both geopolymer the ambient strength decreases with increase in silicate/hydroxide ratios for both Na- and K-based activators. This is attributed to the low water evaporation and less geopolymer structure formation due to excessive sodium silicate and potassium silicate (Chew, 1993). Interestingly the geopolymer with $K_2SiO_3/KOH=3$ exhibited higher compressive strength at all elevated temperatures than ambient temperature, which is also true for Na-based counterpart, however up to 600°C. The increase in compressive strength in the former can be attributed to the lower diffusion coefficient of K^+ at elevated temperatures, which results in higher melting temperature (Bakharev, 2006).

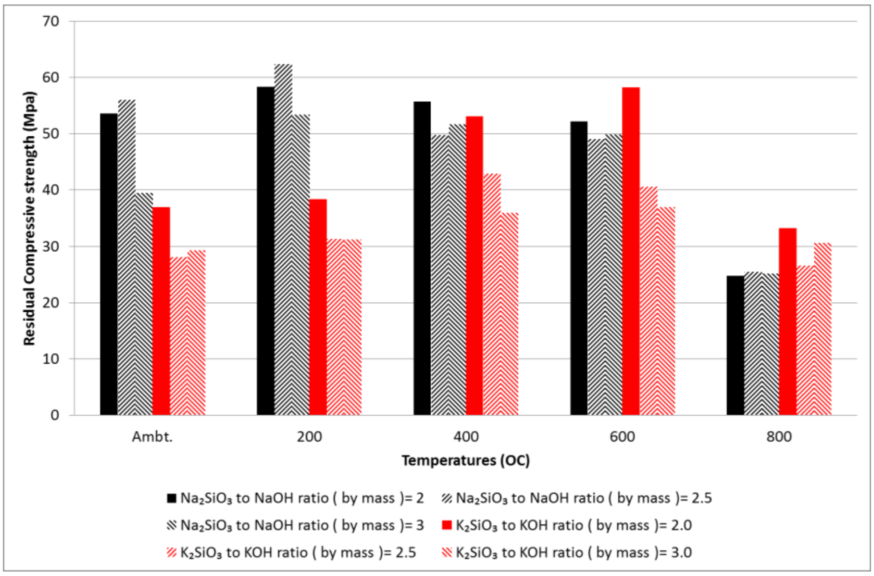


Figure 7 Comparison of compressive strengths of Na- and K-based geopolymer pastes.

The effects of elevated temperatures on physical changes of both Na- and K-based activator synthetized geopolymers are shown in Figures 8-10. Figure 8 shows the formation of cracks on specimens' surface for both geopolymers. It can be seen that up to 400°C no cracks are formed in both geopolymers. However, Na-based geopolymer showed signs of cracks at 600°C and it becomes worst at 800°C, where many wide cracks on the surface are formed. The geopolymer containing K-based activator, however, survived from surface cracking up to 600°C, but fine cracks are formed at 800°C. Figure 9 shows the reduction of mass of both geopolymers at various elevated temperatures. It can be seen that the mass loss of Na-based geopolymer is slightly higher than that of K-based counterpart. An interesting observation is also noted that by increasing the Na_2SiO_3/NaOH ratios the mass loss is slightly increased, which an opposite phenomenon is in K-based system. It can also be seen that up to 400°C significant reduction in mass loss of about 8-10% is observed in both geopolymers and the mass loss becomes stable afterword. In the case of volumetric shrinkage of both geopolymers at elevated temperatures similar results to those of mass loss are also observed, where the K-based geopolymer showed lower shrinkage than its Na-based counterpart at all elevated temperatures.

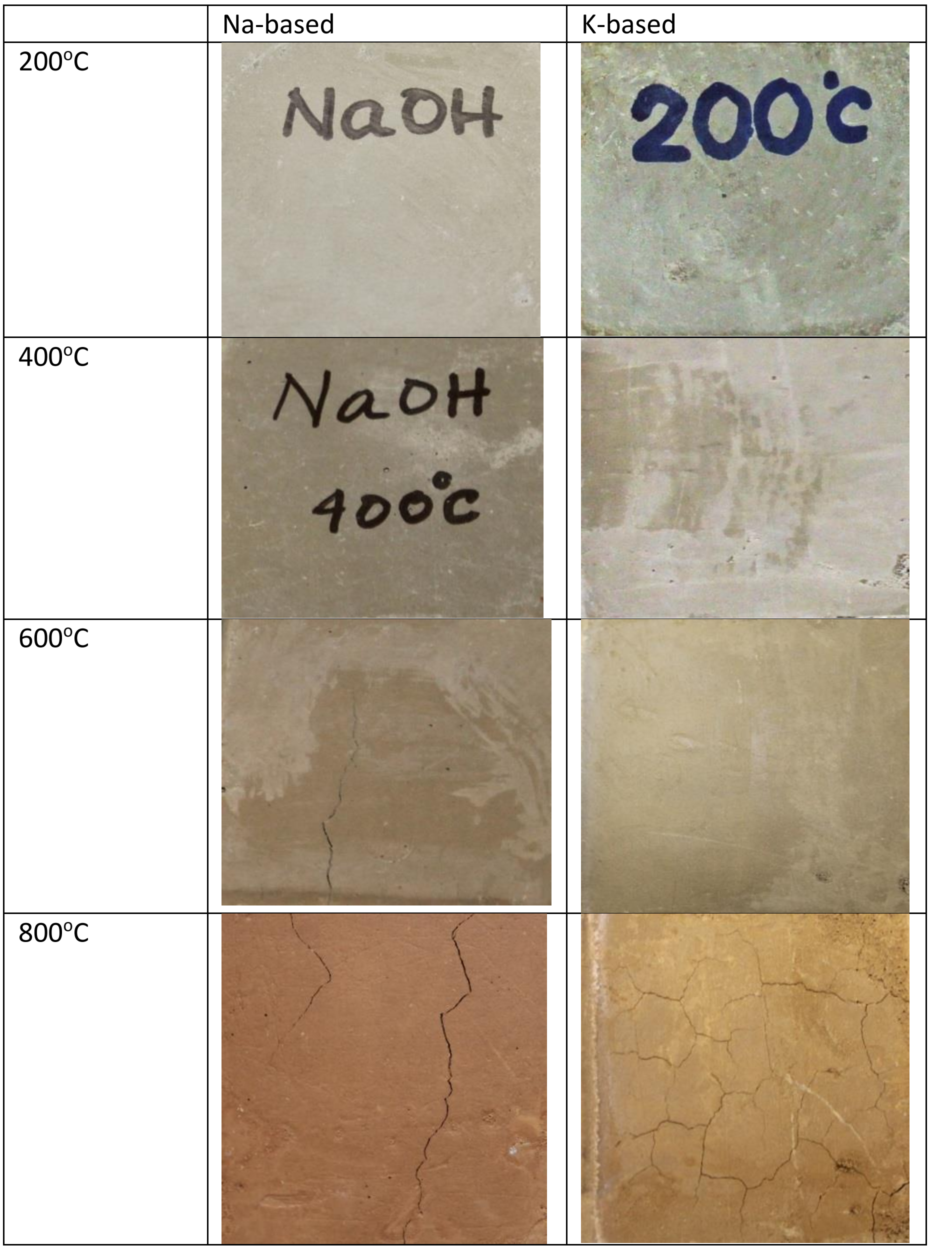


Figure 8 Cracking behaviour of fly ash geopolymers containing Na- and K-based activators at elevated temperatures.

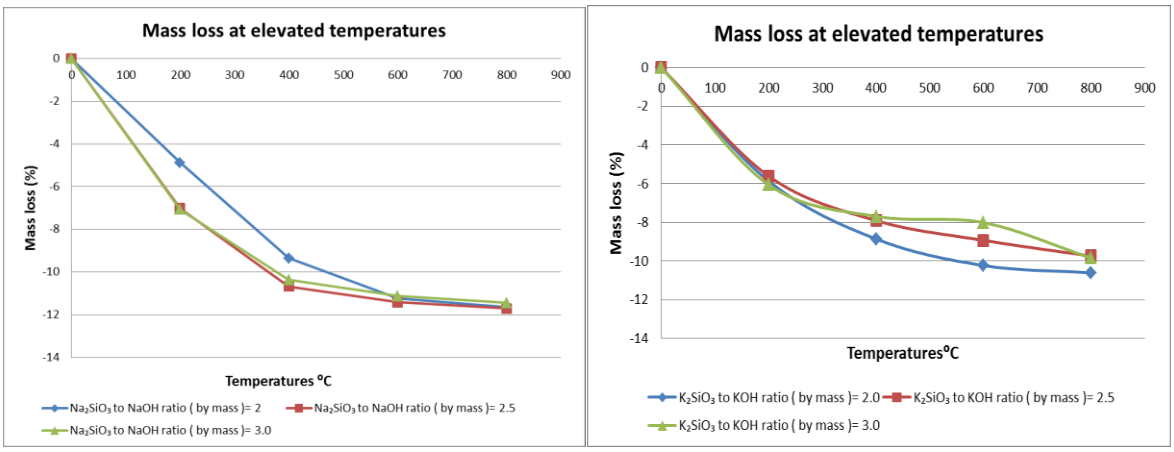


Figure 9 Comparison of mass loss of Na- and K-based geopolymer pastes at elevated temperatures.

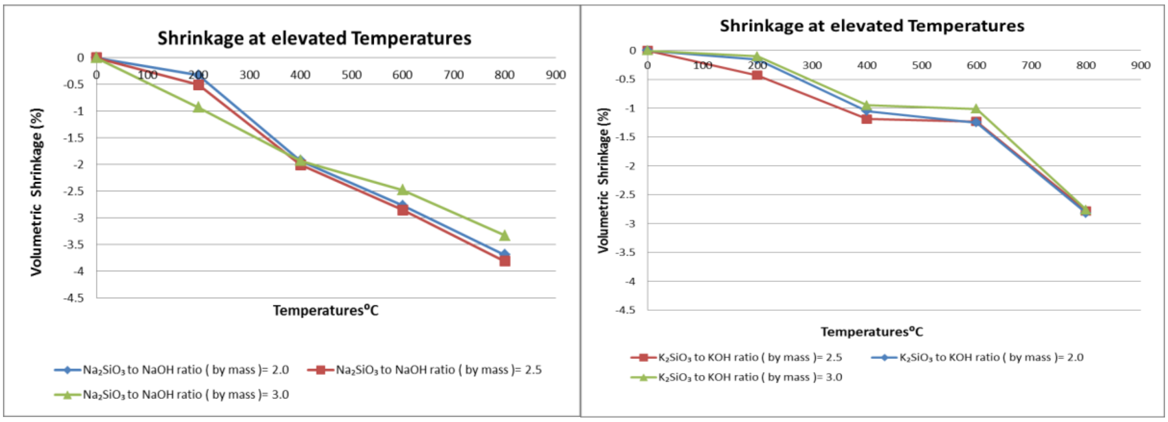


Figure 10 Comparison of volumetric shrinkage of Na- and K-based geopolymer pastes at elevated temperatures.

CONCLUSIONS

Based on limited experimental variables in terms of Na and K-based activators, the ratios of silicate to hydroxide of above activators, elevated temperatures on the residual compressive strengths, volume stability and mass loss of geopolymer pastes the following conclusions can be drawn:

1. The geopolymer pastes containing Na-based activator exhibited higher compressive strength at ambient temperature and higher compressive strength at elevated temperatures up to 400ºC than its K-based counterpart.
2. At 600ºC the compressive strength of geopolymer containing K-based activator is slightly higher than its Na-based counterpart.
3. The geopolymer paste containing K-based activator exhibited higher residual compressive strengths at all elevated temperatures compared to ambient temperature than its Na-based counterpart.
4. The geopolymer paste containing K-based activator with K_2SiO_3/KOH ratio of 3 exhibited the highest residual compressive strengths at all elevated temperatures compared to ambient temperature than its Na-based counterpart.
5. The volume stability and mass loss of geopolymer paste containing K-based activator is higher and lower, respectively than its Na-based system.
6. The geopolymer pastes containing K-based activator exhibited fewer surface cracks than that of Na-based activator.

ACKNOWLEDGMENTS

Grateful acknowledgements are due to Cement Australia for donating class F fly ash from Gladstone power station of Queensland and IMCD Australia Limited for donating potassium silicate in this study.

REFERENCES

Abdulkareem, O.A., Al-bakri, A.M.M., Kamarudin, H., Nizar, I.K. and Saif, A.A. (2014) Effects of elevated temperatures on the thermal behaviour and mechanical performance of fly ash geopolymer paste, mortar and light weight concrete. *Construction and building materials*, Vol.50:337-387.

AS 1012.9 (2014) *Methods of testing concrete - Compressive strength tests - Concrete, mortar and grout specimens*. Standards Australia.

Bakharev, T. (2005) Geopolymeric materials prepared using class F fly ash and elevated temperatures curing. *Cement and concrete research*, Vol. 35:1224-1232.

Bakharev, T. (2006) Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperatures curing. *Cement and concrete research*, Vol. 36:1134-1147.

Chew, M.Y.L. (1993) The assessment of fire damaged concrete. *Building and environment*. Vol.28(1): 97-102.

Davidovits, J. (1991) "Geopolymers-inorganic polymeric new materials". *Journal of Thermal Analysis*, 37 (8):1633–1656.

Guerrieri, M. and Sanjayan, J.G. (2010) Behaviour of combined fly ash/slag based geopolymers when exposed to high temperatures. *Fire and materials*, Vol.34:163-175.

Kong, D.L.Y. and Sanjayan, J.G (2008) Damage behaviour of geopolymer composites exposed to elevated temperatures. *Cement and concrete composites*, Vol. 30:986-991.

Kong, D.L.Y. and Sanjayan, J.G (2010) Effect of elevated temperatures on geopolymer paste, mortar and concrete. *Cement and concrete research*, Vol. 40:334-339.

Kong, D.L.Y., Sanjayan, J.G. and Sagoe-Crentsile, K. (2007) Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures. *Cement and concrete research*, Vol. 37:1583-1589.

Ranjbar, N., Mehrali, M., Alengaram, U.J., Metselaar, H.S.C. and Jumaat, M.Z. (2014) Compressive strength and microstructural analysis of fly ash/palm oil fuel ash based geopolymer mortar under elevated temperatures. *Construction and building materials*, Vol.65:114-121.

Rickard, W.D.A., Temuujin, J. and van-Riessen, A. (2012) Thermal analysis of geopolymer pastes synthesized from five fly ashes of variable compositions. *Journal of non-crystalline solids*, Vol. 358:1830-1839.

Shaikh, F.U.A. and Vimonsatit, V. (2015) Compressive strength of fly ash based geopolymer concrete at elevated temperatures. *Fire and Materials,* Vol. 39:174-188.