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Effect of Temperature on Thermal Properties of Alkali-activated Fly Ash/Slag Binders

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Abstract

Geopolymeric binders exhibit high thermal stability and consequently it is believed that these materials can be extensively used in the construction of infrastructure, where fire safety is of major concern. For such applications, thermal properties play a fundamental role in the heat transfer calculation. This paper aims to provide a comprehensive experimental study of thermal properties of various geopolymeric binders at elevated temperatures. The binders were prepared using alkali-activated low calcium fly ash/ground granulated blast-furnace slag at ratios of 100/0, 50/50, 10/90 and 0/100 wt%. A transient plane source measurement technique was applied to assess the heat capacity and thermal conductivity at temperatures ranging from 23–600 ^{o}C. Data generated was utilised to develop analytical expressions for estimating thermal properties as a function of temperature. The simplified relationships can be used for estimating the fire resistance of structural elements made with geopolymeric materials.

Keywords: Geopolymers, Thermal conductivity, Specific heat, Elevated temperatures, Thermal property models.

1. INTRODUCTION

Alkali-activated slags and fly ashes (or refer to geopolymers) have emerged as innovative building materials with the potential to form an environmentally friendly alternative to ordinary Portland cement (OPC) concrete. These materials are produced by alkali activation of aluminosilicate raw materials (e.g., fly ash or metakaolinite) in a high pH environment and hydrothermal conditions. In comparison with OPC concrete, the greenhouse footprint of geopolymer concrete is 70% lower (van Deventer et al, 2012). Given correct mix design, these alternative binding systems could provide superior mechanical properties and durability to OPC concrete, and be highly profitable.

Research and development of geopolyermic materials started in the 1930s and the number of papers published in this field has grown exponentially in the last 20 years (Palomo et al, 2014). However, the transformation from academic research to on-site field work has been relatively slow. There is a lack of commercial drivers in the market as the benefits of geopolymeric materials are not fully realised by the industry practitioner. One such benefit is the excellent fire resistance of geopolymeric materials, which is attributed to its three-dimensional macromolecular framework (of alkali-activated fly ash) having high thermal stability (Pan et al, 2013).

A recent study has clearly indicated that geopolymeric materials have higher fire performance as compared to OPC materials (Pan and Sanjayan, 2010). When exposed to elevated temperatures, the strength of alkali-activated fly ashes (AAF) increased (due to further geopolymerisation) while the strength of OPC counterparts decreased (due to decomposition of calcium hydroxide). Sarker et al. (2014) studied the thermal spalling of AAF concrete and OPC concrete. When the specimens were exposed to elevated temperatures up to 1000 ^{o}C, the OPC concrete specimens suffered severe spalling, while no spalling was observed on AAF concrete specimens.

Besides mechanical properties and thermal spalling, thermal properties also have a significant influence on the fire response of a structural system. Material with a low thermal conductivity will reduce the amount of heat which flows through it, increasing the fire resistance of structures made from this material. While the effects of temperature on the performance of geopolymers have been investigated, there have been limited investigations into thermal properties of geopolymeric materials. A review of current literature (Subaer and van Riessen, 2007; Duxson, 2006) revealed that data on thermal properties of geopolymers have been preliminary and further research is required to understand these systems. Subaer and van Riessen (2007) investigated thermal expansion and thermal conductivity of geopolymers prepared by metakaolinite, and their results show a similar thermal conductivity obtained in geopolymers, as compared to OPC pastes. However, the specific heat of geopolymer was not reported and the measurement of thermal conductivity was only carried out at ambient temperature in this study. Duxson et al. (2006) studied the effect of humidity on thermal conductivity and specific heat of metakaolin-derived Na, NaK and K geopolymers in the temperature range of 40 to 100 ^{o}C. They found that the thermal conductivity of geopolymers is closely linked with the specific heat. As the specific heat of potassium is lower than that of sodium, the thermal conductivity of K-based geopolymers is also lower than that of Na-based geopolymers.

For a porous material, the thermal transport properties are affected by the pore structure (pore volume and pore interconnectivity) and moisture content. In geopolymerisation, water is required as a reaction intermediate and is released during condensation to form pores and create the biphasic structure (Subaer and van Riessen, 2007). Given that a significant volume fraction of geopolymer composite structures is comprised of water, the thermal properties of geopolymeric materials are expected to vary in a fire, as a result of evaporation. It is also noted that the pore structure varies greatly, depending on the raw materials for the synthesis of geopolymer, and curing regime. In the previous studies (Subaer and van Riessen, 2007; Duxson, 2006), geopolymers were prepared by using metakaolinite, and the samples developed strength under heat curing. Although this regime can easily be achieved in a typical precast concrete factory, it is hard to be implemented for cast in situ applications. In order to offset the limitation of heat curing, a typical method is to manufacture geopolymer by combing fly ash with slags. The fly ash/slag and pure fly ash involve entirely different reaction mechanisms and produce pore structure of distinct characteristics. The fly ash/slag system (Ca-Si system) undergoes a complex reaction that involves hydration of CaO in the presence of Al to form an aluminium-modified calcium silicate hydrate (C-(A)-S-H) gel as a major binding phase. On the other hand, alkali activation of fly ash or metakaolinite (Al-Si system) involves the dissolution of Si, coagulation, and a highly exothermic condensation reaction followed by crystallisation to produce zeolite-like polymers, with a three-dimensional sodium alumina-silicate hydrate (N-A-S-H) gel as a major binding phase (van Deventer et al, 2012). This is different from layered structure for calcium silicate hydrate (C-S-H) gel in Portland cement paste. Therefore, significant variation in thermal conductivity may be found for different type of binders.

This work aims to investigate the thermal properties of the Al-Si (mainly containing fly ash) system and Ca-Si system (slag or fly ash/slag). The thermal properties of the latter have received little attention. Moreover, the previous investigations (Subaer and van Riessen, 2007; Duxson, 2006) of geopolymers only studied the thermal properties over the range of 23–100 °C. In this study, thermal properties of both geopolymeric systems will be measured over the temperature range of 23–600 °C. Data obtained from this study will be used to develop simplified relations for expressing specific heat and thermal conductivity of geopolymers as a function of temperature. These relations are required for analysis of fire resistance of a structural system made with geopolymeric materials.

2. EXPERIMENTAL PROGRAM

2.1. Materials

In this investigation, for the purpose of comparison, cement paste was also prepared. The cement used meets the requirement of ASTM C150 Type I cement. The class F fly ash used in this investigation was mainly a glassy material with some crystalline inclusions of mullite, hematite and quartz. A granulated blast furnace slag was supplied with gypsum, which was pre-blended with slag. The oxide compositions of the binder materials are summarised in Table 1. It is noted that the fly ash has very low calcium content. As a result, the fly ash-based geopolymer mainly consists of calcium-free gel structures.

The alkaline activating agents used in this investigation included sodium hydroxide, sodium silicate and sodium metasilicate. Sodium hydroxide flakes of 98% purity were supplied by Orica Chemicals. Sodium silicate liquid and industrial grade-powdered sodium metasilicate were supplied by PQ Australia. Sodium silicate liquid (Grade D) has the chemical composition: 29.4% SiO_2, 14.7% Na_2O and 55.9% H_2O, with a molecular modulus of Ms=2.06. Sodium metasilicate has the chemical composition: 29% Na_2O, 28% SiO_2 and 43% H_2O, with the Ms=1.0.

Table 1. Chemical analysis by X-Ray Fluorescence of raw materials

Constituent	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	SO_3	Cl	Loss on ignition
Cement (wt%)	19.9	4.7	3.4	0.5	0.2	63.9	1.3	2.6	-	3
Fly ash (wt%)	48.4	30.6	12.1	0.3	0.2	2.7	1.3	-	-	1.7
Slag (wt%)	32.5	13	0.22	0.25	0.21	42.1	5.47	-	-	0.35

2.2. Mix proportion

Samples were prepared without aggregates, since this paper only focuses on one component of concrete, binding phase. Generally, concrete consists of 70% aggregates and 30% binding phase by volume. Although the binding phase constitutes a small fraction of the overall volume, it plays a major role in the determination of thermal properties of concrete because it acts as the continuous phase, whereas the aggregate acts as the dispersed phase.

The samples were prepared in fly ash/slag proportions of 100%/0%, 90%/10%, 50%/50% and 0%/100% (wt-%). The labels representing the above samples are F100, F90S10, F50S50 and S100, respectively. The liquid activator (a combination of sodium hydroxide solution and sodium silicate solution) was used to prepare F100 and F90S10. The concentration of sodium hydroxide solution was 8 M, and the mass ratio of sodium hydroxide solution to sodium silicate solution was 2.5. The ratio of liquid activator to the binder (fly ash + slag) was 0.45 for F100 and F90S10.

It was noted that the dissolution and reaction of slag in strong alkaline media were much faster, as compared to fly ash. As a result, the liquid activator could lead to the quick setting of fresh samples with a high content of slag (F50S50 and S100). To avoid the flash set, the powdered activator (sodium metasilicate) was used to prepare F50S50 and S100. The activator dosage used was 4 wt-% of the total mass of the binder and water to binder ratio was 0.5. The hydrated lime, with a 1 wt-% of the binder, was added to both mixtures of F50S50 and S100. OPC samples with a water to cement ratio of 0.5 were also cast for the purpose of comparison.

2.3. Specimen preparation

The mixing procedures used were summarised as follows. The binders (fly ash, slag or cement) and the liquid components (water or alkali liquid) were mixed in a Hobart mixer for 5 min. When making geopolymer samples, the powder ingredients were dry mixed for 2 min. Then the alkali liquid or water was added, and wet mixing was carried out for 4 min. For powdered activated samples, the dry silicate activator was pre-blended with slag and dry-mixed for 3 min to achieve a homogenous mixture. The hydrated lime was mixed with water in a ratio of 1:3. The lime slurry together with water was then added, and wet mixing was carried out for 4 min. The mixture was poured into the mould in three equal layers. Each layer was vibrated for 20-40 s on a vibration table.

The samples were sealed by using cling wrap and cured for one day in a laboratory environment. Then the samples were removed from the moulds and cured in an oven which was operated at a temperature of 23 ^{o}C and relative humidity of 100%. After 28 days, the samples were kept in the conditioning room until testing. This curing regime was conducted for all samples except F100. Regarding F100, the samples were kept in the moulds and covered by cling wrap and then placed immediately in a preheated oven at 60 ^{o}C. After one day, the samples were removed from the moulds and kept in the conditioning room until testing.

2.4. Test apparatus and procedure

The thermal properties were measured by using a commercially available thermal constants analyser which is illustrated in Fig.1 (a). The model thermal constants analyser is TPS 2500 S. The thermal properties measurements made by this model are reproducible within ±1%. A transient plane source probe is placed between two halves of the sample. When a constant heat source is applied, the temperature in the sensor rises and heat flow in the sample being tested. This measurement technique is described in ISO/DIS 220007 standard (2008). To measure thermal properties at elevated temperatures, the apparatus is connected with a tube furnace in which a specimen was heated to the target temperatures. The paste specimens of 65 x 65 x 25 mm size were sliced from the cylindrical samples before the measurement. Specific heat and thermal conductivity of various binder types were measured at seven temperatures: 23, 100, 200, 300, 400, 500, and 600 °C. In each test, the furnace temperature was raised to the desired temperature and remained at that temperature until the samples reached thermal equilibrium. Then the measurements were carried out.

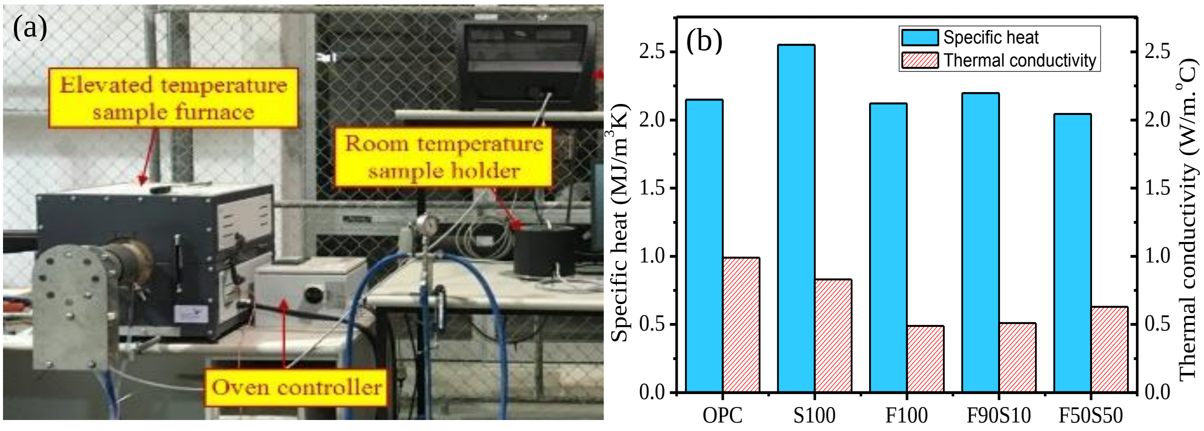

Figure 1. (a) Test apparatus and (b) Thermal properties at ambient temperature

3. RESULTS AND DISCUSSION

3.1. Thermal properties at ambient temperature

At ambient temperature, the variation of thermal conductivity of the cement paste and the geopolymers are demonstrated in Fig. 1(b). The thermal conductivity of slag-based mixture S100 activated with the powder-type activator is slightly lower than that of cement paste. When 50% of slag was replaced by fly ash, the thermal conductivity of F50S50 further decreased from 0.83 to 0.63 W/m·°C. The samples mainly containing fly ash exhibit lower thermal conductivity that is only half of the cement paste. These results suggest that fly ash replacement (in geopolymeric systems) leads to considerable reduction in thermal conductivity. The value of thermal conductivity of Al-Si system (F100) is within the range of thermal conductivity reported in the literature (Subaer and van Riessen, 2007; Duxson, 2006). Subaer and van Riessen (2007) reported that the values of thermal conductivity by using a hot wire method, were 0.55 and 0.91 W/m·°C for geopolymer pastes and mortar containing of 40 wt% quartz aggregates, respectively. Duxson et al. (2006) reported that the thermal conductivity of geopolymers (with different alkali cation) measured by using a laser flash method was between 0.3 to 0.52 W/m·°C. In comparison with the OPC system, the lower thermal conductivity of Al-Si system is due to the different skeletal framework between these two systems. Al-Si geopolymer consists of a three-dimensional alumino-silicate network that is configurated of SiO_4 and AlO_4 tetrahedrons united together by oxygen bridges. On the other hand, OPC system consists of either two or three layers of C-S-H gels, which could roll into fibres. The measured specific heat results of different binders are also illustrated in Fig. 1(b). The values of specific heat of different binder types are similar at ambient temperature, except S100. The specific heat of S100 is approximately 25% higher than that of other samples.

3.2. Effect of temperature on thermal conductivity

The variation of thermal conductivity for different binder types with temperature is presented in Fig. 2(a). The evolution of thermal conductivity shows distinct trends between Al-Si system and other systems. The overall trend of the Al-Si system is that the specific heat of all the samples increases up to 500 °C, then remains almost constant up to 600 °C. Although thermal conductivity for F100 and F90S10 follows a similar trend, a close examination of Fig. 2(a) shows the difference in the range of 200 to 300 ^{o}C. F90S10 shows an increase in thermal conductivity while F100 shows a decrease in thermal conductivity. In comparison with an increase in thermal conductivity of Al-Si system, Ca-Si geopolymers and OPC show a decrease in thermal conductivity with temperatures, and then the thermal conductivity remains almost constant at a higher temperature range. The influence of temperature on thermal conductivity is different between OPC and Ca-Si system. For OPC system, the thermal conductivity initially decreases with temperatures up to 400 °C. In the range of 400–600 ^{o}C, the variation of thermal conductivity is small. For Ca-Si system, a decrease in thermal conductivity can be observed on both S100 and S50F50 at elevated temperatures up to 200 °C. However, the slope of thermal conductivity for S100 is steeper than that for S50F50. At the higher temperature range, the thermal conductivity of these two binders becomes relatively stable. The above mentioned differences in the evolution of thermal conductivity reflect the different physiochemical processes taking place for different binder types at elevated temperatures. For OPC system, the correlation between these processes and the trend in thermal conductivity has been established (Khaliq and Kodur, 2011). The initial steep slope of thermal conductivity up to 400 °C can be attributed to moisture loss at a faster pace, resulting from the evaporation of free and pore water in concrete with a rise in temperature. The minor variation in thermal conductivity between 400 and 500 °C is attributable to the dissociation of small amounts of physically bound water present in concrete as a result of the phase change. Beyond 500 °C, there is a slow decrease in thermal conductivity because of the liberation of a small amount of strongly held moisture left within C-S-H layers. For geopolymeric systems, it has been observed a decrease in porosity at elevated temperatures (Irena et al, 2014). As the thermal conductivity of solid phase is much higher than that of air and water, the decrease in porosity will result in the increase in thermal conductivity of porous materials (e.g. geopolymers and cement pastes). At elevated temperatures, the strength gain of some geopolymers (F100) was observed in our previous study (Pan et al, 2016), indicating the decrease in porosity. A study has continued to investigate effects of temperatures on the porosity of geopolymers. The results will be presented at the conference.

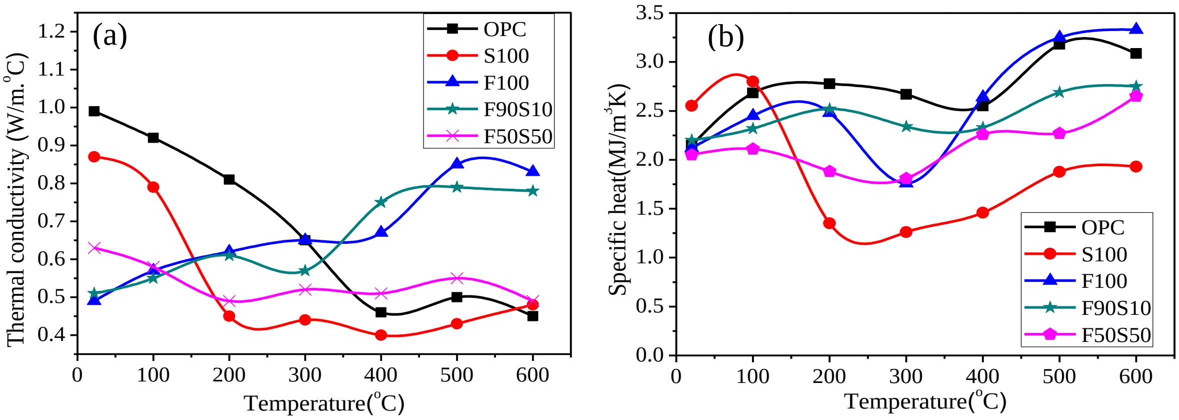

Figure 2. Effect of elevated temperatures on (a) thermal conductivity and (b) specific heat

3.3. Effect of temperature on specific heat

The specific heat of various binder types are presented in Fig. 2(b) as a function of temperature. The specific heat for all binder types shows an increasing trend up to 600 °C. This trend is attributed to the absorption of heat for bending and breaking of hydrogen bonds. Among the investigated binders, it is noted that S100 and F100 show an anomalistic change in specific heat at elevated temperatures. The change for the former is taking place in the range of 100–200 °C while the change for the latter is taking place in the range of 200–300 °C. A comparison of Fig. 2(a) and (b) shows that the thermal conductivity of S100 and F100 also exhibits a sudden change in the same temperature range. The consistency between the specific heat and thermal conductivity results again suggests that some phase transformations may take place in these binders at elevated temperatures. The decrease in specific heat is generally associated with either the heat release or increase in porosity, as a result of phase transformations. This requires considerable future research.

3.4. Empirical models

Data obtained from thermal properties was used to develop empirical models over a temperature range of 20–600 °C. The linear regression analysis was utilised to develop these models. As demonstrated in Fig. 2(a) and (b), both thermal conductivity and specify heat are affected by the type of binder and the range of temperature. Therefore, the empirical models are separately developed for each type of binders. At some temperature ranges, the thermal properties exhibit a sudden change, as a result of the phase transformations. In order to reflect this trend, the thermal property models are also developed in different ranges. The models for thermal conductivity and specific heat are summarised in Eqs. (1) through (5) and Eqs. (6) through (14), respectively. The typical linear regression models of geopolymeric systems, together with coefficient of determination R_2, are presented in Fig. 3.

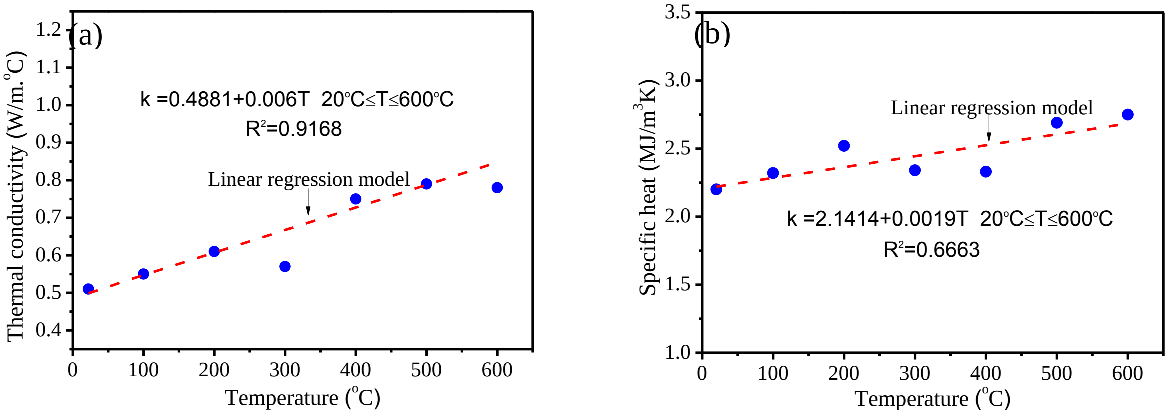

Figure 3. Effect of elevated temperatures on (a) thermal conductivity and (b) specific heat

Thermal conductivity

OPC

$$k = 0.9940 - 0.0010T \qquad 20^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{1}$$

S100

$$k = 0.7636 - 0.0007T \qquad 20^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{2}$$

F50S50

$$k = 0.5885 - 0.0002T \qquad 20^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{3}$$

F90S10

$$k = 0.4927 + 0.0005T \qquad 20^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{4}$$

F100

$$k = 0.4881 + 0.0006T \qquad 20^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{5}$$

Thermal conductivity

OPC

$$k = 2.1714 + 0.0034T \qquad 20^\circ\mathrm{C} \le T \le 200^\circ\mathrm{C} \tag{6}$$

$$k = 2.0235 + 0.0019T \qquad 200^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{7}$$

S100

$$k = 2.9971 - 0.0071T \qquad 20^\circ\mathrm{C} \le T \le 200^\circ\mathrm{C} \tag{8}$$

$$k = 0.8646 + 0.0018T \qquad 200^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{9}$$

F50S50

$$k = 2.1244 - 0.0010T \qquad 20^\circ\mathrm{C} \le T \le 300^\circ\mathrm{C} \tag{10}$$

$$k = 1.1090 + 0.0025T \qquad 300^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{11}$$

F90S10

$$k = 2.2067 + 0.0008T \qquad 20^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{12}$$

F100

$$k = 2.1414 + 0.0019T \qquad 20^\circ\mathrm{C} \le T \le 200^\circ\mathrm{C} \tag{13}$$

$$k = 0.3510 + 0.0053T \qquad 200^\circ\mathrm{C} \le T \le 600^\circ\mathrm{C} \tag{14}$$

4. CONCLUSIONS

At ambient temperature, the thermal conductivity of Al-Si geopolymer system is lower than that of OPC system. This is attributed to the different gel structure between these two types of binders. The C-S-H gel is believed to be the major reaction products for both S100 and OPC. As a result, the measured thermal conductivity for S100 and OPC is similar.

At ambient temperature, the results show a minor variation in the specific heat for all binder types.

At elevated temperatures, the thermal conductivity of Ca-Si geopolymeric system and the OPC system decrease with increasing temperature, while the thermal conductivity of the Al-Si geopolymeric system increases with increasing temperature.

At elevated temperatures, the specific heat for all the binder types generally increases with temperature. However, a sudden drop in specific heat is observed for F100 and S100 in the range of 200–300 °C and 100–200 °C, respectively.

The proposed relationships for thermal properties (at elevated temperatures) can be used for assessing the fire resistance of structures made with geopolymeric materials.

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