Review of research on high-temperature behavior of geopolymer paste

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Abstract. Geopolymer composites have been widely researched during recent years as an alternative to sustainable construction materials, which can minimize CO₂ emission for its application of industry by-products. Past researches on geopolymer show that it has comparable strength and better high temperature stability compared to ordinary Portland cement. In this paper, the high-temperature behavior of geopolymer paste has been discussed through the last data regarding geopolymer, mainly including its bonding performance with steel, stress-strain characteristics, structural analysis of different observation scales and the performance of special geopolymer paste. In summary, some problems that need to be studied in future researches are put forward.

1 Introduction

The term ‘geopolymer’ was invented in 1970’s by Prof. Joseph Davidovits and the French researchers, which is a new eco-friendly cementitious material, also termed as alkali-activated cement, and could be a superior alternative to ordinary Portland cement (OPC) (Shill 2019)[1]. Due to its simple production process, environmental character, and better engineering properties than OPC, in order to enable the civil engineering industry to get faster and better development, geopolymers have also been favored by the majority of researchers. Geopolymer composites is a new type of cementitious material that conforms to the development of the times. The commonly used geopolymers include kaolin based geopolymer, metakaolin based geopolymer and fly-ash based geopolymer.

Comparing to the OPC which degrades in strength irreversibly starting at 200 °C, geopolymer has been regarded as a potential fire-resisting material in civil engineering, which is especially important in high-rise buildings, underground buildings and large-span buildings. The research of geopolymer on the fire resistance is mainly to study the influence of the engineering characteristics of geopolymer when the temperature rises gradually, and the performance is whether the compressive strength changes, or whether there are obvious cracks and so on. About the research on geopolymer is mainly divided into three aspects of the characteristics of geopolymer paste, geopolymer mortar and geopolymer concrete. This paper presents the experiments and conclusions on the fire resistance performance of geopolymer paste in recent years.

2 Bonding behavior during and after exposure to elevated temperatures

The bonding behavior of steel to fly ash based geopolymer paste at fire condition was evaluated, and an extensive experimental study was carried out to investigate the effect of high temperature on the thermal-physical behaviors and mechanical properties of fly ash based geopolymer paste by Jiang (Jiang 2020)[2]. According to the visual observation of OPC and GPC specimens subjected to high temperatures, there was a color change in GPC when the temperature increased to 800 °C. There were fewer visible cracks and no spalling phenomenon in GPC specimens at very high temperatures (800-1200 °C) compared with OPC, indicating that the GPC has better fire-resistance. While OPC completely disintegrated at 800 °C, the GPC still retained some residual bond strength even after exposure to 1200 °C, which indicated that GPC paste had an excellent bond performance at extremely severe temperatures. A positive linear relationship between the residual bond strength (RBS) and residual compressive strength (RCS) indicated that higher compressive strength could result in better bond performance both for GPC and OPC specimens, as shown in Fig1. The XRD results showed that the phases in GPC were much more stable than those in OPC at high temperatures. Furthermore, SEM micrographs demonstrated that the porous system in GPC provided escape routes for water. This characteristic led to better mechanical properties of GPC than that of OPC at elevated temperatures.

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Fig1. Relationship between RBC and RCS(Jiang 2020).

Fig2. Compressive strength of geopolymer after heat treatment(Panjasila 2020).

3 Specific geopolymer paste

Jiang (Jiang 2020)[3] researched the properties of fly ash-based geopolymer paste containing waste glass powder (WPG) at high temperature. The addition of WPG excited reactive silicon and alumina, changed the Si/Al ratio of geopolymers, and thus changed the mechanical properties of the materials, which is similar to (Peem 2020)[4] and (Khan 2020)[5]. It was found that the GPC paste had the best optimum compressive and bonding strengths when the content of WPG was 20%. After exposure to high temperatures (up to 1200°C), the unreacted WPG melted to fill the porous microstructures of the geopolymer matrix, which mitigated the increase of pores, and improved the fire resistance. It was found that Si: Al = 2.5 effectively improved the high temperature resistance of GPC materials, but it was found that Si: Al = 4.17 was better (Peem 2020)[4], the difference of the best Si/Al developed by the two researches may be explained that the latter used a high-calcium fly ash-based geopolymer. For this, it can be verified by the effect of different calcium content on the high temperature resistance of geopolymer.

The changes of compressive strength, microstructure and magnetic properties of high-calcium fly ash based geopolymer at high temperature were studied(Panjasila 2020)[6]. The residual strength of the calcined geopolymer was shown in Fig2. The results showed that the compressive strength was increased at 200°C, and started to adversely affect the properties of specimens at temperatures around 400°C. But at 1000°C, because of the formation of new iron oxide phase, the crystallinity of the paste was increased, the rate of strength decline was actually decreasing. Aziz (Aziz 2019)[7] also suggested that the rearrangement of some amorphous phases to form temperature-stable crystalline phases contributed to the strength of geopolymers. Panjasila also believed that the compressive strength may be related to the magnetic properties of the specimens and that the measurement of magnetic properties can be used as a non-destructive method for structural health monitoring. As for this hypothesis, there should be more experiments to test and refine it in future studies, because it is leading the development of this industry, it is also necessary and innovative to solve practical engineering problems.

4 Stress-strain characteristics at high-temperature

Choi (Choi 2020)[8] used surface fractal dimension analysis method to study the change of mechanics and microstructure of fly ash based geopolymer paste at high temperature, the different dosages of Na₂O geopolymer pastes were exposed to different temperatures by the control variable method. The results showed that the fractal dimension increased with the increase of temperature and Na₂O content, and the compressive strength was proportional to the surface fractal dimension. It showed that the content of Na₂O and the temperature were proportional to the compressive strength in a certain range, as was shown in Fig3. As for the effect of temperature, it can be seen from (Panjasila 2020)[6], (Aziz 2019)[7] and (Zhang 2020)[11] that the intensity will increase in a certain temperature range. Through the fractal geometry method used in this experiment contrast with other methods, the results are much more convincing. It can be supposed that the content of Na₂O on the impact of compressive strength should also exist a maximum, the related tests are worth examining. In connection with the experiments of (Jiang 2020)[3] (Peem 2020)[4], it is conceivable to design an experiment in which Na₂O and reactive SiO₂ and other related chemicals were taken as independent variables, the strength of fly ash-based GPC paste and GPC concrete at high temperature was tested under the best combination.

Fig3. Compressive strengths of the exposed specimens according to the Na₂O content (Choi 2020).

Performance change of GGBFS based geopolymer at high temperatures was carried out (Aziz 2019)[7]. It was found that the unexposed geopolymers had a compressive strength of 95 MPa. The compressive strength decreased to 72 MPa at 800°C but increased to 152 MPa at 1000°C. As can be seen in Fig4 (red-coloured region represents cavern), the crack of geopolymer treated at 1000°C was reduced and partially melted, which meant the crack was healed at high temperature then the compressive strength was improved. Moosavi (Moosavi 2019)[9] also believed that the presence of liquid phase in the composite was an important factor to affect the microstructure and mechanical properties of the composite. At 1000 °C, gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}$), mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and Larnite (Ca_2SiO_4) were also formed in geopolymer paste, and their structures were relatively ordered. It was supposed that the strength increase was mainly due to the rearrangement of amorphous phase to form temperature-stable crystalline phase.

Fig4. Optical microscopy images and schematic representation of crack appearance of GGBFS exposed at (a) 800°C and (b) 1000°C (Aziz 2019).

5 Mixed design and control factors for high temperature applications

The fire resistance of geopolymer was classified into three scales: micro-scale (including crack formation, pore structure changes, densification, sintering, melting), meso-scale (phase composition change: Crystal growth or failure, geopolymer paste transformation) and macro-scale (geopolymer paste thermal deformation) by Lahoti (Lahoti 2019)[10]. Interrelation between micro-, meso-, and macro-scale properties are discussed related to the performance of geopolymer at high temperature exposure.

Researches on the performance of geopolymers at micro-scale show that geopolymers are chemically stable and do not undergo breakdown of chemical structure in contrary to OPC hydration products which undergo severe deterioration on thermal exposure. The factors such as Si/Al ratio, alkali cation type and alkali content are important to determine the chemical structure of geopolymers before and after exposure to elevated

temperatures.

High-temperature exposure causes thermal shrinkage and expansion as well in geopolymers, which in turn causes macro-cracking. It is importance to control the water content in geopolymer mix to regulate the meso-scale thermal deformations. Due to the fact that metakaolin-based geopolymers require a significantly higher amount of water as compared to fly ash-based geopolymers for workability purpose, fly ash-based geopolymers might be preferred for structural fire-resistance applications. Thermal deformations are also influenced by the composition of alkali activating solution as well as the type of alkali cation. Using potassium as alkali cation, thermal shrinkage decreases when compared to using sodium as alkali cation.

Compressive strength of geopolymers can be affected by microstructural changes and phase composition changes, so factors affecting the compressive strength of geopolymers on exposure to elevated temperatures may include the choice of precursor, use of aggregates, total alkali content in geopolymer. It should be noticed that not all geopolymer formulations perform soundly at ambient as well as on high-temperature exposure, tailoring of mix design to produce geopolymers with good thermal stability is essential. With careful mix design, remarkable chemical stability, volume changes, strength endurance, and spalling resistance can be achieved for geopolymers. Mix design factors which need to be controlled include Si/Al ratio, Al/Na ratio, and water/solids ratio other than the factors such as precursor type, alkali cation type, and curing condition. The performance of geopolymer paste as well as the selection of compatible aggregates, fibers and/or fillers, are important considerations for high temperature applications.

In short, to play the best fire resistance of geopolymer paste, it is necessary to strictly control the mixed design and control factors, such as the choice of precursor, use of aggregates, total alkali content in geopolymer and water content, to achieve ideal chemical stability, volume stability, strength endurance and spalling resistance.

6 Conclusions and prospect

From the finding of the recent studies that investigated the high-temperature behavior of geopolymer, the author's views can be summarized in Table 1. Furthermore, some problems that need to be studied in future researches are presented as follows:

- More experiments need to be carried out to research the high-temperature bond behaviour of different types of bars (for example Prestressed steel wire and parallel steel wire bundles) and geopolymer, which can provide fundamental information for use geopolymer in prestressed structures and long span cable structures.

- It is necessary to find an optimal mix proportion to realize the best fire resistance of geopolymer. Experiments can be carried out in which Na_2O and reactive SiO_2 and other related chemicals are taken as independent variables, the strength of fly ash-based GPC paste and GPC concrete at high temperature is tested under the best combination. These experiments may have a great breakthrough in

solving some practical engineering problems.

- According to the construction and use of safety requirements, geopolymer components now need to meet certain high-temperature duration requirements. Under this requirement, the geopolymer component can be subjected to a long period of high temperature resistance test according to the international temperature-rise curve and the relatively practical temperature-rise curve, and is verified by the finite element analysis software, it is necessary to simulate the performance change of the

component in a reasonable and real heating process.

Acknowledgements

This work was financially supported by foundations from Science and Technology Commission of Shanghai Municipality (18070502900; 18ZR1427900). The financial support is appreciated.

Table1. Summary of the literature

Author	Date	Conclusion and opinion
Jiang	2020	Compared with the OPC, the GPC has less visible cracks and no spalling phenomenon, less mass loss and good bonding property at 800,100,1200°C.
Jiang	2020	It is found that the addition of waste glass powder (WPG) excites more active silicon and alumina, thus changes the Si/Al ratio of Geopolymer, and then changes the mechanical properties of the material at high temperature.
Panjasila	2020	The changes of compressive strength, microstructure and magnetic properties of high-calcium fly ash based geopolymer at high temperature were studied. When the geopolymer was heated to 600°C, the strength began to decrease significantly, and the magnetic properties changed from ferromagnetic to paramagnetic at 1200°C,so he hypothesized that compressive strength might be related to the magnetic properties of high calcium fly ash based geopolymer.
Choi	2020	The changes of mechanical and microstructure characteristics of fly ash based geopolymer materials at high temperature were studied by using fractal geometry method. With the increase of temperature and Na ₂ O content, the fractal dimension of the surface of macropores increased, the compressive strength is proportional to the surface fractal dimension.
Aziz	2019	The relative reduction of cracks and partial melting of crushed slag base polymer treated at 1000 °C means the crack healed and the strength increased at high temperature, the strength increase is mainly due to the rearrangement of amorphous phase to form temperature-stable crystalline phase.
Lahoti	2019	The fire resistance of geopolymers was studied on micro scale, meso scale and macro scale.

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