High temperature effect on structure formation and performance of hybrid geopolymers

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Abstract. Fly ash based hybrid geopolymers (HGP) containing different type of mineral admixtures such as portland cement (PC), kaolin and metakaolin (MK) were developed in this study. The improved values of compressive strength, water absorption and water resistance for PC-modified hybrid geopolymers versus MK-modified HGP and reference mix was observed. High-temperature treatment (600 °C) enables to boost compressive strength by 177 % and 55 % as well as water resistance by 34 % and 40 % for MK-modified and kaolin modified HGP, respectively. At the same time, the PC-modified HGP demonstrated a very low thermal resistance, which was confirmed by a rapid drop of compressive strength and distracted structure of the specimen subjected to high temperature.

1. Introduction

Blended binding systems and concrete composites with chemical and/or mineral admixtures represent a new class of construction materials with a wide range of application. Synthesis of these materials is focused on adding new characteristics or improvement of basic properties of traditional construction materials [1–8].

According to the information given in early literature [9–25], hybrid geopolymers are considered to be mixtures consisting of alkali aluminosilicate matrix and modifying chemical and mineral admixtures with different chemical composition, morphology and texture (for exp., fibers, mineral fillers, surfactants etc.).

The selection of certain modifying components generally is based on the necessity of the material to attain new properties or improve certain performance. Basalt fiber, carbon fiber, wood fiber and glass fiber are widely used for reinforcement purposes for hybrid geopolymer systems [9–14]. Rovello etc. reported that introduction of melamine-based epoxy resin into MK-based geopolymer matrix results in thermal resistance and improved compressive strength [15].

Early studies [16] have been demonstrated that incorporation of PC into low calcium fly ash based geopolymer system results in considerable improvement of water resistance (up to 56 %) and reduction of water absorption (by 81.6 %) with a slight increase of compressive strength.

One of the main performance enable to extend the application of geopolymers is considered of their ability to thermal resistance.

There are a number of studies with the experimental data providing the support for thermal resistance of geopolymer systems. The metakaolin based geopolymers with thermal resistant and refractory properties is one of the great examples [17–19]. J. Davidovitz reported that the coefficient of thermal...
expansion in potassium based geopolymers has a close correlation with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as represented in Table 1 [20]:

**Table 1.** Coefficients of thermal expansion in potassium based geopolymers [20]

| $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio | 2   | 3   | 3.5 | 5   | 10  |
|----------------------------------------|-----|-----|-----|-----|-----|
| Coefficient of thermal expansion, $10^{-6}/\degree\text{C}$ | 4   | 6   | 10  | 15  | 25  |
| Corresponding materials                | ceramic, graphite, epoxy resin, steel, copper, aluminium |

It was experimentally proved [21–23], that incorporation aluminosilicate particles and fibers with refractory properties into geopolymers enable to improve their thermal resistance.

Bernal [24] proposed that presence of limestone powder in geopolymer system causes a structure densification under exposure to high temperatures.

The purpose of this work was to study thermal resistance of the experimental hybrid geopolymer pastes incorporating various ultrafine mineral components such as Portland cement, kaolin and metakaolin.

2. Materials and methods

2.1 Materials

Low-calcium fly ash was used as a main aluminosilicate component and sodium hydroxide NaOH (purity of 98 %) as an alkali activator were used to produce hybrid geopolymer pastes. In addition, Portland cement CEM I 42.5N (from Belgorod, Russia), kaolin (from Chelyabinsk, Russia) and laboratory synthesized metakaolin (MK) supplied by were used as ultrafine mineral components (Table 2).

2.2 Methods

Metakaolin (MK) was synthesized in laboratory conditions by drying at 70 °C for 2 hours followed by thermal treatment (dehydration process) at 600 °C for another 2 hours in a lab furnace.

Microstructural characteristics of the produced geopolymer pastes were analyzed with SEM-microscopy using Mira 3 FeSEM (Tescan, Czech Republic) in high-vacuum regime (InBeam). SEM-analysis was performed on fresh chips of the samples. Carbon coating was used as a conductive media.

**Table 2.** Chemical composition of fly ash and mineral additives

| Component       | Oxides content, % wt. | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | K$_2$O | MgO | CaO | P$_2$O$_5$ | N$_2$O | LOI |
|-----------------|-----------------------|---------|-------------|-------------|---------|--------|-----|-----|-----------|--------|-----|
| Fly ash         |                       | 58.98   | 28.29       | 4.63        | 0.97    | 0.65   | 1   | 3.74| 0.36      | 0.63   | 6.07|
| Portland cement |                       | 22.49   | 4.77        | 4.4         | 0.97    | 0.65   | 1   | 3.74| 0.36      |        |     |
| Kaolin          |                       | 53.8    | 43.4        | 1.02        | 0.58    | 0.56   | 0.21| 0.01| 0.06      | 0.03   | 4.2 |
| Metakaolin      |                       | 53.8    | 42.8        | 0.7         | 0.3     | 0.9    |     | 0.15|           | 0.02   | 4   |

3. Experimental part

3.1 Mix proportions and mechanical performance of geopolymers

For this study two series of cubes samples with the size of 20x20x20 mm of different proportions of fly ash and mineral additives were prepared (Table 3).

After the 1st day of curing in laboratory conditions the prepared specimens in the molds were placed in an oven for 24 hours, where temperature was gradually raised to 70 °C and then kept constant for 24 hours followed by normal cooling down in the laboratory environment to the room temperature. After that the samples were demolded and then stored at 22±3 °C and 50% RH until they reached the testing
age. First series of specimens was treated at 600 °C and the second series was stored at 22±3 °C upon testing age. All the samples were tested at the age of 7 days (Table 4).

| Compounds | Fly ash | NaOH | PC | MK | Kaolin |
|-----------|---------|------|----|----|--------|
| GP1       | 95      | 5    | –  | –  | –      |
| GP2       | 57.1    | 38.1 | 4.7| –  | –      |
| GP3       | 57.1    | 38.1 | –  | 4.7| –      |
| GP4       | 57.1    | 38.1 | –  | –  | 4.7    |

Table 3. Dry mix proportion of geopolymer pastes (%), wt.)

| Compounds | Compressive strength, MPa | Water absorption, % | Water resistance  |
|-----------|---------------------------|---------------------|------------------|
| GP1       | 11.1                      | 28                  | 0.43             |
| GP2       | 9.81                      | 28                  | 0.89             |
| GP3       | 3.36                      | 36                  | 0.34             |
| GP4       | 5.1                       | 31                  | 0.43             |

Table 4. Physical and mechanical performance of geopolymer pastes

*Parameters of geopolymer pastes: 1 – before high-temperature treatment; 2 – after high-temperature treatment

The experimental data represented in Table 3 show that PC-modified hybrid geopolymers (HGP) after high thermal treatment had a reduction of compressive strength by 16 % and water resistance by 10 % as well as increase of water absorption by 46 %.

At the same time, the strength performance for reference geopolymer pastes (GP1) after thermal treatment was retained the same, while water resistance boosted up to 81 %.

MK and kaolin modified HGP (GP3 and GP4) demonstrated a considerable improvement of compressive strength by 177 % and 55 %, respectively, when water resistance was also improved by 34 % and by 40 % respectively.

Thus, PC-modified HGP specimens demonstrated a low or not tolerant behavior to high temperature. On the contrary, the specimens modified with MK and kaolin as well as non-modified reference geopolymer mix demonstrated excellent thermal resistance. In addition, it was observed that high temperature treatment has a positive effect on mechanical performance of the discussed hybrid geopolymers.

3.2 Microstructural characterization

In order to establish the relationship between number of parameters such as compressive strength, density, water resistance and water absorption as well as structural characteristics and mineral-and-phase composition, the developed specimens were characterized using SEM-microscopy and XRD-analysis.

The microstructure of several binding systems was studied in this work, which are: reference geopolymer system «fly ash – NaOH» and hybrid geopolymer binder systems «fly ash – PC – NaOH», «fly ash – MK – NaOH» and «fly ash – kaolin – NaOH».

The morphology and microstructural characteristics of the experimental specimens were analyzed at the age of 7 days.

It was observed, that the microstructure of the non-modified geopolymer paste did not have a good compaction and represented by a highly porous matrix. The randomly scattered vitreous zones provide the evidence for low degree of geopolymerization process. In addition, the number of individual needle-like crystal formations of Na-carbonate and Na-hydrocarbonate are found in the system (Figure 1).
Figure 1. Microstructure of non-modified geopolymer paste (GP1) before and after thermal treatment at 600 °C

The presence of high content of water-soluble carbonate formations explains a low degree of reaction of fly ash with NaOH alkaline component, and, therefore results in poor strength development, low values and low water resistance.

The incorporation of PC into geopolymer matrix (Figure 2, a) causes formation of C-S-H gel and tabular-like crystals of Portlandite typical for ordinary Portland cement system (Figure 3), as well as the formation of monolithic vitreous phase typical for geopolymers (Figure 1).

According to the data presented in Table 3, the lowest value of compressive strength is observed for the composition GP3 with MK as a modifying component. The structure of the specimens appeared to be incohesive and crumbly and was not able to support the structure before and after the high-temperature treatment. For this reason, it was not possible to perform SEM characterization for the specimens.
Figure 2. Microstructure of hybrid geopolymer systems GP2 and GP4 a) before and b) after thermal treatment at 600 °C

Figure 3. Microstructure of reference geopolymer paste (GP1)

The XRD patterns demonstrated that the studied geopolymer pastes content more than 70% of vitreous phase and framework aluminosilicates like albite and cancrinite (Figure 4, a) which was indicative of geopolymerization process in the reference geopolymer composition GP1. The phase and mineral composition of the specimen was in a full agreement with the data reported in the earlier study [25–29].
The mineral and phase composition detecting on the corresponding diffractograms for PC-modified hybrid geopolymer specimens (GP2) provide the evidence for both hydration and geopolymerization structure formation mechanisms happening in the systems while hardening (Figure 4, b). In addition, an intensive peak with d-space of 7.914Å appeared on the pattern associated with the formation of zeolite-type crystal formation of heulandite B \( (\text{CaO}, 8\text{Na}_0.4\text{[Al}_2\text{SiO}_7\text{O}_18\text{]} 2\text{H}_2\text{O}) \) a product of pozzolanic reaction between X-ray amorphous aluminosilicate constituent in fly ash and Portlandite. The indicated zeolite formation is characterized by \( \text{Ca}>\text{Na} \) and \( \text{Si}>\text{Al} \) elements ratios similar to those for heulandite B and is in equilibrium with typical phase formation in combined Portland cement and Na-geopolymer binding systems. The presence of heulandite B was confirmed with reference phase from data base ICSD. It is necessary to note that the formation of zeolite minerals in geopolymer systems as much possible at ambient temperature as at high temperature curing conditions and is in agreement with a current statement about low-temperature formation zeolite phases in nature [30, 31].

![Figure 4. Rietveld refinement patterns for: a) non-modified geopolymer and b) PC-modified hybrid geopolymer. Quantitative percentage of present phases calculated by weight](image_url)

The experimental results as well as chemical and microstructural analysis of the studied non-modified (GP1) and modified geopolymers specimens (GP2-GP4) demonstrated that two structure formation mechanisms: hydration and geopolymerization take place in the system concurrently. Therefore, the combination of both mechanisms has a superposition effect allowing for geopolymers attaining new performance such as water-resistance water resistance and refractory properties for Portland cement systems.

4. Conclusion
The analysis of mechanical performance as well as chemical and microstructural characteristics of the experimental geopolymer compositions demonstrated a positive effect of Portland cement, metakaolin and kaolin as mineral additives on water resistance. High temperature treatment at 600 °C of the geopolymer compositions based on reference non-modified GP1 pastes as well as with incorporation of metakaolin and kaolin mineral admixtures GP3 and GP4 leads to strength improvement in the range of 7–76 %, as well the increase of water resistance up to 80 %. However, the addition of Portland cement into geopolymer system helps to improve water resistance and strength performance only when binders cured at ambient condition. The high temperature treatment has a detrimental effect on mechanical performance of the Portland cement modified hybrid geopolymer systems.

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