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Physical properties and powder XRD characterization of coal fly ash-based geopolymer heated up to 1150 °C

Физични свойства и прахова рентгенографска характеристика на получени от въглищна летяща пепел геополимери, нагрети до 1150 °C

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Introduction

Geopolymers are inorganic materials formed by alkali or acid activation of Al- and Si-containing resources through a polycondensation process in which the tetrahedral Si and Al are linked by sharing oxygen atoms. The conceptual model of geopolymerization process involves following overlapping stages: dissolution of the aluminosilicate precursor, speciation, equilibrium, gelation, reorganization, polymerization, and hardening (Duxson et al., 2007). Many studies have revealed that the geopolymer contributes to high compressive strength (Nugteren et al., 2009), good acid resistance (Bakharev, 2005; Song et al., 2005) and excellent fire resistance (Bakharev, 2006). These superior characteristics render geopolymer as promising potential alternative for Portland cement in civil engineering applications. While the ordinary Portland cement degrades and drastically loses strength in temperature above 400 °C (Xiao, Konig, 2004), geopolymer has excellent resistance to elevated temperature. Barbosa and MacKenzie (2003) reported geopolymers having thermal stability up to 1300 °C. The raw materials could be a variety of low cost materials or industrial by-products, such as blast furnace slag, fly and bottom ash, etc. In the territory of Bulgaria there are many potential geopolymer precursors (Nikolov, 2019). Recent studies showed the properties of geopolymers based on local materials such as metakaolinite (Nikolov, 2018), natural zeolite (Nikolov, Rostovsky, 2017; Nikolov et al., 2017), copper slag (Nikolov et al., 2018), fly ash (Nikolov, Barbov, 2018). Detailed reviews of fly ash based geopolymers were done by Lahoti et al. (2019), Xu and Shi (2018), Gollakota et al. (2019), Paizun et al. (2019). In Bulgaria, part of the thermal power plant (TPP) wastes were used in the construction of roads and embankments; the production of blended cements, concrete or mortars. Fly ash from Bulgarian thermal power plants (TPP) could also be used for syntheses of micro- and mesopores zeolites (Barbov, Kalvachev, 2015; Boycheva et al., 2015).

The aim of present study is to examine the physical and structural behaviour of geopolymers based on local fly ash exposed to elevated temperature.

Materials and methods

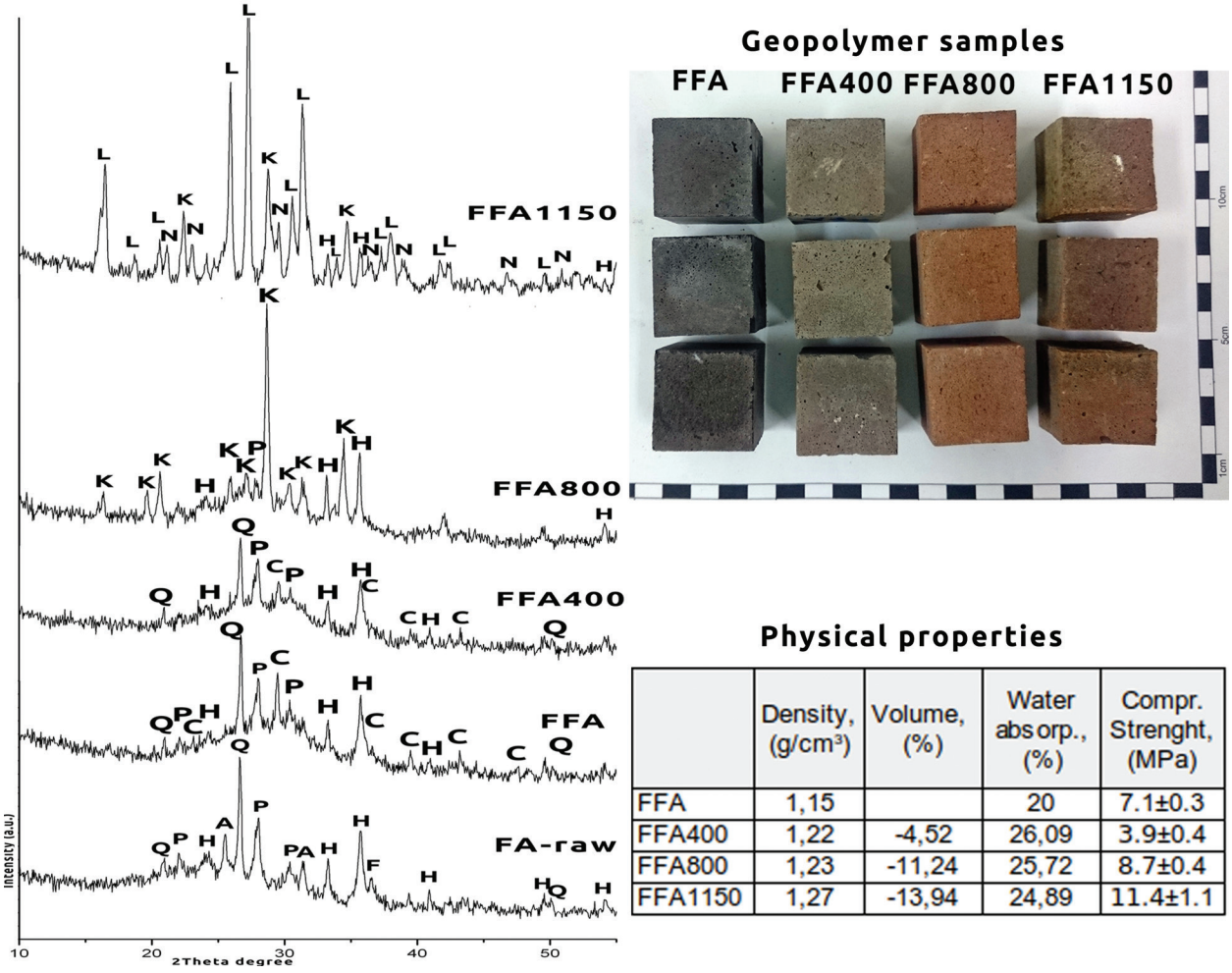
The raw material used in the present study was low calcium coal fly ash collected from TPP Galabovo AES, Bulgaria, with following chemical composition (%): SiO_2 46.18; TiO_2 0.67; Al_2O_3 24.73; Fe_2O_3 10.39; MnO 0.08; MgO 2.36; CaO 8.42; Na_2O 1.43; P_2O_5 0.10; SO_3 4.04, determined by XRF. The alkaline hardener was prepared by using solid KOH pellets, tap water, sodium silicate solution ($MR(SiO_2/Na_2O)=2.98$). The XRD patterns were done by using Philips PW1050 with a Cu Kα source and secondary graphite monochromator. The density was calculated by measuring the volume with digital caliper on 4 places each dimension. The compressive strength was measured on three cube specimens (3.17 mm) each series at rate of load increase of 2400 N/s.

Results

Synthesis of geopolymer paste. The geopolymer in the present work was synthesized based on best performed series B1 in previous study (Nikolov, Barbov, 2018). The molar composition of the activator solution was SiO_2/M_2O=0.70; H_2O/M_2O=10 and it was prepared by dissolving 26.7 g KOH pellets in 19.2 g water and 50 g sodium silicate (per 100 g fly ash). The activator and fly ash were homogenized for 2 min. with mechanical stirrer and poured into steel moulds. The geopolymers were cured in plastic bags in laboratory conditions. The specimens were demoulded after 3 days.

Heating up to 1150 °C. On 180th day the samples were heated in a muffle furnace to 400, 800 and 1150 °C (labelled FFA400, FFA800, FFA1150) with temperature ramp of 5 °C/min and 1 hour hold-up on maximum temperature. The specimens were led to cool down in a closed chamber. There are change in colour caused by oxidation of iron. Density, volume change, water absorption and compressive strength were measured before and after the heat exposure (Fig. 1). Significant shrinkage was observed and the volume of the specimens decreased by 13.94% for heated samples to 1150 °C. The density of the prepared fly-ash geopolymers is relatively low compared to conventional cement pastes – 1.78 g/cm^3. The high water absorption suggests well developed porosity. Heating to 400 °C led to significant shrinkage and decrease of the compressive strength form 7.1 MPa to 3.9 MPa (–45%). The dehydration processes caused internal stresses leading to shrinkage and crack formation. Further heating to 800 °C and 1150 °C showed increase in mechanical properties up to 11.4 MPa accompanied with higher volume changes.

Powder XRD. Fractions of specimens from each series tested on compressive strength were examined by powder XRD (Fig. 1). The raw fly



Geopolymer samples

Physical properties

	Density, (g/cm^3)	Volume, (%)	Water absorp., (%)	Compr. Strenght, (MPa)
FFA	1,15		20	7.1±0.3
FFA400	1,22	-4,52	26,09	3.9±0.4
FFA800	1,23	-11,24	25,72	8.7±0.4
FFA1150	1,27	-13,94	24,89	11.4±1.1

Fig. 1. *On left*, X-ray diffractogram of fly ash (FA-raw), geopolymer (FFA) and heated samples to 400, 800 and 1150 °C. Legend: Q, quartz, P, plagioclase, H, hematite, A, anhydrite, C, Calcite, L, leucite, K, $KAlSiO_4$, N, nepheline. *On right*, geopolymer samples and physical properties.

ash (FA-raw) consists of quartz, hematite, plagioclase and anhydrite. Amorphous phase is visible as halo between 18–30° 2θ. There were slight shift of the amorphous halo to 25–35° 2θ after geopolymerization, which is typical for geopolymers (series FFA). Anhydrite was transformed to calcite by reactions with water, alkali hydroxide and carbon dioxide from air. Hematite, quartz and plagioclase stayed inert and act as filler in geopolymer matric. The heating of the geopolymer specimens to 400 °C was not accompanied with phase changes. A further heating to 800 °C led to a process of crystallization to more energy stable phases. The peaks from diffractograms of series FF800 are related to different species of kalsilite – $KAlSiO_4$ (PDF 50–0436). Calcite and quartz were destructed, while hematite and glassy phase were still present. A crystallization of leucite and nepheline was observed after heating to 1150 °C. Based on peak intensity (FFA800 and FFA1150) some of the $KAlSiO_4$ recrystallized to leucite ($KAlSi_2O_6$). Hematite was stable up to 1150 °C. The crystallization led to significant strength increase and the final strength exceeded the original one by 60%. Leucite and kalsilite are framework silicates commonly presented in refractory materials. The performance of geopolymers prepared using class F fly ash was lower than that of geopolymer materials prepared using metakaolin (Bakharev, 2006). The probable reason for fire resistance degradation is the presence of significant amounts of iron oxide in the fly ash (10.39%) and the degree of geopolymerization of the fly ash.

Conclusion

The geopolymer pastes based on local coal fly ash were characterised by relatively low density (1.15 g/cm^3), high water absorption (20%) and 7.1 MPa compressive strength. The heating to 400 °C was not accompanied with significant phase changes but led to decrease of the compressive strength (–45%) and shrinkage. Further heating to 800 °C and 1150 °C showed increase in mechanical properties to 11.4 MPa and accompanied with crystallization of $KAlSiO_4$, leucite and nepheline.

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