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Novel one-part ferro-phosphate geopolymer cement

Нов еднокомпонентен желязо-фосфатен геополимерен цимент

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Introduction

Geopolymers are synthesized by reaction in both alkaline and acidic medium using alkali hydroxides and silicates or phosphoric acid, respectively (Davidovits, 2008). Generally, the geopolymer precursors are aluminosilicates, but recent studies showed that Fe atoms could substitute part of Al atoms to form ferro-sialate structures (-Fe-O-Si-O-Al-O-). Thus, potential geopolymer precursors are iron-containing raw materials such as laterites, mine tailings, red mud, heavy metals slags, etc. In this group of materials is the fayalite slag – hardly marketable floatation by-product generated by copper producing plants. While alkali activation of fayalite is widely investigated (Komnitsas et al., 2009; Onisei et al., 2018), the acidic activation is still unexplored. To the best of the current author's knowledge – only Katsiki et al. (2017) and Nikolov et al. (2018), separately, activate similar fayalite slags with dilute phosphoric acid. The reaction was rapid resulted in solid ferro-phosphate geopolymer in minutes. In case of using proper retarding agent the setting time could be increased to ensure enough time for homogenization, transportation and moulding. Usually geopolymers are prepared by the reaction of geopolymer powder precursor mixed with alkali or acid activator water solution (Nikolov, 2020). However, handling and working with highly corrosive viscous activator solutions is dangerous and impractical. Those disadvantages could be overcome by the design of so called 'one-part' geopolymer cement systems, where the fresh mixture is prepared by "just add water" to prepared dry geopolymer composition. The dry mixture could be obtained by mixing a solid activator with a solid precursor with or without grinding or calcination step (Luukkonen et al., 2018). The aim of the present study is to develop one-part geopolymer cement based on fayalite slag using suitable dry phosphate reagent.

Materials and methods

The main geopolymer precursor in the present study was fayalite slag. The fayalite slag, also named as iron-silicate fines, is industrial by-product from local copper plant (Aurubis, Bulgaria) with following chemical composition (wt%): Fe_2O_3 58.42; SiO_2 29.34; Al_2O_3 4.40; CaO 2.66; MgO 0.89; Na_2O 0.58; TiO_2 0.30; K_2O 0.71; ZnO 1.32; CuO 0.49; PbO 0.37; MoO_3 0.27; SO_3 0.26. The fayalite slag consists of mainly fayalite, magnetite and pyroxene (Nikolov, 2020). The hardening activator is dry calcium tripolyphosphate with following chemical composition (%): P_2O_5 54.50; CaO 32.84; F 4.25; Fe_2O_3 0.32; SiO_2 1.71; Al_2O_3 0.59; MgO 0.79; Na_2O 0.66; TiO_2 0.30; K_2O 0.14; ZnO 0.04; Cr_2O_3 0.04; SO_3 4.03. The calcium tripolyphosphate ($Ca_5(P_3O_{10})_2$) is commercially available as fertilizer in agriculture, known as super phosphate (SP).

SEM images were obtained by using electron microscope SEM 515 Philips on geopolymer fracture pieces covered with carbon under vacuum. The XRF measurements were performed at Wave-dispersive x-ray fluorescence Spectrometer Rigaku Supermini 200 using pressed tablets. The compressive strength was measured on three cube specimens (3.17 mm) each series at rate of load increase of 2400 N/s. The density was calculated after measuring each specimen dimension with digital calliper.

Results

Synthesis of geopolymers. The fayalite slag was dried to constant mass in oven at 105 °C to eliminate about 10–12% of absorbed water. The slag and different amount of dry calcium tripolyphosphate were grinded together in a ball mill for 2 hours to ensure homogenous dry mixtures. The resulted geopolymer cement were used to prepare geopolymer pastes by "just-add water" method. The water to

Table 1. Composition design, compressive strength, density and water absorption of the prepared geopolymer sample

Series	SP, g	Molar ratio		Compressive strength, MPa	ρ_0, g/cm^3	Water absorption, %
		Fe_2O_3/P_2O_5	H_2O/P_2O			
GFP200	200	4.08	13.01	11.6 ± 0.6	2.24	14.62
GFP250	250	3.27	10.84	17.1 ± 0.8	2.19	14.83
GFP300	300	2.72	9.40	21.0 ± 1.5	2.14	14.98
GFP350	350	2.34	8.36	24.77 ± 1.25	2.09	15.40

solid ratio (w/w) for all series was constant – 0.15. The fresh geopolymer pastes were stirred 2 min with mechanical mixer. The use of retarder agent allowed the increase of setting time to about 15–20 min. The composition design is presented at Table 1 per 1000 g of fayalite slag. The molar ratios were calculated of each geopolymer composition.

Physical and mechanical properties. The compressive strength tests were performed at 14^{-th} day and result with standard deviation is presented in Table 1. The compressive strength steady grows with the increase of the calcium tripolyphosphate to reach 25 MPa for series GFP350. The increase from GFP200 to GFP250 was the most significant – 47%. Contrary to the usual correlation, the compressive strength increases while the density decreases. This could be explained by the difference in the specific density of the raw materials. The fayalite was characterized by 3.85 g/cm^3 specific density, while the super phosphate – 2.85 g/cm^3. Thus, when relatively more SP was used the density decreases despite of the strength increases. In such manner, the water absorption increases with the increase of SP.

SEM. The images of the precursor and prepared geopolymer are presented in Figure 1. The raw fayalite consists of different in size particles of fayalite and magnetite including also submicron grains (Fig. 1a). Figure 1b shows the morphology of the particles of the prepared geopolymer cement. The co-grinding of fayalite slag and SP ensure homogenization. Based on morphology we can assume that particle 1 in Figure 1b is probably phosphate, while particle 2 – fayalite. On Figure 1c we can observe hardened geopolymer, which

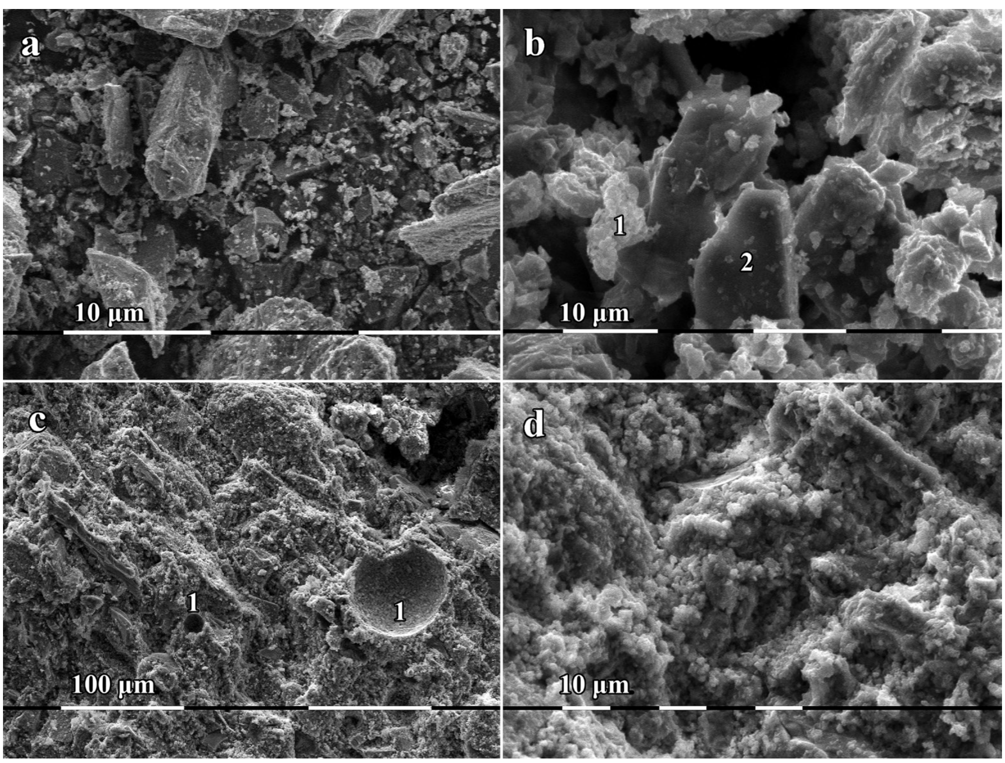

Fig. 1. SEM images of: *a*, raw fayalite; *b*, geopolymer cement (Fayalite + SP); *c–d*, geopolymer GFP250

characterize with presence of spherical pores with diameter up to 100 μm resulted from entrained air during mixing. The structure appears porous which could explain the high water absorption of the samples. The higher magnification (Fig. 1d) shows that surface morphology of the prepared geopolymer was characterized by globular microstructure.

Conclusion

The present study demonstrates a potential usage of commercial super phosphate (calcium tripolyphosphate) as dry activator for geopolymers based on fayalite slag. Co-grinding ensure proper homogeneity and one-part geopolymer was designed and prepared. By "just-add water" fast setting mixture was obtained. The hardened geopolymer was characterized by compressive strength up to 25 MPa on 14^{th} day. Further more detailed studies and optimizations are required to design material with more practical significance.

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