Thermal resistance of alkaline fused phosphate sludge-based geopolymer mortar

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Abstract. The present study investigates the thermal behaviour of phosphate sludge-based geopolymers. Phosphate sludge which is a by-product from phosphate beneficiation processes was activated using the alkaline fusion method to improve the geopolymer activity of this material. Then, the mechanical properties as well as the thermal behaviour of the resulted geopolymer mortar were studied. The effect of sodium hydroxide addition and fusion temperature on the mechanical properties and the thermal behaviour of the geopolymers were assessed using compressive strength tests before and after thermal shock cycles at different temperatures (350, 500, 650 °C). The mineralogical composition of the fused materials was investigated using XRD measurement and the microstructure of the geopolymer mortars was studied using FTIR. The obtained results showed that NaOH content as well as the temperature of fusion are essential parameters controlling the structure and the strength of the developed geopolymeric gel. Exposure to elevated temperatures up to 650 °C induces a decrease in compressive strength between 58 and 71%. However, a further increase in the temperature of exposure till 800 °C induces a development of compressive strength. Overall, geopolymers with good compressive strength up to 40 MPa could be synthesized in the optimum conditions of fusion: 10% of NaOH and 550 °C.

Keywords: high-performance materials, cementitious composites, geopolymer, alkaline fusion, thermal resistance.

Introduction

The valorisation of mine wastes and mine tailing using the geopolymerization technology has attracted scientist's attention recently because of the geopolymer's confinement properties. The main purpose is to explore new utilization of these by-products in order to decrease the environmental impact of their disposal. A variety of mine tailing such as copper (Ahmari, Parameswaran, & Zhang, 2014; Ahmari & Zhang, 2013), vanadium (Jiao, Zhang, & Chen, 2013), tungsten (Pacheco-Torgal, Castro-Gomes, & Jalali, 2008), gold (Caballero, Sánchez, & Ríos, 2014), iron (Kuranchie, Shukla, & Habibi, 2016), coal (Perná, Hanzlíček, & Šupová, 2014) and phosphate mine tailings (Moukannaa et al., 2018) was used to form geopolymers due to its chemical composition especially its aluminosilicate content. However, the geopolymeric activity of non-calcined material like mine tailings is limited due to its low amorphous phase content. Hence, several methods have been experienced to enhance the geopolymeric reactivity of the raw materials such as mechanical, thermal and chemical activation. Each of these activation methods is acting on different aspects of the material properties (particle size, specific area, crystallinity, mineralogical composition...) (Tchadjie & Ekolu, 2017). It has been proved that the thermal activation is an efficient method to improve the reactivity of non-calcined materials by increasing their amorphous content (Hairi, Jameson, Rogers, & MacKenzie, 2015; Zivica, Palou, & Bágel, 2014). Nevertheless, a combination between the chemical and thermal activations has been evidenced to improve the reactivity of the material by modifying their mineralogical composition, generally, converting some phases into soluble aluminosilicates (Kouamo Tchakoute, Elimbi, Diffo Kenne, Mbey, & Njopwouo, 2013).

This method called alkaline fusion consists of mixing the raw material with an alkali source, then heating or calcining at a temperature higher than the melting point of the alkali source to fuse. Then, the resulted material is mixed with an Al source material and activated by sodium silicate or water (Naghsh & Shams, 2017; Xu, Li, Shen, Zhang, & Zhai, 2010). The aim of the present study is to investigate the activation feasibility of phosphate sludge from phosphate mine tailings by alkaline fusion and to study the effect of the fusion parameters on the mechanical properties and thermal resistance of the resulted geopolymers.

Materials and methods

Materials

Phosphate sludge from the Moroccan phosphate beneficiation plant (OCP-SA) was collected from the hydrocyclones of 40 µm during the washing prosses before being mixed with the coarse part of the sludge. The aluminium source used to balance the Al content of the geopolymer mixtures was metakaolin. Sea sand was used as aggregate to prepare the geopolymer mortars.

Figure 1 represent the XRD patterns of the raw materials, metakaolin is mainly consist of amorphous phase, quartz and mullite while phosphate sludge is composed of quartz, fluoroapatite, calcite, dolomite, illite and palygorskite. The chemical composition of the raw materials is presented in Table 1.

Sodium hydroxide pellet and Sodium silicate (24% SiO₂, 14% Na₂O) from Sigma-Aldrich were used in the fusion process and as activator to prepare the geopolymer pastes respectively.

Figure 1. X-ray diffraction patterns of the used raw materials FPS: Fine phosphate sludge (FPS); and MK: Metakaolin.
 F: Fluorapatite (PDF # 00-002-0845); Q: Quartz (PDF # 96-101-1177); C: Calcite (PDF # 01-072-1651); D: Dolomite (PDF # 96-900-4935); I: Illite (PDF # 00-007-0330); P: Palygorskite (PDF # 00-021-0550); M: Mullite (PDF # 96-900-5503)

Table 1. Chemical compositions (wt.%) of the phosphate sludge (FPS) and metakaolin (MK)

Chemical composition (%)										
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LoI ^a
FPS		23.5	3.56	1.52	4.17	31.1	0.54	0.45	14.1	19.3
MK		51.8	34.2	0.5	0.1	0.1	0.6	—	—	12.7

^a: Loss on Ignition.

Mortar preparation

The phosphate sludge was mixed with sodium hydroxide (10, 20 wt%) and calcined using a muffle furnace for 2 h at different temperatures (550 and 800 °C). The resulted powder was grounded to pass through a 100 µm mesh and mixed with metakaolin (40 wt%), then activated with a sodium silicate solution and mixed for 5 min before adding

the sand with an aggregate to binder ratio of 2 and the activator to solid ratio was fixed at 0.4. The resulted paste was further mixed for 5 min, then poured into cylindrical molds ($D = 36$ mm, $H = 72$ mm), vibrated to eliminate air bubbles and covered by plastic sheets to avoid moisture loss for 24 h. The geopolymer samples were then demolded and cured at 60°C for 4 h. a control sample was prepared following the same ratios without fusion in order to evidence the fusion significance on the resulted materials. (see Table 2).

Table 2. Composition of the geopolymers prepared from fused phosphate sludge and metakaolin

Code	Fusion T°	Sand/ CM	% SH	%MK	SS/solid	Water	liq/Sol
F0	28°C	2	20%	40	0.4	84	0.5
F1	800°C	2	10%	40	0.4	84	0.5
F2	550°C	2	10%	40	0.4	84	0.5
F3	800°C	2	20%	40	0.4	84	0.5
F4	550°C	2	20%	40	0.4	84	0.5

Analysis methods

The mineralogical composition of the starting materials and the geopolymer samples were obtained using a Bruker D8 Advance X-ray diffractometer operating with Cu K α radiation. A continuous scan mode was used in the range $2\theta = 5^\circ$ – 70° with a step size of 0.02° and a scanning step of 0.01° . The elemental analysis of the raw materials was performed by X-Ray Fluorescence spectroscopy technique using a Bruker S8 Tiger WD-XRF. The microstructural observations by SEM and EDS analysis were performed via a Guemini apparatus with accelerating voltage being of 20 kV. A Perkin Elmer® Frontier spectrophotometer equipped with an Attenuated Total Reflectance (ATR) accessory and operating in the range of 4000 – 400 cm^{-1} was used to perform the FTIR measurements. The mechanical properties of the synthesized geopolymer mortars were evaluated by compressive strength measurement and conducted using a Technotest electrohydraulic machine with a rate of 0.25 mm/min . The compressive strength (N/mm^2) was calculated by dividing the maximum load applied to each sample by the area of its cross-section. The error was obtained by dividing the standard deviation of three samples' compressive strengths by the square of three. The thermal stability of the geopolymer mortars was assessed by measuring the compressive strength of the mortars after being exposed to different temperatures (350 , 500 , 650°C) for 4 h and a thermal shock at ambient temperature, the microstructure of the treated mortars was analyzed by SEM.

Results and discussion

The results of compressive strength exposed in Figure 2 shows that the alkaline fusion method used to activate the phosphate sludge was efficient in the improvement of the sludge geopolymeric reactivity. This is evidenced by the higher compressive strength of the fused sludge-based geopolymers in comparison with the control sample. The effect of the NaOH content is strongly correlated to the temperature of fusion. At 800°C , the increase of NaOH lead to a compressive strength raise which is generally expected because of the increase of the aluminosilicate dissolution rate (Tchadjé et al., 2015). At 550°C , the addition of sodium hydroxide hinders the development of the sample's strength probably because of alkali excess. The difference in behavior toward NaOH addition between the samples fused at 550 and 800°C could be explained by the fact that the fusion at elevated temperatures induce consumption of more NaOH that is engaged in the formation of Na-rich phases (Ke, Bernal, Ye, Provis, & Yang, 2015). The optimum fusion parameters exhibiting the higher compressive strength were found at the minimum of NaOH 10 wt% and at the lower temperature of fusion 550°C .

Figure 2. Compressive strength of the control sample F0 and the fused phosphate sludge geopolymers at 28 days

Figure 3 illustrates the mineralogical composition of geopolymer samples. The amorphous hump between 20 and 40° 2 θ is characteristic of the geopolymeric phase. The results show the persistence of some original crystalline phases such as quartz which is inert below alkaline conditions. The fluorapatite and calcite phases persisted also but their quantities diminished evidencing their partial participation to the geopolymerization reaction. In addition, some new crystalline phases were formed such as sodium calcium silicate, berlinite (AlPO₄) and cristobalite. These new formed phases were a result of the interaction between the decomposed original phases during the fusion, the available Na⁺ and sodium silicate.

Figure 3. X-ray diffraction patterns of fused phosphate sludge using 10 and 20% of NaOH at temperatures of 550 and 800 °C. F: Fluorapatite (PDF # 00-002-0845); Q: Quartz (PDF # 96-101-1177); C: Calcite (PDF # 01-072-1651); Na: Sodium calcium silicate (PDF # 01-079-1086); B: Berlinite (PDF # 00-003-0447); Cr: Cristobalite (PDF # 96-900-1580)

The SEM images of the geopolymer samples F1 and F2 (see Figure 4) shows the presence of unreacted particles whitening the geopolymeric matrix. For the samples using phosphate sludge fused at 550 °C these unreacted particles are embedded in the geopolymeric matrix and plays a barrier function against cracks propagation (see Figure 4a). In contrast, a separated layer of unreacted particles can be observed in the top of the geopolymer binder (see Figure 4b) which approve the higher compressive strength of the samples fused at low fusion temperature (550 °C) in comparison with the one fused at 800 °C.

Figure 4. SEM images of fused phosphate sludge based geopolymer mortars: (a) F1; (b) F2

The EDX analysis confirms the previous finding showing that the Si and Al content of the sample F2 fused at 550 °C is higher than for the sample F1. In addition, the EDX analysis of F1 sample shows an agglomeration of unreacted particles in the top of the geopolymer binder (see Figure 5b and Table 3).

Figure 5. SEM/EDS micrographs of fused phosphate sludge based geopolymer mortars: (a) F2; (b) F1

Table 3. EDX chemical composition of spectrum 1, 2 and 3 of F1 and F2 samples

Spectrum	Si	Al	Ca	Na	Si/Al	Na/Al
Spectrum 1	18.53	7.33	3.38	8.59	2.53	1.17
Spectrum 2	4.22	1.64	11.11	3.92	2.57	2.39
Spectrum 3	12.17	5.95	3.36	10.49	2.05	1.76

The thermal resistance of the geopolymer samples was evaluated by measuring the compressive strength after exposure to different elevated temperatures and a thermal shock. The results of compressive strength evolution are summarized in Figure 6. all samples showed the same evolution trend regardless of the NaOH content or the temperature of fusion. However, different behaviors were observed depending on the temperature of treatment. Treatment at

Figure 6. Variation of the geopolymer mortars compressive strength before and after heat treatment at several temperatures (350, 500 and 650 °C)

350 °C induce an increase of the geopolymer's compressive strength, which is attributed to the completion of the geopolymerization reaction and the participation of the unreacted particles. Nevertheless, treatment at higher temperatures result in a large compressive strength decline. The treatment at elevated temperatures up to 500 °C induce cracks and an increase of porosity as shown in Figure 7. It is clearly noticed from the SEM images of the geopolymer samples that the unreacted particles were partially or completely dissolved in the matrix after thermal treatment. Overall, the optimum mixture prepared using phosphate sludge fused at 550 °C and 10 wt% preserved a compressive strength of 12.86 MPa after exposure to 650 °C for 4 h.

Figure 7. SEM images of fused phosphate sludge based geopolymers after exposure to high temperatures: (a) F1 exposed to 500 °C; (b) F1 exposed to 650 °C; (c) F2 treated at 500 °C; (d) and (e): F2 treated at 650°C with different magnifications

Conclusions

The present paper investigated the feasibility of using the alkaline fusion method for the activation of phosphate mine tailing mainly phosphate sludge to produce geopolymer mortars and studied the mechanical behavior of the resulted geopolymers after exposure to elevated temperature.

The results showed that the temperature of fusion and the NaOH content are strongly correlated and has a significant impact on the final properties of the geopolymers. The optimum fusion condition was found at 10 wt% of NaOH and 550 °C exhibiting the higher compressive strength. Furthermore, the fusion at 550 °C leads to more homogenous paste, where the unreacted particles are surrounded by the geopolymeric matrix while a treatment at 800 °C induce the formation of layers of the agglomerated unreacted particle in the top of the geopolymer binder which weakens the samples. The compressive strength results after exposure to high temperatures showed that a treatment at 350 °C was beneficial while a treatment at higher temperatures induce a decrease of the geopolymers strength due to the formation of cracks. In essence, geopolymer mortars with good mechanical properties up to 40 MPa were synthesized from fused phosphate sludge at 550 °C using 10% of NaOH. In addition, the geopolymer mortars conserved their structural integrity after exposure to 650 °C.

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