IOP Conference Series: Materials Science and Engineering

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To cite this article: N I Kozhukhova *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **560** 012148

Influence of Fe component from milling yield on characteristics of perlite based geopolymers

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Abstract. The mineral and chemical composition of aluminosilicates used in geopolymer systems is critical for optimal structure formation and the overall performance of the geopolymer products. The composition of alumosilicates can be altered during the technological processing, especially, at the stage of fine milling. This study investigated the effect of aluminosilicate contamination with Fe from milling yield, the characteristics of the aluminosilicates with a metal lining, structure formation, and hardened properties of geopolymers based on different natural and technogenic persilicic aluminosilicates. The formation of Fe-phases due to milling yield was detected by the XRF analysis and the XRD investigation revealed the formation of nanosized ferrous hydroxide or bernalite $Fe(OH)_3(H_2O)_{0.25}$. The volume of an elemental cell of the nanosized bernalite per Fe atom is 4.5 times larger than that of the metallic iron. This results in the disintegration of the matrix, which was observed by SEM and then confirmed by reduced strength performance of geopolymer composites. Based on this study, the negative effect of Fe-phases from milling and nanosized ferrous hydroxide on structural characteristics and service performance of geopolymer composites based on natural and technogenic raw materials was concluded.

1. Introduction

Production of construction materials and composites allows utilization of a wide spectrum of raw components [1]. However, most of the materials need to be dispersed to a certain fineness before being sent to the production process, because the level of dispersity is the key parameter to achieve chemical reactivity of the component and is responsible for the overall performance of construction composites [2, 3].

Mechano-chemical activation is one of the widely used methods to enhance chemical reactivity of natural and technogenic mineral components. The study by Mejdoub [4] demonstrated that the mechano-chemical activation of cement can change not only granulometry of cement particles, but also the reaction ability, such as an addition of even a small amount of activated cement (up to 10%), and can remarkably improve the strength performance of cement binder [4]. The mechano-chemical activation is usually performed in milling units of different types and inside lining and the milling process can be realized in wet or dry conditions [5]. Yet, most of the studies focused on the investigation of microstructural and morphological properties, which are now being changed with milling. An industrial-scale production adapted the application of metallic grinding units that during the milling process tend to form Fe-milling yield from the inside lining and milling bodies contaminating the processed material inside the grinding unit [5-8].

The geopolymer binders based on natural and technogenic raw materials require the mineral powder components to be highly dispersed, therefore the production technology involves milling [9]. Škvára [10] reported that Fe ions in geopolymer binder composition are inactive and do not participate in geopolymerization reactions. Therefore, the higher the concentration of Fe cations in the alkali-aluminosilicate system the lower the reactivity of the geopolymer binder.

The study on alkali-activated binders [11] developed a hypothesis that chemical valency and a coordination number of Fe cations can affect their relevance in structure formation of the geopolymer binder system. Therefore, the cations Fe^{2+} and Fe^{3+} with the coordination number of 5 in alkali-activated aluminosilicate system act the same way as the cations of alkali metals serving as alkaline activators. At the same time, the cations Fe3+ with a coordination number of 4 act similar to the cations Al^{3+} and participate in structure formation; however, this study investigates the iron component in oxide form.

The present research focused on the Fe-milling yield formed from aluminosilicate dispergation represented by nanosized metallic iron, the effect of which in geopolymer systems currently is practically unclear.

2. Materials and methods

In this study, perlite a persilicic alumosilicate material supplied from Mukhor-Talin deposit in Russia and two types of alkaline activators NaOH and KOH were used to prepare and analyze the geopolymer binder.

The X-ray diffraction (XRD) characterization and X-ray fluorescence (XRF) analysis were performed in order to study the mineral composition of perlite and geopolymer binder. Tablet-shaped specimens for XRD and XRF were prepared using a back loading method and analyzed with WorkStation ARL 9900 (Thermo Scientific, USA) spectrometer (using CoKα radiation). The full-profile qualitative XRD analysis was performed using database PDF-2.

An estimation of particle size of metallic Fe in perlite as well as the hydrate Fe-phases in geopolymer binders was calculated using Scherrer equation limited to nano-scale particles:

$$d = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \tag{1}$$

where K is the Scherrer constant or a dimensionless shape factor, which was taken to be 1 as an average value for spherical and granular particles; λ is X-ray wavelength, Å; β is the line broadening at half the maximum intensity, 2θ, radians; θ is the diffraction angle or Bragg angle, degrees.

The volume values of an elemental cell for metallic Fe in perlite and hydrate Fe-phases in geopolymer binders were taken from the Inorganic Crystal Structure Database (ICSD). The microstructural surface analyses of geopolymer binder was carried out on a Mira 3 FesSem scanning electron microscope (SEM) (Tescan, Czech Republic). The accelerating voltage of the electron gun was 7 kV, and the magnification was 3000×. Before examination, a carbon layer was deposited on the surface of the specimen.

Compressive strength and density characteristics of the geopolymer binder were evaluated using three cubes and three beam specimens 70×70×70 mm and 40×40×160 mm, respectively, and the average values of test results were reported [12].

3. Results and discussions

For comparison purposes, in this research perlite was subjected to mechano-chemical activation using two different grinding units in order to reach surface area of 450 m2/kg. The chemical composition of perlite after 2 hours of milling showed that the material processed in planetary mill with metal lining resulted in considerable increase of FeO, up to 69%. However, the mechano-activation in similar conditions in ball mill with uralite lining did not cause any remarkable changes to chemical composition, Table 1, Figure 1.

Table 1. The chemical composition of perlite before (B) and after (A) mechano-chemical activation

Oxide composition, % weight							Remarks
Perlite	*B* before mechano-activation						
SiO_2	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	MgO	
71.97	16.34	4.43	4.63	1.07	0.872	0.74	–
Perlite	*A* in planetary mill						
SiO_2	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	MgO	
71.88	16.3	4.09	4.1	0.73	1.47	0.37	69 % increase of Fe ions
Perlite	*A* in ball mill						
SiO_2	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	MgO	
72	16.42	4.08	4.38	0.93	0.93	0.49	2 % increase of Al ions

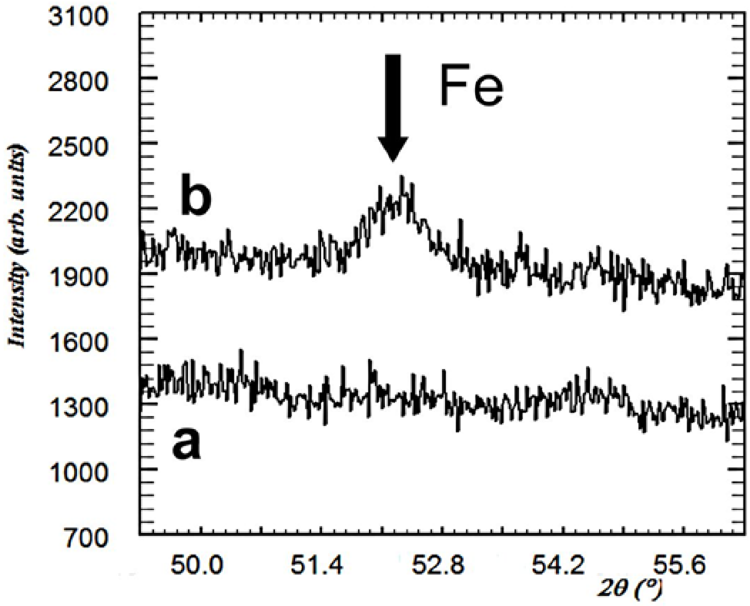
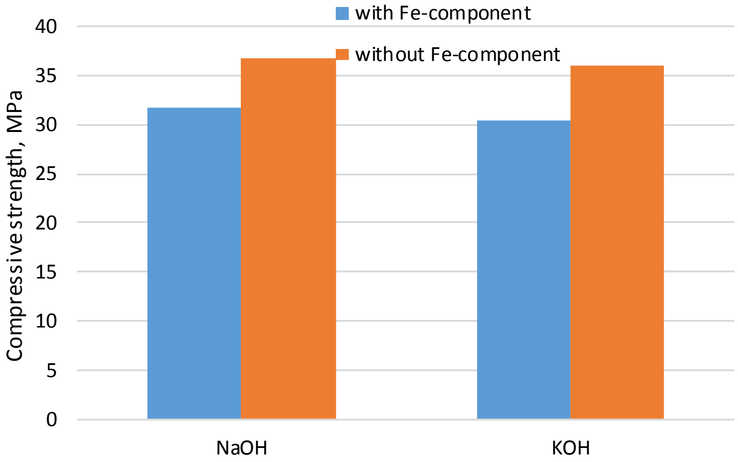


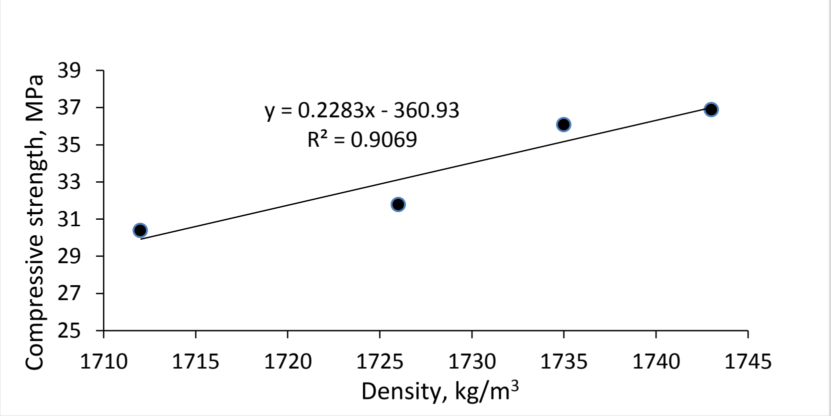
Figure 1. XRD-analysis of the perlite after grinding a – ball mill; b – planetary mill.

At the stage of specimen preparation, the water amount was chosen in order to achieve a given flow in the range of 120–140 mm. The obtained mixtures were cast, compacted using vibration table and then subjected to thermal treatment at 70 oC for 24 hours followed by demolding and additional curing at 22±3 °C and relative humidity of 55 % for another 27 days until the specimens were tested.

Mechanical performance of the geopolymer binder showed that the presence of nanosized metallic iron caused destructive processes when hardening (Figure 2) and results in 13–16 % reduction of compressive strength and up to 1.5% decrease of density.



(a)



(b)

Figure 2. Correlation between compressive strength and density in geopolymers with and without Fe

It follows from the SEM data in Fig. 4 that the specimens containing higher percentage of nanosized metallic Fe showed more loosely packed structure (Figure 3b), whereas the Fe-free specimens demonstrated more dense matrix and integrated structure (Figure 3a).

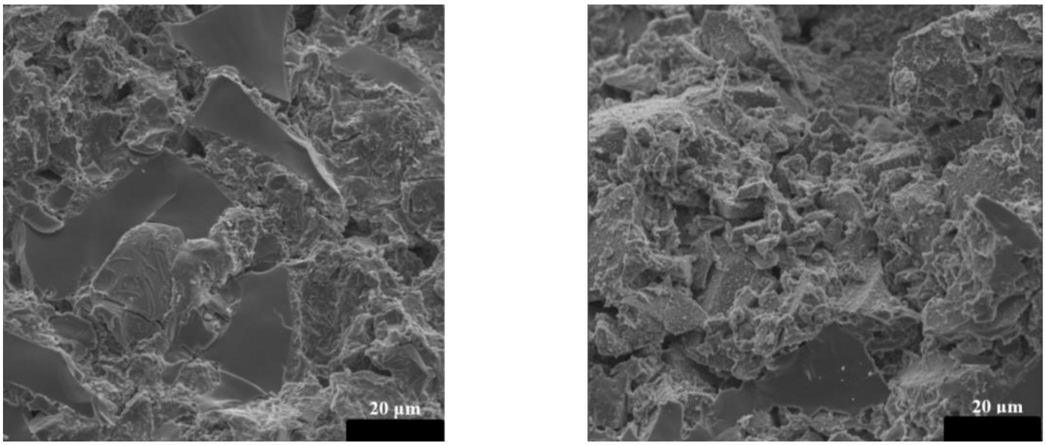


Figure 3. The SEM-images of the geopolymer binders with NaOH: without (a) and with (b) Fe.

The XRD data of the geopolymer binders (Figure 4) lead to the conclusion that the Fe-milling yield in perlite composition after mechano-chemical activation is within nanoscale. In addition, it actively participates in alkaline activation reacting with water molecules or hydroxide OH– ions resulting in the formation of Fe-hydrate phases as bernalite $Fe(OH)_3(H_2O)_{0.25}$.

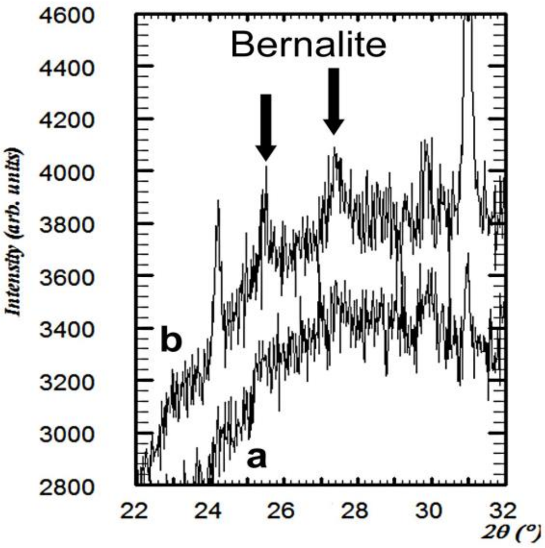


Figure 4. The XRD-pattern of the geopolymer binders with NaOH: without (a) and with (b) Fe.

Due to the fact that the volume of an elemental cell of the nanosized bernalite per Fe atom is 4.5 bigger than that for nanosized metallic iron (Table 2), a disintegration of geopolymer skeleton takes place, causing the reduction of strength and worsen the overall performance of geopolymer concrete.

Table 2. The crystallographic characteristics of Fe-phases

Type of Fe-phase	Parameters of crystal lattice			
	Elemental cell volume of Fe-phase, Å^3	Number of atoms per cell	Elemental cell volume per 1 atom of Fe, Å^3	Crystallite size, nm
α-Fe	23.55	2	12	16
Bernalite $Fe(OH)_3(H_2O)_{0.25}$	431.05	8	53.88	18-19

4. Conclusion

The influence of Fe-bearing oxides contained in the aluminosilicates such as fly ash, slags etc. on various physical, chemical, and mechanical performance is well investigated for geopolymer and alkali-activated binder systems. However, similar effect of metallic iron, a very common product of mechano-chemical activation in grinding units with metal lining, is yet to be investigated.

The effect of Fe-milling yield on the formation and performance of aluminosilicates in geopolymers was studied in this research. The main conclusions may be summarized as follows:

The mechano-chemical activation in a grinding unit with metal lining results in considerable milling yield of Fe affecting the composition of processed perlite, which negatively affects the structural characteristics and strength performance of the perlite-based geopolymer system.

The Fe-milling yield found to be in the form of nanosized metallic Fe that actively reacts in alkaline-aluminosilicate system forming Fe-hydrate phases as bernalite $Fe(OH)_3(H_2O)_{0.25}$. Due to the volume of an elemental cell of the Fe-phases is 4.5 time bigger than that of nanosized of metallic iron, the presence of the highly reactive Fe in the system results in disintegration of alkali-aluminosilicate skeleton and the geopolymer matrix.

Acknowledgments

This research work is financially supported by the Ministry of Education and Science of the Russian Federation in the framework of State Assignment №11.9329.2017/8.9, using equipment of the High Technology Center at BSTU named after V.G. Shukhov.

References

[1] Elistratkin M Yu, Minakova A V, Jamil A N, Kukovitsky V V, Issa Jamal Issa Eleyan 2018 *Construction Materials and Products*. **1(2)** 37–44
[2] Kozhukhova N I, Zhernovsky I V, Sobolev K G 2018 *Bulletin of BSTU named after V G Shukhov*. **4** 5–12
[3] Shekhovtsova J, Zhernovsky I, Kovtun M, Kozhukhova N, Zhernovskaya I, Kearsley E 2018 *Journal of Cleaner Production* **178** 22–33.
[4] Roukaya Mejdoub, Halim Hammi, Mohamed Khitouni, Joan Josep Suñol, Adel M'nif. 2017 *Construction and Building Materials.***152(15)** 1041-1050
[5] Jiajie Li, Michael Hitch 2017 Powder Technology. **308** 13–19
[6] Ermolovich E.A., Ermolovich O.V. 2016 *International Journal of Mining Science and Technology*. **26(6)** 1043-1049
[7] Akshata G, Patil S 2015Powder Technology. **281** 151-158
[8] Sobolev K., Lin Z., Cao Y., Sun H., Flores-Vivian I., Rushing T., Cummins T., Weiss W. J. 2016 Cement and Concrete Composites. **71** 53–62
[9] Fomina E V, Strokova V V, Kozhukhova N I, Fomin A E 2016 *Indian Journal of Science and Technology* **9(22)**
[10] Pawlasová S. Škvára F. 2008 *Alkali Activated Materials*. 523–525.
[11] Zhang Z, Provis J L, Zou J, Reid A, Wang H 2016 *Cement and Concrete Research.* **85** 163–173.
[12] GOST 10180-2012 Concretes. Methods for strength determination using reference specimens. All Union State Standard. 2007.