EFFECT OF KAOLIN ADDITION INTO METAKAOLIN GEOPOLYMER COMPOSITE

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ABSTRACT

Industrially produced metakaolin may contain raw kaolin residues. Therefore, the aim of this work was to determine the impact of kaolin remains on the metakaolin and the final geopolymer quality. A series of mixtures based on metakaolin (Mefisto L05 by CLUZ Nove Straseci, Czech Republic) was prepared with the 0-60 wt% gradual addition of raw kaolin, and the mechanical strength of the final geopolymer products was tested. It was found that up to a 20 wt. % amount of kaolin in metakaolin does not weaken the geopolymer's performance. Moreover, a geopolymer made of metakaolin with 2-4 wt% of kaolin showed slightly better mechanical properties than the geopolymers made from metakaolin itself.

KEYWORDS

Geopolymer, Metakaolin, Kaolin, Mechanical properties, Frost resistance

INTRODUCTION

The number of geopolymer applications increases every day [1-7]. However, there is still a significant number of its properties and details that have to be studied. The influence of basic constituents' composition on geopolymer strength, such as a variety slag-metakaolin ratio [8] or Si/Al metakaolin (MK) ratio [9,10], is being studied. Even so, raw kaolin burning in industrial quantities can lead to the imperfect dehydration of kaolinite. So, the influence of kaolin remains in metakaolin (Mefisto L05, CLUZ Nove Straseci, Czech Republic) was studied in this paper.

Earlier as a main aluminosilicate source metakaolin and fly ash were taken [11], but nowadays the list of geopolymer precursors is significantly increased especially with by-product materials like slag and silica fume [12]. Metakaolin is produced from kaolin, kaolinitic clay or claystone by continual burning. The quality of the burned product depends on the burned amount, particle size, thickness of the layer, and temperature. Therefore, the conversion of kaolinite to metakaolin could not be absolute, which affects further geopolymerization, such as other impurities [13, 14].

In this article the influence of raw kaolin residua (0-60 wt%) in thermally activated kaolin was studied. A test series of compressive and flexural strength was conducted on samples with a variety

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of raw kaolin additions. Also, the mechanical properties of the geopolymers with and without the raw kaolin addition were further characterized by frost resistance.

METHODS

Materials

Mefisto L05, made by the Czech company CLUZ Nove Straseci (Czech Republic) was used with a declared metakaolin content of 95 wt% and impurities such as quartz and muscovite. To remove the residual kaolin in Mefisto L05, the powder was burned at 750 °C for 6 hours. The raw kaolin used was produced by Sedlec Ia (Czech Republic). The alkaline activator was prepared by dissolving NaOH (Lachner, Czech Republic) in sodium water glass from Vodni Sklo, a.s. (Czech Republic) in a volume mass ratio of 1 to 0.15, respectively. As an aggregate, silica sand Strelec ST 92 with 99 wt% of SiO_2 and a particle size of $D_{50} = 0.6$ mm was used.

Sample preparation

Metakaolin and an alkaline activator were mixed (Si/Al = 1.8; Na/Al = 1.0; Na/H2O = 0.7) first for 5 minutes, and a basic geopolymer matrix was obtained. Final mass of alkaline activator depended on the metakaolin or metakaolin+kaolin amount. Then, kaolin and sand were added and stirred for 10 minutes. Sand formed 60 % of the total mixture weight.

To ensure the homogenous distribution of a small amount of kaolin in the samples (5 wt% and lower) the appropriate amount of kaolin was dispersed in approximately 30 g of water, which was required for proper dilution of the alkaline activator. Then, the suspension was added into the already mixed geopolymer matrix. For samples with a kaolin content above 5 wt%, kaolin in the form of a fine, dry powder was added with sand into a geopolymer matrix that helped activate the precursor mixture mechanically.

The weight percentage of kaolin and metakaolin in the samples was 0 to 50 and 100 to 50, respectively. This form of writing was chosen to imitate the impurities percentage in the initial powder.

The mixture was then poured into 40 mm x 40 mm x 160 mm plastic molds under vibration until air bubbles disappeared. The samples were stored indoors in covered molds for 7 days until completely hardened. Then, the samples wrapped in polyethylene foil were cured at laboratory temperature for 28 days to comply with the solidification conditions. All samples were prepared under the same conditions at 20 °C and humidity 45 % and stored for two months after curing before testing.

For XRD and FTIR analyses dry mixtures of metakaolin (MK) and kaolin (K) were prepared in ratio MK:K = 95:5, 85:15 and 65:35.

Sample characterization

Compressive strength and three-point flexural strength tests were performed on a semi-automated press EU 40 Werkstoffprufmaschien, Leipzig according to Standard No. ČSN EN 1015-11(1999) [15] using the standard sample size, i.e., 40 mm x 40 mm x 160 mm.

Frost resistance tests were carried out according to the frost resistance standard CSN 731322 (1969) [16] by alternating freezing and defrosting of water-saturated samples within 50 cycles. Each cycle consisted of 4 hours of freezing at -20 °C and 2 hours of defrosting in water at 20 °C. Before the strength measurements were conducted, all samples were dried at laboratory temperature for 28 days.

X-ray diffractograms were recorded using Rigaku MiniFlex 600 (Ni-filtered, Cu-Kα1,2 radiation) equipped with a NaI(:Tl) scintillation detector and were compared to the relevant records in the ICDD PDF-2 database [17].

Fourier-transformed infrared spectra (FTIR) were recorded by a Nicolet iS50 FTIR spectrometer [18] in the middle infrared region at 400 – 4000 cm^{-1}, with a resolution of 2 cm^{-1} on an ATR diamond crystal, which data were also compared to the relevant records in the HR Inorganics – Minerals database.

Study of the measured samples was carried out on a Quanta 450 (FEI) Scanning Electron Microscope (SEM). The observations of the polished cross-sections were performed in backscattered electron (BSE) mode under a high vacuum. The analytical conditions were the energy of the electron beam at 30 kV and a spot size of 2 mm at a 10 mm working distance. The samples were vacuum-coated with gold to prevent localized charging in the specimen. The semi-quantitative chemical composition of the matrix was analyzed using an energy-dispersive X-ray microanalyzer (EDAX, Apollo X).

A detailed SEM was performed on a Phenom XL Desktop SEM under high-vacuum on the natural sample surface of the polished sections mentioned above with a voltage of 10 kV (SEM) and 15 kV (SEM/EDS).

The elasticity modulus measurement was carried out with a nanoindentation tester by an NHTX S/N: 10-00039 (Anton Paar GmbH, Austria) according to Oliver-Pharr method [19]. The settings were the maximum load of 2 mN, the loading rate of 30 nm/min, and the Poisson's ratio of 0.2.

RESULTS

Influence of kaolin on mechanical properties of geopolymer

The compressive strength of the tested samples with changing kaolin content ranged from 20 to 55 MPa (Table 1). Samples with kaolin content in metakaolin up to 20 wt% showed slightly better compressive mechanical properties in comparison with samples made from pure metakaolin. Changes in flexural strength due to varying kaolin content were negligible and within statistical error, while kaolin content was lower than 20 wt% (Table1). The addition of kaolin above 20 wt% led to a dramatic decrease in both the compressive and flexural mechanical strengths. Hardening process time slowed down with the increasing addition of kaolin.

The addition of kaolin increased mixture viscosity and made mixing difficult, so the porosity of some samples could increase. This could influence the microstructure and thus decreased strength at higher kaolin concentrations.

Tab. 1 - The compressive and flexural strength values [MPa] of the samples with variable kaolin content.

Amount of added kaolin [wt%]	Compressive strength [MPa]	Flexural strength [MPa]
0	47.2 ± 2.2	8.0 ± 0.4
2	52.5 ± 2.5	7.9 ± 0.4
3	52.6 ± 2.5	8.1 ± 0.4
4	52.4 ± 2.5	8.1 ± 0.5
5	55.2 ± 2.6	8.2 ± 0.3
7	53.6 ± 2.5	8.4 ± 0.6
10	53.3 ± 2.5	8.2 ± 0.4
15	52.6 ± 2.5	8.5 ± 0.4
20	52.1 ± 2.4	8.1 ± 0.4
30	40.0 ± 1.9	7.5 ± 0.5
35	32.7 ± 1.5	4.5 ± 0.2
50	21.5 ± 1.0	4.0 ± 0.3

Frost resistance

The compressive and flexural strength after the freezing-defrosting cycles in water was compared with the values of the no-frost sample strength. Samples with 1 wt% of kaolin displayed cracks already after 25 freezing cycles. The cracks were probably caused by unsatisfactorily homogenized kaolin input and, therefore, were not measured. Figure 1 shows flexural and compressive strength after 50 cycles with the highest value reached by samples containing 2-3 wt% of kaolin. The compressive strength even surpassed the highest values before freezing. The reason could be in the prolonged dwell in the proper conditions which aided the polycondensation. Higher addition of kaolin deteriorated the frost resistance probably because of retaining water leading to expansion inside the kaolin particles.
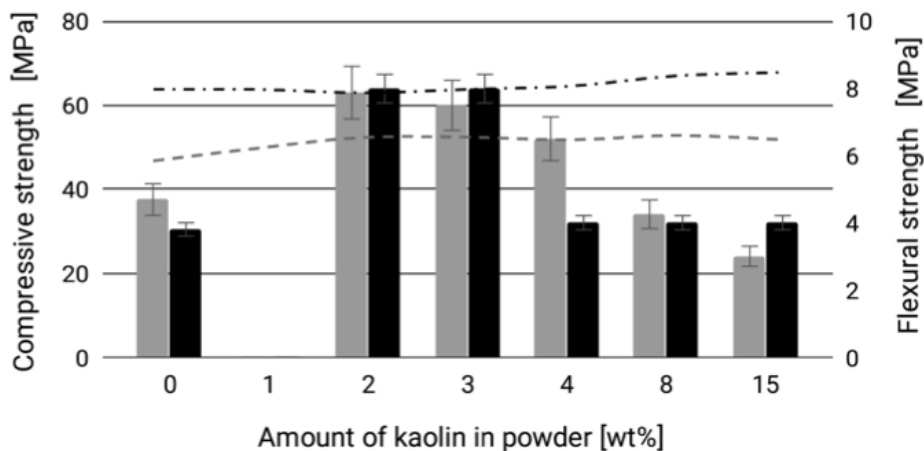

Fig. 1 - The compressive (gray slopes) and flexural (black slopes) strength values of samples affected by kaolin after 50 frost cycles. The gray dashed line shows the values of the no-frost samples' compressive strength, the black dash-dot line shows the flexural strength values of the no-frost samples.

XRD analysis

The amount of raw kaolinite in the industrial metakaolin Mefisto L05 was determined based on peak areas of kaolinite at 12.3^O and 24.8^O. According to five-point calibrations based on metakaolin, mixed metakaolin with kaolin and kaolin the amount of unburned kaolin in Mefisto L05 was determined to be 3.5 ± 0.5 %. Kaolinite in Mefisto L05 is easily visible, and its diffractogram looks similar to the record of the sample with 5 % kaolin addition (MK:K=95:5) (Figure 2). Kaolinite was not found in the metakaolin sample burned in the laboratory kiln, or its amount was under the detection limit. As far as XRPD is a very sensitive method for crystal materials detection, it is possible to say that no kaolinite was presented in burned metakaolin. Quartz was found in all samples.

The presence of kaolinite after geopolymer hardening was observed in the samples with added kaolin (Figure 2, GP [MK:K=95:5]). It means that kaolinite does not participate in polycondenzation. Based on the kaolinite calibrations, its amount in geopolymer was calculated to 5.1 ± 1.0 %, which corresponds with the added amount of kaolin.

Besides quartz, muscovite was detected in the metakaolin Mefisto L05. The amorphous hump of metakaolin is shifted to higher angles and becomes narrower after polycondensation in the matrix, which can mean higher structural organization.
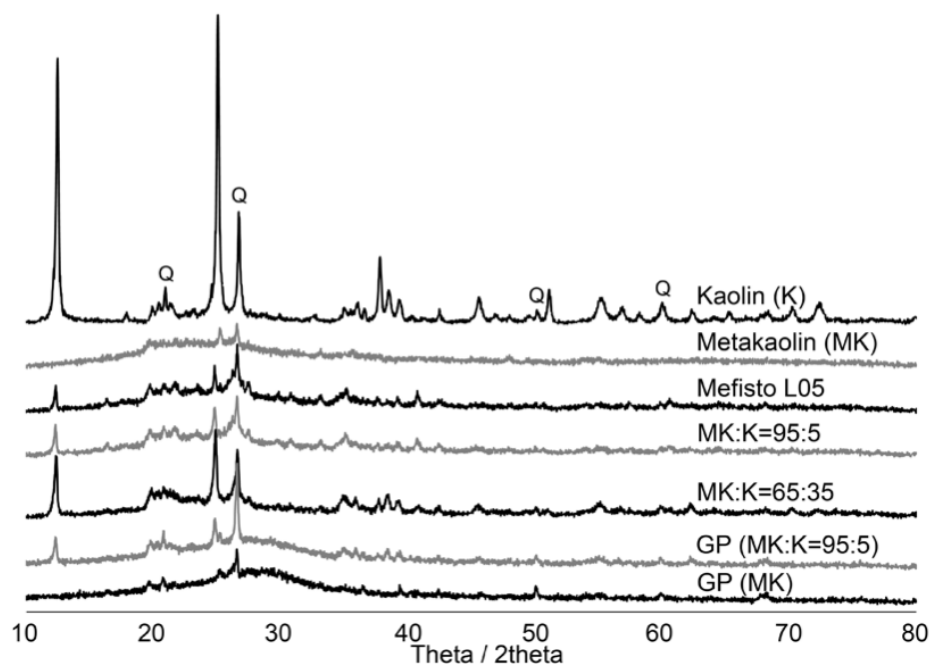

Fig. 2 - A comparison of XRD diffractograms of the metakaolin (MK), raw kaolin (K), and their mixtures (MK:K=95:5 and 65:35); industrial metakaolin Mefisto; the resulting geopolymer made of metakaolin (GP (MK)) and metakaolin with added kaolin (GP (MK:K=95:5)). Q = quartz.

FTIR analysis

The content of kaolinite in the industrial metakaolin Mefisto L05 was very low, and thus, a quantitative analysis based on FTIR spectra was not performed (Figure 3). However, the addition of raw kaolin to the reference-scale samples (MK:K=95:5 and 65:35) is demonstrated by the bands of proportionally graduating height and by the shape with shoulders' referring to the proper kaolin ratio.
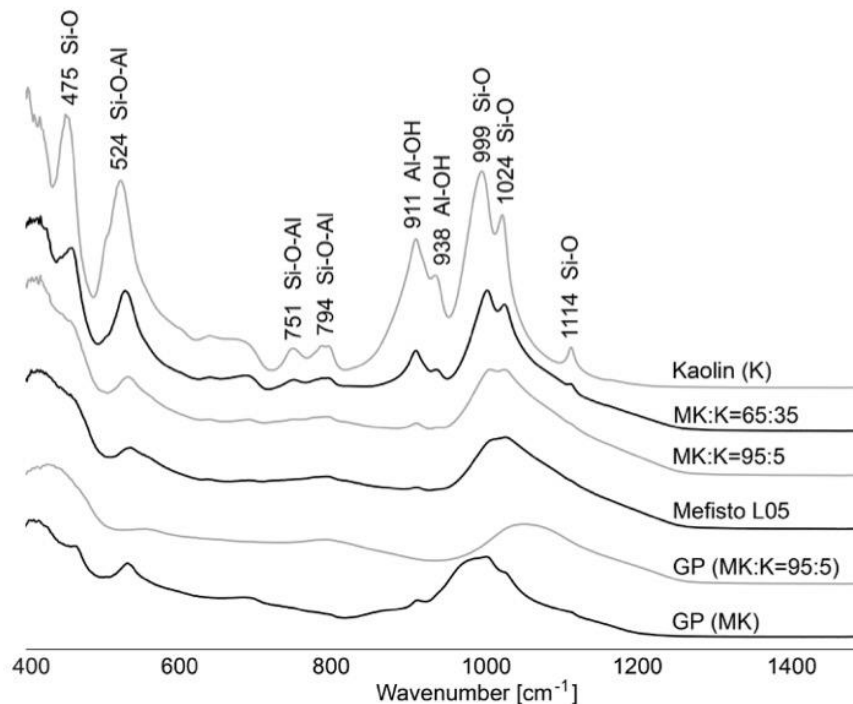
Fig. 3 - FTIR spectra of the industrial metakaolin (Mefisto L05), this one burned in laboratory (Metakaolin (MK)), kaolin (K), their mixtures (MK:K=95:5 and 65:35); and the resulting geopolymer made of metakaolin (GP (MK)) and metakaolin with added kaolin (GP (MK:K=95:5)).

The presence of kaolin in the matrix sample is well seen due to the OH deformation band linked to $2Al^{3+}$ at 911 cm^{-1} and the Si-O-Al stretching band at 524 cm^{-1} [20]. Furthermore, kaolin and the reference-scale samples were compared to the database HR Inorganics I. record of kaolinite in order to confirm the composition. The geopolymer matrix (GP (MK)) band at 930-1070 cm^{-1} with a maximum at 985 cm^{-1} is not so wide, but it shifted to a lower wavenumber in comparison to the metakaolin (MK) main band at 960-1250 cm^{-1} with a maximum at 1035 cm^{-1}. Kaolinite presence is visible in the main band of geopolymer made of metakaolin with a kaolin addition (GP (MK:K=95:5)) as a shoulder at 1032 cm^{-1} and a maximum at 1008 cm^{-1}.

Al-OH stretching bands at 3500-3650 cm^{-1} were also observed in kaolin samples. OH stretching bands of the physically bonded water at 3300-3500 cm^{-1} were observed only in both of the geopolymer samples (GP (MK:K=95:5) and GP (MK)), where the slightly higher absorbance intensity was induced by water in geopolymer matrix.

SEM Analysis

Figure 4 displays the differences between the two microstructures of the matrix with and without kaolin among quartz sand aggregates. The structures differ in their microcracks network. Whereas the matrix without added raw kaolin is more fragmented by numerous fine cracks, the matrix with added kaolin shows fewer but wider cracks. They demarcated the matrix in the areas of relaxed structural strain, unlike the crumbled matrix without raw kaolin. In this matrix, widespread light-grey crumbs were detected and identified by EDAX analyses as residual metakaolin particles (Table 2). The residues of undissolved metakaolin soaked the geopolymer and created harder parts of the matrix. The liquid precursor alone hardened into a softer background matrix that surrounded

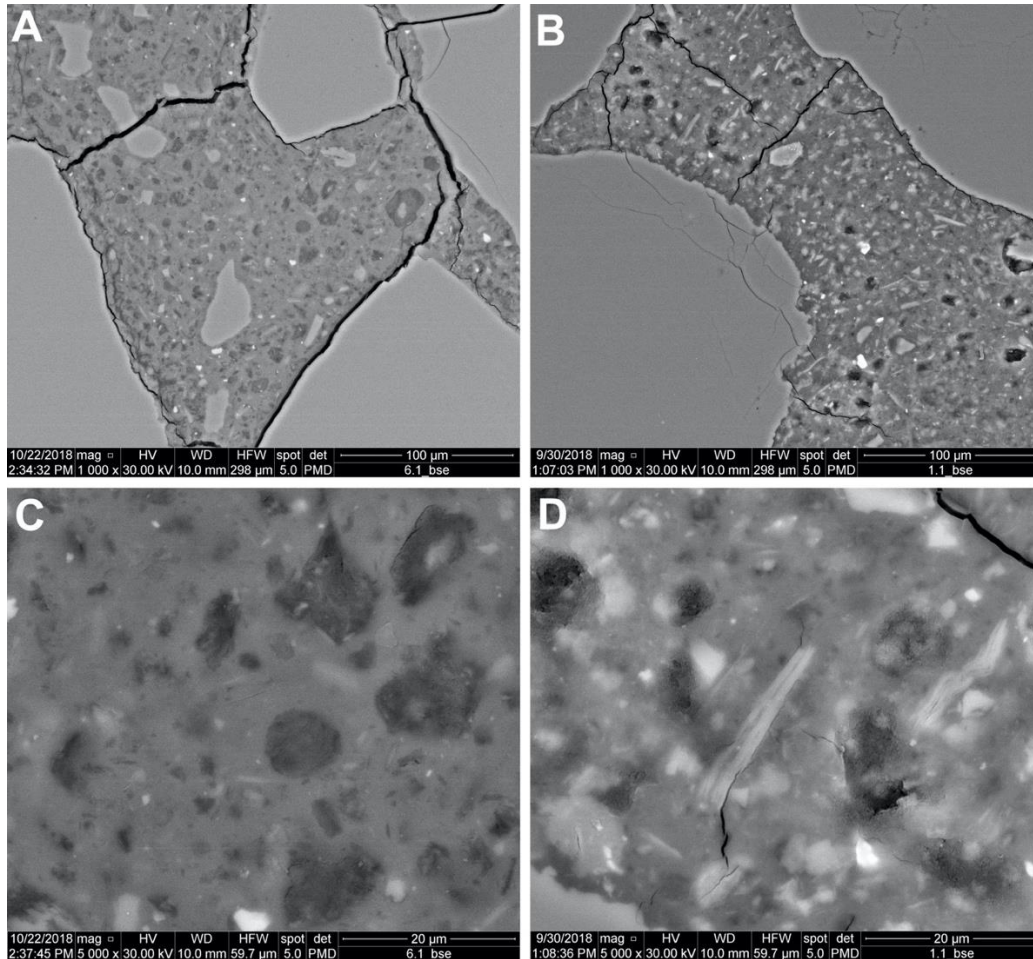all the objects. This is evidenced by the micromechanical properties measured by means of nanoindentation.

Fig. 4 - SEM micrographs of geopolymer made of metakaolin with kaolin (MK:K=95:5) (A; C) and metakaolin (B; D) carried out on a Quanta 450 SEM.

Tab. 2 - EDAX spot analysis [wt%] of the geopolymer matrix-microstructure parts and objects (averaged results). MK = metakaolin, K = kaolin.

Spots in structure	Weight percentage (average results) [wt%]						
	Al_2O_3	SiO_2	Na_2O	K_2O	CaO	FeO	TiO_2
Background	24	61	10	<1	2	<1	<1
MK residues	27	60	7	<1	3	<1	<1
K floccules	36	58	2	<1	<1	<1	<1

The elasticity modulus (E) of the background matrix containing finely dispersed kaolin reached up to 15.2 GPa, unlike the pure matrix, where the results were split into the values of the background matrix (10 GPa) and the metakaolin residues (12 GPa). Both were of lower E than the matrix with kaolin. The differences among micromechanical properties are in accordance with the

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results of the mechanical properties. In the homogeneous microstructure, with a 5 wt% of kaolin, metakaolin was probably better dissolved. This could have been caused by the significantly delayed hardening of the samples with kaolin. During the prolonged dwell in the liquid alkaline medium, the metakaolin had more time to dissolve without "freezing" its whole particles. This could increase monomer-precursor superiority. Thus, the metakaolin can participate in polycondensation towards the structure's densifying and strengthening.

In Figure 5, the most common components of the microstructure are shown in detail: quartz aggregates, mesopores of the size of about 10-20 μm, under 10 μm and smaller particles such as metakaolin residues, quartz, mica, and other impurities.

The added kaolin particles were difficult to detect because of their addition in the form of a colloid suspension. Some bigger kaolin floccules were detected by EDAX and are indicated in Figure 5 by white asterisks. The higher concentration of kaolin slowed down the matrix chaining and setting, which was the reason for the delay in the products' hardening. The floccules reduced the internal strain and partly acted as a structural buffer hindering the spread of microcracks, which contributed to mechanical strength (at least up to the 20 wt% addition of kaolin in metakaolin). For the frost resistance, however, the higher concentration was less effective, probably because of the water retention.
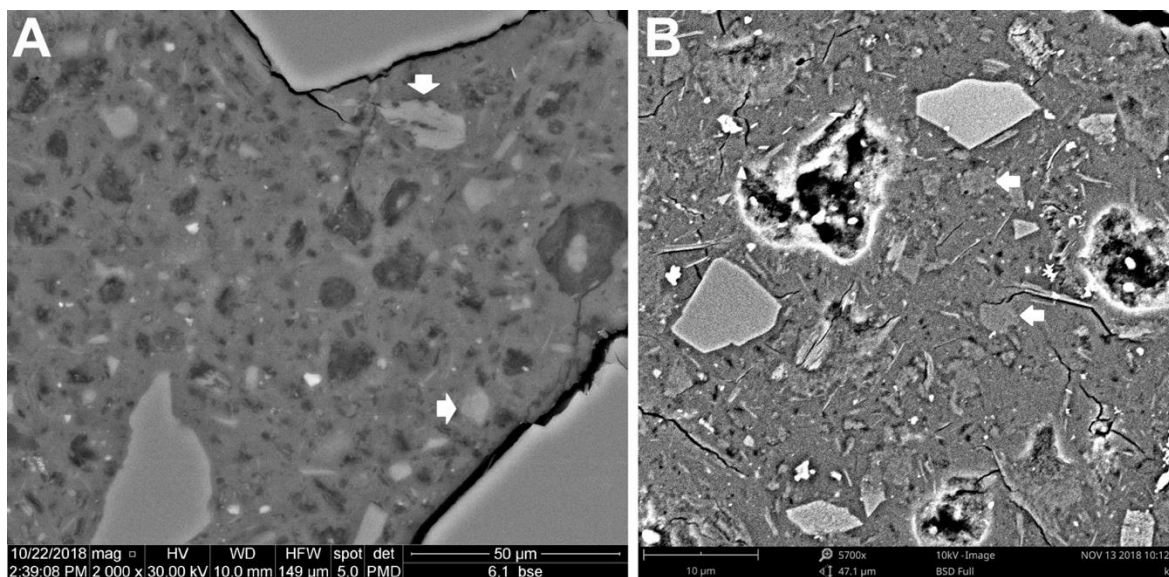

Fig. 5 - Micrographs of geopolymer made of metakaolin with kaolin (MK:K=95:5) with visible particles of kaolin highlighted by white asterisks; (A) carried out on a Quanta 450 SEM, (B) more detailed using a Phenom XL Desktop SEM.

CONCLUSION

This work aimed to study kaolin residues after the industrial metakaolin burning by comparing the influence of the raw kaolin addition to metakaolin on the mechanical properties of the resulting geopolymer products.

Despite the weakness of kaolin and although the raw kaolin is known to be non-convertible into geopolymer chains, it was found that kaolin spoiled neither the polycondensation nor the product solidification. Moreover, it was found out that the solid did not crumble in water in a wide range of kaolin content (2-50 wt%) during testing. A further benefit of the measurement was the finding that

a small amount of kaolin in metakaolin (up to 3 wt%) improved the geopolymer performance in compressive and flexural strength tests after frost-resistance tests in comparison with no-frost samples. Also, the presence of up to 20 wt% of kaolin did not affect the flexural strength of the geopolymer but slightly improved compressive strength. Based on the obtained results, monetary savings in large volume production can be achieved by either admixing raw kaolin into metakaolin or proper regulation of the burning process.

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