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RAW KAOLINITIC CLAYS FROM SERBIA AND THEIR POTENTIAL IN THE PRODUCTION OF EXTRUDED CERAMIC TILES

PRIRODNE KAOLINSKE GLINE IZ SRBIJE I MOGUĆNOST PROIZVODNJE EKSTRUDIRANIH KERAMIČKIH PLOČICA

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Abstract

The present study analyses the usage possibility of the 7 raw kaolinitic clays from Serbia. The characterization of raw materials is done by using instrumental techniques to determine chemical and mineralogical compositions, particle size distribution and behavior during firing (changes in mass, temperature of the system and dimensions). Additionally, refractoriness is determined for each of the materials. The samples are shaped by the extrusion process and fired in a 1000-1250 °C range. The ceramic and technological characteristics of the fired samples are determined, and micromorphology is recorded. It is concluded that most of the tested clays can be used to produce cream-colored extruded ceramic tiles with water absorption between 0.20 and 5.28 % by firing at 1250 °C. The majority of the samples can be used as ceramic tiles for flooring purposes after firing at 1200 °C. Additionally, all samples are found suitable for special purpose roofing tiles production after firing at 1100 °C.

Izvod

Ova studija analizira mogućnost upotrebe 7 prirodnih kaolinskih glina iz Srbije. Karakterizacija sirovina je izvršena korišćenjem instrumentalnih tehnika da bi se odredio hemijski i mineraloški sastav, raspodela veličine čestica, kao i ponašanje tokom pečenja (promena mase, temperature sistema i dimenzija). Dodatno, za svaki od materijala je određena i vatrostalnost. Uzorci su oblikovani postupkom ekstruzije i pečeni u opsegu od 1000-1250 °C. Određivane su keramičke i tehnološke osobine pečenih uzoraka, a evidentirana je i mikromorfologija. Zaključeno je da se većina ispitanih sirovina može koristiti za proizvodnju vučenih keramičkih pločica krem boje sa upijanjem vode u opsegu 0,20-5,28 % pečenjem na 1250 °C. Većina uzoraka se može iskoristiti za proizvodnju pločica za popločavanje podova nakon pečenja na 1200 °C. Dodatno, svi uzorci su se pokazali kao odgovarajući za primenu u proizvodnji crepova od gline za specijalnu namenu pečenjem na 1100 °C.

INTRODUCTION

One of the most significant items in the construction industry is ceramic tile. Ceramic tiles are mostly produced by hydraulic pressing of slurries containing various amounts of kaolinite, feldspars and quartz /1/. The use of raw materials is increasing along with the demand for tiles. Globally, there is a growing threat related to a reliable and inexpensive supply of raw materials for the ceramic industry /2, 3/. While naturally occurring deposits of these separate materials are being devastated, it is convenient to test natural clayey deposits and determine their possible utilization in the industrial production of ceramic materials.

While there are required and additional ways of testing following EN standards, the quality of ceramic tiles is examined using conventional procedures. The important differentiation between ceramic tiles is based on their water absorption, among which the groups absorbing up to 3 % are considered suitable for the production of floor covering tiles, and those that absorb above 10 % are used for interior walls. The same limits are set for both extruded and hydraulically pressed ceramic tiles, /4/. The available literature does not sufficiently cover the topic of extruded ceramic tiles. These kinds of tiles are, for example, very useful for façade applications, owing to great heat and acoustic insulation ability, thus keeping with the current trends towards sustainability /5/. Some studies tested the incorporation of waste glass in the mass to extrude tiles by using 8 % of water, /6/. The others attempted to include rock waste /7, 8/ in ceramic mixtures to obtain tiles by the extrusion process. Besides, Vieira et al. studied the extrusion behavior and microstructure of the extruded tiles produced from kaolinitic clays /9/.

The available studies on ceramic clays from Serbia are scarce /1, 10-12/. Besides, no specified methodology describes the necessary tests to perform with the aim to sufficiently evaluate to usage possibility of a natural clay deposit. This study proposes the methodology to characterize the kaolinitic naturally occurring clays in light of the production of extruded ceramic tiles for different applications. Various instrumental techniques have been employed to determine the chemical and mineralogical composition of the selected samples, their behavior during the firing stage, refractoriness, ceramic and technological properties after firing up to 1250 °C, and microstructure. Most of the raw clays are determined to be applicable in cream-colored extruded roofing and flooring tiles production.

MATERIALS AND METHODS

The 7 composites of ceramic clays from Serbia were tested before the exploitation phase. The samples were marked from CK1 to CK7. Particle size distribution is determined on the as-received raw materials by a standard procedure, that includes wet sieving and precipitation methods, /10/. The samples, pre-dried at 105 °C, were sieved through the standard sieves, and the remains on each sieve were measured with an accuracy of 0.1 %.

The raw samples were dried in an oven at 105 °C to the constant mass and afterward dry-ground in a planetary mill. Then, the raw materials were sieved and the fraction below 0.5 mm is further used.

The chemical composition was determined using the energy dispersive X-ray fluorescence (XRF) technique on a Spectro Xepos instrument using standard and validated reference materials. Binary Co/Pd alloy thick target anode with a 50 W and 60 V X-ray tube operated by Software XRF Analyzer Pro, Version 2.2.2. Polarized and direct excitation were blended in the X-ray tube's excitation mode, /1, 10/.

X-ray diffraction analysis (XRD) of the bulk samples was carried out using the Philips 1050 X-ray powder diffractometer, /1, 10/.

A standard-defined procedure was used to determine the temperature at which materials soften, and so refractoriness is determined by using Seger cones, /13/.

The dry composites were moistened and homogenized in sealed nylon bags for 24 hours. The extrusion process Händle machine was led with applied vacuum, /14/. The samples were extruded into tiles measuring 120×50×14 mm and cubes measuring 30×30×30 mm. The tiles represented laboratory roofing tiles, while the cubes resembled a common brick without voids. The wet (green) samples were used to determine the sensitivity to drying according to Bigot in a baraletograph and plasticity coefficient by Pfefferkorn's method, /15/. The extruded samples were then dried for several days in ambient conditions before being gradually dried in an electrical dryer to attain constant mass.

By using Scheibler's volumetric method, the dried extruded samples were utilized to obtain the percentage of total calcium and magnesium carbonates, /15/.

The firing was conducted in an oxidizing environment electric laboratory oven at 1000 °C, 1100 °C, 1200 °C, and 1250 °C, with 1 h soaking at the final temperature and natural cooling in a closed furnace (firing regime was as follows: 70 °C/h until 200 °C, then 92 °C/h up to 520 °C, afterward 60 °C/h up until 610 °C, and finally 140 °C/h until the final temperature). The regime was slowed down in the critical periods of firing to obtain complete drying and to avoid cracks during the modification of quartz. The cooling phase was performed in a natural environment in the closed furnace to avoid thermal shock. The number of samples of all shapes and firing temperatures was 5 in every composite, to test all the important properties requested by the standard /1, 10/.

Firing shrinkage (FS) and water absorption (WA) were determined in the usual ways /1, 10, 14, 15/. The shrinkage was measured by a caliper which is used to imprint the initial dimensions in the green extruded tiles. Water absorption under vacuum is performed using the apparatus Isovacum A 2012, produced by Gabtech, Italy. The modulus of rupture (MR) was determined by using the Crometro CR4/E1 Gabrielli machine (resolution 1 N, with a range up to 7 kN, and a force increase of 1 N/s).

The 'clinkering' temperature of ceramics, the term recently specified in the literature, is determined as the point at which the samples absorb 6 % of water, which presents the occurrence of the melt and the initiation of liquid-phase sintering. The sintering temperature is considered the moment of maximum consolidation and shrinkage of the matrix when 2 % of absorbed water is reached, /10, 16, 17/.

Using the laboratory hydraulic press Alfred Amsler, CHD, Switzerland, compressive strength (CS) was assessed. The flattened samples of cubes were used to test the compressive strength of the samples fired on each of the peak temperatures defined, /14/.

By employing a MIRA 3 XMU from Tescan and field emission scanning electron microscopy (FE-SEM), the surface micromorphology of the samples was investigated. Samples were coated with Au-Pd in a Fisons instruments chamber before the analysis. The images were captured in a high vacuum environment.

RESULTS AND DISCUSSION

The chemical composition (Fig. 1) of the tested clays showed a loss on ignition (LOI) ranging from 3.6 (CK1) to 6.3 % (CK2). LOI, being below 10 %, is considered adequate in terms of organic matter quantity and the introduced shrinkage and porosity in the case of extruded products from kaolinitic clay, /6/.

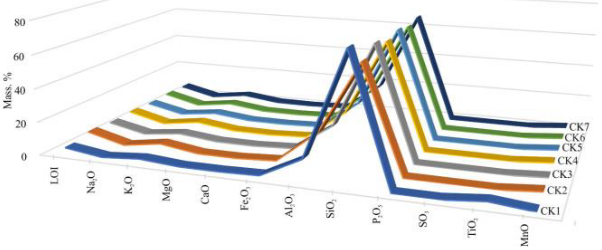

Figure 1. Chemical composition of the raw samples.

The content of SiO_2 varied from 63.3 (CK2) to 75.9 % (CK1) and of Al_2O_3 from 13.2 (CK1) to 21.0 % (CK2). The chemical composition was somewhat comparable to the previously examined clays from Serbia /1, 10/. However, the contents of clay minerals are expected to be lower and, according to the content of Fe_2O_3 and TiO_2, the samples would be paler in color. The contents of Fe_2O_3 were in the 1.1 (CK1) - 1.8 % (CK2) range, which classifies the clays to the light-firing group.

X-ray analysis (Fig. 2) revealed the presence of quartz, kaolinite, illite/mica, albite, orthoclase in all the raw samples. Quartz was the predominant phase, being mostly represented in CK1, and present in the lowest quantity in CK2 and CK3.

The corresponding DSC diagrams (Fig. 3) confirmed the presence of quartz (the peaks at 574 °C, Fig. 3) and its allotropic modification which is recorded as being the highest in CK1, as seen in the XRD analysis (Fig. 2). Besides, the presence of kaolinite and montmorillonite and the existence of trace quantities of hydromica/illite (496-594 °C) and some organic materials (420-437 °C) are also detected, /1, 9/. The samples contained no carbonates, according to the DSC graphs and volumetric total carbonates' content determination results. CK6 appeared to be the only sample containing montmorillonite, according to the endothermic peak that appeared at about 700 °C. The last exothermic peaks in the curves (Fig. 3), found at about 975 °C, which appeared the most intensive in CK2, CK3 and CK4, presented the decom position of metakaolinite to Al-Si spinel, mullite and amorphous silica, /9/.

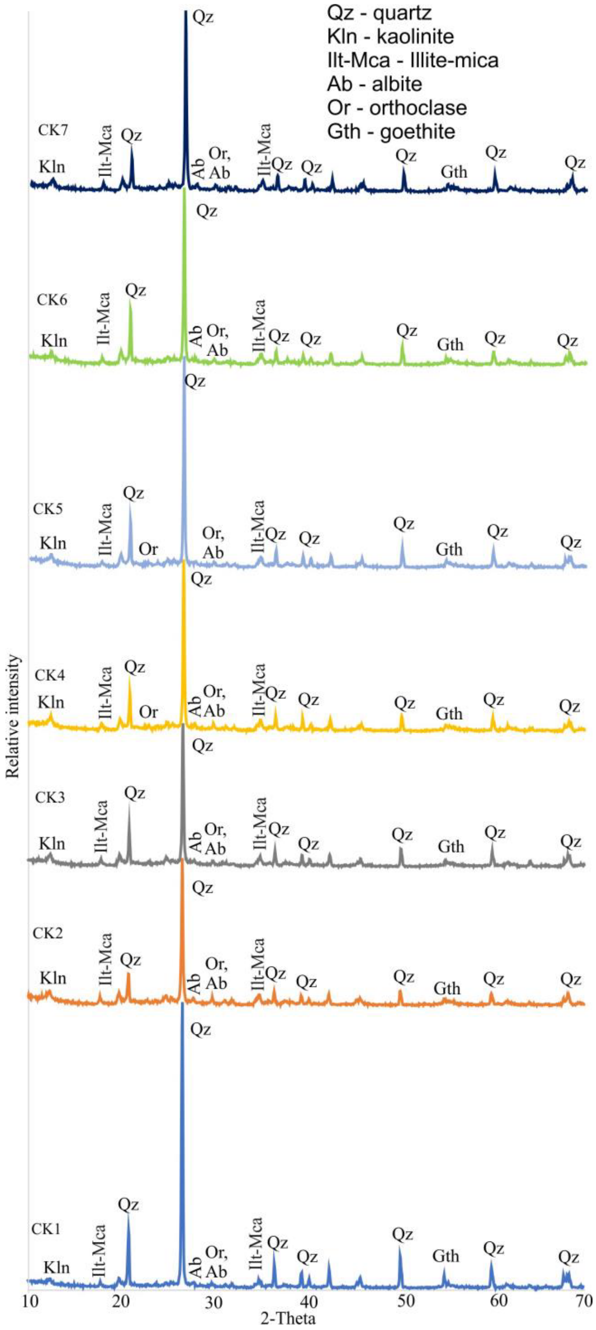

Figure 2. Mineralogical composition of the raw samples.

TG analysis (Table 1) shows that the samples lost water in two steps, where the first corresponds to the loss of adsorbed and interlayer water, which lasted up to 201 °C and amounted to between 0.80 (CK1) and 1.47 % (CK3). The second step is mainly related to the loss of constitutional water that ranged from 3.10 (CK1) to 5.61 % (CK2). The results were in accordance with mineralogical composition (Fig. 2).

Table 1. TG analysis.

	Stage	Temperature Interval (°C)	Maximum on the DTA curve (°C)	Mass loss (%)
CK1	1. 2.	24-166 166-1020	49.3, 127 492	0.80 3.10
CK2	1. 2.	24-166 166-1020	56.4, 133 501	1.08 5.61
CK3	1. 2.	24-191 191-1020	57.0, 137 500	1.47 4.43
CK4	1. 2.	30-174 174-1020	54.5, 134 497	1.30 4.97
CK5	1. 2.	30-174 174-1020	65.4, 135 498	1.12 3.96
CK6	1. 2.	25-201 201-1020	58.8, 137 494, 718	1.34 5.04
CK7	1. 2.	20-184 184-1020	51.6, 126 490	0.90 4.67

Table 2. Particle size distribution.

	Clay (%)	Silt (%)	Sand (%)
CK1	13	44	43
CK2	23	65	12
CK3	23	53	24
CK4	24	59	17
CK5	26	53	21
CK6	26	57	17
CK7	23	53	24

Particle size analyses (Table 2) demonstrated that the clays contained mostly the silt-sized fraction and that the sample CK1 was of the coarsest grain size. The finest particle size distribution was determined in CK2.

According to the behavior of samples during extrusion and drying (Fig. 4), CK2 and CK6 were the most plastic, and, consequently, the most susceptible to drying. At the same time, those samples were of the strongest dry mechanical (compressive and bending) strength. The results conformed with chemical and mineralogical compositions since CK2 contained the highest share of clay minerals, and CK6 was the only sample containing montmorillonite, which significantly increased plasticity. However, all samples were non-susceptible and lowly susceptible to drying, according to Bigot's curves.

The amount of water required to form the samples by the plastic shaping method was determined to be in the 20.0 (CK1) to 26.1 % (CK2) range for a deformation ratio of 2.5 /1/ and was related to the contents of clay minerals. The higher the quantity of the clay minerals, the higher the water demand. Drying shrinkage is considered optimal being between 2.79 (CK1) and 4.21 % (CK6) /6/ and mostly depended on clay minerals type and contents, and also the quantity of quartz. CK1 appeared to contain the highest amount of quartz and the lowest content of clay minerals according to chemical composition, DSC/TG analysis and particle size distribution (Figs. 1 and 3, Tables 1 and 2).

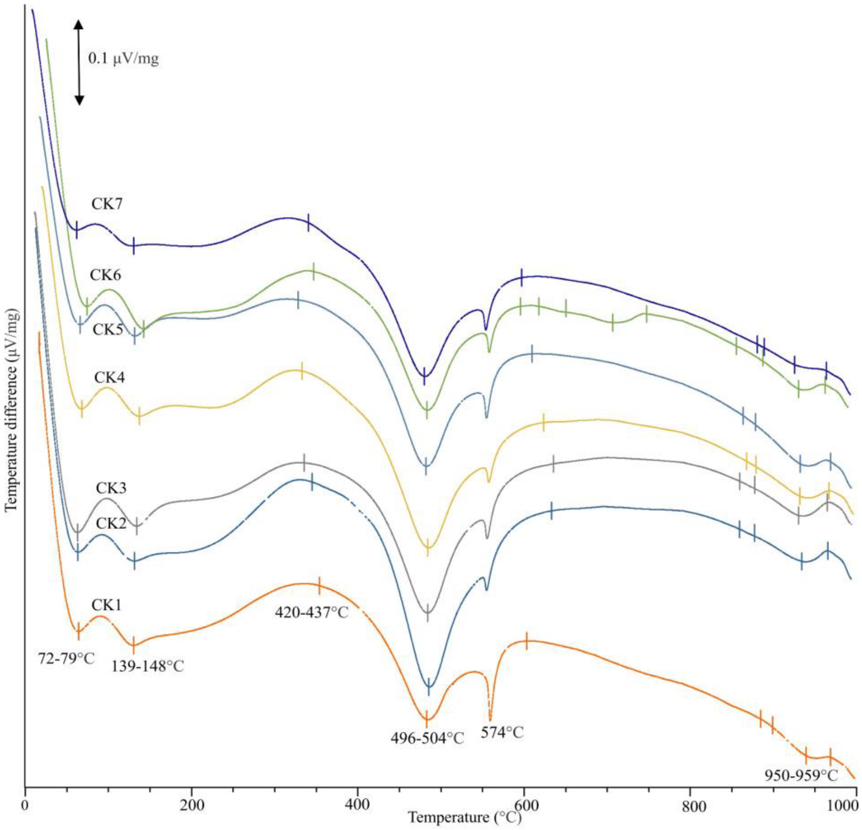

Figure 3. DSC analyses.

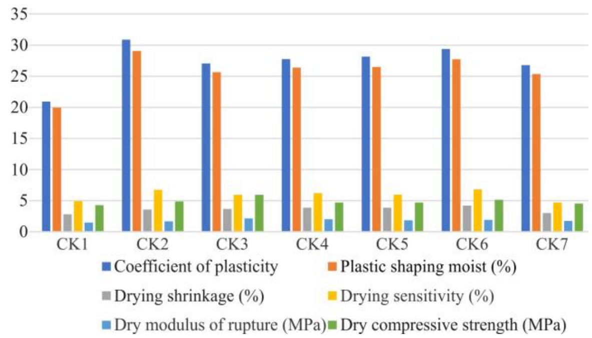

Figure 4. Sample behavior during extrusion and drying processes.

The most important characteristics, determining the latter applicability of ceramic tiles, as defined in the SRPS EN 14411 /4/, are water absorption (WA) and modulus of rupture (MR), Fig. 5. Both parameters showed expected behavior with increasing firing temperature, WA decreased while MR increased (Fig. 4, Table 3), while sharp changes after firing at 1200 °C are noticed. The effect is possibly partly influenced by the fluxing effect of iron which becomes important at these high temperatures /7/. However, the most important influence on this behavior is the formation of secondary mullite. The extruded ceramic tiles fired at the highest temperature satisfied the requirements of the standard as the water absorption was between 0 and 6 %. Besides, these materials are determined applicable to produce low absorbing roofing tiles, considering the limitation of below 20 % for tropical regions, below 12 % in cold climates, and below 7 % in very cold and wet climates, for long periods, including frequent freeze and thaw cycles, /18/.

At the same time, most of the samples acquired the required modulus of rupture of above 13 MPa for extruded ceramic tiles. The only exception was CK1 with minimal MR due to the low content of clay minerals and high share of sand (Fig. 2). Some of the standards declare a minimum modulus of rupture of 18 MPa for ceramic tiles aimed at flooring purposes, /9/. Most of the samples (except CK1) reached above that value after firing at 1200 °C. Concerning the standards for roofing tiles and the demand for them to be above 6.5 MPa, all the samples satisfied these requirements when fired at 1100 °C and above, /8, 18/. The lowest WA and the highest MR, after firing at 1250 °C, were noticed in CK4. The reason for this effect is the relatively high amount of kaolinite and illite/mica in this sample, combined with the highest share of fluxes (albite and orthoclase), as seen from the chemical and mineralogical composition. At a more economical temperature, the samples with the strongest matrix at 1200 °C were found to be CK2 and CK4.

Firing shrinkage mostly increased with temperature (Fig. 5), and is considered satisfactory concerning other studies that found the same results by firing extruded tiles at higher temperatures, but can be problematic when above 4 % /6/.

Higher firing shrinkage at lower temperatures is found in the kaolinitic clay rich in iron with ornamental rock waste addition, compared to this research /8/. The lowest compressive strength for all temperatures was noticed in samples CK1 due to the highest content of sand.

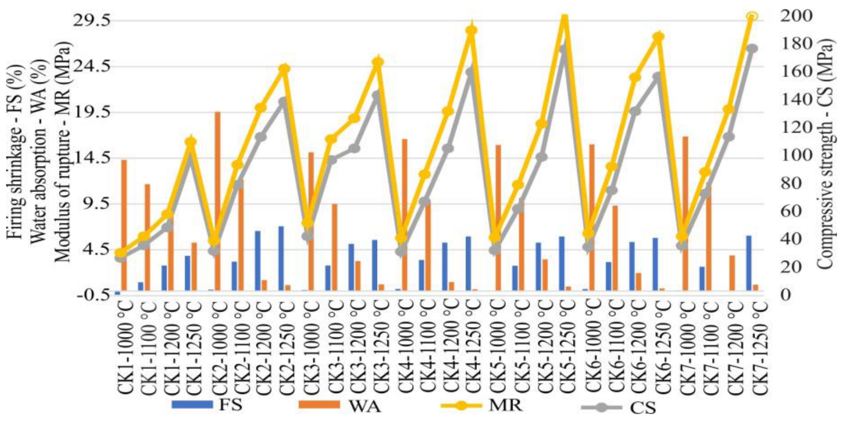

Figure 5. The behavior of the samples on firing.

Table 3. Variation in water absorption (WA) and modulus of rupture (MR) with firing temperature

	1000 °C		1100 °C		1200 °C		1250 °C	
	Min	Max	Min	Max	Min	Max	Min	Max
WA (%)	14.33	19.57	9.33	12.18	0.99	8.23	0.20	5.28
MR (MPa)	3.65	9.78	6.42	19.51	9.46	26.62	11.27	29.98
FS (%)	-0.41	0.23	0.95	3.40	0.04	6.55	3.83	7.83
CS (MPa)	26.92	42.55	36.05	97.07	48.79	132.00	98.82	176.92

Given the sharp changes after 1200 °C in the sintering mechanism according to Fig. 4, it was expected that the sintering temperature is reached at that temperature. The effect is more precisely determined by the methodology described previously, /10/. The ‘clinkering’ temperature ranged from 1143 to 1238 °C, and sintering temperature from 1187 to 1250 °C (Fig. 6). CK1 showed the highest temperature needed to consolidate the sample, due to the lowest content of kaolinite. The refractoriness of all the samples is found to be narrow and from 1486 (CK1) to 1547 °C (CK6). Macro appearance of the samples fired at 1250 °C is presented in Fig. 7.

The microstructure of the samples fired at 1200 °C (Fig. 8) showed no visible closed pores and thus the sintering is considered effective in the well-compacted microstructure. The vitreous matrix is present in all samples, with possibly interconnected quartz and alumina-rich crystals. The image in Fig. 8a, demonstrates the presence of small cracks in the samples CK2, while in others it is not as visible. The result is consistent with the mechanical strength, being the lowest in the group of samples containing cracks (CK2). The stress probably occurred due to formation of secondary mullite and differences among coefficients of thermal expansion of the mullite and the rest of the matrix, while firing at 1200 °C. Besides, a lack of liquid phase development is typical in kaolinitic clays, /9/.

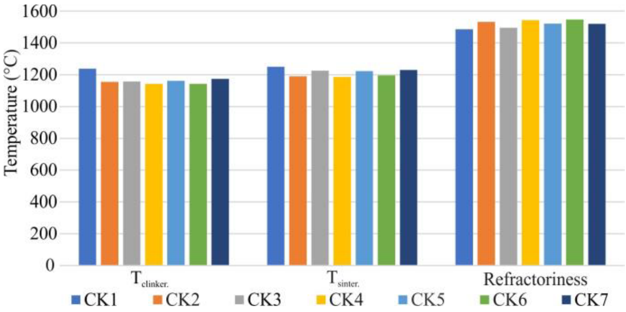

Figure 6. Characteristic temperatures and refractoriness of samples.

Figure 7. Macro appearance of samples fired at 1250 °C.

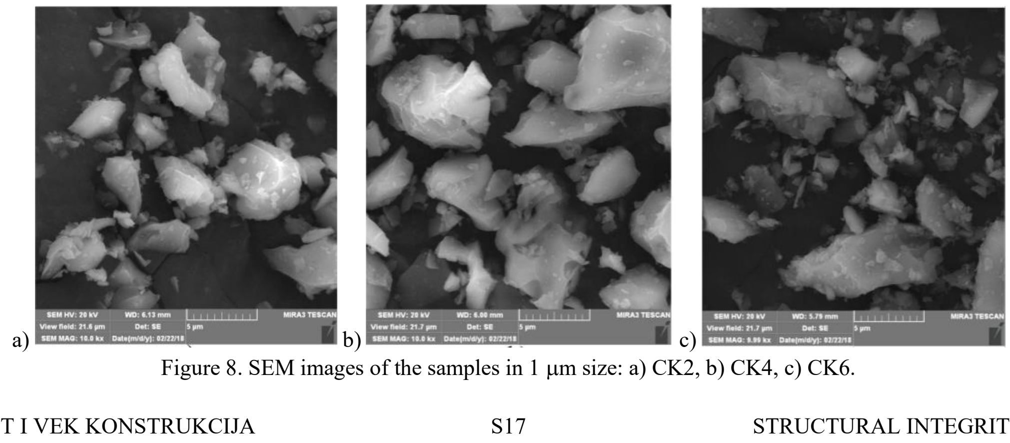

Figure 8. SEM images of the samples in 1 μm size: a) CK2, b) CK4, c) CK6.

CONCLUSION

The presented study shows a methodology to test raw ceramic clays for production by extrusion process. The example of 7 clays from Serbia has concluded that:

- composites predominantly contained quartz, followed by kaolinite, illite/mica, and feldspars,
- the highest plasticity and sensitivity to drying were determined in the samples containing the highest share of clay minerals and the one containing montmorillonite,
- water absorption and modulus of rupture declared the samples fired at 1100 °C suitable for special purpose roofing tiles production, at 1200 °C for extruded ceramic tiles for flooring, and at 1250 °C for extruded ceramic tiles with water absorption between 0.20 and 5.28 %.

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