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ENGINEERING, ENVIRONMENT AND MATERIALS IN PROCESS INDUSTRY EEM2021

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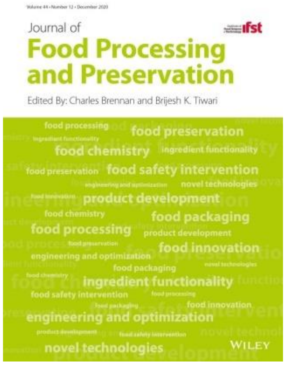

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CHARACTERISTICS AND PHYSICAL-MECHANICAL PROPERTIES OF KAOLINIZED GRANITE

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Abstract

During the long geological past, the rocks of the Adriatic block were formed, which includes the rim of Cer and the Adriatic base. The rim of Cer is characterized by igneous rocks - granite, granodiorite and Paleozoic shale, while the Jadar basin is built of lake sediments that include mainly clay, sand, gravel, sandstone, sandy limestone. Some of these constituents are classified as kaolin raw materials. Kaolin raw materials can be formed during hydrothermal decomposition, kaolinization, which implies physical and chemical changes of various rocks of igneous origin, which contain feldspar and mica, such as granite. As the study of silicate raw materials used in the construction and ceramic industry is a very important and continuous problem, within this paper a more detailed chemical-mineralogical-physical characterization of four kaolinized granite composites (KI, KII, KIII and KIV) from the Beli Majdan deposit-Jadranska Lešnica. Kaolinized granites are formed by subvolcanic decay of granite. In technological terms, these are weakly bound rocks, which are comminuted into smaller aggregates by the grinding process. The techniques used in this study to examine kaolinized granite composite samples included chemical analysis, X-ray diffraction (X-ray), differential thermal analysis (DTA), and ignition tests at three selected temperatures (1000, 1100, and 1250°C). Based on X-ray analysis, it can be concluded that the mineral composition of the kaolinized granite composite "Beli Majdan"-Jadranska Lešnica includes quartz, feldspar, mica, calcite/dolomite and clay minerals. The most common minerals are quartz and feldspar (aluminosilicate containing cations of alkali and alkaline earth metals). Minerals from the mica group as well as carbonates (Ca and Mg) occur in smaller quantities. The results of chemical analysis showed that the Al_2O_3 content in the tested composites ranged from 19.02 to 21.04%, and the Fe_2O_3 content from 1.48 to 1.65%. Additionally, the K_2O content in the tested composites ranges from 5.32 to 6.45%, which indicates the presence of k-feldspar and muscovite, and the Na_2O content from 1.78 to 2.64%. The results of DTA analysis in all four composites indicated the presence of quartz and clay minerals. The ignition color is from brick red to dark brown red. Based on the obtained experimental results, it can be concluded that kaolinized granite "Beli Majdan"-Jadranska Lešnica is a quality raw material for composing ceramic masses in the production of ceramic tiles. It acts as a solvent and can partially or completely replace feldspar in ceramic masses.

Key words: *hydrothermal carbonization, hydrochar, waste biomass, biofuel.*

Introduction

In the ceramic industry, the quality of the final product depends on the physico-chemical and ceramic properties of the raw materials. According to that, testing of silicate raw materials used in the construction and ceramic industries is an important and continuous problem. One of the most commonly used resources in the aforementioned industry in the production of tiles and bricks is clay (Callister 2003). These materials originate of widespread sedimentary rocks, and they are mostly composed of minerals like kaolinite, illite, montmorillonite, but also other aluminosilicates. In addition, they also may contain various impurities (Tsozuéa et al., 2017). Many studies on the characterization of these raw materials have been published so far both in the world and in our country. Due to its beneficial properties and wide utilization that include ceramics manufacture, medical and pharmaceutical application, one of the most commonly used and important clays is kaolin (Garcia-Valles et al., 2020). Kaolin represents mixture of different minerals, of which kaolinite is the most abundant, and in addition it contains certain amounts of quartz, mica, feldspar, illite and montmorillonite (Todorović et al., 2017).

Beside kaolin, one of the raw materials used in the production of ceramic tiles is kaolinized granite. The formation kaolinized granite is associates with surface wear of normal, leucocratic and aplitoid granite, so this type of granite is also the youngest granite type of massif. Kaolinized granite is granite that contains over 5% of kaolinite. This type of granite is formed of a variety of residual primary and secondary minerals during kaolinization. It retains the texture of unaltered granite, and its pattern contains quartz and micas, along with kaolinite, and which partially or completely replace the feldspar site (Todorović et al., 2017, Hergotić 2020). Kaolinized granite is utilized in ceramic industry as an additive and melters and can be used as a substitute for feldspar in the ceramic masses (Filipović-Petrović et al., 2003).

Kaolinized granites in our area are relatively young with a low degree of kaolinization, so the raw material contains, in addition to kaolinite, other minerals: quartz, mica and unchanged feldspar. The area of Loznica is known for its reserves of metallic mineral raw materials, such as antimony, tin, lead, zinc and their accompanying metals silver and gold. The rocks of the Adriatic block (Figure 1) were formed during the Paleozoic, Mesozoic, Cenozoic, and quality sediments were also widespread. The rim of Cer is built of igneous rocks - granite, granodiorite and Paleozoic shales, and the Jadar basin is made of lake, mostly unbound sediments - clay, sand, gravel, sandstone, clay, marl, sandy limestone. Alluvial deposits are most widespread in the valleys of the Drina, Jadar and Lešnica. They are built of gravel, sand and clay and their thickness is about 40 m (http://www.loznica.rs/). Deposits of ceramic and brick clay, refractory clay, kaolin and kaolinized granite stand out from the non-metallic mineral raw materials in the area of Lešnica (Filipović-Petrović et al., 2003).

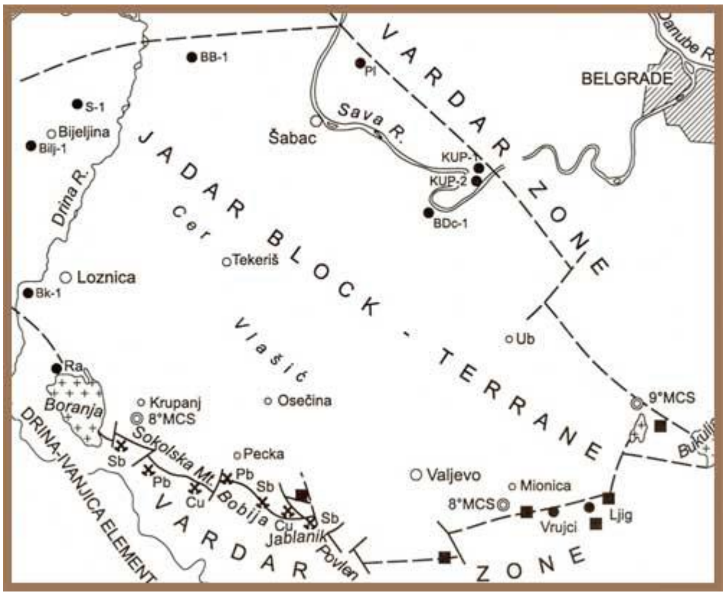

Figure 1. Jadar basin (http://geoliss.mre.gov.rs/?lang=sr&page=geoSzSrbija1)

The paper presents some of the characteristics of kaolinized granite from the Beli Majdan - Jadranska Lešnica deposit. For that purpose, chemical characterization, thermogravimetric (DTA), X-ray diffraction (XRD) analysis and ignition tests were performed. The obtained results will provide insight into the possibility of further application of the analyzed raw material.

Materials and methods

Within this paper a detailed chemical-mineralogical-physical characterization of four kaolinized granite composites (KI, KII, KIII and KIV) from the Beli Majdan deposit-Jadranska Lešnica was performed. All samples were milled in a vibrating ball mill in order to obtain a homogeneous sample and then dried at 105 °C in an oven to constant weight. The samples were then sieved, and a fraction of 0.1 mm was used for characterization of the samples. The techniques used in this study to examine kaolinized granite composite samples included chemical analysis, X-ray diffraction (X-ray), differential thermal analysis (DTA), and ignition tests at three selected temperatures (1000, 1100, and 1250 °C).
Chemical analysis of the feedstock was determined by the following procedures: weight loss was determined by standard gravimetric ASTM D 2974-8 (1993) method, while SiO_2 content was determined by the gravimetric method proposed by Shultz et al. (1972). The content of inorganics, which include Al_2O_3, Fe_2O_3, CaO and MgO were determined using Atomic Absorption Spectrophotometry (AAS Aanalyst 300) by AAS method after acid dissolution proposed by Hseu (2004), while TiO_2, Na_2O and K_2O were determined from the same digested solutions by AES method using the same device.

XRD analysis was used to determine and monitor the phase composition of the samples. Samples were analyzed on an X-ray diffractometer (PHILIPS, model PW-1710), equipped with a curved graphite monochromator and scintillation counter. The intensities of diffracted CuKα X-ray radiation (λ=1.54178 Å) were measured at room temperature at intervals of 0.02° 2θ and time of 0.25 s, and in the range from 3 to 65° 2θ. The X-ray tube was loaded with a voltage of 40 kV and a current of 30 mA, while the slots for directing the primary and diffracted beam were 1° and 0.1 mm.

Thermal analysis (DTA) was performed under air atmosphere using a Netzsch STA-409EP. The sample is heated in the temperature range from 20 to 1000 °C in an air atmosphere at a rate of 10 °C/min.

The behavior of kaolinized granite during firing was tested on test bodies prepared in molds measuring 100x50x9 mm. The test bodies were shaped by manually pressing the raw material into a metal mold. The prepared samples were dried at room temperature for 72h and then in an oven at 105 °C for 4h. The dried samples were placed in a laboratory oven and baked at temperatures of 1000, 1100 and 1250 °C at a heating rate of 5 °C/min. After reaching the appropriate temperature, the samples were heated for another 60 min at the set temperatures. Ceramic properties: total shrinkage, water absorption and color of the baked biscuit were determined on test specimens after baking.

Differential thermal analysis, differential scanning calorimetry (DSC), and differential thermogravimetric (TGA) analyses were performed using a TA Instruments SDT Q600 thermal analysis system. Initial heating was set at 30ºC with a heating rate of 10ºC/min up to 900ºC in an argon atmosphere (the rate varied when weight loss occurred and the weight stabilized) Differential thermal analysis, differential scanning calorimetry (DSC), and differential thermogravimetric (TGA) analyses were performed using a TA Instruments SDT Q600 thermal analysis system. Initial heating was set at 30ºC with a heating rate of 10ºC/min up to 900ºC in an argon atmosphere (the rate varied when weight loss occurred and the weight stabilized) Differential thermal analysis, differential scanning calorimetry (DSC), and differential thermogravimetric (TGA) analyses were performed using a TA Instruments SDT Q600 thermal analysis system. Initial heating was set at 30ºC with a heating rate of 10ºC/min up to 900ºC in an argon atmosphere (the rate varied when weight loss occurred and the weight stabilized).

Results and discussion

Chemical composition of the studied materials, kaolinized granite composites KI, KII, KIII and KIV is shown in Table 1.

Table 1. The chemical composition of starting material

Chemical composition	Content (%)			
	KI	KII	KIII	KIV
L.o.i	4.01	3.48	3.20	3.45
SiO_2	63.88	65.78	64.44	64.62
Al_2O_3	21.04	19.02	19.12	19.20
Fe_2O_3	1.60	1.65	1.48	1.64
TiO_2	0.21	0.22	0.20	0.21
CaO	0.95	0.88	1.22	0.84
MgO	0.30	0.28	0.29	0.26
K_2O	5.41	5.32	6.45	5.75
Na_2O	1.78	2.35	2.02	2.67

The results of chemical analysis showed that the Al_2O_3 content in the tested composites ranged from 19.02 to 21.04%, and the Fe_2O_3 content from 1.48 to 1.65%. The Al_2O_3/Fe_2O_3 ratio could be used to define the possible utilization of material in the ceramic paste formulation. Besides, alkaline fluxes contents (K_2O + Na_2O) are high. Additionally, the K_2O content in the tested composites ranges from 5.32 to 6.45%, which indicates the presence of K-feldspar and muscovite, and the Na_2O content from 1.78 to 2.64%. The MgO and CaO contents indicate that these clayey materials are non-carbonatic. In addition, the Fe_2O_3 and TiO_2 contents determinate the end color of a ceramic piece during firing. High content of this constituents provide dark color of product (Garcia-Valles et al., 2020).

As can be seen from Table 1, all four composites have a similar chemical composition, thus the DTA diagram and X-ray analysis will be shown only for the KI composite, since these curves are similar.

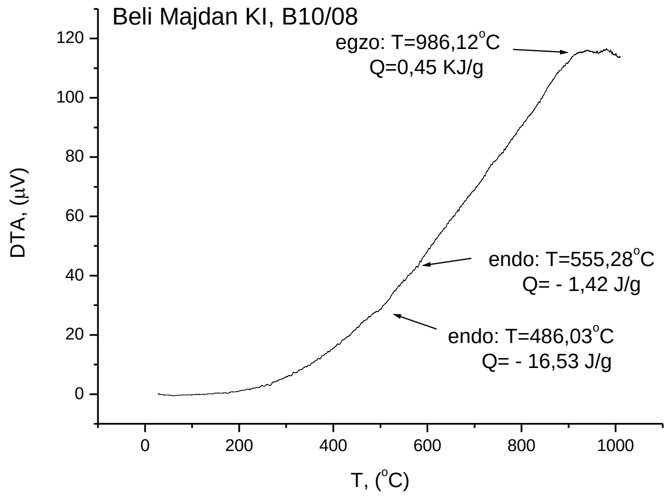

Figure 2. The DTA curve of kaolinized granite composite KI

The differential thermal method (DTA) is most commonly used in laboratory practice to study high-temperature reactions in minerals of ceramic raw materials. The DTA diagram of sample KI is shown on Figure 2. As can be seen in the diagram, two endothermic peaks characteristic of clay materials appear, at temperatures of at 486.03 °C and 555.28 °C, are observed. Those endothermic effects are caused by dehydroxylation of the silicate lattice (clay minerals), which induce the formation of metakaolinite. In addition, no effect for free quartz at 573 °C was expressed. The presence of other mineral species in the examined sample (mica, feldspar, etc.) caused the small temperature shifts of endothermic peaks. Additionally, the exothermic peak is observed at 986.12 °C. This peak probably originated from the formation of new crystalline phases such as γ-Al_2O_3 spinel that contain Si or a 2:1 mullite. Similar observations have been previously published in raw material characterization studies (McConville et al., 1998; Souza et al., 2002, Garcia-Valles et al., 2020).

X-ray analysis of kaolinized granite powder is given in Figure 3. According to this result, it can be concluded that the mineral composition of the kaolinized granite composite includes quartz, feldspar, mica, calcite/dolomite and clay minerals. The most common minerals are quartz and feldspar. Minerals from the mica group as well as carbonates (Ca and Mg) occur in smaller quantities. Besides, peaks characteristic of clay minerals (kaolinite) were not clearly observed on the diffractogram, probably due to overlap with the peaks of other present mineral phases, mainly quartz.

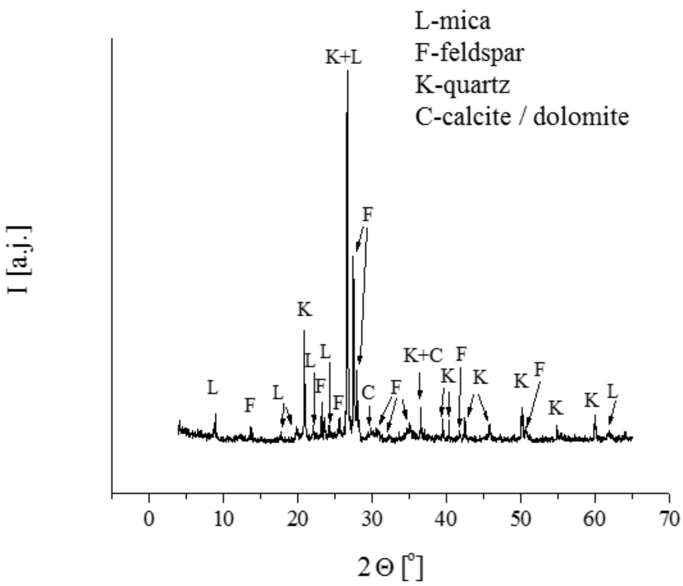

Figure 3. X-ray diffractogram of the kaolinized granite composite KI

Previous studies have shown that the presence of feldspar, as well as the increased content of K_2O and Na_2O in kaolinized granite, indicates the possibility of their utilization as fluxing agents in ceramic masses and tiles production. According to that, kaolinized granites can partially or completely replace feldspar as fluxing agents in the ceramic mass. The share of kaolinized granite in ceramic masses depends on its characteristics, as well as on other raw materials that are constituents (Filipović-Petrović et al., 1998; Filipović-Petrović et al., 2003; Jokanović et al., 2015). Since our results show that feldspar is one of the more dominant minerals in the structure of the tested kaolinized granite, and that the Lešnica granite has a high alkaline flux contents, it can be concluded that this raw material has satisfactory characteristics for use in ceramic masses.

In order to further study the ceramic properties, the tested raw material was baked at three temperatures 1000, 1100 and 1250 °C and total shrinkage, water absorption and color of the baked biscuit according to C.E.C were examined. The obtained results are shown in Table 2. The material exhibited low firing shrinkage at smaller temperatures (1000 and 1100 °C), while at 1250 °C a slightly higher result occurred. Water adsorption shows the opposite trend, so it is noticeable that with increasing of test temperature, the percentage of adsorbed water decreases. Based on results can be concluded that the properties are altered for higher firing temperatures.
The color of the baked biscuit ranges from red brick to brownish red. Clinkering and sintering temperatures are above 1250 °C.

Table 2. Total shrinkage and color of baked biscuit according to C.E.C

Temperature °C	**Ignition color CEC**	**Total shrinkage %**	**Water absorption %**
1000	E_{10}- brick red	1.05	17.33
1100	F_{12}- dark brick red	2.14	14.87
1250	H_9- brown red	5.23	11.52

Conclusion

According to the performed analysis of kaolinized granite Lešnica, it can be concluded that this is a quality raw material that contains a mixture of potassium and sodium feldspar, quartz, minerals from the group of mica and kaolinite. The chemical composition and characteristics of the tested kaolinized granite indicate that this material can be used as one of the constituents of ceramic masses in the production of ceramic tiles, most likely in the role of the fluxing agent.

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