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Characterization of clays from Slatina (Ub, Serbia) for potential uses in the ceramic industry

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Abstract

This study focuses on the mineralogical and thermal properties of clay from "Slatina" deposit, Ub, Serbia. Sampled clays were analysed by XRD, IR spectroscopy, ICP-OES, DTA, specific surface area (SSA), cationic exchange capacity (CEC), gravimetric and grain size measurements. Results show that the studied samples have a medium content of smectite-illite minerals with smaller amount of kaolinite together with quartz, feldspars and goethite. They consist generally of fine particles with medium to high plasticity. Based on their mineral composition and physical properties (grain size, plasticity, CEC) the clays are suitable as raw material for the ceramics industry.

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Keywords: clay; ceramic; potential utilization; characterization; slatina

1. Introduction

Clays play an important part in large number of industries starting from paper, paints, cosmetics, pneumatics, building materials to storage of hazardous waste [1-5]. "The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with dried or fired" [6]. Clays have a complex mineralogy and chemistry and they are essentially composed

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of microcrystalline particles of minerals, referred to as the clay minerals [7]. The clay minerals have characteristics which are mostly depending on their chemistry and structure. Clay minerals are hydrous silicates containing aluminium, potassium and some other cations (Na, Mg). Industrial uses and the quality of clay largely depend on the type and proportion of clay mineral(s) [8]. Clays are constituted from plastic and non-plastic minerals. Minerals that give plasticity to the clay can be kaolinite, montmorillonite, illite, vermiculite, etc., while those mineral constituents which do not impart plasticity to clay are usually minerals like micas, quartz, feldspars, iron oxides and hydroxides like magnetite, hematite, etc. [8].

Traditional single and double firing technology of manufacturing ceramic materials usually uses bodies made up from one clay plus non-plastic materials [9]. Most used bodies are marly clays (illite-chlorite clay with smectite and carbonates), red shale (illite+chlorite±kaolinite±smectite and absence of carbonates) and kaolinite-illite ball clay (+quartz+carbonates or +quartz+feldspars) [9]. In the western part of the Serbia, district of Valjevo, there are several clay deposits and occurrences that are formed with combinations of different types of clay minerals and non-plastic materials. Clay deposit “Slatina” is composed of layers belonging to widespread Neogene sediments that are mostly illite-montmorillonite-kaolinite type. Deposit of quartz sand and fire-resistant ceramic clays "Slatina" was opened in 1965. Under the government of RO “Rudnici nemetala” Valjevo company “Kopovi” JSCo. Ub, became an independent enterprise and started its production in 1989 and at the moment is a leader in production of quartz sand and ceramic clays in western Serbia [10]. According to the company, clay from this layer is sold to the ceramic industry, construction materials industry and to the fire-resistant materials industry [10].

The objective of the present work was to characterize the clays found in one of the widespread clay deposit in the municipal area of Valjevo, Serbia and publish useful data to promote exploitation and application of raw materials in ceramic industries.

2. Materials and methods

2.1. Study area and sampling

The clay samples were collected from exposed faces of the “Slatina” deposit as a raw material and it was obtained in agreement with the governing company “Kopovi” JSCo. Ub, Serbia [10]. The deposit is located 70 km south-west from the capitol city, Belgrade, and according to a geological map of the area, it is composed of Neogene sediments (Fig. 1). Samples, SC and SV, were taken from two different locations in the clay deposit. They have been labelled by governing company and their abbreviations represent industrial application: SC - ceramics and SV - fire-resistant. Samples were dried, crushed and quarted to provide statistically valid samples. The clay fraction (<5 μm) was separated from the bulk samples by sedimentation in distilled water.

2.2. Analytical methods

Grain size measurement (raw samples) and dark field microscopy (<3 μm) were performed to determine the particle size distribution of diffused samples.

Powder and oriented sample X-ray powder diffraction (XRPD) data were obtained with a Philips PW 1710 diffractometer using CuKα radiation with a step size of 0.02 º2θ and scanning time of 1 s per step. The oriented samples were examined air dried (AD), after saturation with ethylene glycol (EG) and after heating at 450 ºC (H). Randomly oriented samples were examined in the intervals 3–60 º2θ and oriented samples from 3 to 15 º2θ.

The chemical composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Thermo Scientific iCAP 6500 Duo ICP-OES spectrometer (Thermo Fisher Scientific, Cambridge, UK) equipped with a RACID86 Charge Injector Device (CID) detector. The cationic exchange capacity (CEC) of the samples was determined after saturation with methylene blue (MB) solution using uniSPEC2 spectrophotometer.

Infrared (IR) spectroscopy was performed in the region between 4000 to 200 cm^{-1} on Perkin Elmer 597 spectrometer using KBr pellet.

Differential thermal analysis (DTA) was performed in air atmosphere using Al_2O_3 as the reference material, temperature range of 50-1000 ºC and heating rate of 10 ºC/min. Measurement were carried out on a modernized A.D.A.M.E.L furnace equipped with Pt-PtRh thermocouple and guided by BK PRECISION XLN15010 programmer. Total mass loss was measured applying gravimetric method on 120, 350, 600 and 1000 ºC.

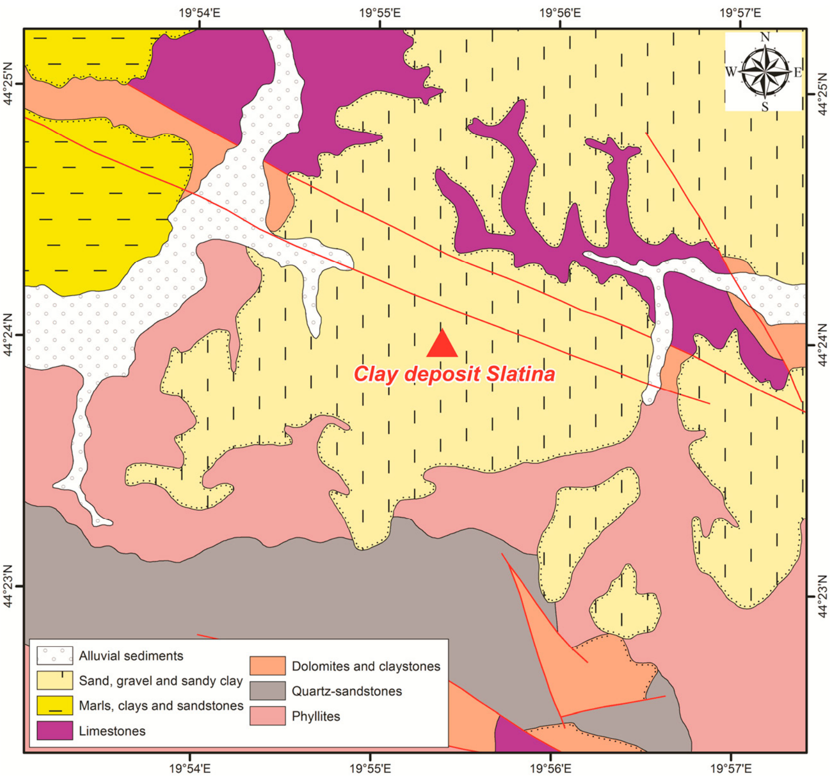

Fig. 1. Geological location of "Slatina" deposit, Ub, Serbia.

3. Results and discussion

Grain size distribution together with dark field microscopy results are shown in Fig. 2 a. Maximum distribution was different when observing raw samples. For sample SC, coarse grain fraction >20 µm (29%) was closely similar to clay fraction (34%). In case of SV sample it was evident that there was a higher content of coarse grain fractions (45%) in regard to clay fraction (24%). After dark field microscopy measurement average grain size was 1 and 0.7 µm for SC and SV samples, respectively with average specific surface area of 89 m^2/g for both samples.

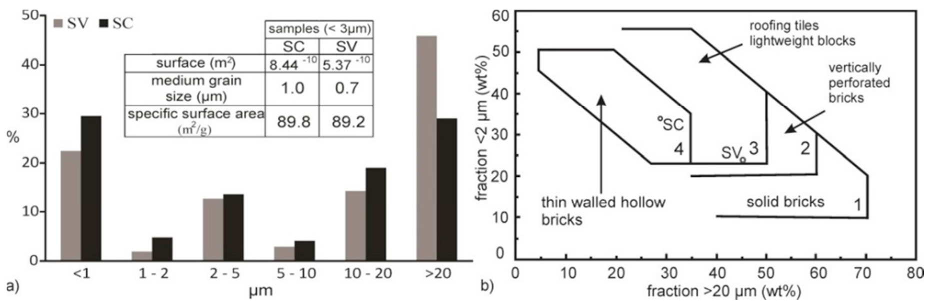

Fig. 2. Grain size distribution for raw samples and samples <3µm (a) and Winkler diagram (b) [11].

Regarding the clay fraction, samples were classified as clayey with a high content of clay fraction (around 30% <1 µm). Application assessment based on average grain size (<2 µm and >20 µm), plotted results in the Winkler's diagram (Fig. 2 b) gave results that indicate suitability for thin walled hollow bricks (SC) and roofing tiles/lightweight blocks (SV) [11,12].

Chemical analysis has shown that the samples are mainly constituted of silica, aluminum, potassium and iron oxides (Table 1). Higher content of SiO_2 and Al_2O_3 together with total mass loss on ignition (LOI) indicate higher content of clay minerals in the samples. Stoichiometric calculations involving the theoretical mineral formulas and chemical composition gave semi-quantitative estimates of the mineralogical composition of the samples. According to the calculation sample SC constitutes from: 45% fine grained smectite-illite mixture, 14% of kaolinite, 19% quartz, 10% feldspars, 7% goethite and 5% of impurities [13]. Sample SV was closely similar to SC: 43% smectite-illite, 11% kaolinite, 18% quartz, 15% feldspars, 7% goethite and 6% of impurities.

Table 1. Chemical compositions of SC and SV samples.

samples	oxides (wt. %)								
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	LOI	total (%)
SC	55.0	21.2	6.4	5.1	1.3	0.5	2.2	9.1	100.8
SV	51.8	19.1	5.9	5.0	1.0	3.0	2.9	9.1	97.9

Cationic exchange capacity (CEC) of the samples after MB saturation was 12.7 and 14.9 eq/g for SC and SV respectively. According to the literature data, samples have CEC values that could be attributed to minerals from illite group [14] and could be classified as medium to high plasticity ball clays [15].

The comparative X-ray powder diffraction diagram of powder and oriented (untreated - AD, glycolated - EG and heated to 450 °C - H) samples are presented in Fig. 3. The XRPD pattern of untreated oriented samples clearly shows peaks corresponding to kaolinite, illite, quartz, feldspars and carbonate minerals. Clay phases were confirmed on oriented samples with peaks on d = 7.2 and 9.9 Å. Quantitative mineral composition obtained by Rietveld refinement of combined chemical and XRD data shows mainly smectite-illite (45%) and kaolinite (14%) clay with 19% of quartz, 10% feldspars and 7% of limonite content for sample SC, while sample SV represents smectite-illite (43%) and kaolinite (11%) clay with 10% of quartz, 15% feldspars and 7% of limonite [13].

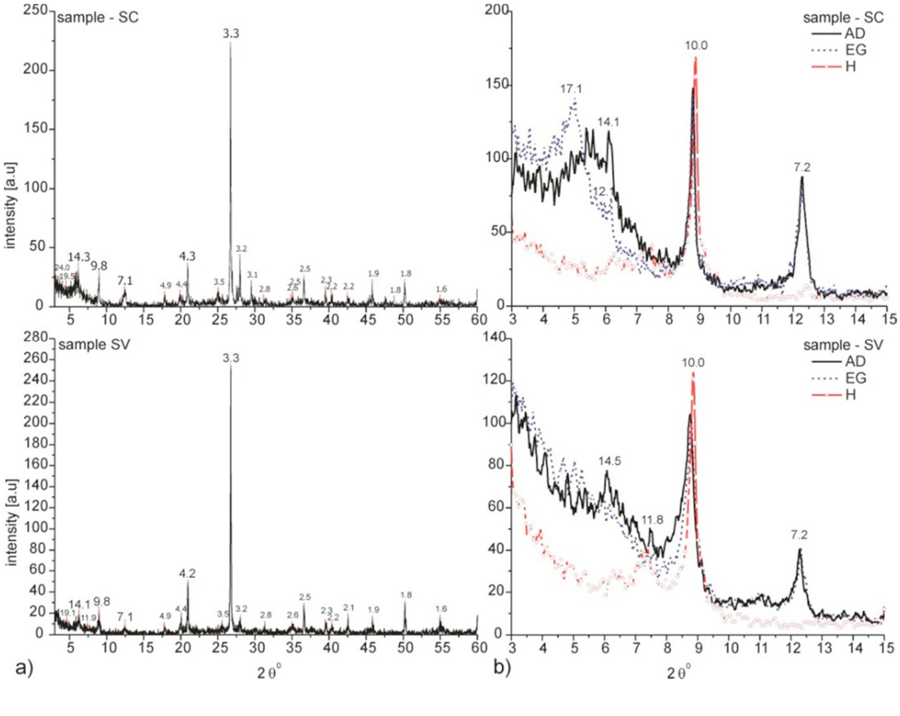

Fig. 3. The comparative X-ray powder diffraction diagram of powder (a) and oriented samples (b) [13]. Peaks are labeled in Å.

IR data of the samples (Fig. 4) shows larger amount of smectite clays with quartz and carbonate minerals for both samples which were in accordance with XRPD data. Bands at 3615, 991 and 921 cm^{-1} correspond to presence hydromica - illite mineral, band at 3612 and 908 cm^{-1} to smectite minerals, while band at 1621 cm^{-1} represent water in the system [16,17]. Major non-clay minerals were also present. Bands at 778 and 692 cm^{-1} corespond to quartz, carbonate minerals are at 1422 cm^{-1}, while band at 778 and 754 cm^{-1} represent feldspars [16]. Visible difference between samples was in the content of carbonate minerals phase, were sample SV have been endowed with higher content than sample SC. Quartz doublet has a higher intensity indicating significant amount of quartz minerals which is in accordance with XRPD data.

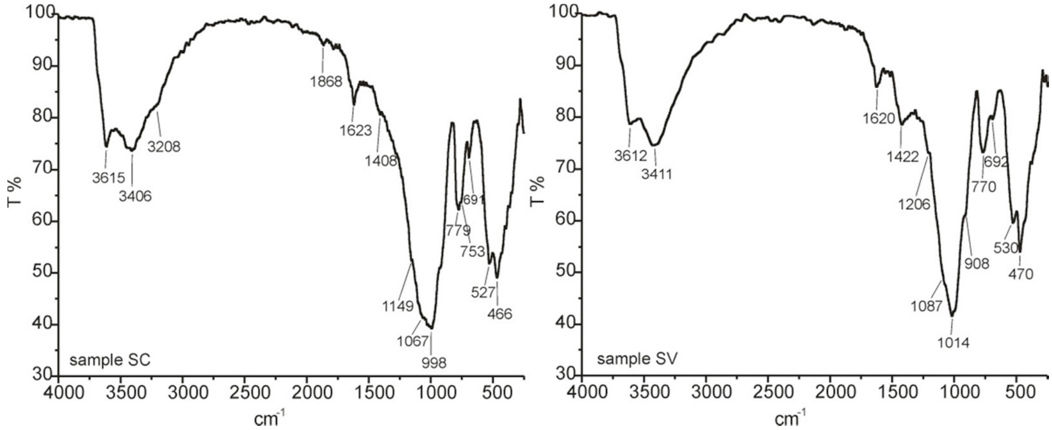

Fig. 4. IR spectra of SC and SV samples.

DTA results have shown couple of events that are endothermic (Fig. 5). First one (100-200 ºC) was associated with loss of moisture and constitutive water, second (300-400 ºC) with iron hydroxide minerals, third (500-600 ºC) with smectite clay content with smaller separate bands of kaolinite clays while events between 800-900 ºC correspond to carbonate minerals [18].

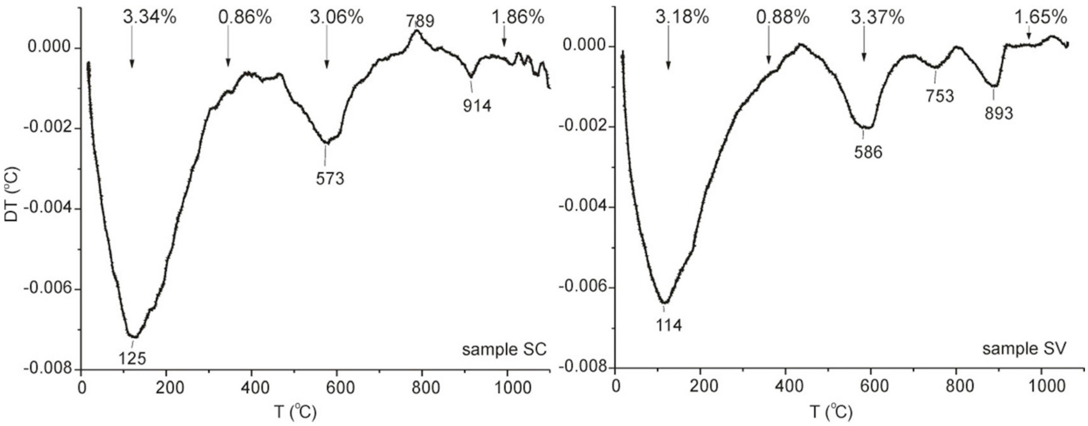

Fig. 5. DTA curves and gravimetric results of selected clay samples.

Loss of mass after gravimetric measurement at given temperatures shows that the samples have significant amount of water in their structure (≈3 wt% (120 ºC)). The highest mass loss was at 600 ºC (3.06 and 3.37 wt%) corresponding to the large endothermic peak associated with smectite minerals. Total mass loss was 9.12 and 9.08 wt% for SC and SV respectively. Loss of mass of around 0.87% at 350 ºC indicates dehydration of goethite and formation of α - Fe_2O_3 [19]. The amount of goethite was estimated as 7% in the samples.

4. Conclusion

The clay from "Slatina" (Ub, Serbia) was characterized by chemical, mineralogical and thermal analysis. All applied methods were in a good agreement. The studied clays from "Slatina" deposit have a medium content of smectite-illite minerals with smaller amount of kaolinite mineral together with quartz and feldspars. Based on their mineral composition and characteristics (grain size, CEC, plasticity), possible application could be in different types of ceramic and construction industries especially for production of tile making, thin walled hollow bricks and roofing tiles/lightweight blocks.

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