RAW CLAYS IN THE PRODUCTION OF CERAMIC AND REFRACTORY TILES

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ABSTRACT

Raw clay samples from Serbia, mainly of kaolinitic, illitic and mixed nature, were tested for their possible application in the production of ceramics. Using various triaxial diagrams, the samples were sorted according to their chemical and bulk mineralogical makeup, and also particle size distribution to determine whether they could be employed in the production of ceramics and refractories. The areas in the ternary graphs determined in earlier studies concerning the expected color after firing and the applicability of the raw clays are checked and extended. The samples' water absorption and flexural strength were assessed using EN standard procedures after they had been hydraulically semi-dry pressed and fired at several peak temperatures between 1100 and 1300 °C. A novel triaxial diagram considering the position of the samples based on firing temperature, water absorption and modulus of rupture is proposed, and the areas of different kinds of ceramic tiles are defined. It is discovered that the different raw clays can be utilized to create refractory, as well as wall and floor tiles. This study supports the rational use of natural sources of raw materials.

1. INTRODUCTION

Sustainable development is a broad goal to make the world a better place by balancing social, economic, and environmental concerns. The sensible use of natural resources is one of the priorities for achieving sustainable development. This entails the integration and harmonization of all sectoral policies' aims and measures, as well as the harmonization of national regulations with EU legislation and their full execution.

The primary problematic aspects in traditional ceramics production are the high use of natural resources and energy (often from non-renewable sources), flue gases, and significant amounts of waste after a product's service life. Another issue is the necessity for mine rehabilitation and reclamation following raw clay extraction [1].

It is estimated that producing one square meter of ceramic tile requires 21–23 kg of raw materials and 30–40 kWh of energy [2]. Huge amounts of clay minerals, quartz and feldspars are needed to form ceramic batches. The share of these materials depends on the intended application of the final products, which is primarily determined based on their water absorption behavior and the modulus of rupture [3]. Since global residential building has been steadily growing since 2021 [4], the demand for ceramic tiles, along with the consumption of raw materials, has also constantly increased. A consistent and affordable supply of raw materials for the ceramic industry is under threat on a global scale, since the naturally occurring deposits of kaolinite, feldspars and quartz are being destroyed and devastated [5,6]. To partly overcome this, natural clayey deposits can be tested to evaluate their usability in industrial ceramics production as the only component [7].

At the time, there were several studies on ceramic and refractory clays from Serbia [3,7-9]. This work shows the applicability of Serbian clays by using various ternary diagrams in the evaluation of deposit quality. Diagrams that connect the particle size distribution, chemical and mineralogical content, and different sorts of clays are shown in this paper. The results are compared to the graph areas defined in earlier studies during the last century, and additional extensions and comments are added and the graph is updated. In addition, for the first time, the application of ternary diagrams was attempted to define the area of application of ceramic products according to European standards [10].

2. MATERIALS AND METHODS

2.1. SAMPLE PREPARATION

The 84 composites of Serbian raw clays originating from 3 deposits (Crne Rovine, Šabac, and Damnjanovića Brdo) were investigated. The detailed results and discussion of two of these deposits were published earlier [7,11]. After the samples arrived at the lab, the samples were dried at 100±5 °C to a constant mass. Then, 4% tap water was added and specimens of 120x25x8 mm were formed using a hydraulic press. An oxidizing atmosphere laboratory electric furnace was used to fire the tiles at temperatures of 1100, 1200, 1250, and 1300 °C with a soaking time of 1 hour. The slow firing regime was applied as defined earlier [11].

2.2. TESTS

The dried raw materials were subjected to a standard procedure that comprises wet sieving and precipitation to establish the particle size distribution [7]. The samples were shredded on a planetary mill, and the fractions with a diameter of less than 0.5 mm were deemed suitable for further testing and pressing of samples. Energy-dispersive X-ray fluorescence, XRF (Spectro Xepos), and X-ray diffraction analysis, XRD (Philips 1050), were used to determine the chemical and mineralogical composition. The complete instrumental methodology, preparation of samples, reference materials, and detection of components are described in detail in earlier studies [7,11].

Water absorption (WA) was determined according to the specifications for ceramic tiles [7,12] in a vacuum using the Isovacum A 2012 by Gabtech, Italy. The three-point modulus of rupture was obtained at room temperature by using the Crometro CR4/E1 (Gabrielli, Italy) [7].

2.3. TERNARY DIAGRAMS IN STUDYING CLAYS

Ternary charts are most effective for representing three variables whose sum is a constant. They constitute the ratios of parameters concerning their position within an equilateral triangle, which is accomplished by normalization of the selected data. The sum of variables can be normalized to 1 or 100. The most common application of ternary plots is in physical chemistry, but they are also used in geology and ceramics, such as Riley`s (1951), Shepard`s (1954), and Winkler`s diagrams (1954) [13-15]. Apart from the diagrams that consider particle size distribution and the classes of sediments and their possible usage in ceramics, there are other interesting examples of ternary diagram applications. Based on chemical composition, there are proposals to divide the samples according to their color after firing and the sort of ceramics that can be obtained [16,17]. Furthermore, a mineralogical composition can also distinguish the usability of clays in ceramics manufacture [16].

In this study, apart from the usual examples of ternary diagrams, it is attempted to use the one composed of firing temperature, water absorption and modulus of rupture to show different groups of ceramic tiles according to their possible utilization (mainly wall and floor tiles) [10].

3. RESULTS AND DISCUSSION

The ranges of the properties of the raw materials are shown in Table 1. Particle size distribution of the materials or previously prepared samples can be used to classify clays in different ways according to Shepard [14] and McManus [18]. The raw clays considered in this study texturally mainly belonged to sandy silty clay and sandy silt (Figure 1a). The clays from Šabac showed the most uniform particle sizes among the three deposits, with a moderate quantity of clay-sized fractions.

The clays from Crne Rovine and Damnjanovića Brdo would be suitable mostly for roof filler slab production, while Šabac and some samples from Damnjanovića Brdo fell outside the ranges for traditional ceramics, based on Winkler`s diagram [15].

According to McManus [18], Figure 1b, the samples belong to the clays inducing low porosity/low permeability and moderately high porosity and permeability (moderately well sorted), which makes them suitable for the construction industry [19].

The samples from the Damnjanovića Brdo deposit, which showed moderately high porosity and permeability, attained the highest modulus of rupture and the lowest water absorption values.

Following the experience in the Italian ceramic tile industry [16], all of the considered raw clays were expected to belong to the white-body group after firing (Figure 2). However, the samples also showed a gray-brownish shade in relatively pale-colored bodies, while the color became darker with increasing firing temperature [7,11]. The composites from the Crne Rovine deposit obtained the darkest shades after firing as a result of the highest quantities of coloring oxides, Figure 2. None of the samples were expected to experience bloating behavior according to Riley [13]. The result was not consistent with the findings in a previous study on clays from Crne Rovine [11], where it was proven that some of the clays experienced bloating even during a slow firing regime owing to the presence of high organic matter content, a parameter which is not considered in Riley`s triaxial graph [11].

By comparing the bulk mineralogy results of the clays studied here, and previous experiences [16] in Figure 3, it is seen that most of the samples can be a good choice to be used in different kinds of structural ceramics production. Some of the samples from Crne Rovine and one from Šabac are found to be outside the previously determined area. The samples containing the highest quantities of clay minerals within the studied deposits were CR17, CR7, CR6, CR1, CR3, and CR12 [11], which have proven to be useful in refractory tile production. Thus, the proposed extended area for structural ceramics application is added to the original graph by Strazzera et al. [16] in Figure 3. The sample containing the highest amount of quartz and feldspars (C-24 in [7]) proved to be usable for the production of ceramic tiles but of a lower quality (water absorption above 5 % and modulus of rupture of 21.49 MPa after firing at 1200 °C). Thus, possible further corrections of the mentioned graph are possible, which needs more testing.

Parameter description	Parameter (%)		Results
Particle size distribution	Clay-sized particles	Minimum Maximum Average Standard Deviation	6 64 26.8 11.8
	Silt-sized particles	Minimum Maximum Average Standard Deviation	30 69 50.6 7.1
	Sand-sized particles	Minimum Maximum Average Standard Deviation	3 56 22.6 9.4
Chemical composition	Loss on ignition	Minimum Maximum Average Standard Deviation	4.18 16.21 7.14 3.14
	SiO_2	Minimum Maximum Average Standard Deviation	48.85 68.96 63.20 5.63
	Al_2O_3	Minimum Maximum Average Standard Deviation	19.10 29.18 22.21 2.62
	Fe_2O_3	Minimum Maximum Average Standard Deviation	1.03 3.33 1.79 0.53
Mineralogical composition	Phyllosilicates	Minimum Maximum Average Standard Deviation	22.35 83.00 47.58 9.73
	Quartz + feldspars	Minimum Maximum Average Standard Deviation	20.50 68.20 48.71 10.95
	Carbonates	Minimum Maximum Average Standard Deviation	0.00 1.80 0.11 0.35

Table 1. *Ranges of the important properties obtained for raw ceramic and refractory clays*

Finally, the ranges of the most important ceramic properties of the tested raw clays are presented (Table 2), which were the basis for defining a novel ternary diagram containing normalized data of the firing temperature, water absorption and modulus of rupture. With the increasing peak firing temperature, water absorption determined in a vacuum decreases, while the modulus of rupture grows, as expected. The samples belonged to various groups according to the resulting quality, from *L* to *G*, Table 2 [10].

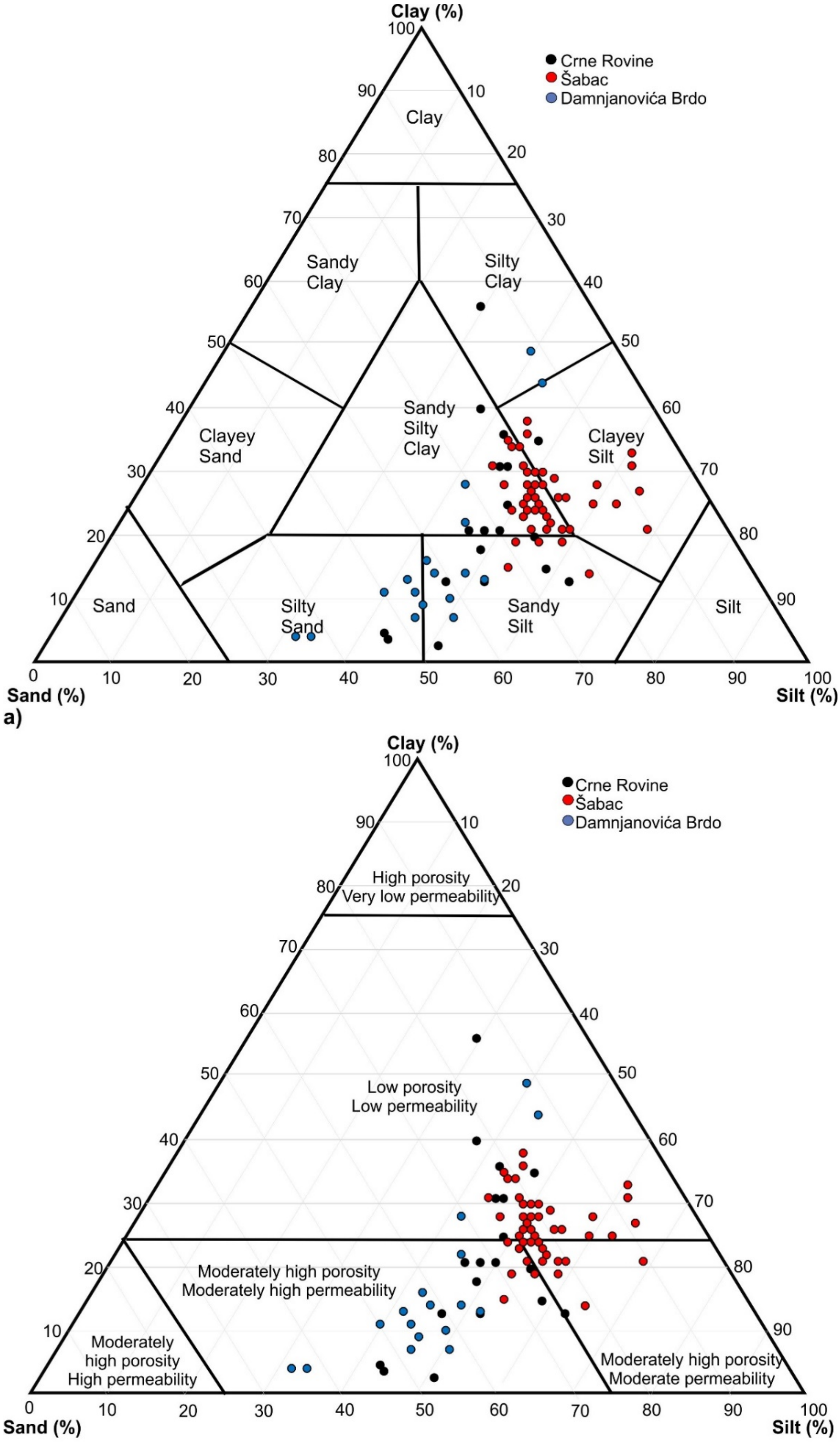

Figure 1. *Plot of the tested samples in diagrams following the relation between sand-, silt-, and clay-sized components after a) Shepard [12], and b) McManus [16]*

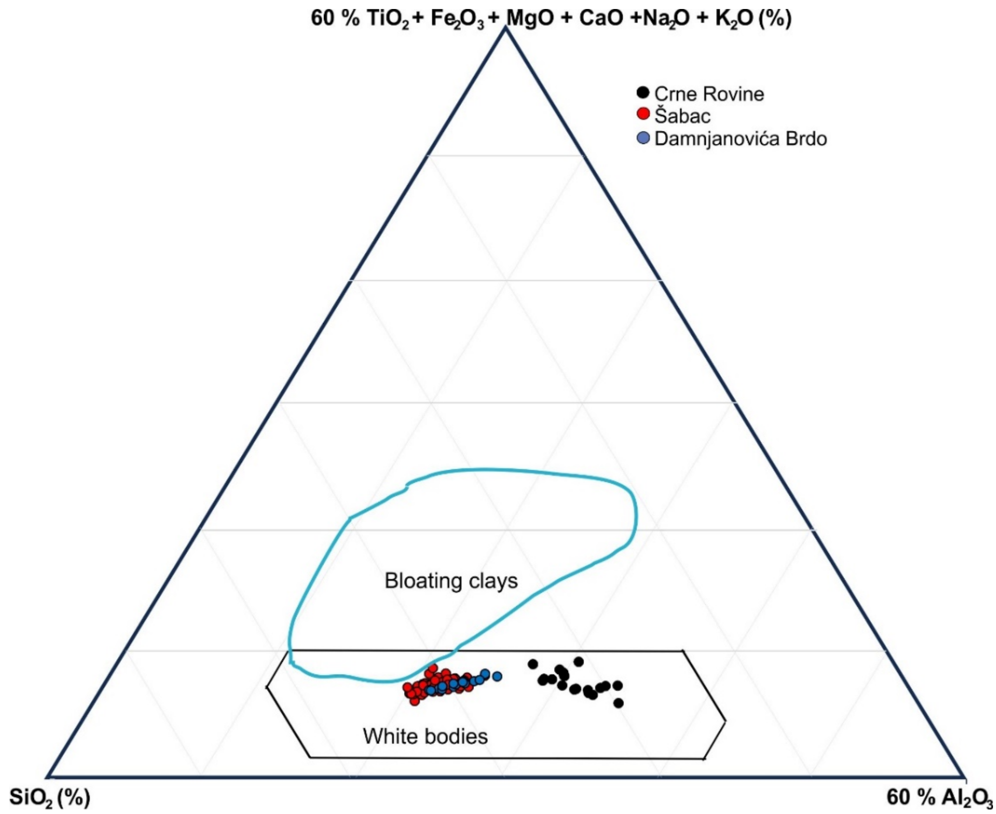

Figure 2. *Position of the tested samples in a diagram following the relation between the sum of coloring and fluxing oxides, Al_2O_3 and SiO_2*

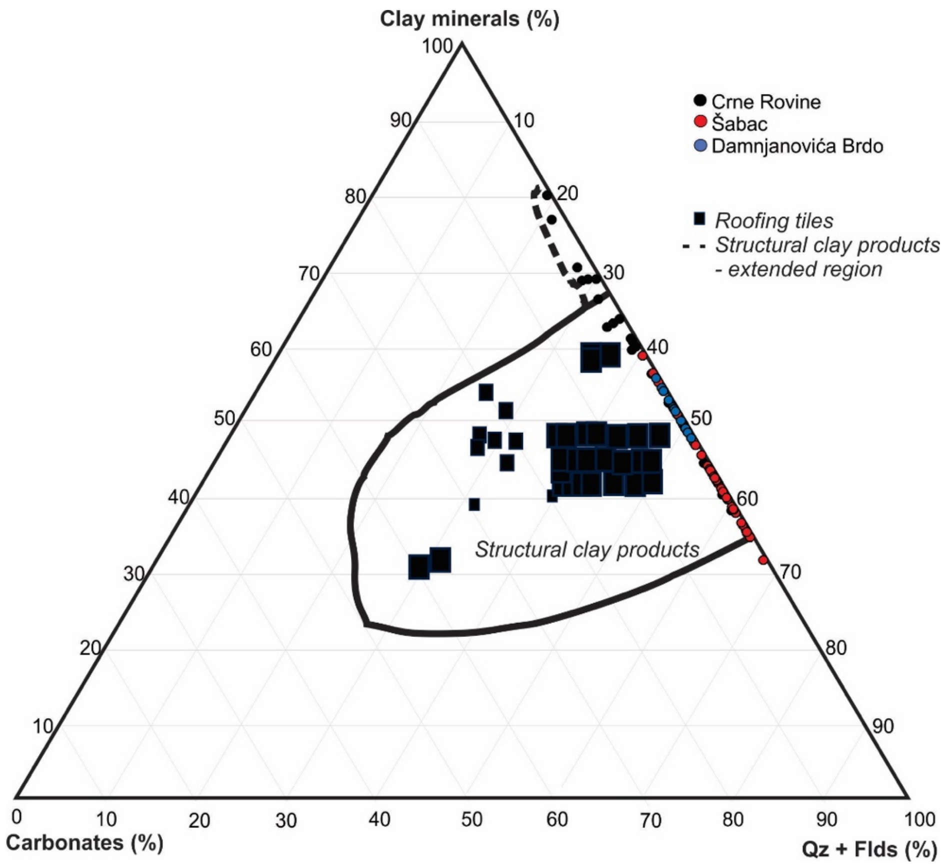

Figure 3. *Fit in a ceramics group based on bulk mineralogy (Qz – quartz, Flds – feldspars), the extended diagram of Strazzera et al. [14]*

Firing temperature (°C)	Value	Modulus of rupture (MPa)	Water absorption (%)
1100	Minimum Maximum Average Standard Deviation	12.12 41.69 22.26 6.83	4.23 11.41 8.12 1.42
1200	Minimum Maximum Average Standard Deviation	17.32 52.12 31.08 7.65	0.15 7.38 4.13 1.38
1250	Minimum Maximum Average Standard Deviation	19.46 52.25 34.06 7.66	0.10 6.93 3.09 1.38
1300	Minimum Maximum Average Standard Deviation	27.16 53.60 40.74 6.82	1.42 6.77 3.81 1.36
Values defined by the standard SRPS EN ISO 14411 [10]			
Annex G		≥ 35	≤ 0.5 %
Annex H		≥ 30	0.5 – 3 %
Annex J		≥ 22	3 – 6 %
Annex K		≥ 18	6 – 10 %
Annex L		≥ 15	> 10 %

Table 2. *Ranges of the ceramic properties of the fired samples and standard-defined values for tiles having a thickness below 7.5 mm*

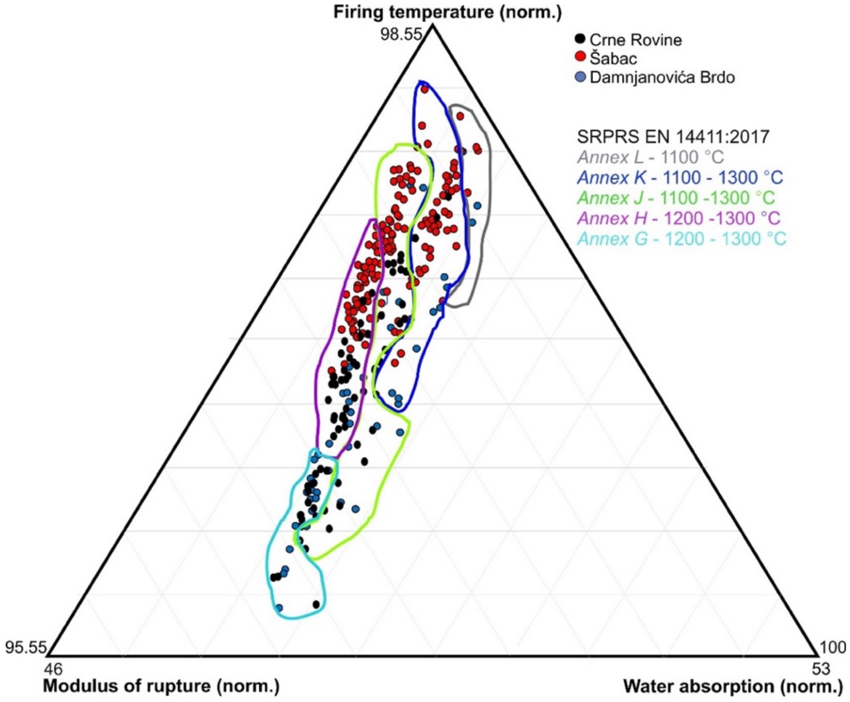

Figure 4. *Sample grouping in accordance with SRPS EN 14411 [10]*

4. CONCLUSIONS

In this study, ceramic and refractory clays from 3 deposits in Serbia are presented using the various kinds of ternary diagrams that show the position of the samples according to granulometry analysis, and also chemical and bulk mineralogical content. The results are compared and confronted with the well-known earlier established areas in those diagrams concerning the use of the clays in the ceramics industry. Based on the previous findings, it appeared that the ceramics with white bodies without bloating could be produced, which was not completely true. The color of the products ranged and contained brownish shades, while some of the samples containing organic matter experienced bloating even under a slow firing regime.

Additionally, a novel ternary diagram to show the areas of EN standard-defined kinds of tiles is shown and proposed.

ACKNOWLEDGEMENTS

This work is supported by the Ministry of Science and Technological Development of the Republic of Serbia, Contract No. 451-03-47/2023-02/200012. The authors are also thankful for the support of the Chilean National Commission on Research and Development (CONICYT) [FONDECYT REGULAR grant number 1180414].

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