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CORELAȚII COMPOZIȚIE-PROCESARE-PROPRIETĂȚI LA OBȚINEREA CERAMICII DE MENAJ. PARTEA a II-a: INFLUENȚA MĂCINĂRII ASUPRA PROPRIETĂȚILOR GLAZURII

CORRELATIONS COMPOSITION-PROCESSING-PROPERTIES FOR TABLEWARE CERAMICS. PART II: INFLUENCE OF GRINDING ON GLAZE PROPERTIES

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This second part of the paper aims to identify the influence of the mechanical processing of the raw mix on glaze properties.

Preliminary tests on grindability were run on each main raw material, showing an initial, large dispersion of the grains size distribution between raw materials at the lowest number of mill rotations. As the number of rotations increases, it was found that the mechanical behavior tends to link to the hardness of the raw materials. Specifically, grains size distributions fall into two different groups of very close, almost identical values: one group for the raw materials having a higher hardness (sand, feldspar) and the other for the lower hardness materials (dolomite and calcium carbonate).

Two sets of raw materials compositions, one for obtaining matte glaze and the other for obtaining glossy glaze were used; each of them was grinded in a laboratory, planetary ball mill at the same number of mill rotations (1000, 2000, 3000, 5000, 7000, 10000 and 13000 rotations) and grain size distributions were measured. The resulting raw mixes were used to glaze already-made ceramic biscuits. Glost firing was made in an industrial tunnel kiln at 1200°C and it was followed by the investigation of optical properties. Also, glaze thermal expansion was measured.

Results reveal that the particle size distribution of the raw mixtures strongly influence glaze color parameters and glaze thermal expansion. This shows a direct influence of the particles size on the investigated properties, as they interact with light. Specifically, as the grinding gets more advanced, the smallest crystals can enter the melt so lowering the number of crystalline particles existing in the glaze. On the other hand, smaller particles scatter the light more than bigger ones; consequently, they behave like opacifiers.

FTIR images of the glazes surface show that the glazes contain a considerable number of crystalline particles embedded in the vitreous matrix. FTIR spectra and maps revealed a decrease in transmittance as the fineness increases.

According to the results, there is no reason to increase the number of rotations higher than 7000 rotations.

Obiectivul celei de a doua părţi a articolului este de a identifica influenţa procesării mecanice a amestecului de materii prime asupra proprietăţilor glazurii.

Au fost realizate analize preliminare a aptitudinii la măcinare pentru fiecare materie primă principală. S-a constatat o importantă dispersie a distribuţiei granulometrice la un număr mic de rotaţii ale morii. Pe măsură ce numărul de rotaţii creşte, comportamentul mecanic tinde să fie corelat cu duritatea materialelor. Astfel, distribuţiile granulometrice se regăsesc în două grupuri distincte, care conţin, fiecare, valori foarte apropiate: primul grup pentru materialele care prezintă duritate mai mare (nisip, feldspat) şi celălalt pentru cele cu duritate mai mică (dolomită şi carbonat de calciu).

Au fost utilizate două serii de compoziţii de materii prime, una pentru glazuri mate şi alta pentru glazuri lucioase; fiecare dintre ele au fost măcinate într-o moară planetară cu bile la acelaşi număr de rotaţii ale morii (1000, 2000, 3000, 5000, 7000, 10000 şi 13000 rotaţii) şi a fost determinată distribuţia granulometrică. Amestecurile de materii prime rezultate au fost utilizate pentru glazurarea unor suporturi ceramice. Arderea de glazură s-a realizat într-un cuptor tunel industrial la 1200°C, cu ardere rapidă şi a fost urmată de investigarea proprietăţilor optice şi dilatarea termică a glazurii.

Rezultatele dovedesc că distribuţia granulometrică a granulelor influenţează puternic parametrii de culoare ai glazurii şi dilatarea ei termică. Aceasta arată influenţa directă a dimensiunii particulelor asupra proprietăţilor investigate, datorită interacţiunii lor cu lumina. Pe măsură ce măcinarea devine mai avansată, cele mai mici particule intră în topitură şi, în consecinţă, numărul celor care rămân ca fază cristalină scade. Pe de altă parte, particulele de dimensiuni mai mici produc o dispersie mai importantă a luminii (se comportă ca opacifianţi). Imaginile FTIR ale suprafețelor glazurilor arată un număr mare de particule cristaline dispersate în faza vitroasă. Spectrele și cartografierile FTIR evidențiază o scădere a transmitanței cu creșterea fineții de măcinare.

Conform rezultatelor, numărul maxim de rotații a morii este de 7000 rotații, după care apare supramăcinarea.

Keywords: *tableware ceramics, grinding, glaze, color*

1. Introduction

Correlations composition-processing-properties were largely investigated on all scales, from the atomic to macroscopic scales, in both academic and industrial environments. These investigations were targeting, on one hand, a fundamental understanding and, on another, to improve product properties and/or to reduce heat and energy consumptions. In the first part of the

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article, correlations composition-properties for the tableware ceramic mass (biscuit) were addressed [1]. This second part deals with correlations processing-properties of the tableware glaze, from an industrial viewpoint. As the temperature of the glost firing depends on thermal analysis results of the glaze, in this second part of the article it was considered only the influence of the mechanical processing, i.e. the grinding on some glaze properties.

Grinding the raw materials in ceramic industry aims for reducing particle size and, also, for narrowing the particle size distribution to an optimal one, corresponding to each application. Benefits and drawbacks of grinding are related mainly to the reducing of the particle size. On one hand, smaller particle size means a higher specific surface area, thus a higher surface energy and a higher reactivity; another advantage is that, smaller particles size could allow for a higher homogeneity of the raw mix, given a proper mixing. [Note that homogeneity vs. number of rotations of the mill has not been addressed in this paper and could make the subject of a further research.] Therefore, heat consumption is decreased and product quality increases. The main drawback is the high energy consumption of the grinding process. As a rule of thumb, the higher the hardness of a raw material, the lower the grindability and the higher the energy consumption. Nowadays, even though raw materials have different grindabilities, they are grinded together, for the benefit of obtaining a higher homogeneity of the raw mix.

Wet/dry grinding systems are available, each having their advantages and disadvantages. Amount of grinding media, shape and size/size distribution of the grinding media play also an important role on the effectiveness of the grinding process. Various indices such as particles shape/size factors, specific surface area of the raw mix, Rosin-Rammler-Sperling-Benet indices etc. can be used to assess the effectiveness of the grinding process.

Glazes should provide a series of features/properties, such as:

- a good compatibility with the ceramic body; differences between thermal expansions of the two components translate in stresses [2]. If these stresses exceed a certain limit they could affect integrity, inducing defects such as *crazing* and *shivering*;
- transparent or opaque glazes;
- glossy or matte glazes;
- having a certain color.

Matte glazes can be obtained by: i) devitrification, by properly adjusting the cooling phase (studies were conducted on the glass crystallization and the consecutive effects on opacity [3] and on optimization of processing time-temperature [4]), ii) incorporating some coarser raw materials into the raw glaze, inclusions that will not melt entirely (they can cause light scattering), iii) other less common ways (some oxides that can enter combinations with silica and grow in crystals, even at normal cooling rates; sandblasting). These matte glazes are high in alumina content; glazes that are high in glass formers (SiO_2, B_2O_3) are glossy. However, the thermal processing features, i.e. the cooling rate influences the appearance of the glaze, meaning that the same glaze composition cooled differently can lead to either matte or glossy glazes.

Color of the glaze is of a paramount importance when selling the product, so matte glazes and glossy glazes are to be color characterized. Under varying circumstances, colorants can give different results. Several variables can influence glaze color: glaze composition, firing temperature (some colorants give different colors at different temperatures) and kiln's atmosphere during firing.

Grinding plays, also, an important role for colorants: optical behavior is influenced by the size of particles and their distribution; also, by the particles shape. Berthier et al. [5] studied – among others – the influence of crystals shape on transmittance spectra of transparent glass–ceramics with different crystal shapes, reporting higher transmittance for cubic crystals as compared to spherical crystals. Basically, particles higher than a given size will remain crystalline and will act as reflectors while particles smaller than that limit can melt, thus being useless. Larger than the optimum size crystals will provide a low coloring intensity – due to the small number of particles – while particles of smaller size tend to melt, thus decreasing color intensity. As it is known that a good reflection requires the existence of fine crystalline particles in the glaze, the best option is, for each colorant will exist a given, narrow particle size distribution. As a conclusion, colorants should have a high melting point and a low solubility in the melt and a proper particle size distribution. Also, they should feature a high refraction index because coloring power depends on it.

Transmittance in the visible spectra of glass–ceramics is given by two mechanisms: their crystal sizes are much smaller than the wavelength of light or there is an insignificant difference between the refractive index of vitreous matrix and the crystals. [5] Light interaction with glaze consists of several phenomena [5, 6]:

- light reflection given by equation (1);

$$I_r = I_0 \left(\frac{n_g - n_c}{n_g + n_c}\right)^2 \quad (1)$$

where I_0 and I_r are the incident and reflected light intensity, n_g, n_c are the refractive indices for glass and crystals;

- atomic absorption and scattering. The intensity of the scattered light can be obtained by the Eq. (2)

$$I = I_0 e^{-Sx} \quad (2)$$

where S is the scattering coefficient, x the optical path length.

The scattering coefficient S is directly related to both the number density of the scattering particles and their squared size:

$$S = KN\pi r^2 \tag{3}$$

where N are the number density of the scattering particles, r is the size of the scattering particles, and K is a scattering factor.

K increases with particle size, reaches a maximum when the particle-size is close to the light wavelength, and decreases for larger particle-sizes, approaching a constant value for being much higher the light wavelength. [1]

Schabbach et al. [7] mentioned that, in a multicomponent optical system it is important to consider not only the pigments but, also, the other crystals [and, also, glaze thickness] that may still coexist with the vitreous phase, through their collective contribution to the optical properties of the glaze. Reflectance (color), is related to the amount of absorbed and scattered light; these ones depend on the light wavelength, and, also, on the grain size, for all, pigments, and, in our case, other crystals. Other crystals can be nonmelted, big quartz grains or they may come from partial vitreous phase recrystallization during glaze cooling. Partyka and Lis [8] confirmed the influence of the grinding on glaze optical properties. They observed that, by solely decreasing quartz grain size, glaze gloss is strongly influenced (with no influence on color) while using very fine grain size of feldspars and reducing quartz grain size lead to both visible glossy and whiteness improvements. Dinescu [6] also mentioned that grinding increases glaze lightness but decreases color intensity because some amount of the pigment may become an opacifier – without explaining the mechanism.

Liu et al. [9] confirmed a strong linear correlation between the refractive index and the grain size in HfO_2 thin films, and therefore, the mechanism of the refractive index inhomogeneity of the HfO_2 thin films is the crystallization effect.

The influence of grinding fineness on glaze thermal expansion, color parameters and on the glazes surface features will be investigated on turquoise-colored glazes.

2. Experimental

Two sets of glazes, one of 7 matte glazes and the other of 7 glossy glazes were made to identify possible correlations mechanical processing (grinding)-properties. The raw materials were grinded in a laboratory mill, using alumina grinding media, for 1000, 2000, 3000, 5000, 7000, 10000 and 13000 rotations. Sedigraph III Plus has been used to obtain all particle size distributions. Note that 1000 rotations refer to the absolute number of rotations of the planetary ball mill (taking about 5 minutes of grinding).

Cylindrical samples were glost fired in an industrial tunnel kiln at 1200°C with a short firing cycle to measure glaze thermal expansion, along with glazed plates that were subjected to optical properties measurements.

FTIR data were obtained by using a Thermo Scientific Nicolet iN10 MX in ATR (Attenuated Total Reflection) mode, mainly to obtain microscopy images of the glaze surfaces. Additionally, there were obtained FTIR spectra and maps. The aim was to characterize surface morphology and samples transmittance changes that may be influenced due to the grinding progress. No interest was paid to obtain the *precise* mineralogical composition; however, X-ray diffraction on glazed biscuits were attempted with no success. Results showed a highly crystalline structure, with no indication of the existence of the vitreous matrix. The most probable explanation is, in our trials the diffraction pattern belongs [also] to the ceramic substrate (biscuit) and not to the thin layer of tens of microns of glaze.

2.1. Preliminary tests

Grindability of the main raw materials was assessed by grinding each raw material in a laboratory mill at the same number of rotations and by sieving on a sieve with mesh size of 38µm. Residues were obtained and plotted in Fig. 1. The lowest grindability was observed for sand, followed by feldspar and dolomite. Initially, at 1000 rotations, differences were recorded for the residue of all raw materials with a clearly separated value for calcium carbonate. At 9000 rotations both calcium carbonate and dolomite had almost the same residue (around 2%) and a similar behavior has been recorded for the pair sand-feldspar (around 20%). This concludes to: by grinding each raw material at a time, at 9000 rotations, particles coarser than 38µm do exist in a significant amount (~20%), and nearly all of them are made of either sand or feldspar. All other raw materials grinded at 9000 rotations have particle size distribution ranging to up to 38µm, basically.

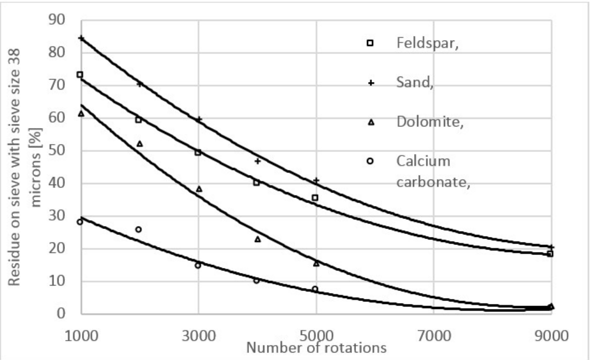


Fig. 1 - Residue on sieve with mesh size of 38µm at different number of rotations/*Variația reziduului pe sita cu dimensiunea ochiului de 38µm în funcție de numărul de rotații.*

Table 1

Raw mixtures composition (in weight percentages)/*Compozițiile amestecurilor de materii prime (în procente masice)*

Raw materials	Feldspar, %	Sand, %	Calcium carbonate, %	Dolomite, %	Kaolin, %	$BaCO_3$, %	Metakaolinite, %	ZnO, %	$ZrSiO_4$, %
Matte glazes	32.92	17.63	14.10	7.06	12.93	4.70	10.66	-	-
Glossy glazes	34.04	29.79	6.38	10.65	12.76	3.19	-	2.13	1.06

2.2. Materials and preparation

Raw materials, given in Table 1, were proportioned and wet grinded in a laboratory mill. Pigments (3 coloring agents for obtaining a turquoise glaze) were grinded with raw mixtures. To remove the influence of the amount of pigments, for all raw mixes they were added as 5% in weight. Slurry was sieved on the 45 microns sieve, then dried in the drying oven at 100°C and sieved again on the 160 microns sieve. The particle size distribution was analyzed by Sedigraph III Plus.

Cylindrical samples obtained by pressing 5 grams of material at 60 bars were tested for thermal expansion test after glost firing. For the optical properties, the raw mix was laid on biscuit plates. The glazed plates were also glost fired at a maximum temperature of 1200°C and optical properties were determined on the resulting glaze. Measurements were made by a BYK Colorimeter in CIE Lab color space (where *L* stands for the lightness, *a* and *b* for the green–red and blue–yellow color components). Each specimen was measured in three distinct points and the result was averaged.

3. Results and discussions

3.1. Particle size distribution analysis

D80 values for both sets of matte and glossy glaze were plotted in Fig. 3, showing that the fineness of grinding increases as the number of rotations increases. The two evolutions are similar, with some small differences recorded.

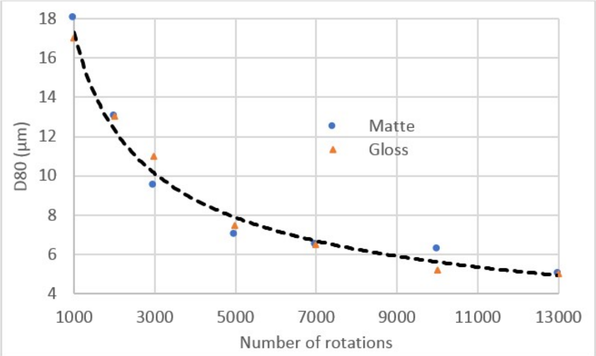


Fig. 2 - D80 versus on the number of rotations for the matte and glossy glazes/*Variația lui D80 în funcție de numărul de rotații ale morii pentru glazurile mate și lucioase.*

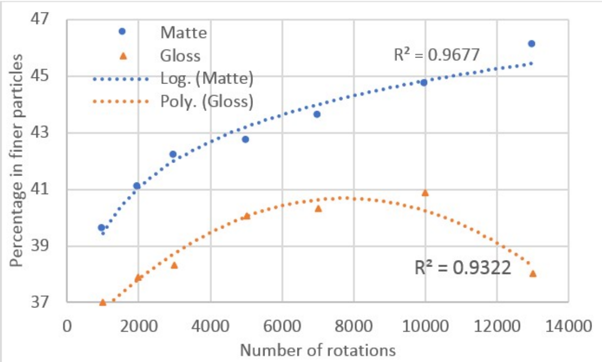


Fig. 3 - The percentage of particles with diameters less than 1μm vs. number of rotations for both types of glaze (logarithmic and polynomial functions were used for regression analysis for matte and, respectively, gloss glazes)/*Procentajul de particule cu diametrul mai mic de 1μm în funcție de numărul de rotații pentru ambele tipuri de glazuri (pentru analiza de regresie au fost folosite funcția logaritmică și polinomială pentru glazura mată, respectiv lucioasă).*

A parameter recorded by the particle size analysis is the percentage of particles less than 1μm. Results of these measurements are plotted in Fig. 3 for both matte and gloss glazes. Initially, the percentage of fine particles was 37% for the glossy glaze and 39.6% for the matte one. This is consistent with the raw mix composition given in Table 1: glossy glaze contains a higher amount of sand and feldspar, which are raw materials with a lower grindability (see Fig. 1), thus a lower amount of smaller particles should be found. As the number of rotations increases, the percentage of particles under one micron increases, as the raw material begins to grind; trends look similar and almost parallel up to 10000 rotations. However, the smaller the particle diameter, the higher the possibility of particle agglomeration. Particle agglomeration occurred, in our case, for the matte glaze raw materials grinded at 13000 rotations, showing a decrease of about 3% of the finer particles from the preceding result (at 10000 rotations). However, the D80 value decreased, as shown in Fig. 2.

Fig. 4 presents a comparison between matte glazes made by grinding raw materials at 7000 and 13000 rotations. Macroscopic glaze defects (glaze *crawling*) appeared for the glaze made by grinding the raw mix at 13000 rotations. Along with the - possible – apparition of the agglomeration phenomenon, this result confirms the ineffectiveness of advanced grinding.

As a conclusion, results demonstrate that grinding fineness depends on the number of mill rotations. However, by exceeding the number of rotations the benefit could be smaller than the energy consumption, while particle agglomeration and glaze defects can occur. By analyzing Figs. 2-4, it results that 7000 could be the highest number of rotations needed.

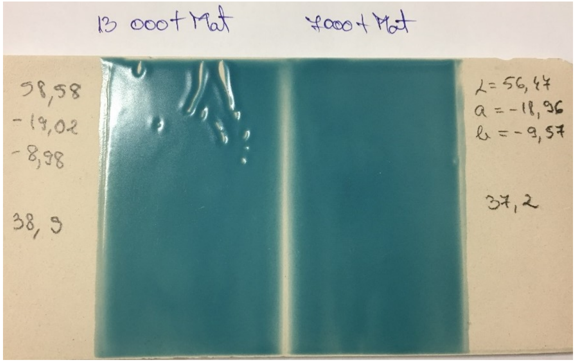


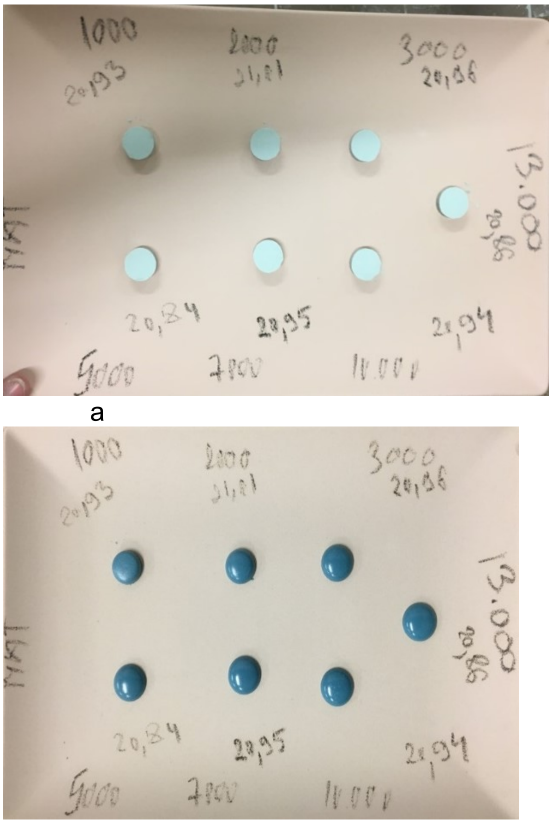
Fig. 4 - Matte glaze obtained by grinding at 7000 (to the right)/13000 (to the left) rotations showing glaze defects (crawling) for the 13000 rotations-made matte glazes due to overgrinding/*Glazura mată măcinată la 7000 (în dreapta) şi 13000 rotaţii (în stânga). Retragerea de glazură (în stânga) apare la glazurile mate măcinate la 13000 rotaţii datorită supramăcinării.*

3.2. Glaze thermal expansion

Glazes thermal expansion was investigated by obtaining the difference in size between the samples measured with a precision caliper before - Fig. 5, a) - and after - Fig. 5, b) - glost firing at 1200°C in an industrial tunnel kiln. Almost every sample increased by size, except for the case of the sample grinded at the lowest number of rotations (1000 rotations), which showed a contraction. A simple inspection revealed that, unlike the other samples, the one grinded at 1000 rotations had a rough surface, which can be attributed to the existence of large SiO_2 incompletely melted crystals. The less glossy appearance of the surface also confirmed that the percentage of vitreous phase is lower than for the other 6 samples.

Figure 6 plots the evolutions of the measured thermal expansion with the number of rotations for the matte and glossy glazes.

As revealed by particle size analysis, the raw mixes obtained by grinding the raw materials at only 1000 rotations are characterized by the coarsest particles. Specimens made of these raw mixes for both categories of glazes, showed contraction after firing. By increasing the number of rotations, the expansion increases up to 7000 rotations, after which it remains quasiconstant for both matte and glossy glazes. As it can be expected, as the grinding process increases the fineness of both categories of glazes with the number of rotations, so does the amount of vitreous phase and, consequently, the thermal expansion. As the glossy glaze contains a higher amount of sand, starting from 5000 rotations the thermal expansion of the glossy glaze becomes slightly higher than that of the matte glaze. A possible explanation is, sand reached a certain fineness that allows him to enter more in the vitreous phase, fineness which becomes bounded at 7000 rotations. As a conclusion, further grinding of the raw mixtures above 7000 rotations will have no or little effect and, therefore, is not necessary.



a

b

Fig. 5 - Glaze samples a) green; b) fired/*Specimene de glazură a) crude; b) arse.*

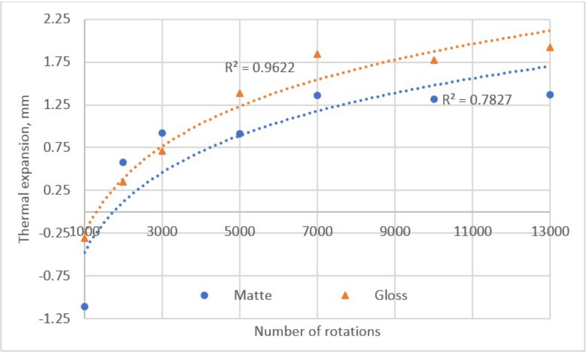


Fig. 6 - Thermal expansion variations vs. number of rotations for both types of glaze (logarithmic functions were used in regression analysis for both matte and glossy glazes)/*Evoluţia dilatării termice în funcţie de numărul de rotaţii pentru ambele glazuri (au fost folosite funcţii de tip logaritmic în analiza de regresie).*

A visual inspection of the Fig. 7 confirm that the matte glaze obtained at 1000 rotations has a higher roughness of its surface, most probably due to the coarser quartz grains that were not melted.

Fig. 7 - Glazes obtained by grinding raw mixtures for matte glazes at 1000 (left) and 2000 (right) rotations, showing a visible, higher roughness of the surface for 1000 rotations / *Glazuri mate obţinute prin măcinarea materiilor prime la 1000 (stânga) şi 2000 rotaţii (dreapta). Rugozitatea suprafeţei din stanga este vizibil mai mare.*

3.3. Optical properties

Optical properties such as color (*L*, *a* and *b* parameters) and gloss/matte of the glazes were measured by the colorimeter, to study the influence of the grinding progress.

Fig. 8 confirm the influence of the grinding progress over the matte and is consistent to the theory relating optical behavior of crystalline particles and their size and to the published experimental results [6-8]. As the number and the size of the crystalline particles' changes with the grinding progress, color intensity is also affected and even color itself can be slightly changed, as it is shown in Figs. 9 and 10.

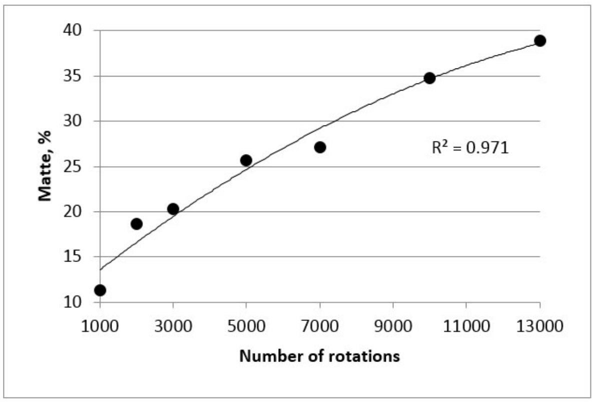


Fig. 8 - Matte trend vs. the number of rotations for the matte glaze (polynomial function was used in regression analysis) / *Evoluţia matizării cu numărul de rotaţii pentru glazura mată (în analiza de regresie a fost folosită o funcţie polinomială).*

"*a*" parameter evolution is given in Fig. 9, showing a clear shift towards green for both glazes, that confirm the influence of the grinding on this parameter. However, results are not neatly separated for each type of glaze. A completely different case was found for the evolutions of "*b*" parameter trend vs. the number of rotations for both categories of glazes. Although both categories of glazes experienced a shift towards blue at around 7000 rotations when a minimum value of "*b*" was obtained (more visible for the matte glaze), evolutions are individualized for matte and glossy glazes, with a clear gap between them. While each trend confirms the clear influence of the fineness, this gap is, most probably, due to the influence of the raw mixtures' compositions, i.e. to the difference between the two compositions.

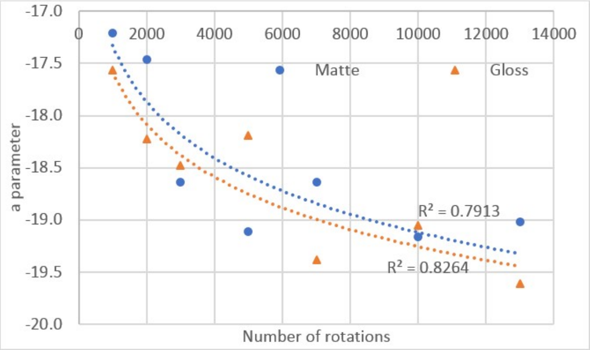


Fig. 9 - "*a*" parameter trend vs. the number of rotations for both categories of glazes, showing a shift towards green (logarithmic functions were used in regression analysis for both matte and glossy glazes) / *Evoluţia parametrului "a" cu numărul de rotații pentru ambele tipuri de glazuri, prezentând o tendință de virare a culorii către verde.*

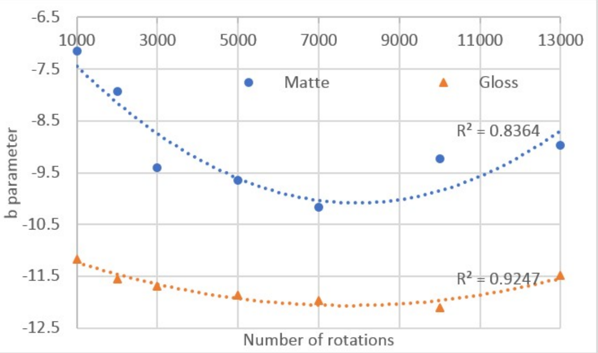


Fig. 10 - "*b*" parameter trend vs. the number of rotations for both categories of glazes, showing a maximum shift towards blue at around 7000 rotations (polynomial functions were used in regression analysis for both matte and glossy glazes) / *Evoluţia parametrului "b" cu numărul de rotații pentru ambele tipuri de glazuri, prezentând un viraj maxim al culorii către albastru la 7000 rotații.*

The clearly identified trends in Figs. 9 and 10 are explained by the changes in the number and in the size of the crystalline particles and the related optical phenomena at the interfaces existing between different solid (crystalline, vitreous), gaseous (pores, surface) media.

Fig. 11 confirm the influence of the fineness on the L parameter. A first, abrupt decrease can be observed when increasing the number of rotations from 1000 to 2000, and then a constant, lower slope decrease continues to 5000 rotations; this is followed by an increase in *L* value in the next steps.

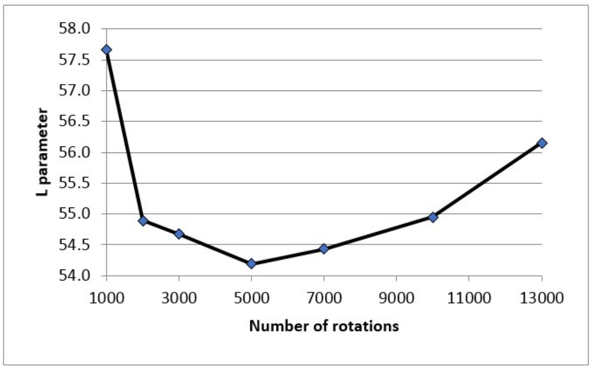


Fig. 11 - Lightness (L parameter) trend vs. the number of rotations for the glossy glaze / *Evoluția parametrului L cu numărul de rotații pentru glazura lucioasă.*

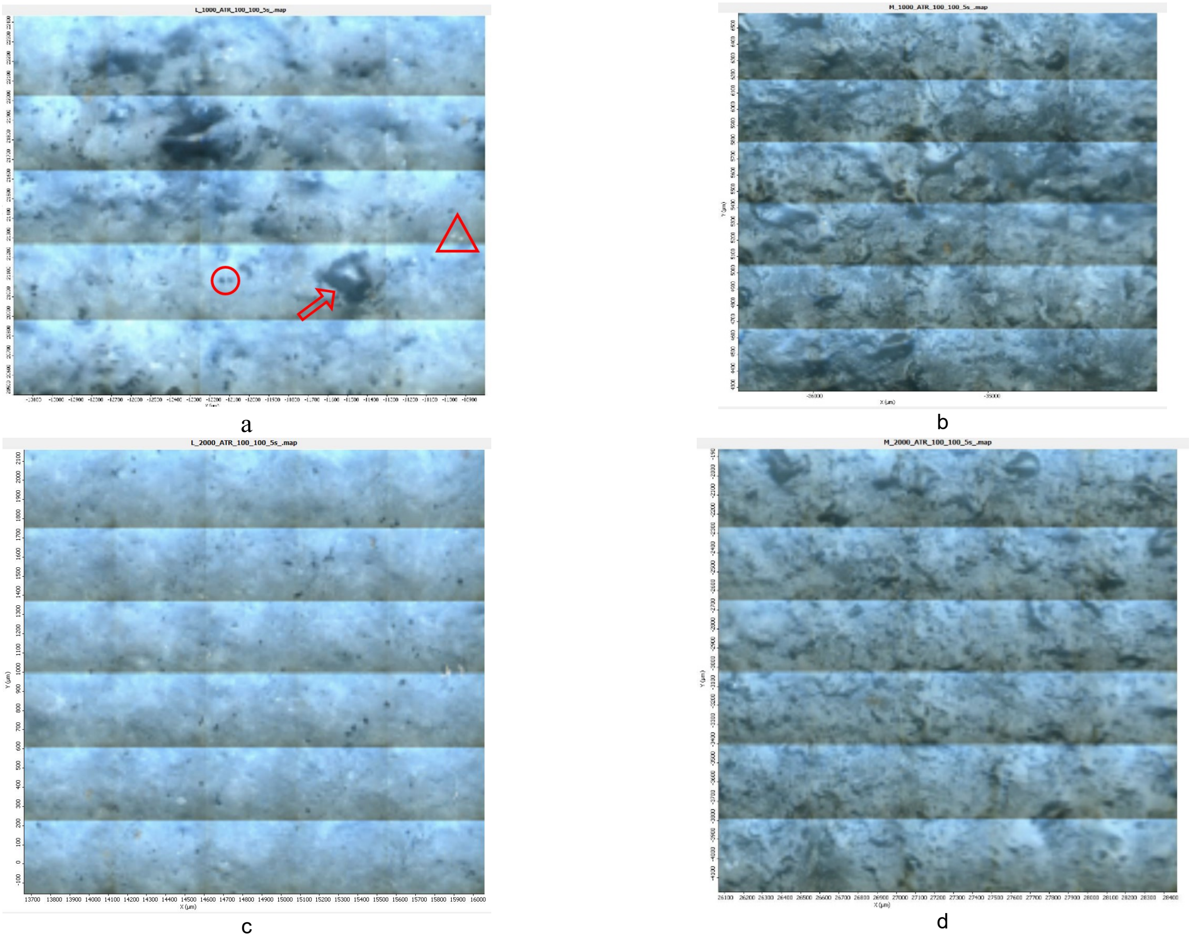
The decrease correlate well with the increase in scattering due to the reducing in particle size with the grinding progress. The increase observed after 5000 rotations and mostly starting from 10000 rotations it is more difficult to explain – further investigations, such as SEM analysis in transversal sections – may give an insight. Hypothesis could be: possible agglomeration phenomena when overgrinding or changes in glaze thickness and different glaze-biscuit interaction (interlayer) consecutive to an increase in melted phase fluidity at firing.

FTIR analysis was recorded on an area of 2x2 mm.

In Fig. 12 are shown FTIR images of the surface of the:

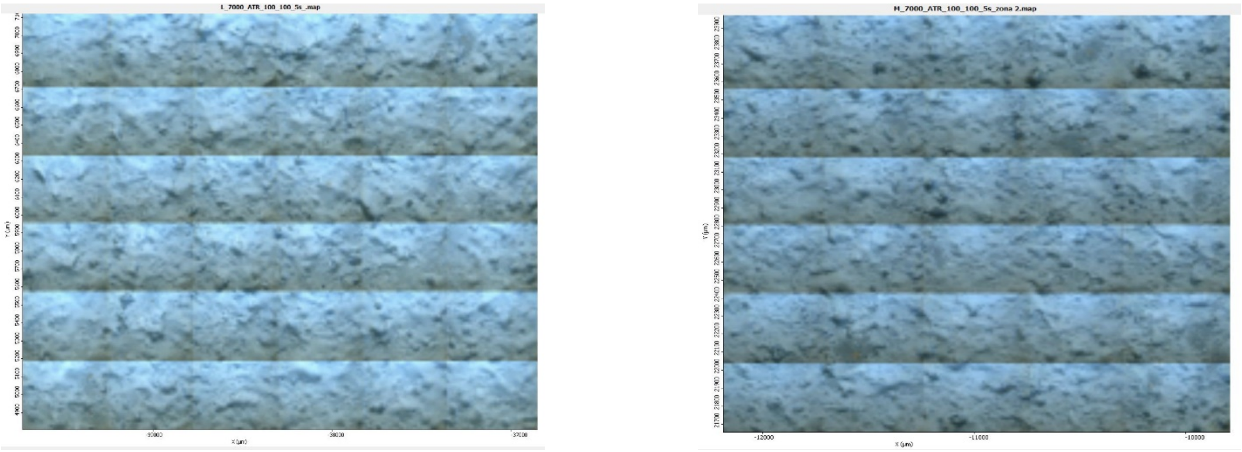
- glossy glaze when the raw mixture was grinded at: a) - 1000 rotations, c) 2000 rotations, and e) 7000 rotations;
- matte glaze when the raw mixture at: b) - 1000 rotations, d) - 2000 rotations, and f) - 7000 rotations.

For both series, the increase in the number of rotations of the mill is clearly influencing the morphology of the surface and the uniformity of the grain spatial distribution. Specifically, for the glossy glaze, image a) show some defects that may be large grains or blisters of more than 200 microns (indicated by an arrow), along with – probably – quartz grains of roughly the same size – 30 µm (encircled in Fig. 12 a) and – probably – some wollastonite (within the triangle in Fig. 12 a). Image c) show a glaze surface featuring a higher uniformity in the existing grains distribution. Image e) show an increase in roughness of the surface. A possible explanation of this phenomenon can be the following reasoning: this raw mixture has the smallest grains size among the three of them (see Fig. 2). Comparing to previous cases, these particles enter sooner in the melted phase that covers, in that case, the majority of the particles. This early melting lead to a decrease of the melted



a b

c d



e

f

Fig. 12 - FTIR images of the surface of glossy glaze – images a), c) and e) – and matte glaze – images b), d) and f) / *Imagini FTIR ale suprafetei glazurilor lucioase – imaginile a), c) și e) și a glazurilor mate – imaginile b), d) și f).*

phase's viscosity; the melted phase can penetrate the ceramic support through its pores in a higher amount than in cases a) and c), thus creating a wider intermediate layer between glaze and ceramic support (and a stronger bonding).

Further investigations must be done in the future on SEM images on transversal sections of the specimens to confirm these assumptions.

Although the same trend of increasing homogeneity can be observed for the second series of matte glazes on images b), d) and f), there are clear differences on how the surface looks between the two series. These differences are due to the differences in raw mixtures compositions (Table 1).

An overall analysis of the FTIR spectra presented in Fig. 13 indicate a decrease in Transmittance with the increase in number of rotations. This observation confirms the known fact that already referred optical phenomena taking place at the interface between vitreous matrix and crystalline grain are influenced by the size of the grain. Specifically, by decreasing the crystal size, the scattering increases and particles behave more as opacifiers. Glazes grinded at 1000 and 2000 have a close pattern along the almost all range of wavenumbers and so does the pair 7000-10000 rotations. Although these two pairs show different transmittance values, they have similar

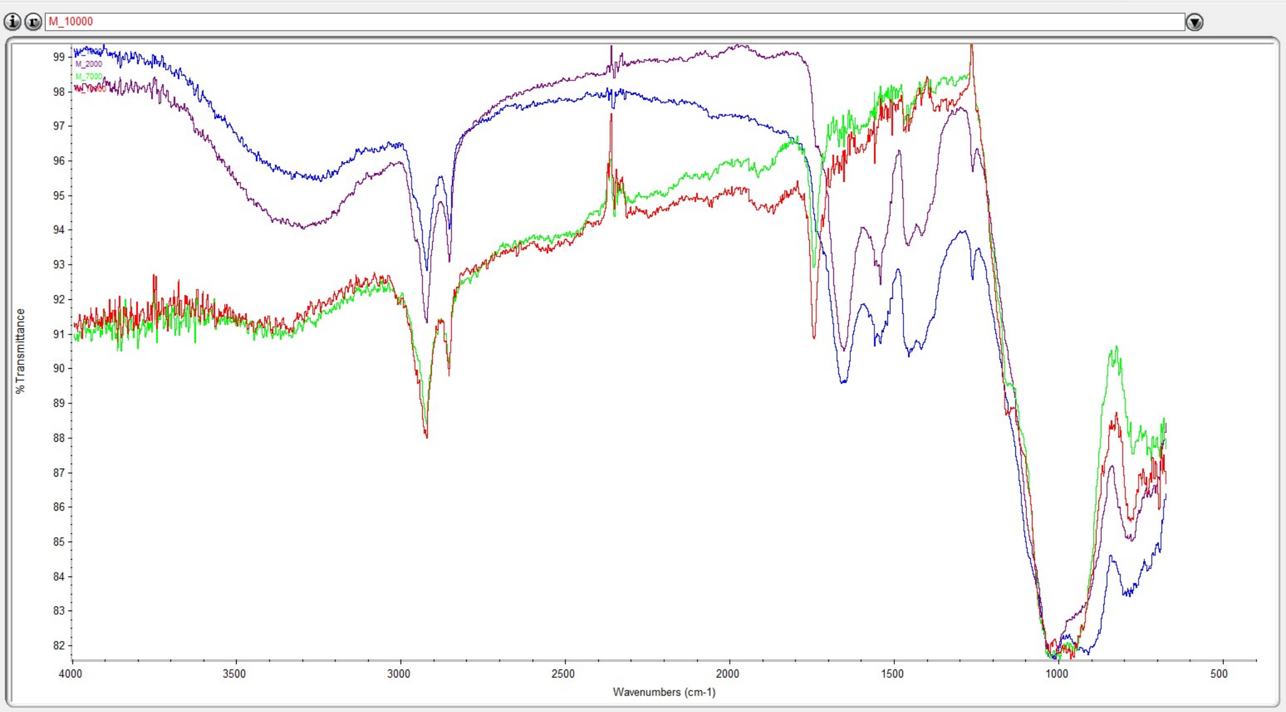
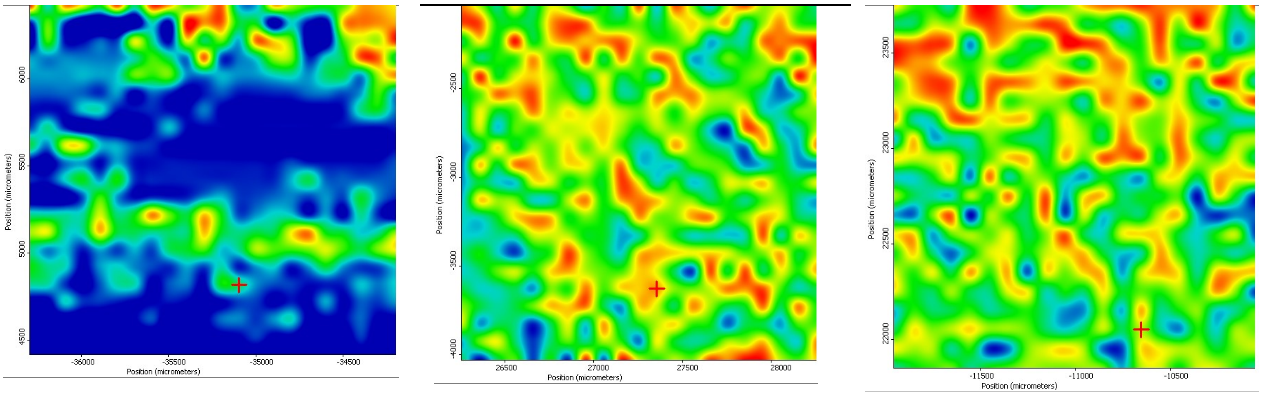


Fig. 13 – FTIR spectra of the matte glazes grinded at 1000 (blue), 2000 (indigo), 7000 (green) and 10000 (red) rotations
Spectre FTIR ale glazurilor mate măcinate la 1000 (albastru), 2000 (indigo), 7000 (verde) şi 10000 (roşu) rotaţii.



a) at 1000 rotations b) at 2000 rotations c) at 7000 rotations

Fig. 14 - FTIR maps of the matte glazes grinded at a) 1000, b) 2000, c) 7000 rotations at a wavelength of 940cm^{-1}

Cartografieri FTIR ale glazurilor mate măcinate la a) 1000, b) 2000, c) 7000 rotaţii la o lungime de undă de 940cm^{-1}.

behaviors, such as common peaks in the region 2800-3000 cm^{-1} and a common large band at around 1000 cm^{-1}. Note that inhomogeneities recorded in FTIR images at 1000 and 2000 rotations influence the transmittance values more than it was recorded for the other pair made of 7000-10000. Therefore, higher differences in transmittance were recorded between the two glazes grinded at the lowest number of rotations (undergrinded).

According to [10, 11], overall, FTIR spectra indicate the existence of various Si-O-Si and Si-O-Ca (and, possibly, with Al) bridges/bonds.

The visual examination of FTIR maps given in Fig. 14, show an inhomogeneity of the optical behavior of the glaze obtained at 1000 rotations, that is due to the phases and chemical inhomogeneity of the glaze itself. Blue areas correspond to higher values of the transmittance; therefore, transmittance decreases as grinding progresses. Note that these maps are recorded at one wavelength.

4.Conclusions

Two sets of glazes, with 7 glazes per set, obtained by grinding in the laboratory mill at a different number of rotations were made. The raw mixtures were grinded at 1000, 2000, 3000, 5000, 7000, 10000 and 13000 rotations, and the glazes were analyzed for particle size distribution, thermal expansion, FTIR (some samples) and optical properties (matte and *L, a, b* parameters in Hunter diagram).

Preliminary grindability tests made for each raw material show that feldspar and sand behave the same at grinding (each converge to a specific, very close value of residue at 9000 rotations), and so does dolomite and calcium carbonate. Grinded at 9000 rotations separately, sand and feldspar still have about 20% of the grains higher than 38µm while dolomite and calcium carbonate have only around 2%.

FTIR microscopy revealed that the glaze contains an important number of crystalline particles, some of them protruding at the surface and some being covered by a layer of vitreous matrix. It was observed both at a visual inspection and by FTIR microscopy that at an insufficient number of rotations (called undergrinding) - such as at 1000 rotations – [possibly] big quartz particles/agglomerates which are inclusions in the vitreous matrix were not dissolved yet and the samples surfaces morphology suggest inhomogeneity. Note that surface roughness negatively influences not only the aesthetics but also the hygiene, by providing microorganisms with an increasing chance to remain trapped at the glaze surface.

It was observed that by increasing the number of rotations (at further grinding) the surface becomes smoother. For example, inclusions of more than 200µm that can be found at 1000 rotations disappear at 2000 rotations for the glossy glaze. Matte glaze surfaces are more difficult to be analyzed; further investigations of SEM in transversal section and X-ray diffractometry will be needed for both types of glazes. An issue arises at this point as, at fast firing as it is the case here, films of glazes of a thickness less than 100µm will experience different transformations as compared to samples of millimeters in thickness.

On the other hand, increasing too much the number of rotations (overgrinding) lead to the apparition of macroscopic glaze defects (crawling) at 13000 rotations and to the formation of agglomerates in the raw mixtures.

Along with FTIR microscopy, recorded IR spectra and maps show an increase in the glaze surfaces' homogeneity with the progress of grinding, and, also, a decrease in transmittance. This decrease in transmittance is related to optical phenomena (scattering, absorption) and the refractive index that are related also to the size of the crystalline grain. By increasing the number of rotations of the mill the crystalline grains size decreases; the smaller the size is, the higher the scattering and refractions index become, and, consequently, particles behave more like opacifiers. Therefore, not only the pigments are important when evaluating optical properties but, also, other possible crystals existing in the glaze (and their size) should be, collectively, considered.

Optical properties (matte and *L, a, b* parameters in Hunter diagram) were measured and the grinding influence over them was confirmed. Matte parameter evolved as expected from literature, confirming the above explanations about the correlation of the optical phenomena and grain size. For the glossy glaze, of an interest is the *L* parameter; this one decreased to up to 5000-7000 rotations (which can be explained by the same opacifying effect of decreasing grain size) but clearly increased after 7000 rotations. It could be supposed that crystalline agglomerates are formed at overgrinding, agglomerates that do not melt easily. "*a*" parameter decreased nonlinearly with the number of rotations, but the two series of matte and glossy glazes were virtually indistinguishable. "*b*" parameter has distinct trends for the two series of glazes, with an extreme point at 7000 rotations. The gap between the two distinct series can be attributed to the influence of composition. All these results can be explained by the reduction in the number and size of the refractors (crystals) consecutive to advanced grinding and by the referred optical phenomena taking place at different, existing interfaces.

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