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Influence of mineralogical composition of applied ball clays on properties of porcelain tiles

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Abstract

Relations between quality of ball clays applied in raw materials batches for manufacture of porcelain tiles, and physical properties and microstructure of obtained tiles, were investigated. Studied clays constituted 35% of the batch, while the other components were unchangeable. Stoch index, new IR 3620/3700 index and XRIR index (Stoch index multiplied by IR 3620/3700 index), were proposed to take into account crystallinity of kaolinite and contents of illite and smectites in studied clays. Relationship between XRIR index value of clay, and water absorption and abrasion resistance of the obtained ceramic material, was found. Water absorption of the tile is also correlated with grain size distribution and bending strength of used clay. Optimal ball clay for porcelain tile production should exhibit: Stoch index – min. 4.3; IR 3620/3700 index – min. 1.2; XRIR index – min. 4.8; grain size median – max. 0.27 μm; bending strength after drying – min. 8.0 MPa.

Keywords: A. Firing; B. Microstructure-final; D. Clays; D. Porcelain stoneware

1. Introduction

Porcelain tiles belong to the group of ceramic materials obtained by forming of appropriate ceramic batch under high pressure (35–45 MPa), and its single fast-firing (40–50 min cycle) in roller kilns at a temperature up to maximum 1200–1230 °C [1]. They have very compact microstructure, with water absorption and open porosity being close to zero. Thanks to that, porcelain tile possess very good physical and mechanical properties, including high hardness, bending strength and abrasion resistance.

Advantageous properties of porcelain tiles are distinctly related to mineral composition of raw materials used, as well as to process of ceramic batch preparation and its firing. Plastic ball clays, kaolin, feldspar-quartz raw materials and pure quartz sand are commonly the main components of such a batch, in appropriate proportions [2–5]. Each of these components plays specific function in the technological process. Low content of colouring oxides (Fe_2O_3, TiO_2) is the common feature of all these raw materials. During firing, thermal decomposition of the majority of initial crystalline phases occurs (except of quartz), while new crystalline phases (especially mullite) and chemically differentiated glassy phase are formed [6,7].

Plastic white-firing clays (ball clays) assure good moulding properties of ceramic batch and high mechanical strength of raw tile after drying. Presence of kaolinite promotes mullite formation, while occurrence of illite and smectites contributes to formation of glassy phase assuring good densification of ceramic body during its firing [8,9]. This resulted in very low porosity and water absorption, as well as better mechanical properties of this material [1]. High whiteness after firing of the applied clays contributes to similar whiteness of the obtained ceramic material.

Ball clays are these components of ceramic batch for porcelain tiles production, which have the largest qualitative variability among applied raw materials [10]. This strongly influences basic parameters of obtained tiles. In Poland, as sources of ball clays are very limited, the domestic production assures max. 1/5 of demand. Furthermore, quality parameters of these clays are not optimal for the porcelain tiles production.

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The majority of demand is met by imports – primarily from Donetsk region (Ukraine) and Meissen region (Germany), with smaller amounts coming from the Czech Republic and other countries [11,12].

2. Materials and methods

Thirteen ball clays currently used or planned to be used in the Polish ceramic tiles industry for porcelain tiles production [11], were investigated in the study (Table 1).

Mineral composition of studied clays was established by means of XRD, DTA/TG, MIR and SEM/EDS methods. X-ray diffraction data (XRD) were obtained using Panalytical X'Pert Pro diffractometer equipped with Cu Kα radiation source. Diffraction patterns were recorded between 3° and 70° 2θ, with a step 0.008° 2θ. Analyses were carried out on three types of clay samples: air-dried clay, clay after vaporization by ethylene-glycol for 24 h, and clay after heating at 560 °C for 1 h. Differential thermal analysis (DTA/TG) was made by TAInstruments DTS 2960. Temperature increase rate from room temperature to 1100 °C was 10 °C/min. The middle infrared spectra (MIR) were measured by Bio-Rad FTS 60 V Fourier spectrometer in the spectral range 400–4000 cm^{-1}. The KBr pressed disc technique was used. Representative samples of clays were also investigated by SEM and EDS. Samples were carbon-coated. SEM observations were made by FEJ Nova Nano SEM200 scanning microscope at 18 keV, equipped with EDAX X-ray spectrometer.

In grain analysis, share of >100 μm grain fraction was initially measured by wet screen analysis. Particle size distribution of <100 μm grain fraction was determined by Micromeritics Sedigraph 5100 particle size analyser. Sample was prepared in the form of suspension in the water solution of sodium phosphate $Na_4P_2O_7$. Additionally, specific surface was determined by BET method, which use phenomenon of physical absorption of gas molecules on the surface of the solid body (according to Brunauer–Emmett–Teller theory). For measurement of some technological parameters, five samples of each clay were humidified (humidity ca. 7%). Then, beams were formed under the pressure of 20 MPa, and dried in an oven at temperature of 110 °C for 24 h until stable weight was achieved. For such beams, bending strength after drying at 110 °C was determined. Later on, these samples were fast fired for 30 min to the maximum temperature 1250 °C, soaked for 15 min and then cooled at a rate 50 °C/min. to room temperature. Water absorption after firing has been established by weighting of dry beam sample fired at 1250 °C, boiling it in distilled water for 2 h and weighting again.

In the second part of the study, ceramic batches, each containing 35% of one of 13 studied clays, were prepared. Other components were the same at each batch, i.e.: feldspar-quartz raw material from Polish company Strzeblowskie KSM (25%), feldspar-quartz raw material from the Czech company KMK Granit (25%), washed kaolin (10%) and quartz sand (5%) from the Polish company KPK Grudzeń Las. They are typical for such ceramic batches used in the Polish porcelain tiles plants. All the batches, with addition of water (solid content 66%) were ground in laboratory ball mill to grain size <0.045 mm, dried at 105–110 °C for 3 h, comminuted in impact mill with 6% addition of water, pressed at 40 MPa, dried at 150 °C for 1 h, and finally burned in industrial roller kiln at max. temperature of 1200 °C (total firing cycle: 42 min).

For obtained ceramic materials, the following physical parameters were measured: water absorption – according to EN ISO 10545-3 standard, flexural strength – according to EN ISO 10545-4 standard, abrasion resistance – according to EN ISO 10545-6 standard.

Polished samples of the same ceramic materials were examined by Cameca SX100 electron probe micro-analyser together with WDS X-Ray spectrometer, in BSE mode. Microstructure and phase composition of these materials, as well as phases and pores distribution, were analysed. For more detailed analysis of distribution of the main phases, chemical mapping was made for Al, Si, and K. Parameters of this mapping were as follows: Al and Si – 15 kV, 10 nA, 20 ms/pixel, K – 15 kV, 20 nA, 50 ms/pixel. Such chemical mapping allowed to assess location of the main phases in the studied ceramic materials [13]. Areas exhibiting high Si content were classified as quartz grains. Areas showing high Al content were interpreted as areas, were mullite nanocrystals occur within "kaolin" glassy phase, obtained by decomposition of clay minerals. Areas with high K content and moderate content of Si

Table 1
List of ball clays investigated in the study.

No.	Producer/plant	Grade of clay	Symbol of clay	Symbol of ceramic material
1.	Ekoceramika – Janina mine	JB1W	P1	MP1
2.	Bolesławieckie ZMO – Czerwona Woda mine	CWW	P2	MP2
3.	F. Jopek Ceramika – Zapniów mine	G3S	P3	MP3
4.	Vesco – Novoandreyevskoye mine	Granitic	U1	MU1
5.	Donbas Clays – Mertsalovo plant	DBY-4	U2	MU2
6.	Druzhkovskoye Rudoupravlenye – Noworayskoye mine	DN-0	U3	MU3
7.	Druzhkovskoye Rudoupravlenye – Zapadodonskoye mine	ZD-1	U4	MU4
8.	Druzhkovskoye Rudoupravlenye – Oktiabrskoye mine	OKT-1	U5	MU5
9.	Donkerampromsyryo – Toretskoye mine	K-28	U6	MU6
10.	Tschasov-Yar Refractory Combine – Tschasov-Yar mine	Cz-0	U7	MU7
11.	Stephan Schmidt Meissen – Kamenz plant	12087	G1	MG1
12.	Stephan Schmidt Meissen – Kamenz plant	14329	G2	MG2
13.	LB Minerals – Skalna mine	B3	C1	MC1

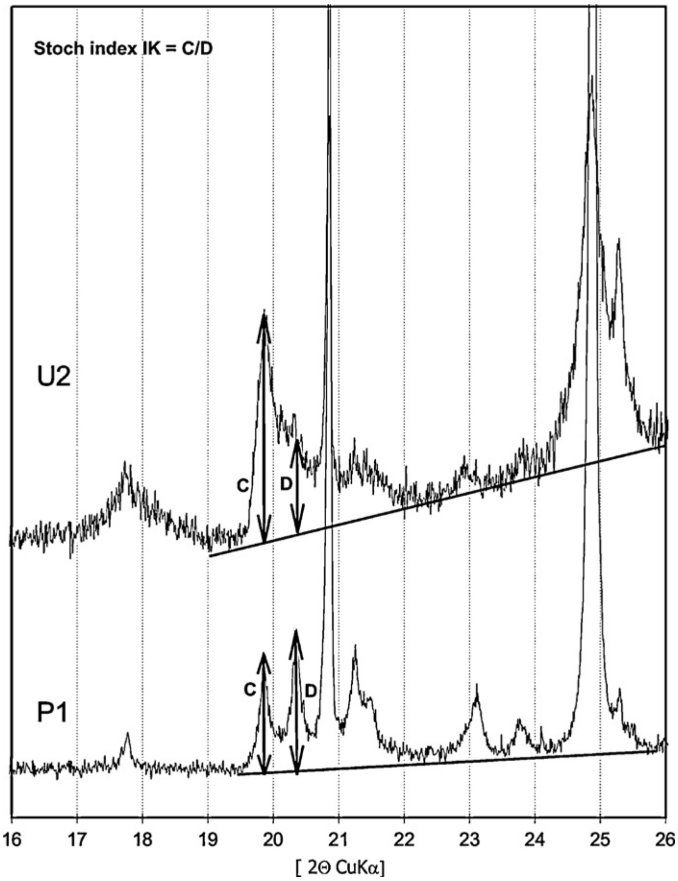

Fig. 1. Stoch index (IK) for P1 and U2 clay.

and Al were classified as occurrences of mostly ''feldspar'' glassy phase after feldspars melting [8].

3. Results

3.1. Mineralogical characteristics of investigated clays

Phase composition of investigated clays is differentiated. Three main components – kaolinite, illite and quartz – prevail in each clay, but their proportions are variable. Illite/smectite (I/S) mixed-layered minerals are additional, very important components of Ukrainian clays. It should be pointed out that degree of structural order (crystallinity) of kaolinite is strongly diverse. It is confirmed by, e.g. values of Stoch index (Fig. 1) calculated from XRD analysis [14,15], and values of Kissinger index (Fig. 2) established on the basis of DTA analysis [16]. Lower value of Stoch index is strictly related to higher degree of kaolinite structural order, while value of Kissinger index – inversely. The highest structural order of kaolinite is observed in case of Polish clays from Bolesławiec area (clays P1 and P2 in Table 1), while the lowest order – for Ukrainian clays (Table 2, Figs. 1 and 2). It is correlated with the size and shape of kaolinite plates in investigated clay. For example, their size for P1 and P2 clays reaches even 10 μm, while for Ukrainian clays it commonly amounts to 0.5–1 μm, hardly ever up to 3 μm. Structural order of illite, illustrated e.g. by Kübler index [17], is also the highest in case of the Polish P1 and P2 clays, the German G2 clay, and the Czech C1 clay, while the lowest for Ukrainian clays (Table 2). Plates of illite in P1 and P2 clays have commonly size of 0.3–0.5 μm, whereas in Ukrainian clays – often under 0.1 μm. I/S mixed-layered minerals specimens in Ukrainian clays are always smaller than 0.1 μm.

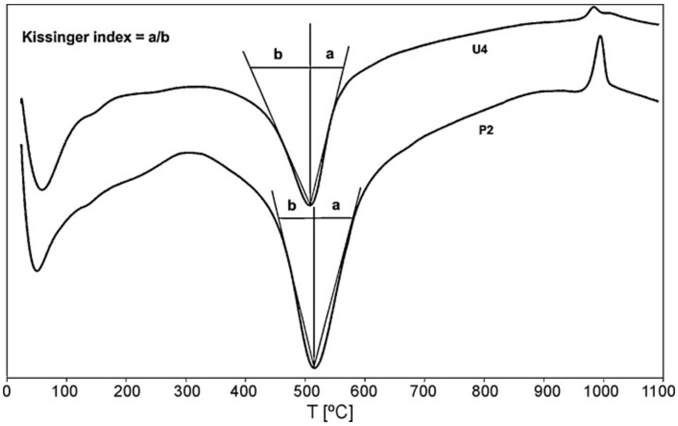

Fig. 2. Kissinger index for P2 and U4 clay.

On the basis of XRD and DTA/TG analyses, kaolinite content in studied Polish clays was estimated at over 50%, in German and

Table 2
Indices related to crystallinity of kaolinite (Stoch and Kissinger index), to crystallinity of illite (Kübler index), to proportion of illite + smectite/kaolinite (proposed IR 3620/3700 index) and proposed combined XRIR index for investigated clays.

No.	Clay	Stoch index	Kissinger index	Kübler index	IR 3620/3700 index	XRIR index
1.	P1	0.94	1.25	0.12	0.86	0.81
2.	P2	0.97	1.09	0.14	0.84	0.81
3.	P3	2.00	0.83	0.18	0.99	1.98
4.	U1	4.50	0.63	0.28	1.00	4.50
5.	U2	3.57	0.80	0.27	1.14	4.07
6.	U3	3.63	0.58	0.23	1.00	3.63
7.	U4	3.60	0.61	0.30	1.09	3.92
8.	U5	3.34	0.74	0.25	1.29	4.31
9.	U6	4.33	0.47	0.29	1.19	5.15
10.	U7	3.91	0.55	0.29	1.20	4.69
11.	G1	2.80	0.58	0.21	0.90	2.52
12.	G2	3.67	0.71	0.12	0.94	3.45
13.	C1	2.88	0.65	0.10	0.85	2.45

Table 3
Content of clay minerals in investigated clays estimated on the basis of DTA/TG analysis (presence of minerals confirmed by XRD analysis).

No.	Clay	Kaolinite	Illite[a]	Smectite
1.	P1	52	7	1
2.	P2	55	8	1
3.	P3	68	19	1
4.	U1	36	34	–
5.	U2	19	78	–
6.	U3	34	48	–
7.	U4	35	41	–
8.	U5	38	19	–
9.	U6	25	58	–
10.	U7	17	73	–
11.	G1	49	29	2
12.	G2	28	12	1
13.	C1	45	20	1

[a] For Ukrainian clays – total amount of illite and I/S mixed-layered minerals.

Czech clays between 28 and 49%, while in Ukrainian clays it was very variable depending on grade: from only 16% to 46%. The share of the second important component – illite – varied from less than 10% in P1 and P2 clays to ca. 20% in P3 and C1 grades and even 29% in G1 clay. In Ukrainian clays, total content of illite and I/S mixed-layered minerals was estimated, varying from ca. 20% to even over 70%. Another clay mineral – montmorillonite – was observed in investigated Polish, German and Czech clays, but in amounts below 2% (Table 3).

In MIR spectroscopy analyses, in case of kaolinite two bands are very characteristic: 3620 cm^{-1} band connected with vibration from inner hydroxyl groups and 3700 cm^{-1} band related to *in phase* vibration of hydroxyl groups [18]. Also other clay minerals – illite and dioctaedric smectite – show on MIR spectra very important band related to hydroxyl groups vibration at the range 3620–3635 cm^{-1} (and another one, very wide between 3400 and 3440 cm^{-1}), but do not demonstrate 3700 cm^{-1} band [19]. So, comparison of intensity of 3620 cm^{-1} band (related to kaolinite, but also to illite and smectite – if 3400–3440 cm^{-1} band confirms it) to intensity of 3700 cm^{-1} band (related only to kaolinite) allows estimating the proportion of illite + smectite content to kaolinite content. Such relation was proposed by author as a new IR 3620/3700 index (Fig. 3). When IR 3620/3700 index rises, sum of illite and smectite in relation to kaolinite also increases [20]. In investigated clays, the lowest values of IR 3620/3700 index were observed for P1, P2 and C1 clays (ca. 0.85), while the highest values – confirming very significant share of illite and I/S minerals – for Ukrainian clays (Table 2).

Mineralogical composition of clays is strongly correlated with their grain size distribution. Ukrainian clays are extremely fine-grained, with median value commonly below 0.5 μm and content of grains <2 μm over 80% (including 35–45% of <0.2 μm grains). It is confirmed by BET surface area values, ranging between 34 and 50 m^2/g (Table 4). Polish clays P1 and P2, and German clays G1 and G2 are much coarser, showing also lower BET surface area values (Table 4).

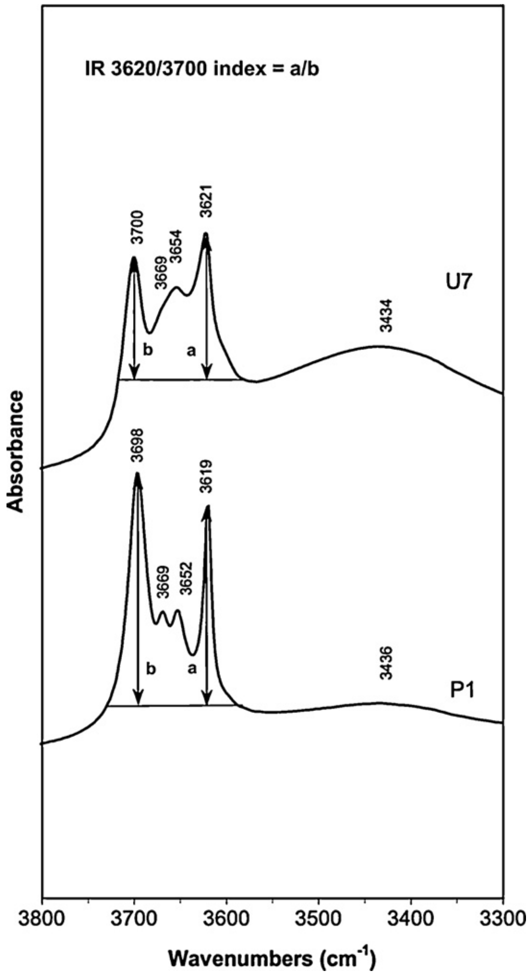

Fig. 3. Proposed IR 3620/3700 index for P1 and U7 clay.

Distinct variability of technological properties of investigated clays is the consequence of the differences of their mineralogical and grain size composition mentioned above. Ukrainian clays are regarded as highly plastic clays, as their bending strength after drying at 110 °C is usually higher than 7 MPa. Other studied clays are plastic (2–3 MPa), with the exception of P1 and P2 clays

Table 4
Grain median, BET surface area, average bending strength after drying and average water absorption after firing of investigated clays.

No.	Grade	Grain median (μm)	BET surface area (m^2/g)	Bending strength after drying at 110 °C (MPa)	Water absorption after firing at 1250 °C (%)
1.	P1	2.54	12.3	1.7 ± 0.2	12.64 ± 1.12
2.	P2	1.89	14.7	1.9 ± 0.2	11.72 ± 0.76
3.	P3	1.09	28.9	2.8 ± 0.2	0.20 ± 0.02
4.	U1	0.48	45.7	5.2 ± 0.4	0.29 ± 0.06
5.	U2	0.27	39.5	7.0 ± 0.8	0.21 ± 0.03
6.	U3	0.33	36.0	7.1 ± 0.5	0.23 ± 0.05
7.	U4	0.54	34.0	8.7 ± 0.3	0.22 ± 0.04
8.	U5	0.49	36.7	8.0 ± 0.4	0.25 ± 0.04
9.	U6	0.28	46.5	8.4 ± 0.7	0.22 ± 0.04
10.	U7	0.23	50.1	7.7 ± 0.5	0.28 ± 0.05
11.	G1	1.32	13.8	2.6 ± 0.4	4.58 ± 0.26
12.	G2	2.36	30.0	2.2 ± 0.1	3.15 ± 0.29
13.	C1	0.73	26.6	2.2 ± 0.3	2.95 ± 0.28

which show bending strength values less than 2 MPa (Table 4). Ukrainian clays, as well as P3 clay, exhibit good sintering properties, illustrated by very low values (under 0.3%) of water absorption after firing at 1250 °C. On the contrary, P1 and P2 clays do not show good sintering properties, while sinterability of the German and Czech clays is medium (Table 4).

3.2. Properties of obtained ceramic tiles

The basic physical parameters of obtained ceramic tiles, manufactured from batches with use of the studied clays, along with methodology described in point 2, are shown in Table 5. Assumption of the standard composition of ceramic batch with only one variable component – white-firing ball clay, was the starting point for establishment of influence of applied clay characteristics on physical properties of received ceramic materials. Only in a few cases these materials met requirements of EN 14411 standard for porcelain tiles. It was especially difficult to fulfil requirements in case of water absorption (max. 0.5%), what was obtained (or almost obtained) only for a few materials manufactured from batches containing Ukrainian clays (MU4, MU5, MU2, MU6). Other produced materials,

Table 5
Basic technological parameters of ceramic materials obtained by firing at 1200 °C from batches with use of individual grades of investigated ball clays.

Ceramic material	MP1	MP2	MP3	MU1	MU2	MU3	MU4	MU5	MU6	MU7	MG2	MG1	MC1
Water absorption (%)	3.52 ± 0.31	3.73 ± 0.24	2.83 ± 0.25	1.14 ± 0.24	0.53 ± 0.08	1.12 ± 0.23	0.29 ± 0.05	0.50 ± 0.08	0.53 ± 0.09	0.73 ± 0.13	2.11 ± 0.12	2.90 ± 0.27	2.25 ± 0.21
Flexural strength (MPa)	47.1 ± 5.5	67.0 ± 7.0	63.9 ± 4.6	45.9 ± 3.5	61.5 ± 7.0	49.0 ± 3.5	77.2 ± 2.7	71.8 ± 3.6	48.8 ± 4.1	63.4 ± 4.2	39.8 ± 5.0	56.4 ± 2.6	68.3 ± 9.3
Abrasion resistance (mm^3)	184 ± 21	205 ± 22	158 ± 11	126 ± 10	117 ± 13	167 ± 12	116 ± 4	116 ± 6	117 ± 8	156 ± 10	131 ± 20	169 ± 8	147 ± 20

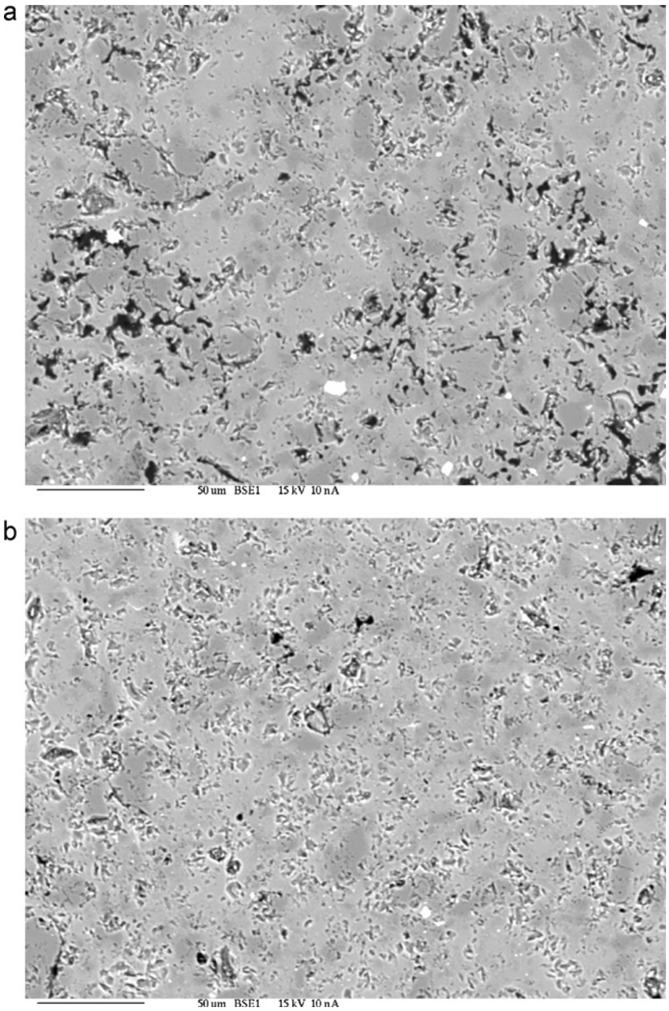

Fig. 4. SEM BSE picture of polished ceramic materials obtained after firing at 1200 °C: (a) MP3 and (b) MU4.

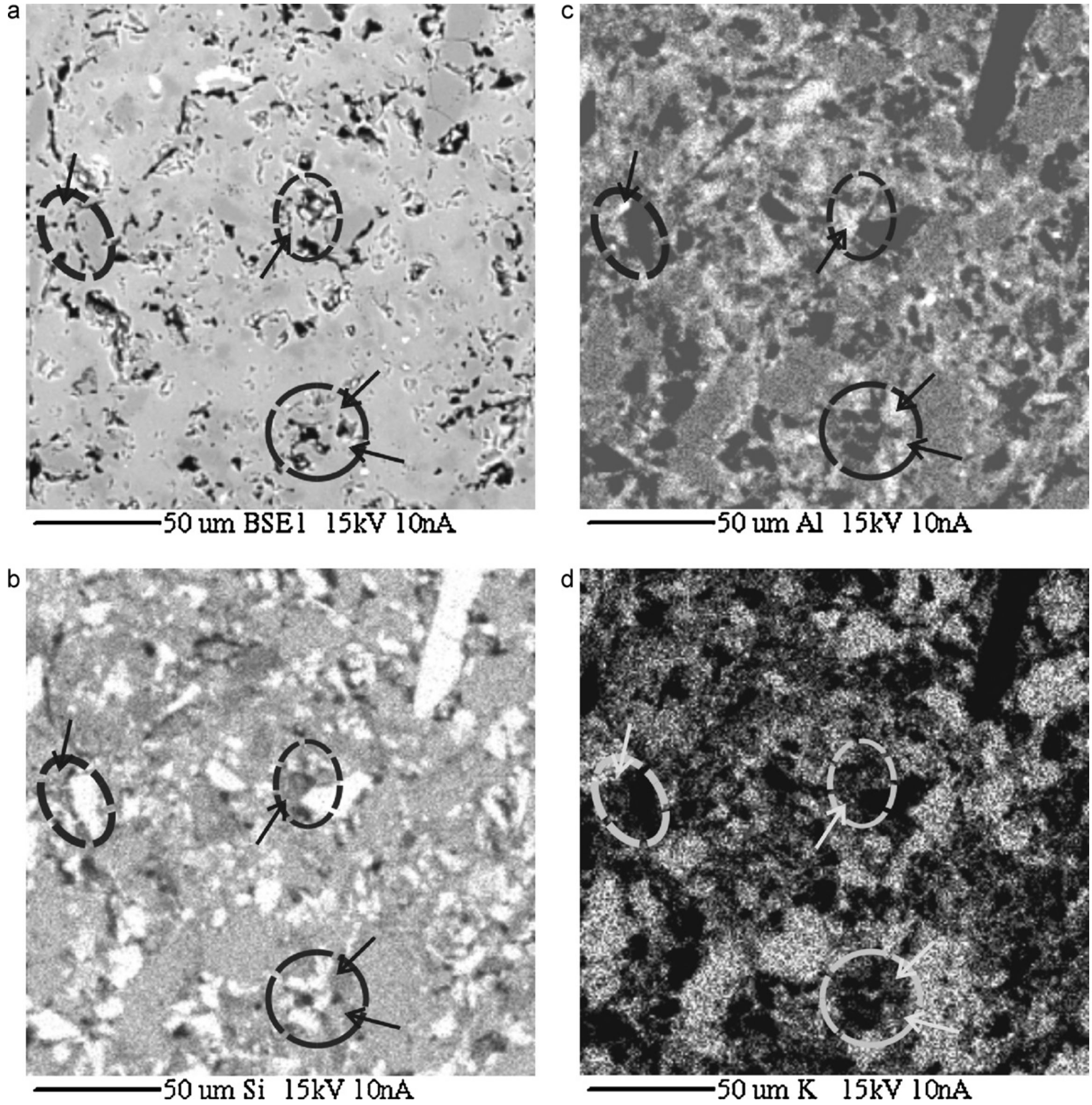

Fig. 5. SEM picture of MP1 ceramic material: (a) picture in BSE mode; (b)–(d) maps of content of the main elements: (b) Si, (c) Al, (d) K. Examples of areas of ‘‘kaolin’’ glassy phase presence near pores and small quartz grains are shown in circles by arrows.

made from batches with use of the Polish, German and Czech clays, were more porous, with water absorption value over 2% (Table 5). However, all obtained materials met requirements regarding flexural strength (min. 35 MPa) and abrasion resistance (max. 175 mm^3). The only exception was higher value of volume removed in case of MP1 and MP2 materials (Table 5).

EPMA(BSE)/WDS observations confirmed that the main phases of the obtained ceramic materials are: residual quartz, newly formed mullite and – primarily – aluminosilicate glassy phase exhibiting diverse chemical composition. Tiles obtained from batches with use of the Polish, German and Czech clays (MP1, MP2, MP3, MG1, MG2, MC1) are not well sintered (Fig. 4). Mullite is commonly not detectable by this method, because it probably forms nanocrystals within glassy phase [21]. Aluminosilicate glassy phase constitute the majority of the material, but its microstructure is partly porous. It should be underlined, that pores concentrate mostly between small quartz grains, being related to ‘‘kaolin’’ variety of glassy phase (showing high Al content and low K content), formed mostly as a result of clay minerals decomposition (Fig. 5). Typical Al_2O_3 content in this glassy phase ranges between 20 and 25%, what suggests moderate presence of mullite nanocrystals.

Tiles produced from batches containing Ukrainian clays are commonly well sintered, exhibiting marginal total porosity (Fig. 6). Their microstructure is more homogenous. Mullite forms exclusively nanocrystals within glassy phase. The main component – glassy phase – exhibits minimal porosity. Also in this case glassy phase shows differentiated chemical composition, and two varieties can be distinguished: ‘‘kaolin’’ and ‘‘feldspar’’ glassy phase. Porosity of ‘‘kaolin’’ glassy phase is minimal, while typical Al_2O_3 content in this phase amounts to

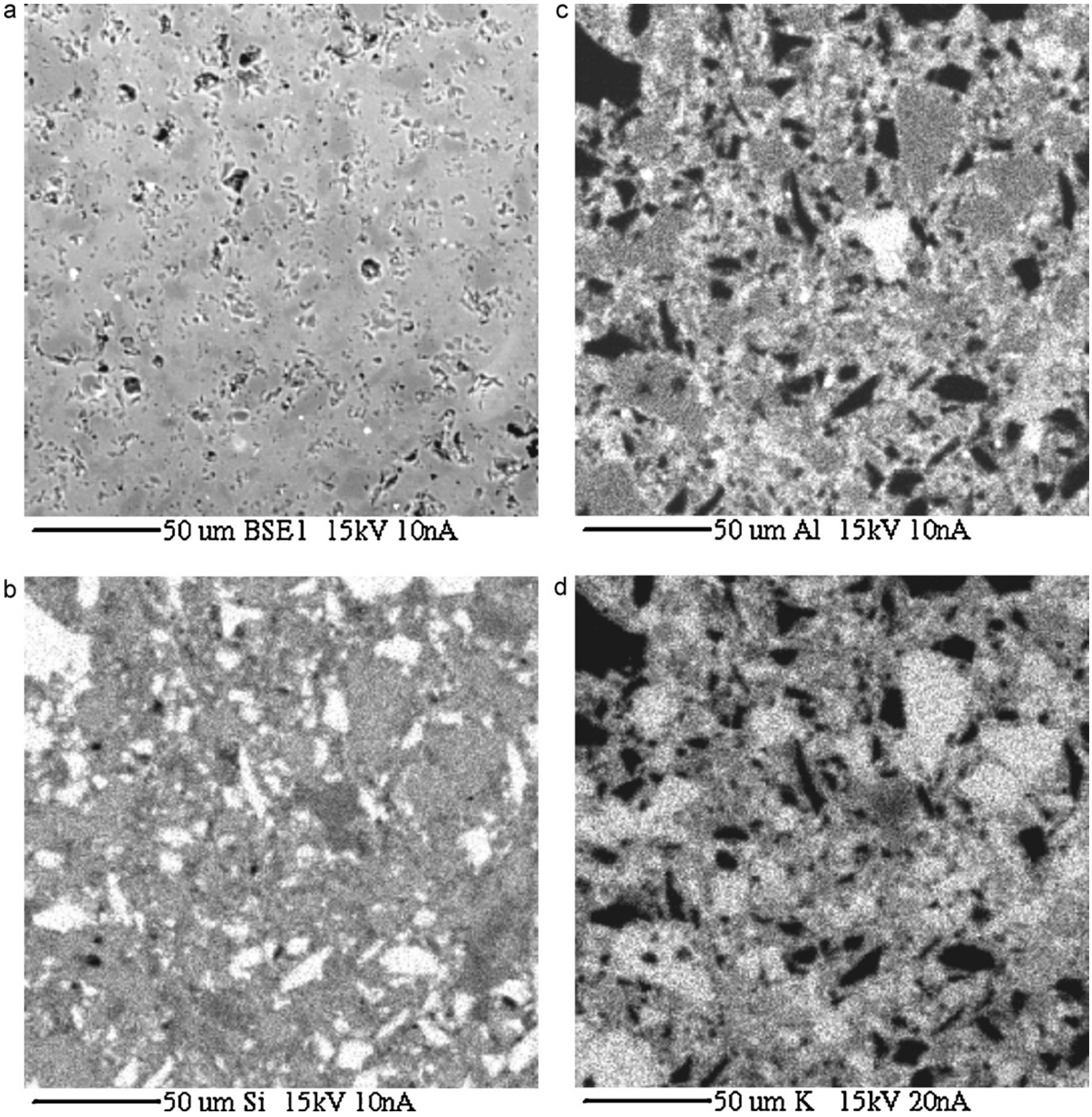

Fig. 6. SEM picture of MU2 ceramic material: (a) picture in BSE mode; (b)–(d) maps of content of the main elements: (b) Si, (c) Al, and (d) K.

even 32%, what suggests significant amounts of mullite nanocrystals.

Studies of microstructures of the obtained ceramic materials lead to a conclusion, that due to short time of firing (total cycle: 42 min) their initial microstructure strongly maintains set-up and morphology of the initial phases occurring in ceramic batch, in green tile after pressing. Quantity of the formed mullite only (as nanocrystals) in such materials is much smaller than in typical porcelain materials. Short time of firing unables diffusion of individual chemical components within glassy phase being formed. This explains the fact that chemical composition of this phase is very differentiated. As it was mentioned above, two basic types of such glassy phase can be distinguished: ‘‘feldspar’’ glassy phase in the places where feldspar grain were previously located, and ‘‘kaolin’’ glassy phase formed from clay minerals, in the areas between small grains of quartz [8]. In case of materials showing higher porosity (MP1, MP2, MP3, MG1, MG2, MC1), pores are distinctly concentrated in the areas of ‘‘kaolin’’ glassy phase, around small grains of quartz. It leads to a conclusion that mineralogical and technological characteristics of the applied clay have strong influence on the level of sintering of produced material. Taking into account the diversity of mineralogical composition of used clays, two factors seem to be the most important: the level of structural order of kaolinite and total content of illite and smectite. Lower structural order of kaolinite and – in parallel – higher share of illite and smectite lead to higher reactivity of clay minerals and initiation of phase reactions in lower temperatures. As a result, such materials (i.e. MU materials) are better sintered, showing lower porosity and water absorption.

4. Discussion

Basic physical parameters and microstructure of ceramic tiles obtained from batches with only one variable component – type of applied ball clay, are distinctly diverse. They exhibit the largest difference in case of water absorption after firing at 1200 °C, values of which vary between 0.29% and 3.73%. Values of flexural strength and abrasion resistance can differ – one to another – sometimes even almost two times (Table 5).

All components of ceramic batch were unchangeable, except for studied ball clays. Technology of manufacture of all ceramic materials was also fixed. So, large differences in values of basic physical parameters of received materials seem to be a consequence of diverse mineralogical composition of applied clays and their various interactions with other components of ceramic batch during firing process. Quantity and features (such as crystallinity) of clay minerals, occurring in particular grades of these clays, have – according to the study results – crucial influence on key physical parameters and microstructure of obtained tiles. It is anticipated, that they are related primarily to:

- quantity of mullite formed during firing (primarily as mullite nanocrystals within aluminosilicate glassy phase), what depends on the share of clay minerals – mainly kaolinite – in the clay, as well as on their various tendency to phase transformation related to structural order (crystallinity) of occurring clay minerals [22];
- high specific surface and strong reactivity of the clay (e.g. in contact with feldspar), directly proportional to participation of illite and I/S mixed-layered minerals; it distinctly influences intensity of batch sintering with formation of aluminosilicate glassy phase;
- plasticity of ball clays before firing, related to share of particular clay minerals and their structural order; it affects properties of ceramic batch after pressing and drying.

Applied clays should also exhibit very low content of colouring oxides, influencing whiteness of received tiles. It is not so easy to fulfil these requirements in case of plastic clays, as they contain some amounts of iron and titanium oxides (e.g. hematite, anatase, rutile), as well as clay minerals with low structural order and common isomorphic substitutions of iron ions [23].

Taking into account all these aspects, key factors influencing phase transformations in applied clay and its interaction with other components of the ceramic batch, seem to be the following:

- participation and type of kaolinite occurring in investigated clay, as well as its structural order (crystallinity);
- share of other very fine-grained clay minerals (i.e. illite, smectite, I/S mixed-layered minerals) exhibiting low isomorphic substitutions of iron ions in their structure;
- grain size distribution of applied clays related directly to type of clay minerals appearing in such clays; their bending strength after drying being a consequence of clays' mineral composition and grain size distribution as well.

According to results of the study, water absorption (WA) of received tiles was very variable, depending on type of clay used. To establish a correlation between properties of applied clay and water absorption of obtained ceramic material, some relationships between value of the latter parameter and values of a few indices related to type and share of clay minerals in used clays, were investigated.

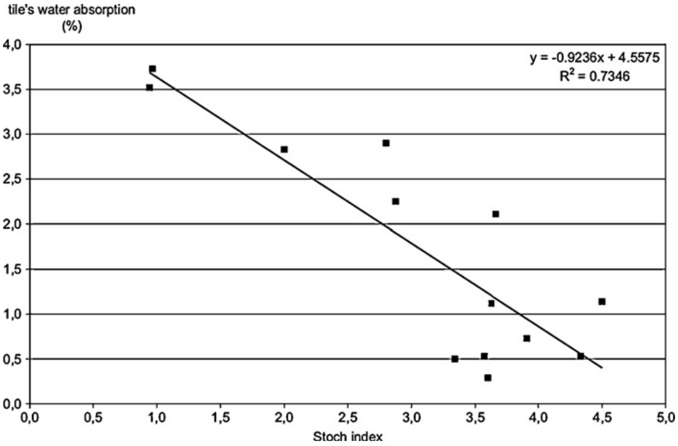

Fig. 7. Dependence of tile's water absorption on Stoch index of kaolinite occurring in applied clay.

At the beginning, potential relationship between structural order of the main clay mineral – kaolinite – in applied clay, expressed by Stoch index, and tile's water absorption, was investigated. Dependence of value of water absorption of tile on value of Stoch index for applied clay can be expressed by linear function: $y = -0.9236x + 4.5575$ (where y – WA in %, x – Stoch index value). It shows good coefficient of determination $R^2 = 0.7346$.[1] With growth of Stoch index value, WA value of tile is decreasing, reaching limit of 0.5% at Stoch index value ca. 4.3 (Fig. 7). In other words: higher Stoch index value means lower structural order of kaolinite in investigated clay. It is related to lower grain size (kaolinite crystals with lower structural order are finer), higher plasticity and higher specific surface of such a clay. Thanks to that, the clay shows higher reactivity with other components of ceramic batch, what – finally – results in better sinterability and lower porosity and water absorption of ceramic tile.

Potential relationship between participation of very fine-grained clay minerals – illite, smectite, I/S mixed-layered minerals – in applied clay, expressed by IR 3620/3700 index proposed by author, and water absorption of obtained tile, was also investigated. Dependence of value of tile's water absorption on value of IR 3620/3700 index for applied clay can be expressed by linear function: $y = -7.1103x + 8.9753$ (where y – WA in %, x – IR 3620/3700 index value). It shows good coefficient of determination $R^2 = 0.7312$. With growth of IR 3620/3700 index value, WA value of tile is decreasing, reaching limit of 0.5% at IR 3620/3700 index value ca. 1.2 (Fig. 8). In other words: higher IR 3620/3700 index value means higher share of illite + smectite, in comparison to kaolinite. It results in lower grain size distribution (specimens of illite, smectite, and I/S mixed-layered minerals are much smaller than kaolinite plates), giving higher plasticity and

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[1] For all relationships presented in the paper, relevance of fixed coefficient of determination was affirmed at confidence level $p = 99\%$.

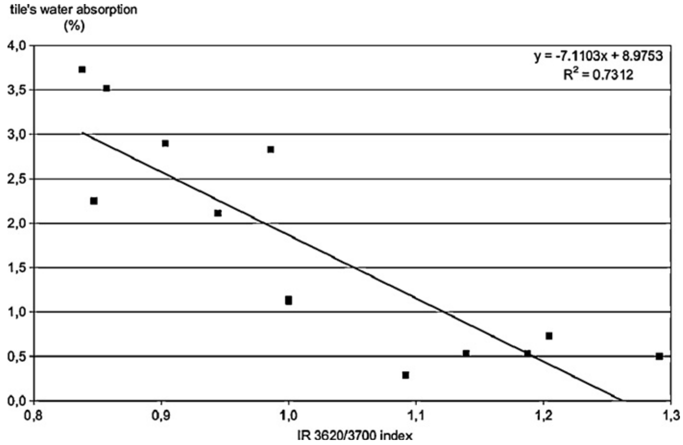

Fig. 8. Dependence of tile's water absorption on IR 3620/3700 index for applied clay.

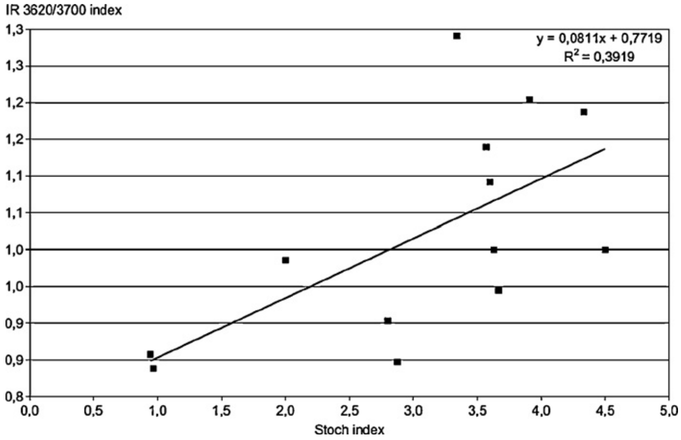

Fig. 10. Weak relation between Stoch index of kaolinite and IR 3620/3700 index for applied clay.

higher specific surface of such a clay. Thanks to that, clay exhibits higher reactivity with other components of ceramic batch, what improves formation of higher amounts of aluminosilicate glassy phase, and – finally – results in more sintered microstructure of received tile, with lower porosity and water absorption values.

Taking into account the influence of both mentioned above factors (i.e.: structural order of kaolinite and participation of illite, smectite, and I/S mixed-layered minerals in studied clay) on value of water absorption of obtained tiles, the introduction of a new index was proposed. This index, marked as XRIR index (*X-Ray analysis*, *Infra Red analysis*), is the product of Stoch index and IR 3620/3700 index (Table 2). Very good correlation between this index and value of water absorption of obtained tile was found. Dependence of value of tile's water absorption on value of XRIR index for applied clay can be expressed by linear function: $y = -0.8117x + 4.3465$ (where y – WA in %, x – XRIR index value). It shows very good coefficient of determination $R^2 = 0.8738$. Along with growth of XRIR index value, tile's WA value is decreasing, reaching limit of 0.5% at XRIR index value ca. 4.8 (Fig. 9). XRIR index, as it is the product of two previously analysed indices, expresses two-dimensional correlation of water absorption of received tile with these two analysed factors. Usefulness of such product index is additionally emphasized by the fact, that there is only a poor relation between Stoch index and IR 3620/3700 index (Fig. 10).

Some relationships between value of the other important physical parameter of tile – abrasion resistance, and values of a few indices related to type and share of clay minerals in used clays, were also investigated. Strong correlation between tile's abrasion resistance and value of proposed XRIR index was found. This dependence can be expressed by linear function: $y = -16.66x + 201.03$ (where y – abrasion resistance in mm^3, x – XRIR index value). It shows good coefficient of determination $R^2 = 0.6607$. With growth of XRIR index value, the abrasion resistance of tile is improving, down to limit of 175 mm^3 at XRIR index value ca. 1.4 (Fig. 11). No correlation between flexural strength of obtained tile and values of discussed indices, related to type and share of clay minerals in applied clays, was found. However, all obtained materials met requirements regarding flexural strength (Table 5).

Due to confirmed relationships between structural order of kaolinite and share of fine-grained clay minerals, and water absorption of received tiles, similar correlation of grain size

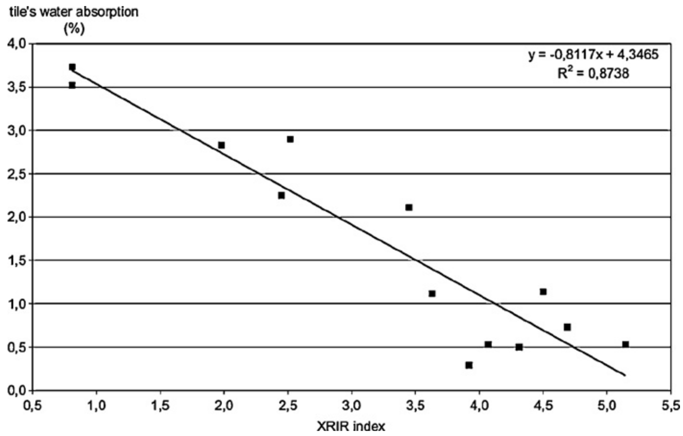

Fig. 9. Dependence of tile's water absorption on XRIR index for applied clay.

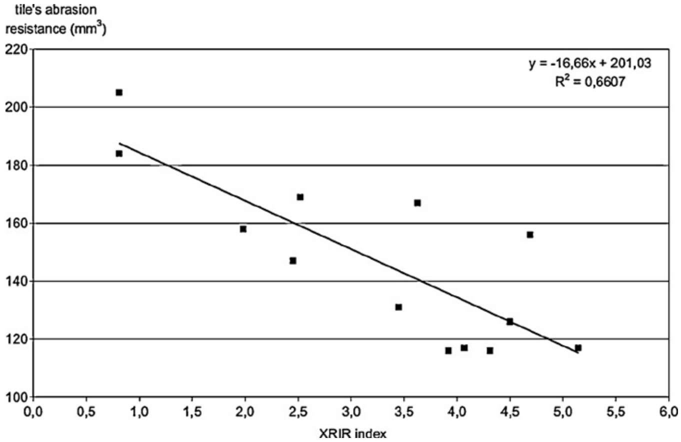

Fig. 11. Dependence of tile's abrasion resistance on XRIR index for applied clay.

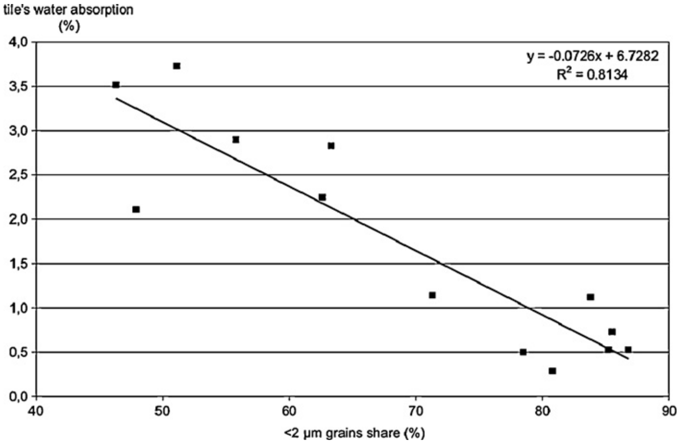

Fig. 12. Dependence of tile's water absorption on <2 µm grains share in applied clay.

median of applied clay and tile's water absorption was also investigated and found good. This dependence can be expressed by logarithmic function: $y = 1.2602\ \ln(x) + 2.1664$ (where y – WA in %, x – grain size median in µm). It shows good coefficient of determination $R^2 = 0.7443$. With decrease of grain size median of used clay, water absorption of received tile is also decreasing, reaching limit of 0.5% at median value ca. 0.27 µm. Other parameter of grain size distribution of clay – share of <2 µm grains – is even better correlated with tile's water absorption. This dependence can be expressed by linear function: $y = -0.0726x + 6.7282$ (where y – WA in %, x – share of <2 µm grains in %). It shows very good coefficient of determination $R^2 = 0.8134$. With growth of share of <2 µm grains to ca. 85%, water absorption of received tile is reaching limit of 0.5% (Fig. 12).

Potential relationship of water absorption of obtained tiles and bending strength of used clays after drying at 110 °C, was also studied. This parameter is strictly related to quantity and type of clay minerals occurring in clay, as well as to its grain size distribution [24]. Such dependence can be expressed by linear function: $y = -0.4079x + 3.7622$ (where y – WA in %, x – bending strength after drying at 110 °C in MPa). It shows very good coefficient of determination $R^2 = 0.8741$. With growth of clay' s bending strength value up to ca. 8.0 MPa, water absorption of received tile is reaching the limit of 0.5% (Fig. 13).

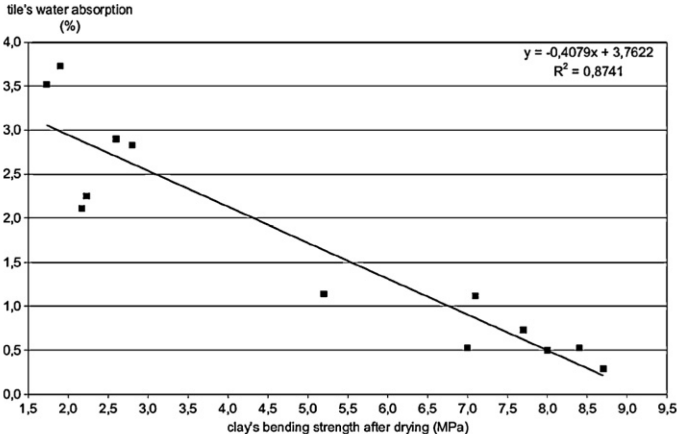

Fig. 13. Dependence of tile's water absorption on bending strength after drying of applied clay.

5. Conclusions

Studies on dependence of some physical properties of obtained porcelain tiles (especially water absorption being the key parameter classifying tile as porcelain tile) on quality of applied ball clays allowed to define a few important features of the optimal plastic ball clay for the production of these tiles. Some indices reflecting mineral composition of ball clays, i.e. Stoch index and – proposed by author – IR 3620/3700 and XRIR indices, seem to be the most important. These indices are connected with the structural order of kaolinite and proportion of total amount of fine-grained illite and smectite to the amount of coarser-grained clay mineral – kaolinite. The other important features of ball clays – also related to their mineral composition – are: grain size distribution and bending strength after drying. Assuming – in the ceramic batch – unchangeable content of other raw materials (feldspar-quartz raw materials, washed kaolin, quartz sand), the optimal ball clay for porcelain tile production should exhibit:

- Stoch index – min. 4.3;
- IR 3620/3700 index (proposed by author) – min. 1.2;
- XRIR index (proposed by author), i.e. Stoch index multiplied by IR 3620/3700 index – min. 4.8;
- grain size median – max. 0.27 µm;
- bending strength after drying at 110 °C – min. 8.0 MPa.

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