



Composition and ceramic properties of ball clays for porcelain stoneware tiles manufacture in Poland

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ABSTRACT

The paper presents the results of investigations of mineralogical, grain and chemical composition, and ceramic properties of 18 white-firing ball clays from five producing regions in eastern and central Europe. Relationships between the bending strength of the clay after drying and its grain size and mineralogical composition were studied. High contents of illite and illite/smectite minerals in the clay, and low crystallinity of kaolinite and illite, strongly influenced plasticity but also improved sinterability, as appropriate phase transitions of clay minerals began at lower temperatures. The clays were also highly reactive towards other components of the ceramic batches for porcelain stoneware tile production. The ball clays from the Donetsk region in Eastern Ukraine are recommended for the porcelain stoneware tile production in Poland, while the Polish, German and Czech clays may be used only as supplementary components.

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1. Introduction

Porcelain stoneware tiles are very strongly sintered ceramic materials with water absorption and open porosity close to zero (Manfredini et al., 1995). They possess perfect physical and mechanical properties like high hardness, abrasion resistance and bending strength. These features of porcelain stoneware tiles are considerably related to the mineralogical composition of the raw materials: plastic ball clays, kaolin, feldspar–quartz and pure quartz sand (Abadir et al., 2002; Leonelli et al., 2001). Each of these components has specific function in the technological process but low content of coloring oxides (Fe_2O_3 and TiO_2) should be their common feature. Plastic ball clays for porcelain stoneware tile production have the largest qualitative variability among applied raw materials (Andreola et al., 2009). They should guarantee good molding properties of ceramic batch and high mechanical strength of dried tile before firing. Presence of kaolinite promotes mullite formation, while occurrence of illite and smectites influences glassy phase formation and good densification of the ceramic body during firing (De Noni et al., 2008; Ferrari and Gualtieri, 2006). High whiteness after firing of the applied clays contributes to similar whiteness of the obtained ceramic material.

Plastic ball clays are commonly composed of kaolinite (25–80%), illite and mica (10–30%), and fine-grained quartz. Sometimes, illite/smectite (I/S) mixed-layered minerals also occur. A small amount of organic matter—up to 0.5 mass %—is also typical (Wilson, 1998). The ceramic properties of plastic ball clays depend on the content of the clay minerals (especially I/S minerals) but also on the level of crystallinity of kaolinite and illite. These features influence grain size distribution and specific BET surface area of the clays. Plastic ball clays contain commonly large amounts of grains $< 1 \mu\text{m}$ (50–90%), and even $< 0.2 \mu\text{m}$ (25–40%). The grain size of clay is, in general, inversely proportional to the specific BET surface area and plasticity. Levels of crystallinity of kaolinite and illite are the other factors influencing the plasticity of a clay (Dondi et al., 2003; Stoch, 1964). Therefore, optimal ball clays should contain higher amounts of low-ordered kaolinite and illite and some amounts of I/S minerals. They should demonstrate high bending strength after drying at 110°C , i.e. over 3 MPa (sometimes even 8–10 MPa), and high specific BET surface areas of 20–50 m^2/g . Due to these features, optimal plastic ball clays ought to have good sintering properties, as the phase transitions of clay minerals start at relatively low temperatures. Such plastic ball clays are also highly reactive towards other components of the ceramic batch for porcelain stoneware tile production, especially against feldspars (Das Kshama et al., 1992; Dondi et al., 2003, 2008; Galos and Wyszomirski, 2004).

The Polish ceramic tile industry was quickly developing in recent years, especially regarding porcelain stoneware tile production. Their manufacture capacities rose from zero in 1994 to ca. 60 million m^2 per year recently (Galos, 2007). Domestic suppliers assure the Polish

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Table 1
The Polish, Ukrainian, German and Czech ball clays investigated in the study.

No.	Producer/plant	Location	Grade of clay	Symbol of clay
1.	Ekoceramika–Janina mine	SW Poland	JB1W	P1
2.	Bolesławieckie ZMO–Czerwona Woda mine	SW Poland	CWW	P2
3.	F. Jopek Ceramika–Zapniów mine	Central Poland	G3S	P3
4.	Glinkop–Żarnów mine	Central Poland	Żarnów	P4
5.	Vesco–Novoandreyevskoye mine	Eastern Ukraine	Granitic	U1
6.	Donbas Clays–Mertsalovo plant	Eastern Ukraine	DBY-4	U2
7.	Donbas Clays–Mertsalovo plant	Eastern Ukraine	HD-3	U3
8.	Donbas Clays–Mertsalovo plant	Eastern Ukraine	HD-2	U4
9.	Druzhkovskoye Rudoupravlenye–Noworayskoye mine	Eastern Ukraine	DN-0	U5
10.	Druzhkovskoye Rudoupravlenye–Zapadodonskoye mine	Eastern Ukraine	ZD-1	U6
11.	Druzhkovskoye Rudoupravlenye–Oktiabrskoye mine	Eastern Ukraine	OKT-1	U7
12.	Donkerampromsyryo–Toretskoye mine	Eastern Ukraine	K-28	U8
13.	Donkerampromsyryo–Toretskoye mine	Eastern Ukraine	K-26	U9
14.	Tschasov-Yar Refractory Combine–Tschasov-Yar mine	Eastern Ukraine	Cz-0	U10
15.	Tschasov-Yar Refractory Combine–Tschasov-Yar mine	Eastern Ukraine	Cz-1	U11
16.	Stephan Schmidt Meissen–Kamenz plant	Eastern Germany	12090	G1
17.	Stephan Schmidt Meissen–Kamenz plant	Eastern Germany	14329	G2
18.	LB Minerals–Skalna mine	Western Czech Rep.	B3	C1

porcelain stoneware tile industry most of the raw materials, with the exception of ball clays. Ball clays' sources in Poland are very scarce. The domestic production meets at most 20% of demand. Moreover, quality parameters of the Polish clays are not optimal for the porcelain stoneware tile production. This is why the majority of demand is met

by imports, primarily from the Donetsk region (Eastern Ukraine), and Saxony region (Eastern Germany), while smaller amounts are coming from the Czech Republic and other countries (Galos, 2010).

The paper presents mineralogical characteristics of the clays currently used or possible for application in the Polish ceramic tile industry (Galos, 2007, 2010). Their technological properties in respect to their suitability for the production of porcelain stoneware tiles, are also described.

2. Materials and methods

Eighteen ball clays were examined in this study (Table 1). For all the clays, the mineralogical, grain size, chemical, and technological properties were accomplished.

The mineralogical composition of the clays was examined by means of XRD, DTA/TG, MIR and SEM/EDS methods. X-ray diffraction data (XRD) were obtained using the Panalytical X'Pert Pro diffractometer equipped with a Cu K α radiation source. Diffraction patterns were recorded between 3 and 70° 2 θ , with steps 0.008° 2 θ , of three types of samples (raw, glycolated, and heated at 560 °C). Differential thermal analysis (DTA/TG) was made by the TAInstruments DTS 2960, coupled with the quadropole mass spectrometer Balzer ThermoStar GSD300 for analysis of evolved gases (EGA), in flowing synthetic air (flow 50 cm³/min). Temperature increase rate from room temperature to 1040 °C was 10 °C/min. The infrared spectra of KBr discs were measured by the Bio-Rad FTS 60V Fourier spectrometer in the spectral range 400–4000 cm⁻¹. SEM observations were made by the FEJ Nova Nano SEM200 scanning microscope at 18 keV, equipped with EDAX X-ray spectrometer. Samples were carbon-coated.

For grain analysis, the content of >100 μ m grains was measured by wet screen. Particle size distribution <100 μ m was determined by the Micromeritics Sedigraph 5100 analyzer. Additionally, the specific surface was determined by the BET method.

The chemical composition was determined by ICP-AES, using the Jarrasell Ash Enviro spectrometer and Perkin Elmer 6000 spectrometer. A sample of 0.25 g was dissolved in 10 ml of HCl–HNO₃–HClO₄–HF at

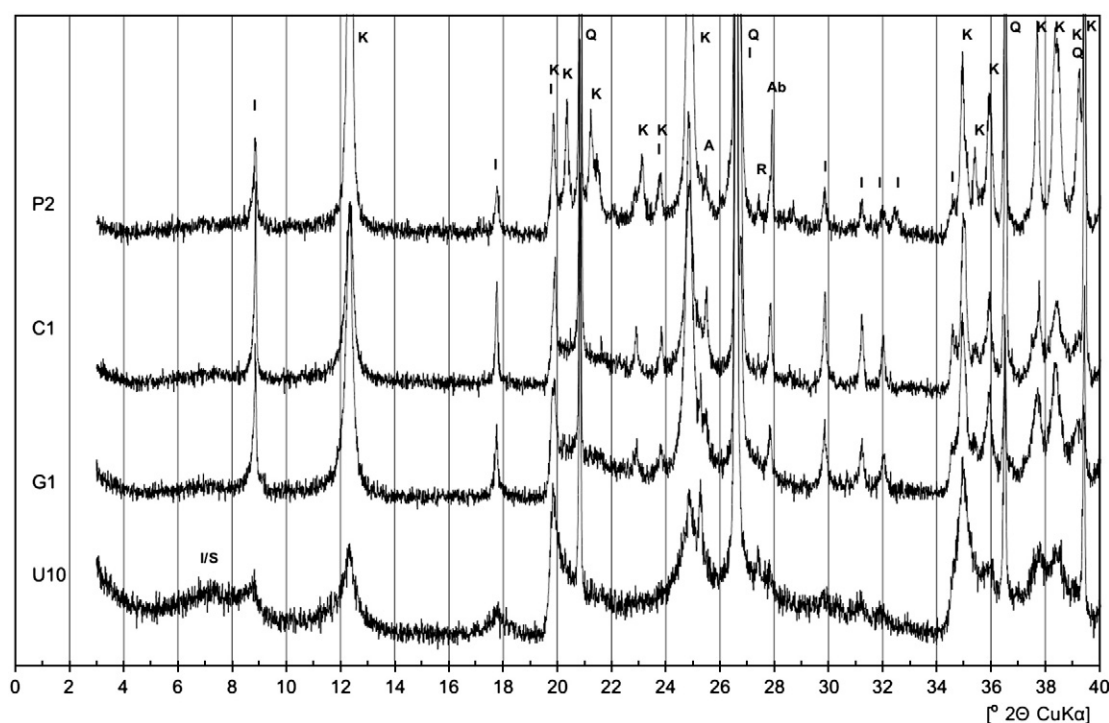


Fig. 1. X-ray patterns of the clays. A–anatase, Ab–albite, I–illite, I/S–mixed-layered illite–smectite, K–kaolinite, Q–quartz, R–rutile.

Table 2

Crystallinity of kaolinite on the basis of X-ray analysis (Stoch index, Hinckley index) and DTA analysis (Kissinger index), and crystallinity of illite (Kübler index) of the clays.

Clay	Stoch index	Hinckley index	Kübler index ($^{\circ}2\theta$)	Kissinger index
P1	0.94	1.46	0.12	1.25
P2	0.97	1.50	0.14	1.09
P3	2.00	0.88	0.18	0.83
P4	1.45	1.20	0.14	1.22
U1	4.50	0.14	0.28	0.63
U2	3.57	0.09	0.27	0.80
U3	3.91	0.15	0.29	0.69
U4	3.02	0.17	0.28	0.53
U5	3.29	0.14	0.23	0.62
U6	3.60	0.11	0.30	0.61
U7	3.34	0.06	0.25	0.74
U8	4.33	0.07	0.29	0.47
U9	4.00	0.05	0.24	0.52
U10	3.91	0.07	0.29	0.55
U11	4.61	0.04	0.32	0.64
G1	3.17	0.24	0.09	0.57
G2	3.67	0.09	0.12	0.71
C1	2.88	0.10	0.10	0.65

Table 3

Content of the clay minerals in the clays estimated by DTA/TG analysis.

Clay	Kaolinite	Illite*	Smectite
P1	52	7	1
P2	55	8	1
P3	68	19	1
P4	46	9	1
U1	36	34	–
U2	19	78	–
U3	19	54	–
U4	27	64	–
U5	34	48	–
U6	35	41	–
U7	38	19	–
U8	25	58	–
U9	30	43	–
U10	17	73	–
U11	16	66	–
G1	32	5	1
G2	28	12	1
C1	45	20	1

* For Ukrainian clays—total amount of illite and I/S mixed-layered minerals.

200 °C. The experimental error for all components was ± 0.01 mass %. The content of total carbon and organic carbon was determined by the Leco CR-12 analyzer. The analytical error was ± 0.05 mass %.

To examine the technological parameters, samples of clays were humidified. Shaped plates and beams were formed and dried at 110 °C for 24 h until mass constancy. Then, these samples were heated during 30 min to the maximum temperature of 1250 °C, kept at 1250 °C for 15 min and then cooled at a rate of 50 °C/min to room temperature. Make-up water, MW (%), was determined as: $MW = (M_w/M_d) \cdot 100/M_d$, where M_w and M_d are the mass of green and dried plates. Linear drying shrinkage, S_d (%), was calculated as: $S_d = (L_0 - L_d) \cdot 100/L_0$, where L_0 and L_d are the lengths of green and dried plates. Bending strength after drying at 110 °C, R_{bd} (MPa), was determined as: $R_{bd} = 3 \cdot F_d \cdot L_d / 2 \cdot b_d \cdot h_d$, where: F_d —breaking load for dried sample (in N), L_d —distance between supports for dried sample (mm), b_d —dried sample width (mm) and h_d —dried sample thickness (mm). Linear firing shrinkage, S_f (%), was calculated as: $S_f = (L_d - L_f) \cdot 100/L_d$, where L_d and L_f are the length of dried and fired plates. Water absorption after firing, WA (%), was determined by

weighting of dry beam samples fired at 1250 °C, boiling it in distilled water for 2 h and weighting again. Water absorption after firing at 1250 °C was calculated as: $WA = (M_{fs} - M_{fd}) \cdot 100/M_{fd}$, where M_{fs} —mass of fired water saturated beam and M_{fd} —mass of fired dry beam. Bending strength after firing at 1250 °C, R_{bf} (MPa), was established as follows: $R_{bf} = 3 \cdot F_f \cdot L_f / 2 \cdot b_f \cdot h_f$, where: F_f —breaking load for fired sample (in N), L_f —distance between supports for fired sample (mm), b_f —fired sample width (mm) and h_f —fired sample thickness (mm). The surface activity of clay minerals was evaluated by the methylene blue index (MBI) (Avena et al., 2001), measured according to ASTM C 837 on unbuffered dispersions (original pH, experimental uncertainty 0.5 meq/100 g). The color of the bodies fired at 1250 °C were measured and classified in terms of L^* , a^* and b^* parameters from the CIE Lab system, using the X-Rite SP62 spectrophotometer.

In the final part of the study, ceramic batches were prepared. Each of them contained 35% of one of 13 clays. Other components were the same in every batch, i.e.: feldspar–quartz from the Polish company Strzeblowski KSM (25%), feldspar–quartz from the Czech company KMK Granit (25%), washed kaolin (10%), and quartz sand (5%) from

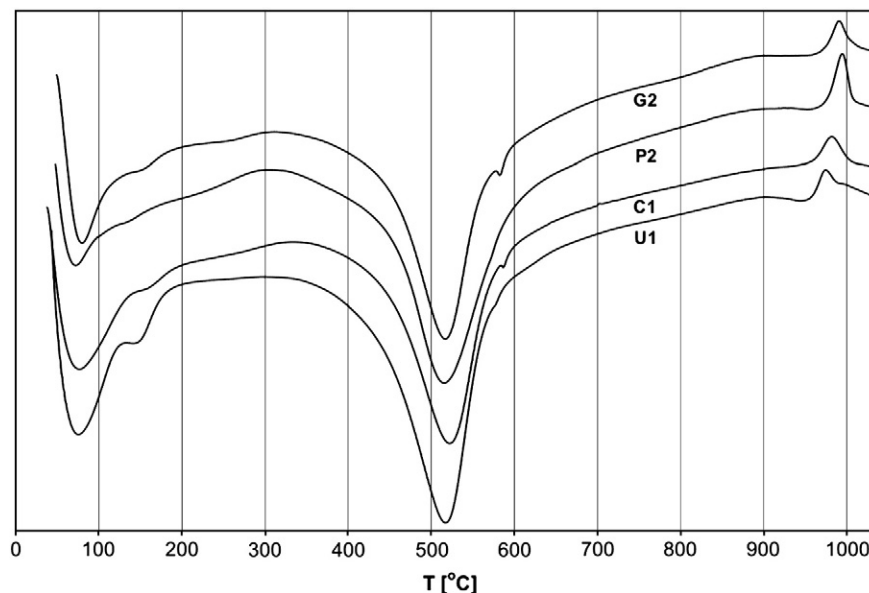


Fig. 2. DTA curves of clays.

the Polish company KPK Grudzeń Las. They are typical for such ceramic batches used in the Polish porcelain stoneware tile plants (Galos, 2010). All the batches were ground to grain size <0.045 mm, dried at 105–110 °C for 3 h, milled in impact mill with 6% addition of water, pressed at 40 MPa, dried at 150 °C for 1 h, and finally fired in industrial roll furnace at 1200 °C (total firing cycle: 42 min). The following physical parameters of the tiles were measured: water absorption according to the EN ISO 10545-3 standard, flexural strength according to the EN ISO 10545-4 standard, abrasion resistance according to the EN ISO 10545-6 standard.

3. Results

3.1. Mineralogical composition

Three main components of all studied clays were: kaolinite, illite and quartz. The common accessory minerals in almost all clays were: titanium oxide as anatase and rutile, and unweathered albite. Only in the Ukrainian clays, mixed-layered illite–smectite is another important component (Fig. 1).

The crystallinity of kaolinite in the clays was very variable. It can be estimated from X-ray analysis by the Stoch index (Stoch, 1974), the Hinckley index (Hinckley, 1963) or the Aparicio–Galan–Ferrell index (Aparicio et al., 2006). In this study, the Stoch index was recognized as the most adequate, because of low intensity of the X-ray 110 and 111 kaolinite reflections of the Ukrainian and German clays. The crystallinity of illite was estimated with by the Kübler index, defined as width at half maximum of the 002 illite reflection, expressed by 2θ (Guggenheim et al., 2002; Kübler, 1966).

Kaolinite in clays from SW Poland (P1 and P2) was well ordered. The Stoch index was <1.0 , while the Hinckley index was high (ca. 1.5). Kaolinite in clays from central Poland (P3 and P4), Saxonian clays (G1, G2), and the Czech grade (C1) was moderately ordered. In Ukrainian clays, kaolinite was represented by *fire clay kaolinite*, with the Stoch index >3.0 and the Hinckley index <0.2 (Table 2).

The high crystallinity of illite in P1 and P2 clays was confirmed by sharp 002 and 004 reflections and a low Kübler index of 0.12–0.14°. Of similar crystallinity were the illites in P4, G1, G2 and C1. An illite of lower crystallinity was found in P3 (Table 2). Two main illite reflections in the Ukrainian clays were broadened and weak, with Kübler index between 0.24° and 0.32°.

Presence of smectite or mixed-layered illite/smectite was not confirmed by X-ray analysis in the Polish, German and Czech clays, even after glycolation and heating. The specific feature of Ukrainian clays was the diverse quantity of highly disordered I/S minerals indicated by the pronounced background of the 001 reflections and disappearance of this reflection after glycolation and after heating to 560 °C. Simultaneously, the intensity of the 10 Å reflection, common for illite and I/S minerals (Moore and Reynolds 1989; Rösler and Starke, 1967) was observed. The 10 Å reflection was weak for U1 and U7, indicating low contents of I/S minerals.

The DTA curves revealed illite dehydration, illite and kaolinite dehydroxylation, and an exothermic effect at ca. 980 °C (transition into metakaolinite) for all studied clays (Fig. 2). Smectite dehydration (140–170 °C) was observed for almost all clays except for P2 and C1. This effect was particularly strong for the Ukrainian clays. The endothermic quartz transition at 573 °C was observed for the German and Czech clays, and weakly for the Polish clays, except for P3.

Analysis of DTA/TG curves allowed to estimate the contents of the main clay minerals. It was assumed that the theoretical mass loss

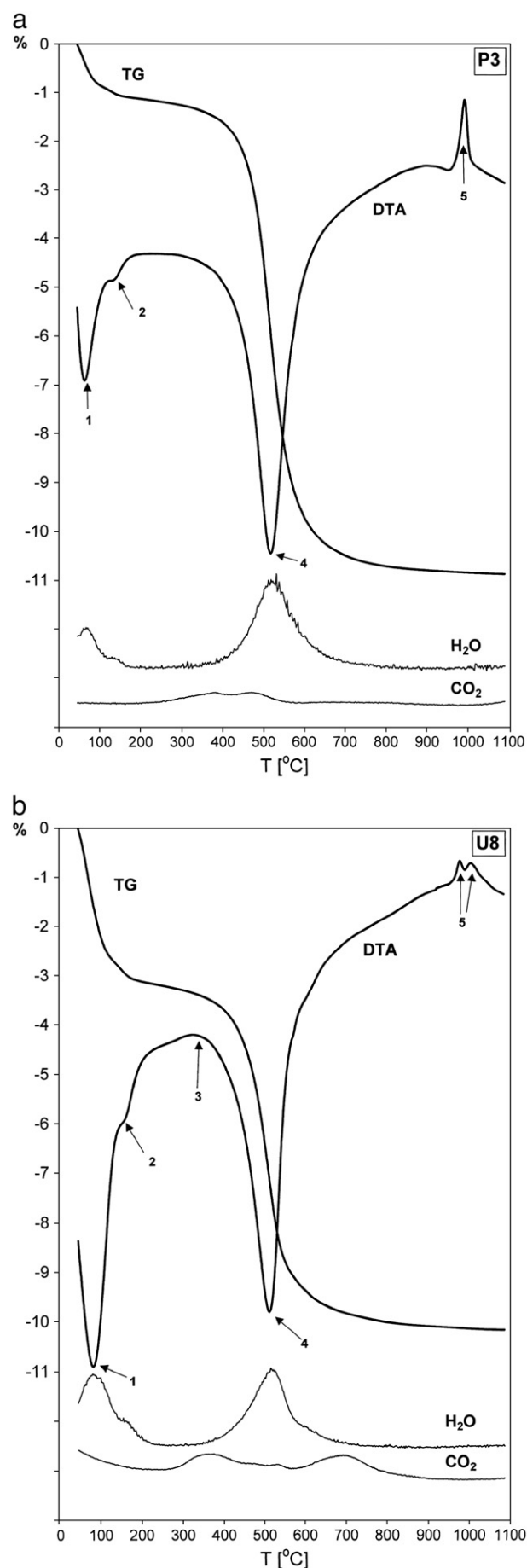


Fig. 3. DTA, TG and EGA analyses (H_2O , CO_2) of selected clays. Symbols: a—P3, b—U8; 1—endothermic effect of illite dehydration, 2—endothermic effect of smectite dehydration, 3—exothermic decomposition of organic matter, 4—endothermic effect of kaolinite and illite dehydroxylation, 5—exothermic effect of mullite-like phase formation.

resulting from illite dehydration amounted to 5%, smectite dehydration 14%, illite dehydroxylation 5% and kaolinite dehydroxylation—12% (Kościówko and Wyrwicki (1996)). For Ukrainian clays it was assumed that the mass loss due to smectite dehydration was partly caused by I/S mineral dehydration. Therefore, in this case the total content of illite and I/S mineral was estimated (Table 3). It varied between 40% and 75%, with the exception for U1 and U7 (Table 3). The other clays showed higher illite contents (even up to 20%). Marginal amounts of smectite were found in P3 and C1.

The kaolinite content exceeded 45% for all the Polish clays (68% in P3) and the Czech clay. The kaolinite content in the German clays was around 30%, while for the Ukrainian clays 17–38% (Table 3).

The shape of kaolinite dehydroxylation effect on the DTA curve also allowed assessing the level of kaolinite crystallinity using the Kissinger index (Kissinger, 1957). It was the highest for P1, P2 and P4 (Table 2), confirming the highest level of kaolinite crystallinity among the studied clays. The Kissinger index of the Ukrainian, German and Czech clays was <0.8 indicating the low level of kaolinite crystallinity.

The presence of the highly disordered variety of kaolinite, especially in the Ukrainian clays, was also confirmed by some additional observations (Kakali et al., 2001), i.e.:

- The temperature of kaolinite dehydroxylation maximum was the highest for clays from SW Poland (P1, P2); for Ukrainian clays it is lower by 10–15 °C; and

- The shape of the kaolinite exothermic effect at ca. 980–990 °C was the most sharp for P1 and P2, moderate for other Polish, German and Czech clays, and the most weak, very broadened and usually double for the majority of Ukrainian clays.

EGA analysis, performed in parallel to DTA/TG analysis, disclosed the presence of organic matter. The shape of the DTA curve in the range of 200–400 °C suggested the occurrence of organic matter especially in case of P1, P2, P4, G1, G2, and C1, showing a broad exothermic effect due to decomposition of the organic matter. The comparison of DTA and EGA curves showed that some organic matter was present in all the Ukrainian clays, and was decomposed in two stages: at 300–400 °C and 600–800 °C. The highest CO₂ emission in EGA analysis was found for U1, U6, U8, U10 and U11, the lowest one for P3 (Fig. 3).

The infrared spectra confirmed the high diversity of the clays. For clay minerals, the most important bands were related to the stretching vibrations of O–H groups. For kaolinite, 3620 cm⁻¹ band of inner hydroxyl groups and sharp 3700 cm⁻¹ band of in-phase

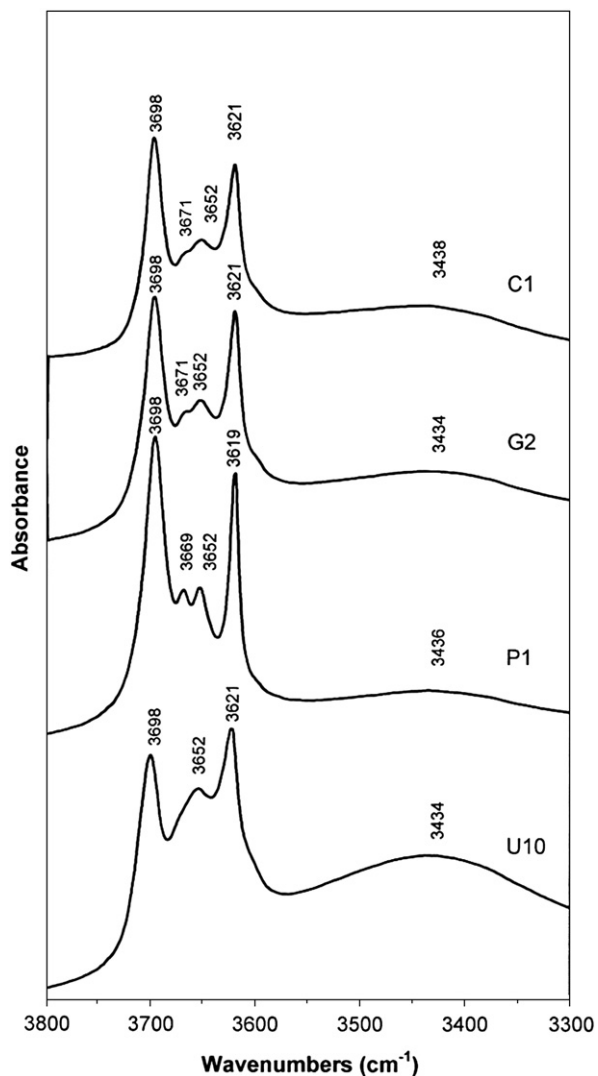


Fig. 4. MIR spectra of some clays.

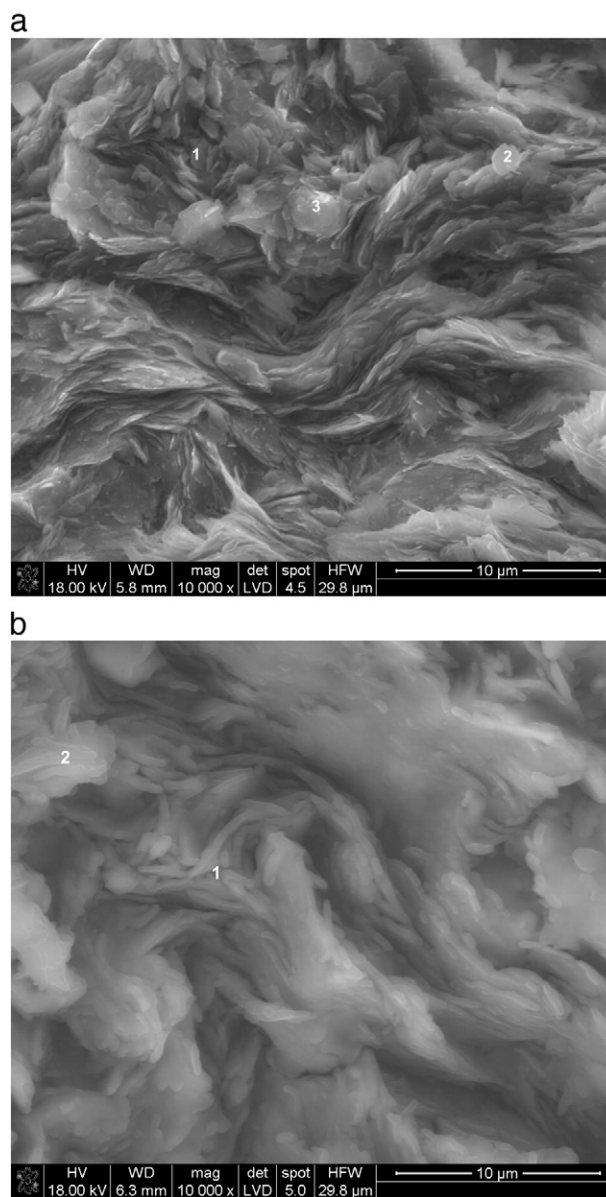


Fig. 5. a. Banded large plates of kaolinite, smaller plates of illite (1, 2), sometimes rounded grains of quartz (3) in P2 clay. b. Aggregates of small illite crystals, probably together with mixed-layered illite/smectite particles (1, 2) in U2.

vibrations of surface hydroxyl groups, were the strongest. Two other bands at 3653 cm^{-1} and 3669 cm^{-1} related to out-of-plane vibrations were characteristic of well-ordered kaolinite (Balan et al., 2001; Farmer, 2000). Disordered kaolinite showed only one of these bands at 3653 cm^{-1} (Farmer, 1974; Galan et al., 1996). Such spectra were observed for all the Ukrainian clays, while P3, P4, G1, G2 and C1 clays showed only small bands at $3668\text{--}3671\text{ cm}^{-1}$. The 3669 cm^{-1} band was clearly visible only for P1 and P2 (Fig. 4).

Montmorillonite and other dioctahedral smectites (or mixed-layered minerals containing smectite layers), showed a strong $3620\text{--}3630\text{ cm}^{-1}$ band, a weak broadened band with maximum at 3435 cm^{-1} , and a very weak broadened band with 1630 cm^{-1} maximum. Unfortunately, $3620\text{--}3630\text{ cm}^{-1}$ band coincided with the strong 3620 cm^{-1} kaolinite band, making the identification of dioctahedral difficult (Madejova 2003). However, the presence of dioctahedral smectites can be deduced by comparing the intensity of the 3620 cm^{-1} and 3700 cm^{-1} kaolinite bands, the asymmetric shape of the 3620 cm^{-1} band and the presence of the wide 3435 cm^{-1} band. Dioctahedral smectites (or mixed-layered minerals with smectite layers) were found in all the Ukrainian clays, and probably also in G1, G2, C1 and P3.

Muscovite and illite group showed strong 3635 cm^{-1} band coinciding with the strong 3620 cm^{-1} kaolinite and $3620\text{--}3630\text{ cm}^{-1}$ smectite band. Their weak broadened band with ca. 3400 cm^{-1} maximum coincided with wide 3435 cm^{-1} smectite band (Farmer, 1974). Thus, the presence of illite in the studied clays could not be confirmed.

Various contents of quartz was illustrated by intensity differences of ca. 1164 , 800 and 780 cm^{-1} bands (Farmer, 1974), especially well seen for P1, P2, G1, G2 and C1.

SEM/EDS analysis proved that the studied Polish clays contained coarse ($2\text{--}10\text{ }\mu\text{m}$), up to $0.2\text{ }\mu\text{m}$ thick kaolinite particles (Fig. 5). Sometimes they form booklet aggregates with thickness up to $15\text{ }\mu\text{m}$. Smaller particles of kaolinite occurred occasionally. Illite mostly formed small plates of $0.1\text{--}0.5\text{ }\mu\text{m}$ size, rarely aggregates of such plates (up to $10\text{ }\mu\text{m}$). The quartz grains were usually small ($1\text{--}5\text{ }\mu\text{m}$). Large, unweathered feldspar grains were occasionally found. In the Ukrainian clays the kaolinite particles were much smaller ($0.5\text{--}1\text{ }\mu\text{m}$), rarely forming larger aggregates. Illite and I/S mineral particles were $<0.1\text{--}0.2\text{ }\mu\text{m}$, but often formed larger aggregates (Fig. 5). Quartz grains were of $1\text{--}10\text{ }\mu\text{m}$ size. In the German and Czech clays, kaolinite

particles had $0.5\text{--}3\text{ }\mu\text{m}$, while illite particles were of $0.2\text{--}0.5\text{ }\mu\text{m}$. Both kaolinite and illite often formed larger aggregates. Predominant size of the quartz grains was $5\text{--}10\text{ }\mu\text{m}$, in German clays sometimes even up to $30\text{ }\mu\text{m}$.

3.2. Grain size

The clays exhibited a large variation of grain sizes. The Ukrainian clays from Donetsk area are very fine-grained clays, with median diameter $<0.5\text{ }\mu\text{m}$ (Fig. 6) and with $>80\%$ of grains $<2\text{ }\mu\text{m}$. The content of grains $<0.2\text{ }\mu\text{m}$ in these clays is one of the largest of all clays in the world (Kielski et al., 2005), exceeding 40% for U8, U10 and U11. It is correlated with large specific BET surface area values of $34\text{--}50\text{ m}^2/\text{g}$ (Table 4). The BET surface area of P3, P4, G2 and C1 was $26\text{--}31\text{ m}^2/\text{g}$ due to the content of fine-grained clay minerals. P1, P2 and G1 were coarse-grained, with median diameter around $2\text{--}3\text{ }\mu\text{m}$, a specific BET surface area $<20\text{ m}^2/\text{g}$ and with ca. 50% (or less) of grains $<2\text{ }\mu\text{m}$.

3.3. Chemical composition

The Al_2O_3 content varied between 19 mass % and 31 mass %, depending on the content of clay minerals. The largest content was found for Ukrainian clays and P3. The higher SiO_2 contents in P1, P2, P4 and G1 was due to the significant quartz content. The Fe_2O_3 content did not exceed 1.2 mass % in Ukrainian, German and Polish clays, but it is much higher in C1. The TiO_2 content in Ukrainian clays and in P3 and P4 are two times higher than in P1 and P2 (Table 5). The high K_2O content in the Ukrainian clays (even 3 mass % in U7) was related to considerable illite and I/S minerals content. Enhanced contents of MgO , CaO and Na_2O in the Ukrainian clays in comparison to other studied clays also suggest the presence of smectite or I/S minerals. Organic carbon was found in the Polish clays, G1, U10 and U11 (Table 5). As the analytical error was ± 0.05 mass %, the carbon content in the other clays was <0.05 mass %.

3.4. Ceramic properties

The Ukrainian clays were very plastic (bending strength after drying: $5\text{--}9\text{ MPa}$), P1, P2 and P4 were medium plastic ($<2\text{ MPa}$) and P3, G1, G2 and C1 were plastic ($2\text{--}3\text{ MPa}$). This was, in general,

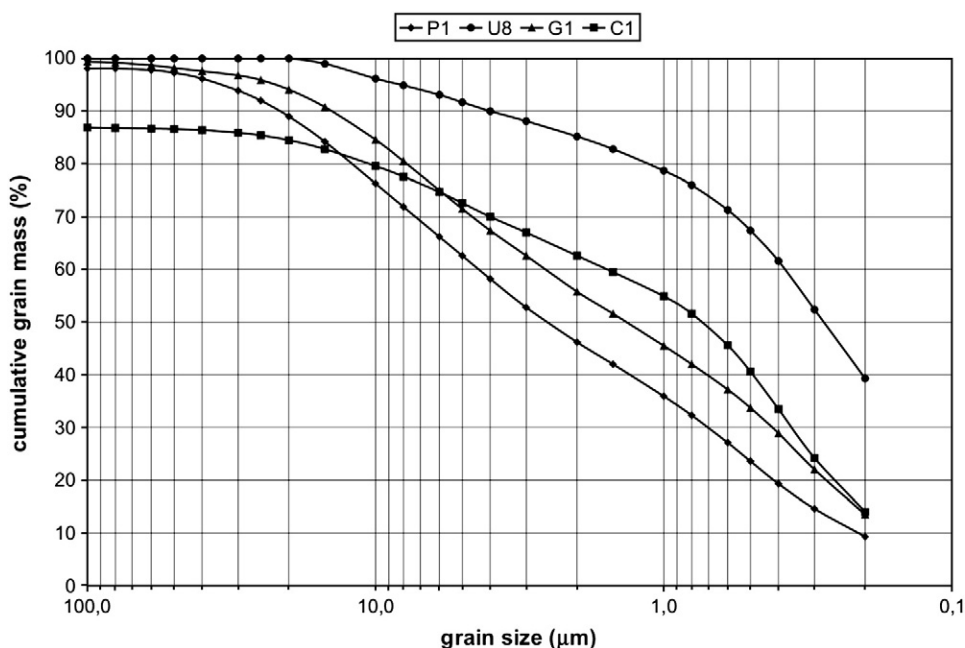


Fig. 6. Cumulative grain size distribution of some clays.

Table 4
Grain size analysis of the clays.

Clay	Median diameter (μm)	Specific BET surface area (m^2/g)	Fraction $<2 \mu\text{m}$ (%)
P1	2.54	12.3	46.3
P2	1.89	14.7	51.1
P3	1.09	28.9	63.3
P4	1.47	30.8	54.4
U1	0.48	45.7	71.3
U2	0.27	39.5	86.8
U3	0.34	39.0	66.2
U4	0.31	40.0	87.4
U5	0.42	44.0	80.5
U6	0.54	34.0	80.8
U7	0.49	36.7	78.5
U8	0.28	46.5	85.2
U9	0.36	46.6	81.1
U10	0.23	50.1	85.5
U11	0.27	49.4	80.9
G1	3.58	20.9	41.1
G2	2.36	30.0	47.9
C1	0.73	26.6	62.6

consistent with the values of methylene blue index (Table 6), which is a kind of indicator of clay's plasticity related to surface activity of clay minerals, particle size distribution and mineralogical composition (Dondi et al., 2008). The only important exception was the very high MBI value for U8 and its low value for U2 and U3 (Table 6). Ukrainian clays and the Polish P3 grade show very good sintering properties, with water absorption after firing at 1250 °C below 0.3% (Table 6). Sinterability of the other Polish clays is very weak, with water absorption values between 8 and 12% (Table 6).

Ceramic tiles, manufactured from batches containing 35% of clay exhibited different basic parameters (Table 7). It illustrates the influence of applied clay on physical properties of manufactured ceramic materials. Only for a few of these materials, made from batches containing Ukrainian clays (U2, U6, U7 and U8), the water absorption values are close to criterion of the EN 14411 standard for porcelain stoneware tiles (max. 0.5%). Other produced tiles made with the Polish, German and Czech clays, were much more porous (Table 7). The majority of the tiles met the requirements of flexural strength (min 35 MPa) and abrasion resistance (max. 175 mm³). The exceptions were tiles from P1 and P2.

Table 5
Chemical composition of the clays (mass %, content of C_{total} and C_{org} included).

Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	Na ₂ O	K ₂ O	LOI	C_{total}	Including: C_{org}
P1	62.66	22.70	0.91	0.61	0.29	0.13	0.27	1.39	9.60	0.23	0.14
P2	60.75	24.50	0.94	0.53	0.35	0.10	0.08	1.67	9.56	0.26	0.19
P3	50.04	31.01	1.07	1.51	0.46	0.22	0.22	2.16	12.24	0.13	0.13
P4	65.93	19.78	0.88	1.32	0.32	0.15	0.21	1.56	8.57	0.62	0.62
U1	57.03	26.48	0.75	1.38	0.45	0.39	0.50	2.11	11.32	n.d.	n.d.
U2	53.82	28.81	1.08	1.39	0.66	0.37	0.54	2.74	10.10	n.d.	n.d.
U3	58.70	24.38	0.79	1.44	0.54	0.25	0.60	2.75	10.86	n.d.	n.d.
U4	50.11	29.33	0.73	1.32	0.59	0.33	0.62	2.60	14.29	n.d.	n.d.
U5	53.22	28.09	1.06	1.23	0.51	0.33	0.50	2.10	11.92	n.d.	n.d.
U6	53.44	27.11	1.15	1.22	0.63	0.22	0.66	2.52	11.46	n.d.	n.d.
U7	54.81	26.94	0.81	1.38	0.61	0.25	0.65	3.01	10.29	n.d.	n.d.
U8	51.95	28.73	0.94	1.55	0.63	0.29	0.65	2.81	12.56	n.d.	n.d.
U9	52.66	26.80	0.77	1.53	0.59	0.27	0.62	2.62	12.60	n.d.	n.d.
U10	55.37	25.91	0.90	1.11	0.67	0.36	0.36	2.20	13.84	0.10	0.10
U11	55.34	24.95	1.09	1.25	0.72	0.43	0.43	2.41	13.69	0.15	0.15
G1	70.86	18.14	0.83	1.16	0.22	0.12	0.20	2.06	7.03	0.13	0.08
G2	55.32	25.76	1.15	1.72	0.28	0.29	0.22	1.55	13.04	n.d.	n.d.
C1	57.81	26.43	1.83	0.92	0.31	0.23	0.17	2.22	10.48	n.d.	n.d.
Experimental error	± 0.01	± 0.01	± 0.01	± 0.01	± 0.01	± 0.01	± 0.01	± 0.01	± 0.01	± 0.05	± 0.05

n.d.—not determined.

Table 6
Comparison of technological properties of the clays.

Clay	Make-up water ^a (%)	Drying shrinkage ^a (%)	Firing shrinkage ^b (%)	Water absorption after firing ^b (%)	Bending strength after drying ^a (MPa)	Bending strength after firing ^b (MPa)	Methylene blue index MBI (meq/100 g)	Color parameters after firing ^b :		
								L (%)	a	b
P1	23.0 ± 0.2	2.9 ± 0.3	4.8 ± 0.3	12.64 ± 1.12	1.7 ± 0.2	17.6 ± 1.2	2.5	85.9	1.2	13.5
P2	26.1 ± 0.1	2.2 ± 0.6	6.7 ± 0.6	11.72 ± 0.76	1.9 ± 0.2	26.6 ± 1.4	2.8	86.3	1.2	12.6
P3	23.3 ± 0.1	6.3 ± 0.3	8.5 ± 0.3	0.20 ± 0.02	2.8 ± 0.2	52.5 ± 0.8	5.6	79.1	2.2	18.3
P4	22.7 ± 0.5	6.5 ± 0.7	4.3 ± 0.6	10.87 ± 0.67	1.3 ± 0.2	22.7 ± 0.7	3.5	79.8	1.9	12.6
U1	30.8 ± 0.2	10.4 ± 0.3	8.8 ± 0.4	0.29 ± 0.06	5.2 ± 0.4	47.6 ± 0.5	10.0	83.3	1.2	13.0
U2	28.4 ± 0.1	9.8 ± 0.5	8.6 ± 0.6	0.21 ± 0.03	7.0 ± 0.8	49.4 ± 0.5	5.0	78.1	1.8	13.7
U3	26.2 ± 0.3	7.3 ± 0.4	6.7 ± 0.5	0.16 ± 0.05	7.3 ± 0.6	38.9 ± 2.2	6.2	71.1	1.2	13.0
U4	29.4 ± 0.2	9.2 ± 0.9	6.6 ± 0.7	0.27 ± 0.08	9.1 ± 0.8	37.1 ± 2.4	15.6	74.3	0.6	10.1
U5	27.5 ± 0.3	10.0 ± 0.9	7.2 ± 0.5	0.16 ± 0.05	8.1 ± 0.2	50.1 ± 1.5	17.0	79.9	1.1	15.3
U6	30.3 ± 0.1	9.2 ± 0.2	6.3 ± 0.4	0.22 ± 0.04	8.7 ± 0.3	50.4 ± 0.8	15.6	77.4	1.9	13.5
U7	29.6 ± 0.1	10.1 ± 0.3	8.7 ± 0.5	0.25 ± 0.04	8.0 ± 0.4	48.5 ± 0.5	15.0	78.0	1.5	13.1
U8	28.1 ± 0.1	9.7 ± 0.2	6.4 ± 0.3	0.22 ± 0.04	8.4 ± 0.7	50.2 ± 0.5	44.2	76.7	2.0	13.4
U9	27.9 ± 0.5	10.0 ± 1.5	4.7 ± 0.9	0.68 ± 0.11	8.1 ± 0.7	23.9 ± 1.6	21.9	74.6	1.4	14.1
U10	29.8 ± 0.1	8.8 ± 0.6	7.1 ± 0.6	0.28 ± 0.05	7.7 ± 0.5	51.8 ± 0.7	22.2	74.7	2.1	13.1
U11	31.2 ± 0.2	9.7 ± 1.3	6.4 ± 0.5	0.18 ± 0.04	8.4 ± 0.6	29.0 ± 0.8	27.2	72.5	0.5	11.1
G1	22.4 ± 0.3	6.5 ± 0.3	3.6 ± 0.2	5.59 ± 0.25	2.5 ± 0.2	21.8 ± 1.2	6.2	79.0	0.4	8.6
G2	21.4 ± 0.2	7.1 ± 0.4	6.5 ± 0.4	3.15 ± 0.29	2.2 ± 0.1	33.9 ± 0.4	11.3	71.4	2.8	15.8
C1	20.4 ± 0.6	5.5 ± 0.4	7.4 ± 0.3	2.95 ± 0.28	2.2 ± 0.3	17.7 ± 0.5	4.7	80.8	4.0	35.1

^a At 110 °C.

^b At 1250 °C.

Table 7
Basic technological parameters of ceramic tiles obtained by firing at 1200 °C.

Clay	P1	P2	P3	U1	U2	U5	U6	U7	U8	U10	G1	G2	C1
Water absorption (%)	3.52	3.73	2.83	1.14	0.53	1.12	0.29	0.50	0.53	0.73	2.11	2.90	2.25
Flexural strength (MPa)	47.1	67.0	63.9	45.9	61.5	49.0	77.2	71.8	48.8	63.4	39.8	56.4	68.3
Abrasion resistance (mm ³)	184	205	158	126	117	167	116	116	117	156	131	169	147

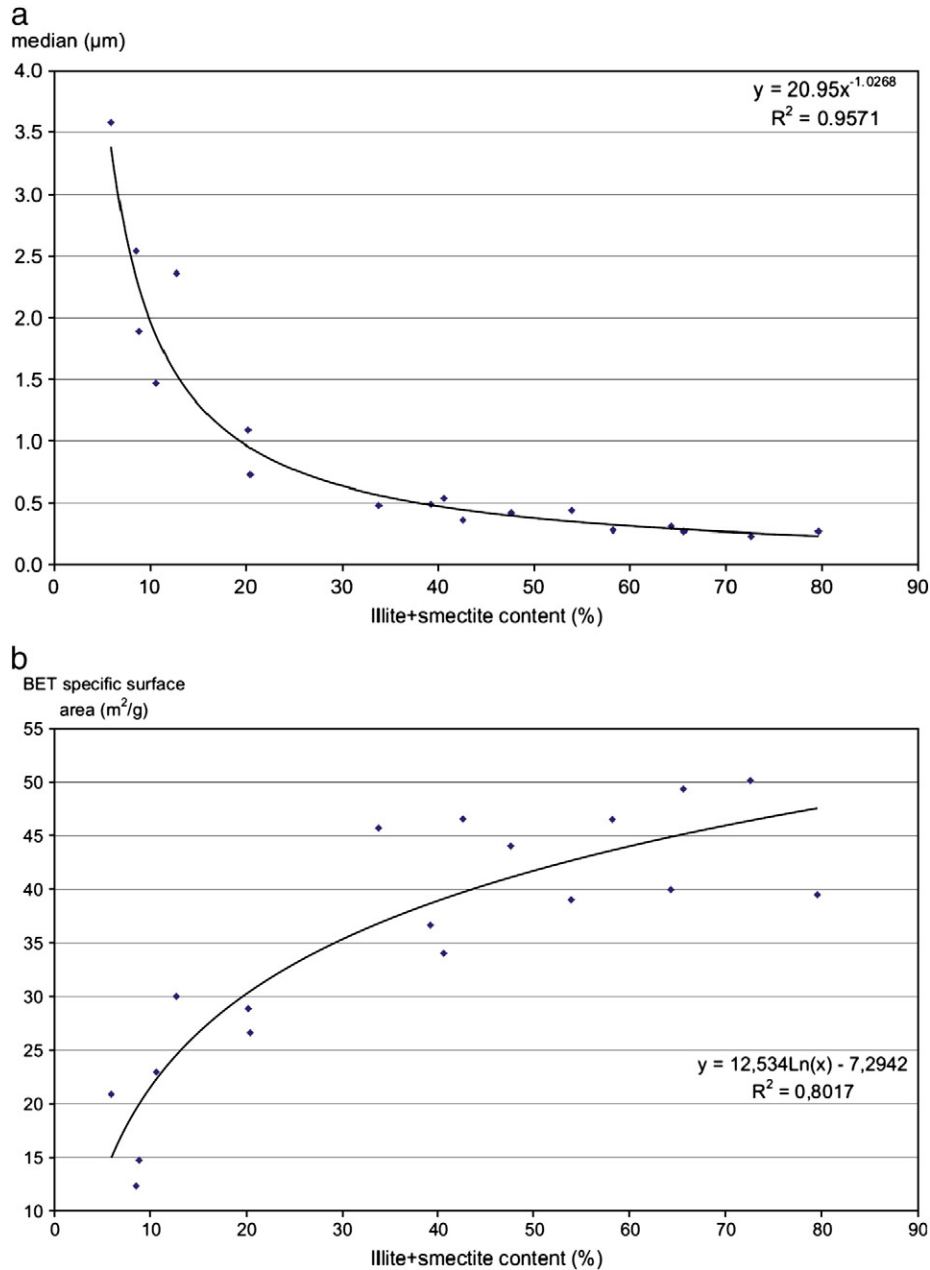


Fig. 7. Correlation between total quantity of illite, smectite and mixed-layered illite/smectite and: a) grain size median diameter, b) BET specific surface area.

4. Discussion

Illite, smectites and mixed-layered illite/smectite were the most fine-grained mineral components of the studied ball clays. A strong correlation was found between the total content of these minerals and: (i) grain median diameter, and (ii) the specific BET surface area (Fig. 7). Especially for the first relation, a very high coefficient of determination $R^2 = 0.9571$ ¹

was found (correlation expressed by an exponential function). For the second relation this coefficient was $R^2 = 0.8017$ (correlation expressed by a logarithmic function).

Bending strength after drying is one of the common measures of plasticity. Its relation to granulometry and mineral composition was also confirmed in the case of the 18 studied clays. There was very good correlation between the bending strength after drying and: (i) the total illite and smectite content (expressed by a logarithmic function), and (ii) the content of <2 µm grains (expressed by an exponential function). Their coefficients of determination R^2 exceeded 0.8 (Fig. 8).

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

The behavior of ball clay during firing depended on the type and content of clay minerals, especially illite and I/S minerals, but also grain size distribution and specific surface area (Ferrari and Gualtieri, 2006). Decomposition of illite, smectite and I/S minerals at lower temperatures than in the case of kaolinite also strongly influences sinterability of the formed ceramic material (Liebermann and Schulle, 1999), expressed e.g. by the value of water absorption after firing. Kaolinite and illite crystallinity also affected the sintering process, as phase transitions of well-ordered kaolinite and illite start at higher temperatures than in the case of the disordered varieties (Aras, 2004). There was found a good correlation between water absorption after firing at 1250 °C and: (i) total illite and smectite content (expressed by an exponential function), and (ii) the content of <2 µm grains (expressed by an exponential function). In both cases, coefficients of determination R^2 were close to 0.8 (Fig. 9). However, the correlation between the water absorption after firing at 1250 °C, and both the BET specific surface and grain median diameter, was found worse, with the coefficient of determination R^2 around 65%.

Water absorption of tiles obtained from batches containing 35% of clays was very variable. It distinctly depended on the type of the clay used. There was a good correlation between the content of <2 µm grains and water absorption of the tiles (expressed by a linear function), with $R^2=0.8134$ (Fig. 10a). The relationship between water absorption of the tiles, and the bending strength of the clays after drying at 110 °C was strictly related to quantity and type of clay minerals in the clays, as well as to its grain size distribution (Dondi et al., 2003). The correlation was good (Fig. 10b), with $R^2=0.8969$ (expressed by a logarithmic function).

5. Conclusions

Intense development of porcelain stoneware tile production in Poland increased demand for high quality raw materials. Plastic ball clays are components for porcelain stoneware tile production having the largest qualitative variability. The domestic sources of ball

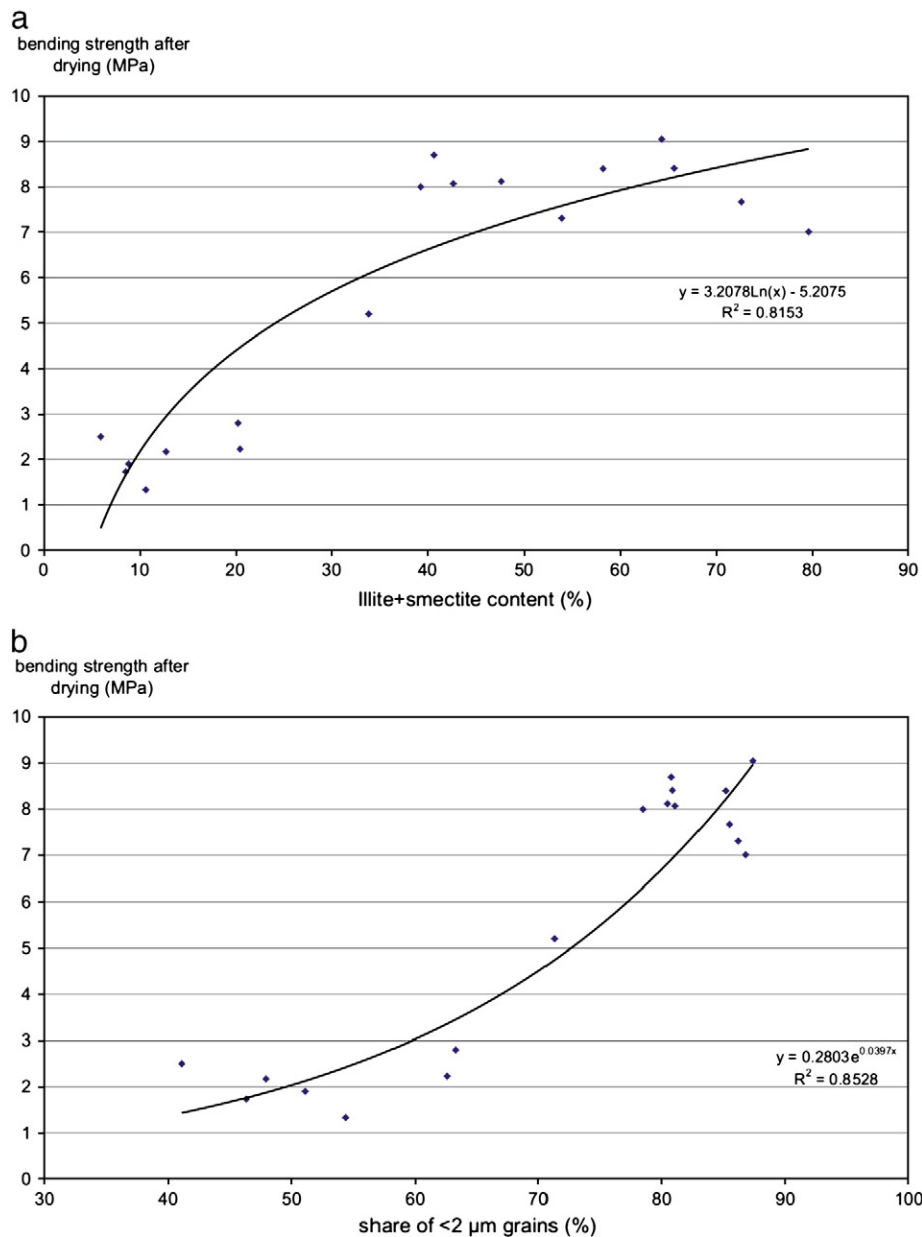


Fig. 8. Correlation between bending strength of the clays after drying and: a) total quantity of illite, smectite and mixed-layered illite/smectite, b) content of grains <2 µm.

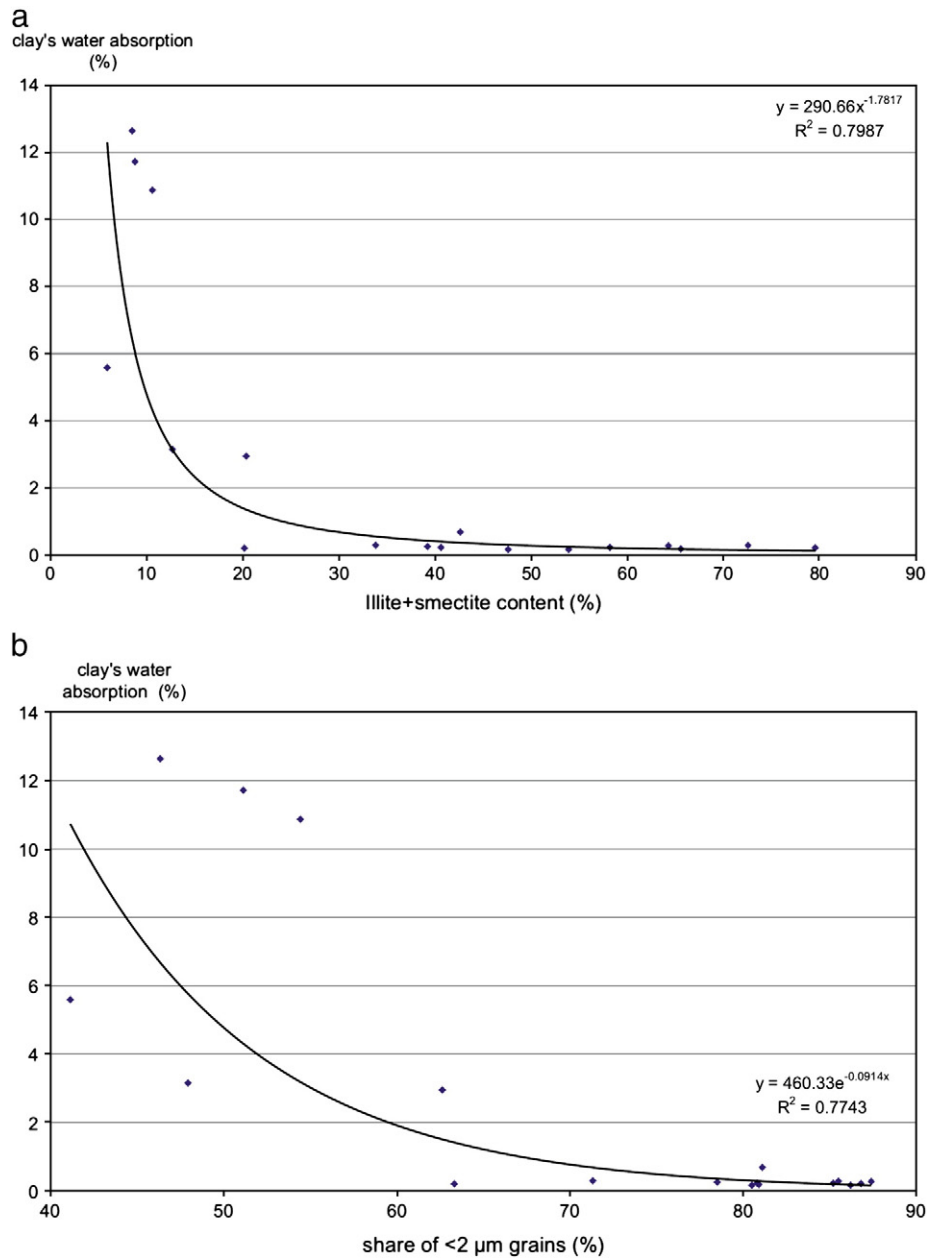


Fig. 9. Correlation between water absorption of the clays after firing at 1250 °C and: a) total quantity of illite, smectite and mixed-layered illite/smectite, b) content of grains <2 μm.

clays in Poland are scarce, so demand for them was met by imports of appropriate clays, mainly from Ukraine and Eastern Germany.

White-firing plastic ball clays from a few producing regions in eastern and central Europe (southwestern Poland, central Poland, eastern Ukraine, eastern Germany and western part of the Czech Republic) demonstrated the large variability of mineral, grain and chemical composition as well as of ceramic properties.

Studies on composition and ceramic properties of numerous clays from central and eastern Europe prove that only Ukrainian grades were optimal for porcelain stoneware tiles production. They contained mixed-layered illite/smectite minerals and low-ordered fine-grained varieties of kaolinite and illite, relatively low contents of Fe₂O₃ and TiO₂, and usually low contents of organic carbon. As a consequence, they were characterized by high plasticity, excellent sintering properties and high whiteness after firing. Application of the Ukrainian ball clays in the batches for porcelain stoneware tile manufacture allowed obtaining ceramic materials, which met the

requirements of the EN 14411 standard. Clays from southwestern Poland and also from Eastern Germany, showed very high whiteness after firing. Due to the presence of well-ordered coarse-grained varieties of kaolinite and illite, they were medium plastic. Their sinterability was weak or very weak. Clays from central Poland and one Czech clay showed intermediate properties. Relatively high contents of coloring oxides were their main disadvantages.

Relations between illite + smectite content and grain composition and specific BET surface area were confirmed for 18 clays. Relationships between the bending strength after drying, and its granulometry and mineralogical composition, were reported.

Increasing contents of illite and I/S minerals, as well as low crystallinity of kaolinite and illite, strongly influenced the process of sintering, as the phase transitions began at relatively low temperatures. Due to such mineralogical and grain composition, plastic ball clays were also highly reactive with other components of ceramic batches for porcelain stoneware tile production.

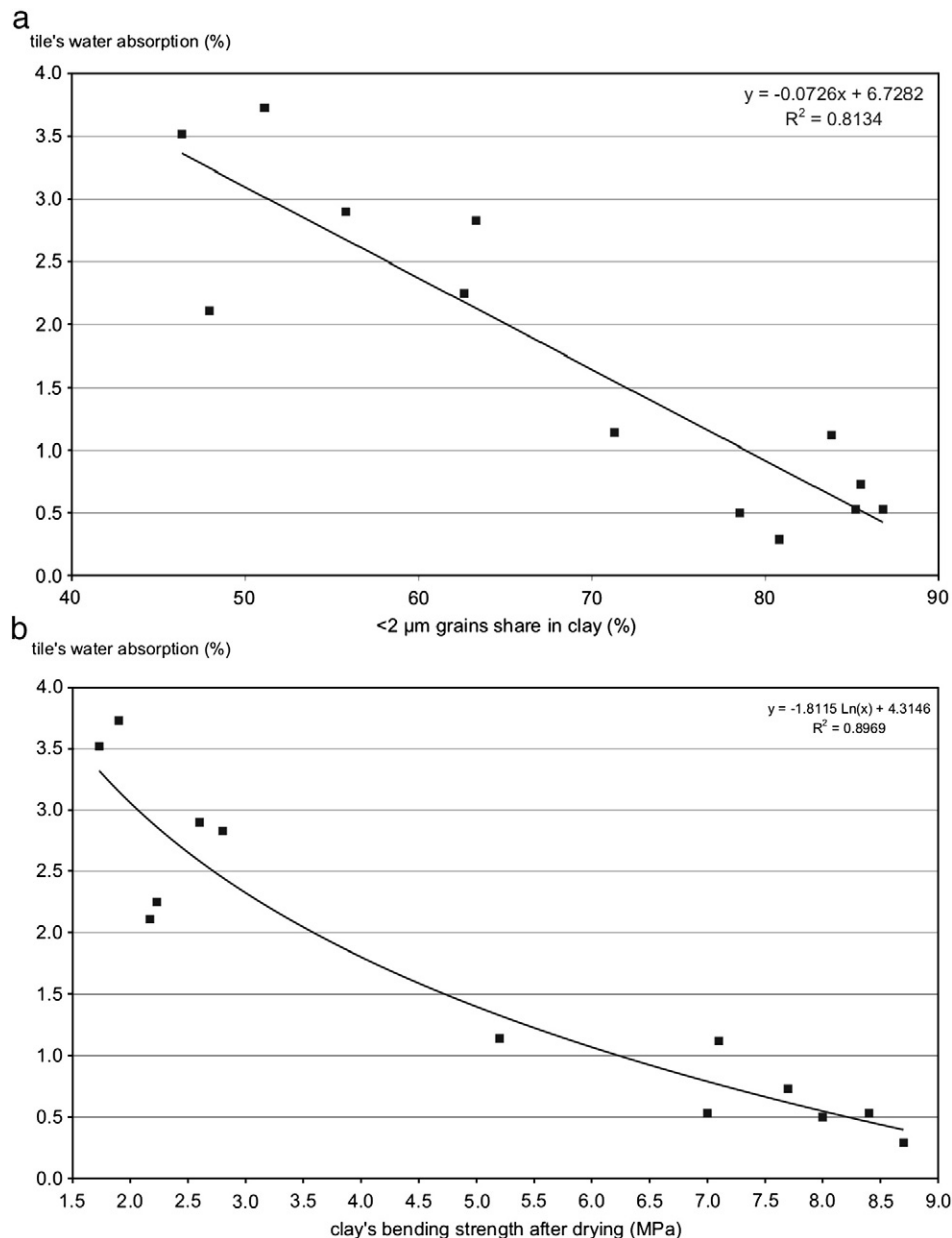


Fig. 10. Correlation between water absorption of the tile and: a) content of grains <2 μm in applied clay, b) bending strength after drying of the clay.

Due to their composition and ceramic properties, the Ukrainian clays from the Donetsk region should be the main type of ball clay used. Other clays may be utilized only as supplementary components.

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