THE EFFECT OF SHAPING AND FIRING TECHNOLOGY ON THE PROPERTIES OF CERAMIC TILES BASED ON TWO DIFFERENT KAOLINIC CLAYS

VPLIV TEHNOLOGIJE OBLIKOVANJA IN ŽGANJA DVEH RAZLIČNIH KAOLINSKIH GLIN NA LASTNOSTI KERAMIČNIH PLOŠČIC

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Two types of different kaolinic clays currently used in a Czech refractory and the ceramic-tile industry in particular, with different ratios between the main non-plastic (quartz) and the main plastic components (kaolinite), were tested for their applicability in the production of ceramic bodies by dry pressing and extruding from a plastic body. Depending on different firing cycles (fast and slow firing processes) at 1090–1170 °C, the opportunities for using both clays for dry pressing and moulding from a plastic body were documented. Fired bodies made from a plastic body have a lower porosity than dry-pressed bodies after the utilization of the same firing cycle. Plastic moulding is not a very suitable technology for fast firing due to the fact that the test samples are more inclined to bloating during the fast-firing process. According to the theoretical models using the pore-size distribution, dry-pressed bodies have a higher probability of frost resistance than the moulded bodies.

Keywords: ceramic body, dry pressing, plastic moulding, pore-size distribution, frost resistance

Preizkušena je bila uporabnost dveh različnih kaolinskih glin z različnim razmerjem glavne neplastične (kremen) in glavne plastične komponente (kaolin), ki se ju sedaj uporablja v češki industriji ognjevzdržnih materialov in keramičnih ploščic. Preskušena je bila njihova uporabnost za proizvodnjo keramičnih teles s suhim stiskanjem in ekstrudiranjem. Dokumentirane so možnosti uporabe obeh vrst glin pri različnih ciklih žganja (hiter in počasen proces žganja) pri 1090–1170 °C za suho stiskanje in oblikovanje v orodjih plastičnih teles. Žgana telesa, izdelana iz plastičnih teles, imajo manjšo poroznost v primerjavi s suho stiskanimi telesi po enakem ciklu žganja. Stiskanje v orodjih ni primerna tehnologija za hitro žganje zaradi dejstva, da so preizkusni vzorci bolj nagnjeni k napihovanju med procesom hitrega žganja. Suho stisnjena telesa imajo, skladno z modelom, ki temelji na razporeditvi velikosti por, večjo verjetnost za odpornost proti zmrzovanju v primerjavi s telesi, stisnjenimi v orodju.

Ključne besede: keramično telo, suho stiskanje, stiskanje v orodju, razporeditev velikosti por, odpornost proti zmrzali

1 INTRODUCTION

There are several clay types for ceramic production, the selection of which, for a specific ceramic application, is associated with the proper evaluation of, among others, sinterability, i.e., the dependence between the firing temperature and the physical and mechanical properties of a body (given mainly by the porosity thereof). In a simplified way, the basic types of ceramic clay are clearly divided into three basic categories – porous, refractory and stoneware – according to Czech standard no. 72 1330.

Kaolinic clays are used in ceramic technology mainly for their typically high refractoriness and possible use in raw-material mixtures designated for fast firing. In terms of the formation method, their use is entirely universal – they are used in the mixtures for dry pressing, plastic moulding, as well as slip casting, usually due to their very good deflocculation. The ceramic-body properties are strongly dependent on the used clay type, as well as on the mineralogical composition, granulometry[1–4], and the technological conditions of the ceramic-body production, such as the shaping method[5] and the firing mode[6–10]. The ceramic-body properties can also be

significantly modified by using various clay types, mainly in terms of the calcite content[3,5].

The aim of our experimental work was to assess the impact of using two mineralogically different (in terms of the quartz content) kaolinic clays on a body microstructure based on the shaping method and firing temperature, while using an identical type of the non-plastic component in a raw-material mixture with clay. For the laboratory experiments, two types of well-sintering kaolinic clays, identified as C and QC, were selected.

2 MATERIALS AND METHODS

2.1 Raw materials and test samples

Kaolinic clay C is in the group of kaolinic-type refractory clays. It features a very good binding power (min. 70 %) and sinterability (the indicated maximum sintering temperature is 1150 °C). It is normally used for the production of refractory materials (such as fireclay), as well as the production of tiles and building stoneware. For its very good sinterability even at the firing temperatures around 1000 °C, it is currently also used as a cor-

Table 1: Chemical composition in mass fractions (w/%) of the tested clays and quartz sand
Tabela 1: Kemijska sestava v masnih deležih (w/%) preizkušenih glin in kremenovega peska

Material	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	TiO$_2$	CaO	MgO	K$_2$O	Na$_2$O	LOI
Clay C	48.60	33.50	2.64	0.00	0.76	0.12	0.30	2.19	2.18	10.80
Clay QC	72.90	20.90	1.70	0.00	1.70	0.20	0.30	2.00	0.30	5.10
Quartz sand	81.32	9.20	1.25	0.03	0.14	0.67	0.34	2.96	1.92	0.73

rection material in brickware production (e.g., in the production of clay roof tiles to reduce the water absorption of the fired body) where the body frost resistance is required.
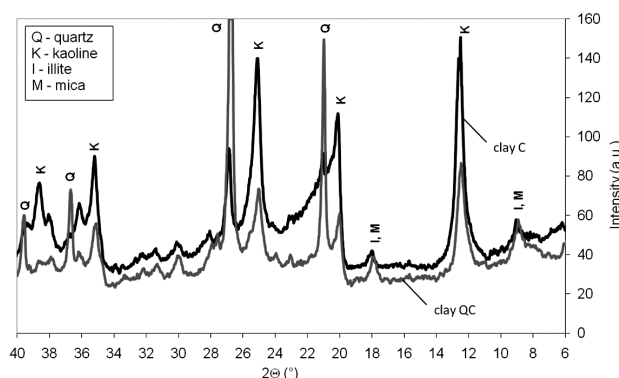
Kaolinic clay QC is stoneware clay with similar properties as clay C but with a lower plasticity due to a higher content of quartz in the C clay. The mineralogical composition (**Figure 1**) of both clays determined on the basis of the X-ray diffraction analysis clearly proves the difference between the two tested clays in terms of the contents of quartz and kaolinite. This fact is also supported by the chemical composition (**Table 1**). Both clays were supplied in a dry and ground condition directly from the supplier.

Quartz sand was used as the non-plastic material in all the test mixtures. The chemical composition of quartz sand (**Table 1**) approximates the commercially sold feldspar Z43KNa50 (marked according to the Czech standard 72 1370). The used quartz sand is normally employed as the aggregate in concrete with a fraction of 0–4 mm. For the purposes of the experimental work, the quartz sand was dry grounded in the laboratory ball mill to a fineness corresponding to the mass fraction w = 15 % residue of quartz-sand grains on a 0.063 mm sieve.

Table 2: Criteria for indirect determination of frost resistance
Tabela 2: Merila za posredno določanje odpornosti proti zmrzovanju

	T_{value}	DF	$r_{50\ \%}$/μm
Frost resistance	<0.75	>70	>1.65
Limited frost resistance	0.75–0.85	50–70	0.60–1.65
At risk from frost	>0.75	<55	<0.60

The test samples for dry pressing and moulding were prepared from the mixture in the weight ratio of 40 % clay and 60 % quartz sand. The raw-material mixtures

Figure 1: Mineralogical composition of the used clays (X-Ray diffraction)
Slika 1: Mineraloška sestava uporabljenih glin (rentgenska difrakcija)

for the production of the test samples were dry-mixed for 24 h in a homogenizer. The mixture was then moistened with 10 % and the moistened mixture was pressed through a 1 mm sieve to prepare the pressing granulate. This was then stirred in a closed vessel in the homogenizer for 12 h in order to achieve even moisture of the pressing granulate. The testing samples with a green-body size of 100 mm × 50 mm × 10 mm were uniaxially pressed at 20 MPa. The plastic body from the homogenized raw-material mixture was prepared by dosing the mixing water in such a quantity that would ensure a deformation ratio according to the Pfefferkorn method[11] allowing the plastic body to achieve a value of 0.7. The testing samples with the dimensions of 100 mm × 50 mm × 15 mm and 100 mm × 20 mm × 20 mm used for the thermal dilatometric test (**Figure 3**) were prepared by hand with the help of a metal form after a 48 h ageing of the plastic body.

Drying in air at a temperature of about 21 °C was followed by the final drying in the laboratory drier at 110 °C to achieve a constant weight. The test samples were fired in the laboratory electric furnace by:

a) fast firing with the maximum possible temperature increase and with a 10-minute soaking time at the maximum firing temperature (identified as the FAST mode),

b) standard firing according to the Czech standard 72 1082 as follows: 20–800 °C, with a heating rate of 400 °C/h; and from 800 °C to the firing temperature with a heating rate of 200 °C/h, incorporating a 1 h soaking time at the maximum firing temperature (identified as the SLOW mode).

In order to compare both firing cycles (FAST and SLOW), Bullers rings as the firing-temperature identifiers, based on the measured diameters of the rings after the firing process, were used. The equivalent firing temperature according to Bullers rings FTB (the standardized identifier of the firing temperature) was determined.

The properties of the fired test samples were tested according to:

- EN ISO 10545-3: vacuum water absorption E_2, bulk density B, apparent density T, apparent porosity P;
- EN ISO 10545-4: modulus of rupture MOR;
  Czech standard CSN 72 1073: firing shrinkage FS.

The indirect frost resistance of the fired test samples was determined via the pore-size distribution (high-pressure mercury porosimetry). The limit value for the mean pore radius $r_{50\ \%}$ (**Table 2**) was defined[12,13]. Frost resistance according to durability factor DF was defined[14,15]:

Table 3: Properties of pure clays C and QC
Tabela 3: Lastnosti čistih glin C in QC

	Clay C					Clay QC				
Mixing water (w/%)	35.7					26.5				
Drying shrinkage (%)	−5.4					−4.7				
Sintering temperature (°C)	1090					1170				
Refractoriness (°C)	1720 °C					1570 °C				
Firing temperature (°C)	1000	1100	1200	1300	1400	1000	1100	1200	1300	1400
Firing shrinkage (%)	−9.9	−17.3	−18.7	−17.2	−16.0	−9.9	−14.3	−16.3	−13.2	− 12.1
Bulk density (kg m⁻³)	1777	2388	2456	2463	2231	1886	2227	2375	1890	1645

$$DF = \frac{3.2}{PV} + 2.4P_3 \qquad (1)$$

where

PV is the pore volume (m³ g⁻¹),

P_3 is the pore volume (%) for the pores with a diameter >3 μm (% of PV).

Durability factor represents a more precise formulation of the saturation value (T_{value}) according to the German standard DIN 52251, part 3:

$$T-value = \frac{E_1}{E_2} \qquad (2)$$

where

E_1 is the cold-water absorption after a 24 h wetting of the fired test samples at the water temperature of 20 °C (w(%))

E_2 is the vacuum water absorption after the wetting of the fired test samples in a vacuum of 30 mbar (w(%)).

The saturation value of 0.75, for example, means that on freezing of the water, 25 % of the open pores are still available as the expansion area. The limit values are stated in **Table 2**.

3 RESULTS AND DISCUSSIONS

3.1 Properties of pure clays

Clay C features high refractoriness (1720 °C), while clay QC can be used in the refractory production only for less demanding applications due to its lower refractoriness (1570 °C) and body bloating (the secondary porosity formation) at a firing temperature above 1200 °C. This results in the reduced length changes made by firing, higher water absorption (**Figure 2**), and a lower bulk density of the body after the firing at 1300 °C and 1400 °C (**Table 3**). The proportion of the closed porosity increases with the firing temperature of above 1200 °C even in the case of clay C, but does not significantly affect the body water absorption. The advantages of clay QC include smaller size changes and deformations during firing and drying.

Clay C features a very low sintering temperature of 1090 °C (according to the Czech standard 72 1072 it is the contractual firing-temperature value, at which the body water absorption reaches $E = 2$ %), while the zero water absorption was determined between 1100 °C and the maximum tested firing temperature was 1400 °C.
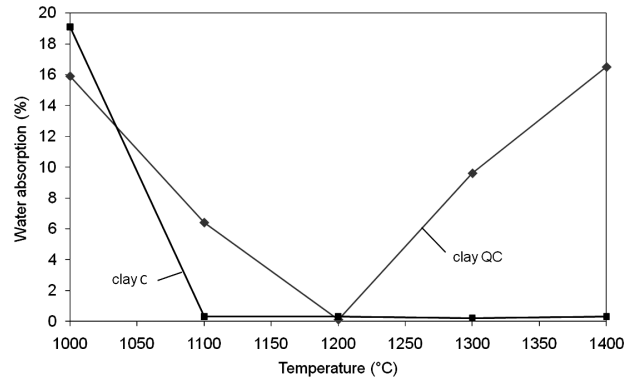

Figure 2: Sinterability of the test samples of the tested kaolinic clays
Slika 2: Sposobnosti sintranja preizkušanih kaolinitnih glin

The curve showing the water absorption and the firing-temperature dependence of clay C (**Figure 2**) reveals no significant minimum that would define the maximum sintering temperature. On the other hand, the clay-QC curve shows the maximum sintering temperature very clearly (around 1200 °C); in this case a significant body bloating occurs, causing an increase in the water absorption (and the corresponding reduction in the bulk density) when the above temperature is exceeded.

The dilatometric curves in **Figure 3** clearly indicate a much better sinterability of clay C, which results in a significantly higher shrinkage during the firing process. The body of clay C starts to shrink already at a temperature of approximately 800 °C, while clay QC
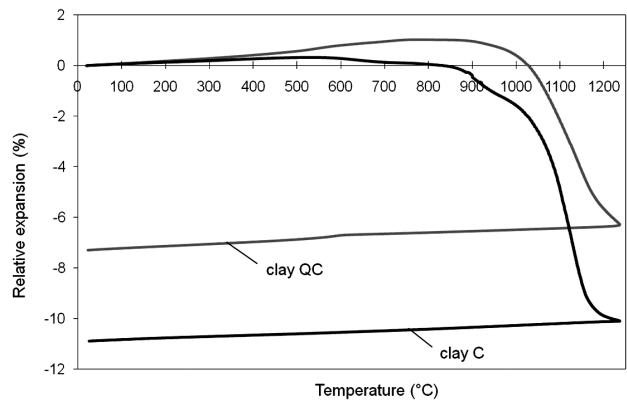

Figure 3: Relative expansion during the firing of green samples of clay C and QC (the heating rate of 3 °C/min)
Slika 3: Relativno širjenje med žganjem zelenih vzorcev gline C in QC (hitrost ogrevanja 3 °C/min)

shrinks at a higher temperature – at around 1025 °C. The dilatometric measurement (**Figure 3**) can also determine the coefficient of linear thermal expansion α of the fired bodies made of both clays, which is much higher for clay QC ($\alpha_{20-500\,°C} = 95.3 \cdot 10^{-7}\,K^{-1}$) than for clay C ($\alpha_{20-500\,°C} = 68.5 \cdot 10^{-7}\,K^{-1}$). This mainly relates to the higher content of quartz in clay QC.

3.2 Properties of the raw-material-mixture test samples

The dry-pressed and plastic moulded samples have a significantly different water content in the raw-material mixture, which is approximately twice as high in the plastic body as in the granulate for dry pressing. This also corresponds to the drying shrinkage that is almost zero in the case of the dry-pressed green samples, whereas the value of the plastic samples is around 5 % (more in the green test samples on the basis of clay C). Clay C with higher clay content requires a higher quantity of mixing water to achieve a plastic body with a deformation ratio of 0.6 according to Pfefferkorn. Dried green samples from the plastic body feature a higher bulk density than dried green test samples prepared by dry pressing.

The fired-body properties based on the used clay type, shaping method, and firing temperature are stated in **Tables 5** and **6**. We can make the following conclusions based on the stated results:

The bodies made of a plastic body feature a much lower porosity (i.e., a lower water absorption and apparent porosity, a higher bulk density) than the bodies made by dry pressing at the same temperature and in the same firing mode. The cause of this can be a higher bulk den-

sity of the plastic, dried green samples compared with the dried green samples prepared by dry pressing (**Table 4**). This fact also affected the higher modulus of the rupture of the bodies prepared by plastic moulding.

Table 4: Properties of the green samples
Tabela 4: Lastnosti zelenih vzorcev

Clay	Sample	Mixing water ($w/\%$)	Drying shrinkage (%)	Bulk density (kg m^{-3})
C	dry pressed	10.6	–0.1	1907
	moulded	23.1	–5.1	1985
QC	dry pressed	10.5	0.0	1949
	moulded	20.6	–4.7	1974

The plastic samples are very sensitive to the FAST firing. After the fast firing at 1150 °C, these bodies already featured significant deformations as a result of bloating, and therefore they were fired at lower temperatures with the SLOW-firing program.

The dry-pressed fired bodies feature a better pore-size distribution in terms of the frost resistance described on the basis of the T_{value}. The difference between the cold-water absorption E_1 and the vacuum water absorption E_2 is negligible in the case of the fired bodies moulded from a plastic body; however, the difference between the results of both water-absorption determination methods (E_1 and E_2) exceeds by as much as 50 % in the case of the dry-pressed fired bodies. The T_{value} decreases with the increasing firing temperature.

The increased firing temperature reduces the total volume of the pores in the body in all the cases.

Using the dry-pressing method, the fired bodies based on clay QC feature a higher bulk density than the

Table 5: Properties of the fired test samples based on clay C
Tabela 5: Lastnosti preizkusnih vzorcev na osnovi gline C po preizkusu žganja

Mixture	Firing cycle	FTB (°C)	FS (%)	E_1 (%)	E_2 (%)	T_{value}	B (kg m^{-3})	P (%)	T (kg m^{-3})	MOR (MPa)
				Dry pressed from granulate						
C11	FAST1120	1025	–4.1	6.8	8.6	0.79	2119	18.1	2588	18.0
C12	FAST1150	1070	–4.8	4.1	6.8	0.60	2184	14.8	2564	23.9
C13	FAST1170	1095	–5.3	2.3	5.4	0.43	2239	12.0	2544	26.6
				Moulded from a plastic body						
C21	FAST1120	1025	–5.0	3.3	3.3	1.00	2210	7.3	2383	27.1
C22	SLOW1090	1030	–5.0	3.4	3.4	1.00	2202	7.5	2382	27.9
C23	SLOW1120	1080	–5.1	2.2	2.2	1.00	2374	5.2	2505	29.8

Table 6: Properties of the fired test samples based on clay QC
Tabela 6: Lastnosti preizkusnih vzorcev na osnovi gline QC po preizkusu žganja

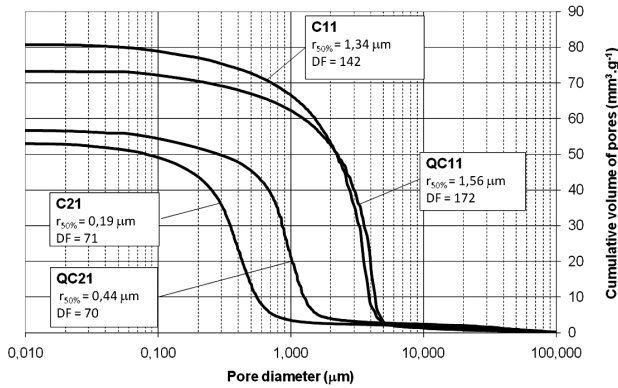| Mixture	Firing cycle	FTB (°C)	FS (%)	E_1 (%)	E_2 (%)	T_{value}	B (kg m^{-3})	P (%)	T (kg m^{-3})	MOR (MPa)
				Dry pressed from granulate						
QC11	FAST1120	1025	–3.1	5.5	7.3	0.75	2174	15.9	2584	21.0
QC12	FAST1150	1070	–4.9	1.7	4.1	0.41	2304	9.4	2544	26.4
QC13	FAST1170	1095	–5.7	0.9	3.0	0.30	2340	7.0	2516	34.6
				Moulded from a plastic body						
QC21	FAST1120	1025	–4.3	3.9	4.0	0.98	2208	8.7	2410	25.6
QC22	SLOW1090	1030	–4.2	4.2	4.3	0.98	2200	9.5	2440	24.2
QC23	SLOW1120	1080	–6.6	1.1	1.1	1.00	2366	2.7	2432	29.9

Figure 4: Pore-size distribution of fired bodies – influence of the type of the used clay and the type of shaping (after FAST firing at 1120 °C)
Slika 4: Razporeditev velikosti por žganih teles – vpliv vrste uporabljene gline in načina oblikovanja (po hitrem žganju pri 1120 °C)
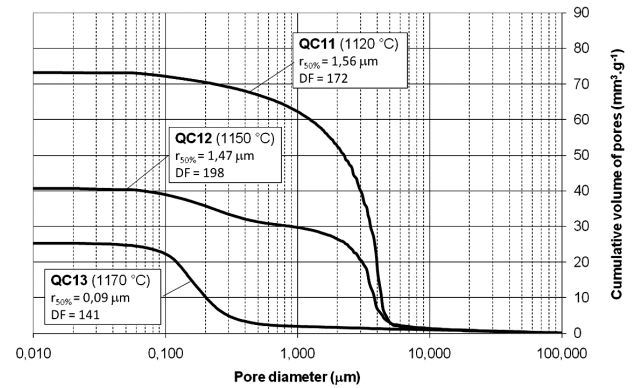

Figure 6: Pore-size distribution of fired dry-pressed bodies based on clay QC – influence of the firing temperature (the FAST cycle)
Slika 6: Razporeditev velikosti por žganih in suho stisnjenih teles iz gline QC – vpliv temperature žganja (hiter cikel žganja)

bodies made on the basis of clay C. The same conclusion applies even to the highest firing temperature (SLOW 1120) of the plastic samples; however, the situation is opposite after the firing at the lower testing temperatures (SLOW 1090 and FAST 1120).

After an identical firing method, the plastic body features a significantly lower volume of pores with lower mean values of pore radiuses $r_{50\%}$ and durability factor *DF* than the dry-pressed body (**Figure 4**). In terms of pore-size distribution in the body, the dry-pressed bodies have a higher probability of frost resistance, although the primary reason for frost resistance is the volume of pores[16], featured by the bodies with a lower plasticity. The impact of the firing-temperature increase on the porous-structure properties is more significant in the case of the body based on clay QC (**Figure 6**), while the total volume of pores and the mean pore radius $r_{50\%}$ reduce significantly with the increasing firing temperature. On the other hand, the ratio of bigger pores increases with the increasing firing temperature in the case of the body based on clay C (**Figure 5**), which also increases the durability factor *DF*.
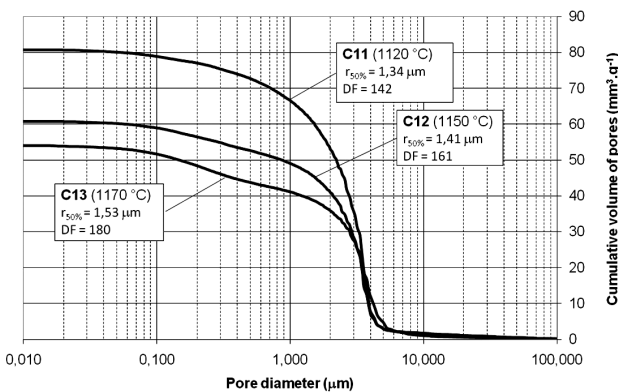
Comparing the pictures of the microstructures of the dry-pressed body (SEM) and the plastic body (samples C11 and C21 in **Figure 7**), we can see a more compact structure of the plastic body (C21) with a significantly lower content of the pores. The impact of temperature on the microstructure formation is documented on the dry-pressed body based on clay QC (**Figure 8**), where we can see the pore-size-reduction process with the increasing firing temperature, as well as the closed porosity formation.
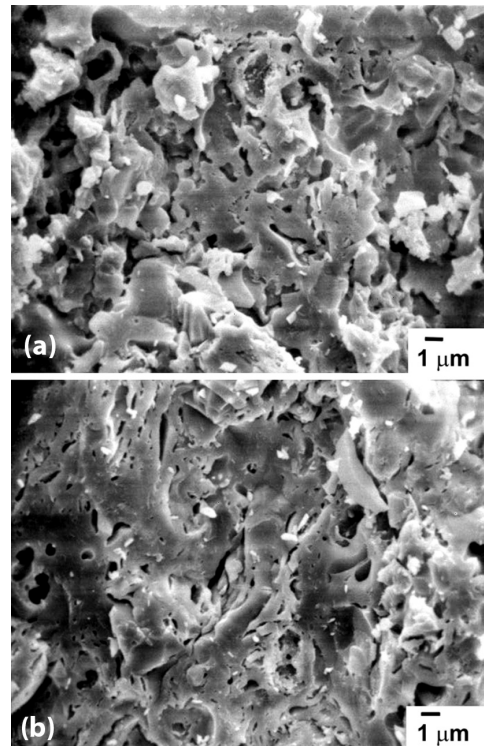

Figure 7: Microstructure of fired bodies (SEM, magn. 2000-times) after the FAST cycle at 1120 °C – effect of the shaping type: a) C11, b) C21
Slika 7: Mikrostruktura žganih teles (SEM, povečava 2000-kratna) pri hitrem ciklu žganja na 1120 °C – učinek na oblikovanje: a) C11, b) C21

Figure 5: Pore-size distribution of fired dry-pressed bodies based on clay C – influence of the firing temperature (the FAST cycle)
Slika 5: Razporeditev velikosti por žganih in suho stisnjenih teles iz gline C – vpliv temperature žganja (hiter cikel žganja)
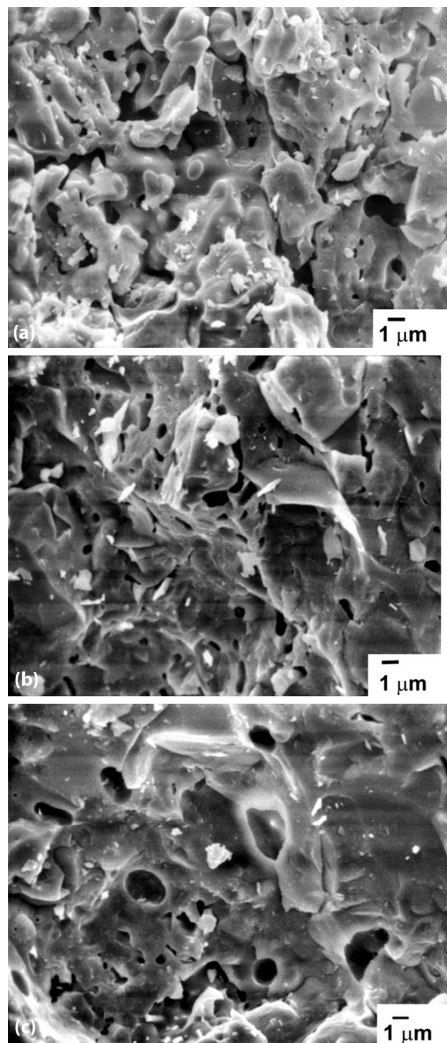
Figure 8: Microstructure of fired bodies (SEM, magn. 2000-times) – effect of the firing temperature: a) QC11 (1120°C), b) QC12 (1150 °C), c) QC13 (1170 °C)

Slika 8: Mikrostruktura žganih teles (SEM, povečava 2000-kratna) – učinek temperature žganja: a) QC11 (1120 °C), b) QC12 (1150 °C), c) QC13 (1170 °C)

4 CONCLUSIONS

Both the shaping method and the mineralogical composition of the used clay have a significant impact on the moulding properties, mainly on the fired-body properties. The conducted experiment revealed that the plastic samples are more compact after firing than the adequate, fired, dry-pressed samples. On the other hand, the dry-pressed bodies contain a higher proportion of pores in their microstructure, which results in better body characteristics in terms of frost resistance based on the available models (durability factor DF, mean pore radius $r_{50\,\%}$ and T_{value}). A higher proportion of the non-plastic component (quartz) in the clay QC mainly affects its lower shrinkage by drying and mixing the water volume.

5 REFERENCES

[1] G. Cultrone, E. Sebastián, K. Elert, M. J. de la Torre, O. Cazalla, C. Rodriguez–Navarro, Influence of mineralogy and firing temperature on the porosity of bricks, Journal of the European Ceramic Society, 24 (**2004**), 547–564

[2] V. Beltran, E. Sanchez, J. García, F. Ferrando, Extruded rustic floor tile: II. Impact of the composition on the body's behaviour during firing and fired product characristics, Tile & Brick Int., 12 (**1996**), 320–326

[3] S. Freyburg, A. Schwarz, Influence of the clay type on the pore structure of structural ceramics, Journal of the European Ceramic Society, 27 (**2007**), 1727–1733

[4] O. Széwald, I. Kotsis, Setting the optimal technological parameters for producing ceramic substrates, Ceramics international, 27 (**2001**), 467–471

[5] M. I. Carretero, M. Dondi, B. Fabbri, M. Raimondo, The influence of shaping and firing technology on ceramic properties of calcareous and non-clacareous illitic-chloritic clays, Appl. Clay Sci., 20 (**2002**), 301–306

[6] K. Ikeda, H. Kim, K. Kaizu, A. Higashi, Influence of firing temperature on frost resistance of roofing tiles, Journal of the European Ceramic Society, 24 (**2004**), 3671–3677

[7] M. Sveda, The effect of firing temperature and dwell time on the frost resistance of a clay roofing tile, Ziegelindustrie International, 59 (**2004**), 36–40

[8] O. Delbrouck, J. Janssen, R. Ottenburgs, P. Van Oyen, W. Viaene, Evolution of porosity in extruded stoneware as a function of firing temperature, Applied Clay Science, 8 (**1993**), 187–192

[9] F. Gonzales-Garcia, V. Romero-Acosta, G. Garcia-Ramos, M. Gonzales-Rodriguez, Firing transformations of mixtures of clays containing illite, kaolinite and calcium carbonate used by ornamental tile industries, Appl. Clay Sci., 5 (**1990**), 361–365

[10] M. M. Jordan, A. Boix, T. Sanfeliu, C. De la Fuente, Firing transformations of cretaceous clays used in the manufacturing of ceramic tiles, Appl. Clay Sci., 14 (**1999**), 225–234

[11] C. O. Modesto, A. M. Bernardin, Determination of clay plasticity: Indentation method versus Pfefferkorn method, Appl. Clay Sci., 40 (**2008**), 15–19

[12] L. Franke, H. Bentrup, Evaluation of the frost resistance of brick in regard to long service life. Part 1, Ziegelindustrie International, 46 (**1993**), 483–492

[13] L. Franke, H. Bentrup, Evaluation of the frost resistance of brick in regard to long service life. Part 2, Ziegelindustrie International, 46 (**1993**), 529–536

[14] M. Maage, Frost resistance and pore distribution of bricks. Part 1, Ziegelindustrie International, 43 (**1990**), 472–481

[15] M. Maage, Frost resistance and pore distribution of bricks. Part 1, Ziegelindustrie International, 43 (**1990**), 582–588

[16] M. Sveda, Frost resistance of brick knowledge about the relationship between pore structure and frost resistance, Am. Ceram. Soc. Bull., 80 (**2001**), 46–48