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Dry pressed ceramic tiles based on fly ash–clay body: Influence of fly ash granulometry and pentasodium triphosphate addition

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Abstract

Fly ash from brown coal (70 wt.%) and stoneware clay (30 wt.%) were used for the dry pressed ceramic tiles (according to EN 14411) raw materials mixture. The effects of fly ash milling and pentasodium triphosphate addition as a deflocculant and fluxing agent on the properties of green body (flexural strength, bulk density) and fired body (EN ISO 10545—water absorption, bulk density, true density, apparent porosity, flexural strength, frost resistance) were studied and explained as a function of the firing temperature (1000–1150 °C). Fly ash milling (corresponding to 5 wt.% residue of fly ash grains on 0.063 mm sieve) increased the sintering abilities of the fly ash–clay body. A similar effect was achieved by 1.3 wt.% pentasodium triphosphate (PST) addition with an increase in green body flexural strength and a decrease in water content of the granulate. Fly ash–clay bodies can be frost resistant with water absorption above 10% due to positive pore size distribution, which were examined using the high-pressure mercury porosimetry method.

Keywords: Ceramic tile; Fly ash; Pentasodium triphosphate; Pore size distribution

1. Introduction

The Czech Republic depends on coal power plants for 62% of its electric requirement (based on figures from the year 2006). Coal power plants produce a significant number of energy by-products (fly ash, FGD gypsum). Just the power plant in Melnik, of which the fly ash has been used in this work, produces 22 000–28 000 tons of fly ash per month during the winter and 15 additional coal power plants in the Czech Republic produce similar quantities of fly ash.

Publications dealing with the use of power plant fly ash for ceramic tiles production [1] and brickmaking [2,3] appear at the beginning of the eighties of the last century. Experiments concerning use of stone mining wastes for ceramic tiles production showed perspective results [4–8]. The influence of fly ash quantity (20–80%) on the properties of mixtures with variable quantities of clay, calcite and feldspar has been published in recent years [9]. Other researches evaluated the influence of different waste such as tincal solid waste [10], blast furnace slag [11] or paper mill sludge [12] with fly ash and clay admixtures on the properties of the resulting materials. In all cases, the optimum dosage has been found for these wastes in order to improve the physical and mechanical properties of the final body. Conversely only few studies [3] solve the problem of fly ash grain size (milling) influence on the properties of green or fired fly ash–clay body.

Even if electric power plant fly ash is a very fine-grained raw material (Table 1), its granulometry does not reach the necessary parameters suitable for the production of dry pressed ceramic tiles. In general, the grain fineness is considered correct if the residue on a 0.063 mm sieve is lower than 5%. It is general knowledge that the raw materials mixture granulometry plays a very important role in the sintering process [13–15]. The present article aims to explain on how much fly ash milling can influence the properties of the fired body. The other goal was to explain the influence of pentasodium triphosphate, usually used as deflocculant for ceramics in order to increase the strength of dried green body and to decrease the firing temperature (mainly used as fluxing agent) or to avoid additional fly ash milling.

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Table 1
Granulometry of typical power plant fly ashes from brown coal in Czech Republic.

Power plant (town)	Melnik	Chvaletice	Opatovice
Sieve residue on 0.063 mm (wt.%)	43.0	40.0	25.6
Mineralogical composition: mullite, quartz, amorphous glass phase			

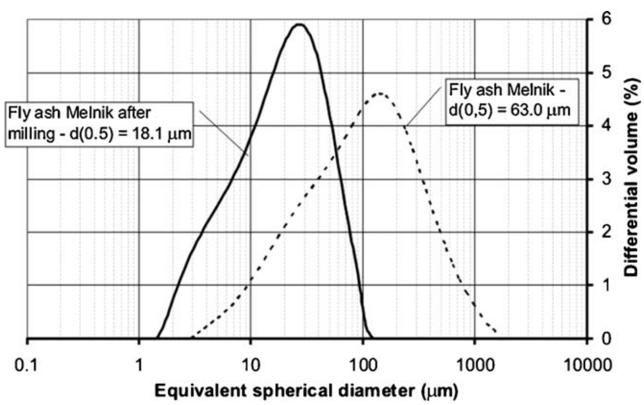


Fig. 1. Granulometry of used fly ash—influence of milling process on mean equivalent spherical diameter of grains $d(0.5)$.

2. Materials and methods

2.1. Raw materials and their properties

The used fly ash exhibited low loss on ignition (1.2 wt.%) which corresponds to the combustion of organic substances and culminates at 480 °C (according to DTA and TG analyses—see Fig. 2). The fly ash contains only grains under 1.5 mm. The difference between non-milled and milled fly ash is the equivalent mean spherical diameter of the grains $d(0.5)$ documented in Fig. 1 (particle size analyzer Mastersizer 2000). The granulometry of the fly ash has also been analyzed according to residue (in wt.%) on a sieve with a mesh diameter of 0.063 mm. Fly ash grains residue decreased from 43.0 wt.% (non-milled fly ash) to 5.0 wt.% (milled fly ash) after dry milling in the laboratory ball mill.

A plastic stoneware clay was used with high binding capacity content 70 wt.% of grains less than 2 μm (according to sedimentation analyses). The stoneware clay is primary composed of quartz, kaolinite, montmorillonite, feldspars, illite and mica. The average chemical composition is specified in Table 2.

The technology of the dry pressed ceramic tiles production requires a flexural strength of more than 2.0 MPa for dried green body. For small sized ceramic tiles, a flexural strength of 1.5 MPa is sufficient. The fly ash–clay raw materials mixture met this requirement with a minimum quantity of 30 wt.% of used stoneware clay.

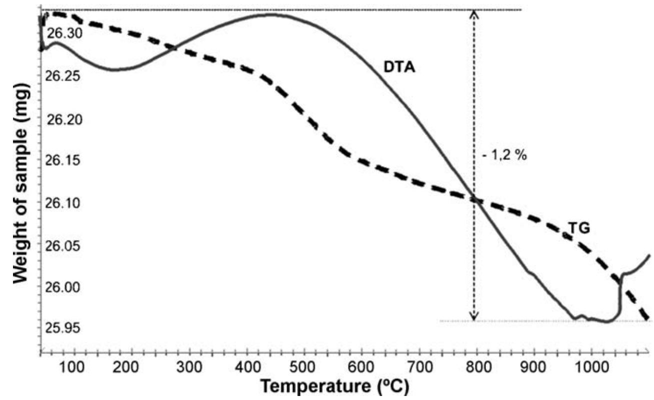


Fig. 2. DTA and TG curve of used fly ash.

2.2. Preparation of test samples and test methods

The use of deflocculants in the production of dry pressed ceramic tiles is presently a standard procedure. Within the experiment, the influence of pentasodium triphosphate $Na_5P_3O_{10}$ and sodium water glass $Na_2O \cdot nSiO_2$ (molar ratio SiO_2/Na_2O, $m = 1.6$) has been verified, both commonly used as deflocculants in ceramics. Their fluxing effect can also not be omitted [16,17]—the pentasodium triphosphate has its melting temperature at 620 °C. To determine the optimum deflocculant dosage, the flow viscometer method was used for the suspension made from the proposed material mixture with the addition of water 100%. The deflocculant has been gradually added to the suspension with an increase of 0.2 wt.% from the dry fly ash–clay mixture weight.

The raw material mixtures for the production of the test samples were dry-mixed for 12 h in the homogenizer. The mixture was then moistened at the relevant pressure moisture (in the case of the use of deflocculant, it was dissolved into this water) and the moistened mixture was pressed through the 1 mm sieve. The granulate was thus prepared and subsequently mixed for 12 h in the closed vase of the homogenizer to reach a homogenous moisture. Testing samples with a green body size of 100 mm × 50 mm × 8 mm were unaxially pressed at 20 MPa.

The green bodies were fired at temperatures of 1000, 1050, 1100 and 1150 °C with 10 min soaking time at the maximum temperature. The firing process of the test samples was performed in the electric laboratory furnace with regard to the organic substance enclosed in the fly ash: this combustion should not cause bloating of the test samples at the highest firing temperatures. The firing proceeded as follows: 20–450 °C

Table 2
Average chemical composition of used raw materials (wt.%).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	LOI	S
Clay	61.2	18.8	4.1	1.5	1.4	1.4	0.4	1.9	9.3	–
Fly ash	57.3	29.3	5.1	1.7	2.2	1.4	1.6	0.1	1.2	0.1

Table 3
Summary of criteria for indirect determination of frost resistance.

	$r_{50\%}$ (μm)	T-value	F
Frost resistance	>1.65	<0.75	>70
Limited frost resistance	0.60–1.65	0.75–0.85	50–70
At risk from frost	<0.60	>0.85	<55

the heating rate 8 °C/min, at the range 450–600 °C heating rate 4 °C/min, at 600 °C 15 min soaking time, from 600 °C to the firing temperature 4 °C/min. The subsequent cooling proceeded spontaneously following the natural cooling rate of the furnace. After firing, the body properties were defined according to the official standard EN ISO 10545 (water absorption, bulk density, apparent porosity, apparent density, flexural strength) and EN 202 (frost resistance—number of cycles increased up to 100 instead of required 50). The pore size distribution was defined by means of the method of high-pressure mercury porosimetry (Thermo Finnigan Pascal 140/240) with subsequent evaluation based on the available models of the indirect determination of the frost resistance based on the Maage's coefficient F [18,19], mean pore radius $r_{50\%}$ [20,21] and saturation ratio T-value, which is the ratio of the water absorption at cold (at the laboratory temperature) and the vacuum (at the vacuum 30 Bar) according to German standard DIN 52251 – 3. These models have been mostly created for brick bodies (Table 3). Water absorption has great influence on the body frost resistance [22].

3. Results and discussion

3.1. Effect of pentasodium triphosphate addition on the green body properties

With regard to the fly ash–clay mixture, the water glass cannot be used as deflocculant due to its instantaneous effect. On the contrary, pentasodium triphosphate is very efficient and the optimum dosage is about 1.3% (Fig. 3). At this dosage, the suspension viscosity was lowered by approx. 32.5% (the time of the suspension flow in viscometer is decreased from 20.0 s to 13.4 s). For this reason, the testing samples of granulate with 1.3 wt.% of the pentasodium triphosphate and without its addition were prepared using different quantities of water in order to define the optimum pressure moisture at which the dried green body will have the required flexural strength of 2.0 MPa. The addition of PST decreases the required pressure moisture from approx. 19.5% to 12.0% (Fig. 4). Using the same granulate moisture (16%), the flexural strength of the green body without deflocculant is about 0.9 MPa at a bulk density of 1600 kg m^{-3} the deflocculant increases the flexural strength up to 4.5 MPa (bulk density 1720 kg m^{-3}). Fly ash–clay dry pressed test samples for firing were prepared according to Table 4. Composition was selected among materials that achieved the required flexural strength of the dried green bodies.

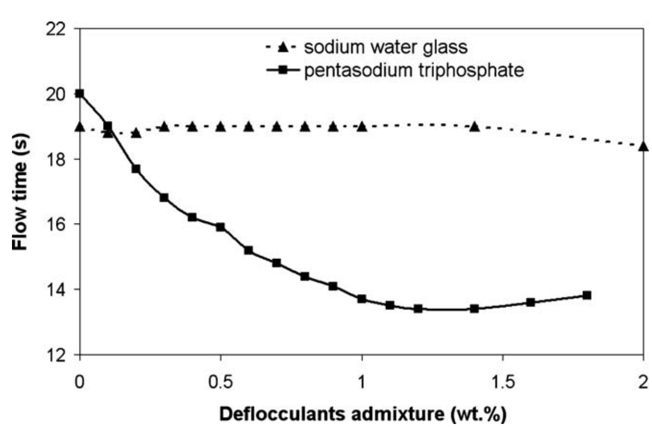


Fig. 3. Effect of deflocculants addition on the viscosity of fly ash–clay suspension.

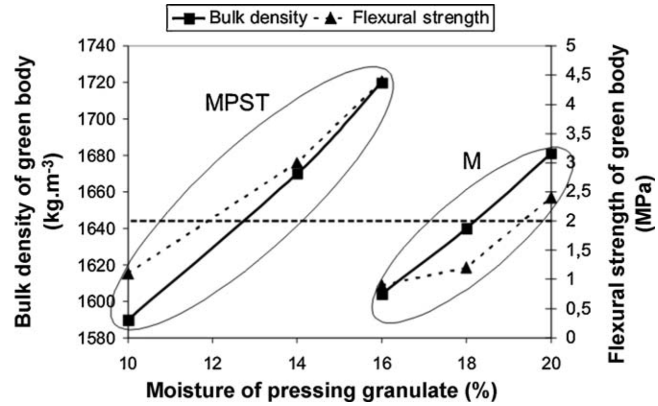


Fig. 4. Properties of green body depending on pressing granulate moisture and pentasodium triphosphate addition.

3.2. Properties of fired bodies

As expected, the physical and mechanical properties of the samples improved as the firing temperature increases. Enhancement is more evident in samples made using the milled fly ash which are denser (lower water absorption, higher bulk density and flexural strength). Milling fly ash decreases the firing temperature about 150 °C to achieve similar water absorption of the fired bodies (in comparison of samples M-1000 and N-1150, for example). The addition of pentasodium triphosphate also confirmed its fluxing capability. But the use of the milled fly ash with PST addition only induces a secondary porosity (bloating) of bodies fired at 1150 °C—Fig. 5. The bloating process is characterized by intensive firing shrinkage and bulk density decreasing due to rising of closed porosity with typical true density decreasing of bloated body (MPST-1150 in Table 5).

Addition of PST makes possible the production of materials with lower firing shrinkage and flexural strength when

Table 4
Batch compositions.

Batch		Water content	Deflocculant
MPST	70 wt.% milled fly	13 wt.%	1.3 wt.% PST
M	ash + 30 wt.% clay	20 wt.%	–
NPST	70 wt.% non-milled fly	13 wt.%	1.3 wt.% PST
N	ash + 30 wt.% clay	20 wt.%	–

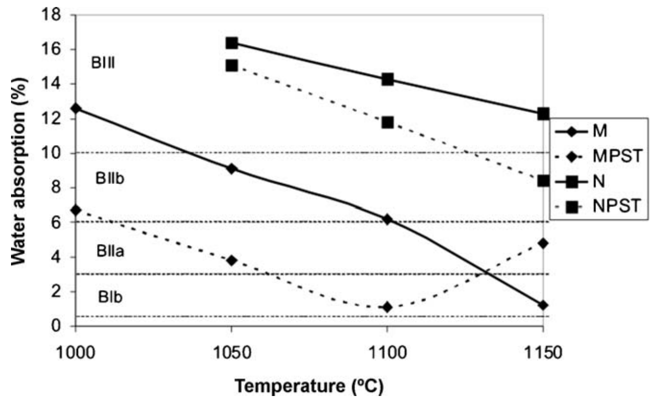


Fig. 5. Effect of firing temperature on water absorption.

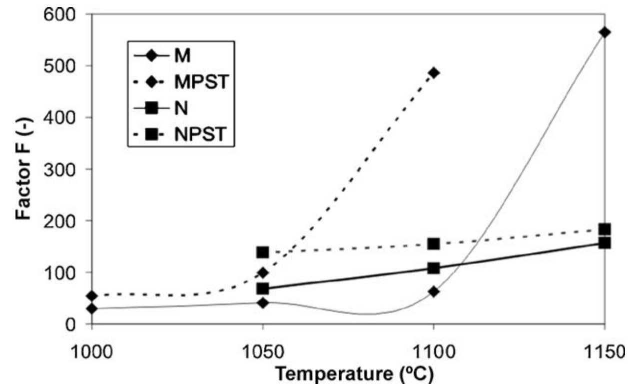


Fig. 6. Maage's coefficient of frost resistance F depending on firing temperature.

comparing fired bodies with a same water absorption (for example MPST-1000 with firing shrinkage 6.9% and M-1100 with firing shrinkage 10.6%). The lower flexural strength of materials containing PST is caused by their higher closed porosity which is displayed by the lower true density.

Bodies made using non-milled fly ash or those containing pentasodium triphosphate show a high portion of closed porosity, proven by the low values of the apparent density coexisting with similar water absorption or apparent porosity. The flexural strength of the fired bodies meets the EN 14411 standard required for individual groups of dry pressed ceramic tiles (BIa, BIb, BIIa, BIIb, BIII) according to water absorption. The addition of PST increased the flexural strength of the milled fly ash based fired bodies especially when increasing the firing temperature.

3.3. Pore structure and frost resistance of fired bodies

The porous structure (pore size distribution) of the fly ash–clay bodies is very advantageous especially in case of non-milled fly ash addition. The porous structure with advantageous pore size distribution is only the premise for the frost resistance of these bodies at the lowest firing temperatures—the frost resistant fly ash–clay body was prepared at the firing temperature of 1000 °C corresponding to the group BIII, and complies with the norm EN 202. A positive pore size distribution of fired fly ash–clay bodies is not always a guarantee of their frost resistance in the event that water absorption is high. Fly ash–clay body made with non-milled fly ash and fired at 1050 °C (N-1050) with water absorption 16.4% was classified as not frost resistant after 100 freezing–thawing cycles (−20 °C/+20 °C) according to EN 202. The same problem with frost resistance was determined in fly ash–clay body made with milled fly ash and fired at 1000 °C (M-1000) with 12.6% water absorption. Other bodies are frost resistant—no visual changes have been observed on tested fired fly ash–clay bodies after 100 freezing–thawing cycles. The pore size distribution of samples made with non-milled fly ash is generally more advantageous for frost resistance (mainly at lower firing temperatures)—it can be evaluated based on the saturation ration *T*-value, Maage's factor F (Fig. 6) and mean pore radius $r_{50\%}$.

The prevailing size (diameter) of the pores resulting in materials made with non-milled fly ash falls within the range

Table 5
Properties of fly ash–clay bodies after firing.

Firing temperature (°C)	Batch	Flexural strength (MPa)	Bulk density (kg m^{-3})	Apparent porosity (%)	True density (kg m^{-3})	Firing shrinkage (%)
1000	M	15.8	1990	25.1	2660	−5.5
	MPST	21.5	2230	14.2	2600	−6.9
1050	M	18.9	2160	19.6	2680	−8.0
	MPST	29.7	2370	9.0	2600	−9.6
1100	M	28.4	2300	14.2	2680	−10.6
	MPST	31.3	2460	2.3	2530	−11.2
1150	M	34.1	2500	3.1	2580	−14.3
	MPST	16.4	2030	9.8	2250	−7.3
1050	N	16.8	1690	27.7	2330	−3.2
	NPST	14.8	1660	25.1	2220	−3.8
1100	N	17.2	1780	25.4	2390	−4.9
	NPST	18.1	1830	21.6	2340	−6.0
1150	N	24.9	1860	22.6	2400	−7.1
	NPST	20.6	1910	16.1	2270	−7.2

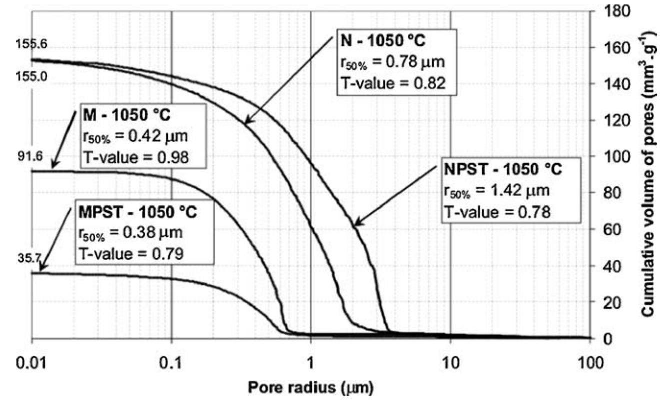


Fig. 7. Pore size distribution of fly ash–clay bodies fired at 1050 °C.

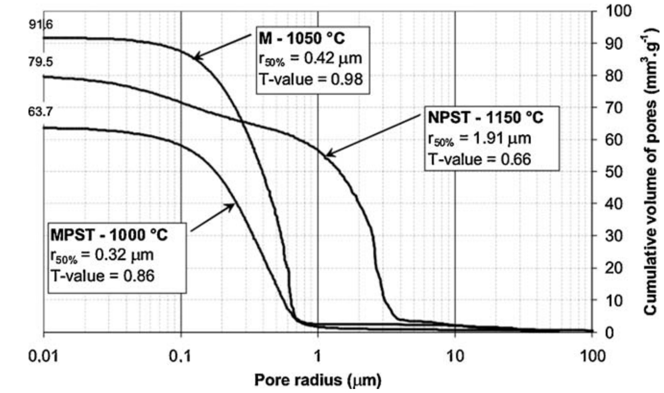


Fig. 9. Pore size distribution of fly ash–clay bodies suitable for ceramic tiles of group BIIb according to EN 14411.

3.00–5.00 μm, which is more and more dominant with the rising temperature—i.e. the pore sizes are found at a restricted range. For bodies made with milled fly ash, the pore size falls in the range of 1.00–1.25 μm. The advantage of bodies made with non-milled fly ash is the higher mean pore radius $r_{50\%}$ which is caused by the larger porosity of larger fly ash grains compared to the milled fly ash. The series of graphs reported in Figs. 7 and 8 clearly show the considerably quicker sintering (pore disappearance) of bodies made with fly ash having a lower mean spherical diameter of grains $d(0.5)$ (milled fly ash in Fig. 1). The influence of pentasodium triphosphate on pore volume of test samples made with non-milled fly ash and fired at 1050 °C is not evident. Conversely the mean pore radius $r_{50\%}$ is increased.

A firing cycle up to 1100 °C considerably decreases of the total porosity of bodies made with non-milled fly ash. It means that the effect of pentasodium triphosphate as a fluxing promoter at lower firing temperatures (Figs. 5 and 6) also requires the use of milled fly ash in the powder mixture with stoneware clay.

Ceramic tiles of the group BIIb according to EN 14411, for instance, can be produced in several technologic procedures, thanks to the comparison of fired bodies' water absorption (Fig. 5):

- with use of milled fly ash at the firing temperature of 1050 °C or
- with use of milled fly ash and 1.3% of pentasodium triphosphate at the firing temperature of 1000 °C or
- with use of non-milled (untreated) fly ash and 1.3% of pentasodium triphosphate at the firing temperature of 1150 °C.

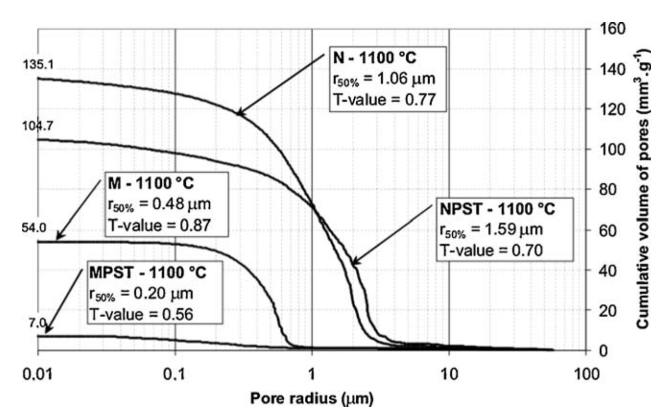
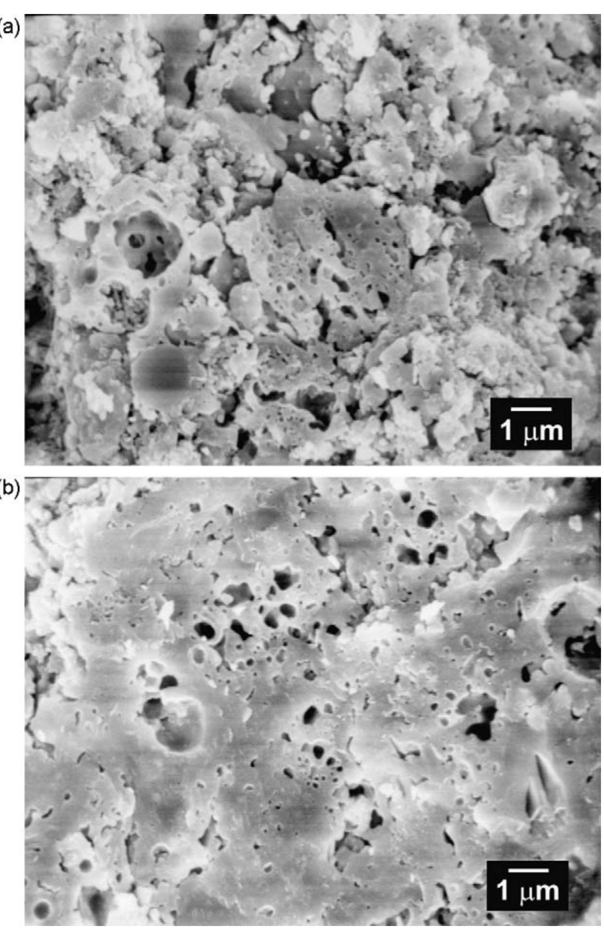


Fig. 8. Pore size distribution of fly ash–clay bodies fired at 1100 °C.

In other words, the final bodies have water absorption within the range of 6–10%, but the difference in pore size distribution (Fig. 9) is considerable. As for the indirect methods of frost resistance evaluation, the body of type NPST-1150 has the most

(a)



(b)

Fig. 10. Microstructure of fly ash–clay body after firing at 1000 °C: (a) batch M and (b) batch MPST (REM 2000×).

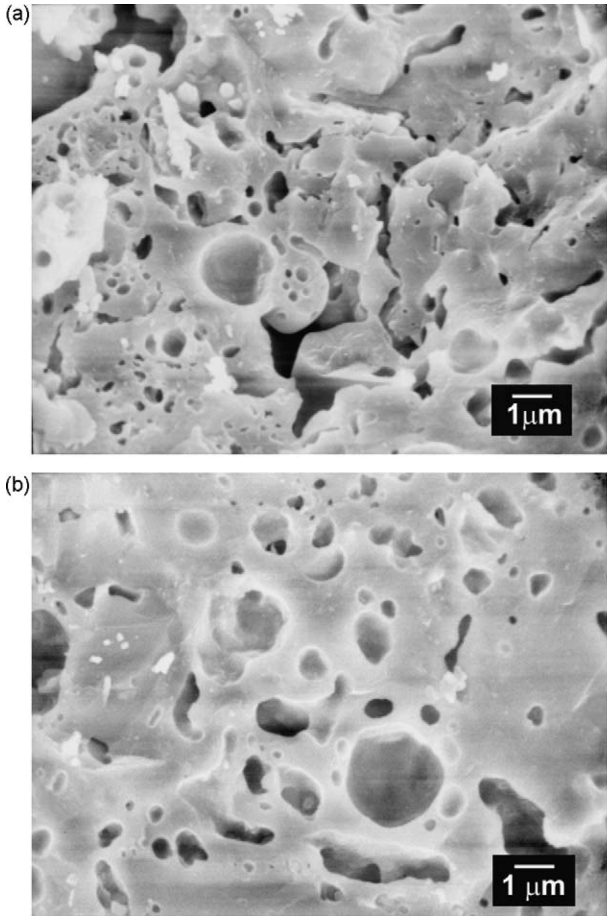


Fig. 11. Microstructure of fly ash–clay body after firing at 1150 °C: (a) batch N and (b) batch NPST (REM 2000×).

suitable pore structure distribution, having also the least bulk density of 1910 kg m^{-3} thanks to the high closed porosity ratio (true density only 2270 kg m^{-3}).

The PST fluxing influence is also evident in the pore size distribution in the body. For example materials made with milled fly ash and fired at 1000 °C, showed that the pore volume decreased in most evaluated intervals, except these of diameter 1.0–1.5 μm and 5.0–3.0 μm. This means that such pores are advantageous for the frost resistance of these materials. This fact also manifests itself at the higher values of the parameters F and $r_{50\%}$ and at the lower T-value. In general, at this temperature, the deflocculant decreases the water absorption by nearly one half and adjusts the pore size distribution for the increase of body frost resistance. The positive effect of the deflocculant on the body sintering is also documented in Figs. 10 and 11, where it is displayed the more dense microstructure of deflocculated bodies. In materials containing non-milled fly ash such effect is not greatly visible (and this is also obvious from the results of Table 5).

4. Conclusions

As a relatively fine-grain secondary raw material, fly ash is not too acceptable for the economical production of dry pressed ceramic tiles, unless it is milled. Fly ash milling enable more intensive sintering of the fly ash–clay bodies with the possibility of decreasing in firing temperature in comparison with the use of non-milled fly ash. But non-milled fly ash enable to create a frost resistant body with higher water absorption thanks to more positive pore size distribution in comparison with the use of milled fly ash.

Pentasodium triphosphate addition decrease pressing moisture content to achieve required flexural strength of dried fly ash–clay green body. Pentasodium triphosphate is advantageous due to its strong fluxing effect, which is even exhibited at 1000 °C. The fluxing effect of PST also increases the amount of small grains in fly ash.

Acknowledgements

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