Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 2879–2885
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

The effect of fluidized fly ash on the properties of dry pressed ceramic tiles based on fly ash–clay body

Radomir Sokolar *, Lucie Vodova

Brno University of Technology, Faculty of Civil Engineering, Institute of Technology of Building Materials and Components, Veveri 331/95, 602 00 Brno, Czech Republic

Received 22 March 2011; received in revised form 29 April 2011; accepted 2 May 2011
Available online 10 May 2011

Abstract

Stoneware clay (40 wt.%), classical high-temperature fly ash and fluidized fly ash from two different power plants used in various mixing ratios were the base raw materials for the mixture for production of dry pressed ceramic tiles of the BIII group according to EN 14411. The influence of an increasing addition of fluidized fly ash in the raw material mixture and the granulometry of fly ashes (milling) on the properties of the fired fly ash–clay body have been studied after firing at 1080 °C (water absorption, bulk density, apparent density, apparent porosity and bending strength). Fluidized fly ash reduces firing shrinkage and increases the porosity of the body, which is more remarkable when non-milled fluidized fly ash is used. It is possible to use max. 20 wt.% of fluidized fly ash in the fly ash–clay mixture so that the properties of the fired body meet the requirements of the BIII Group for a body of dry pressed ceramic tiles. The fluidized fly ash dramatically increases the content of sulphur dioxide in flue gases during the firing.

Key words : B. Porosity; Dry pressed ceramic tiles; Fly ash; Firing shrinkage; Sulphur oxide

1. Introduction

The fluidized technology is one of the most up-to-date methods for burning of coal and other sorts of fuel in thermal power plants. In conjunction with desulphurization, this is the most efficient method for the limitation of harmful emissions (especially sulphur dioxide) in the air. Fluidized fly ashes are generated during burning a fine grain mixture of coal powder, fly ash and limestone or dolomite in fluidized-bed boilers, which are burning the air-borne coal dust at lower temperatures (usually up to 900 °C) in comparison with the classic burning on fire grates where the burning temperature is up to 1450 °C.

The fly ash–clay mixtures for the single-firing process technology for the dry pressed ceramic tiles were developed experimentally, using kaolinic stoneware clay as the basic raw material and classical high temperature fly ash [1,2]. The bodies prepared by this method show a high shrinkage after firing, often even in the reduction cores, in comparison with standard bodies based on natural resources. The limited shrinkage after firing the fly ash–clay mixture may be achieved by the addition of limestone [3,4], which however decreases the bending strength of the body [3]. Blast furnace slag [5] with a high content of CaO in the mixture and with fly ash may also decrease the firing shrinkage of body at firing temperatures up to 1150 °C, much like the low alkali pyrophyllite [6]. Paper mill sludge with high content of CaO (43.1%) in the mixture with coal fly ash decrease firing shrinkage [7]. Tincal ore waste [8], talc [9] and metal finishing wastes [10] in the fly ash mixture behave as a flux, and, on the contrary, the firing shrinkage of the body increases with increased proportions of those materials in raw materials mixture. Fluidized fly ash was used successfully during the preparation of glass–ceramic materials [11,12]. Fluidized fly ash shows a worse sinterability (higher water absorption, porosity) than classical high temperature fly ash [13]. It is possible to improve the sintering activity of fly ash mixtures by milling - their water absorption after firing decreases [1,14].

The aim of the experimental part of the article is an evaluation of the influence of fluidized fly ash addition to the base material mixture which consists of classical high temperature fly ash from power plant and kaolinic clay. The goal is to find the optimum amount of fluidized fly ash which may decrease the body firing shrinkage due to reaction by calcium compounds in the fluidized

* Corresponding author. Tel.: +420 54114 7501; fax: +420 54114 7502.
E-mail address: sokolar.r@fce.vutbr.cz (R. Sokolar).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.05.005

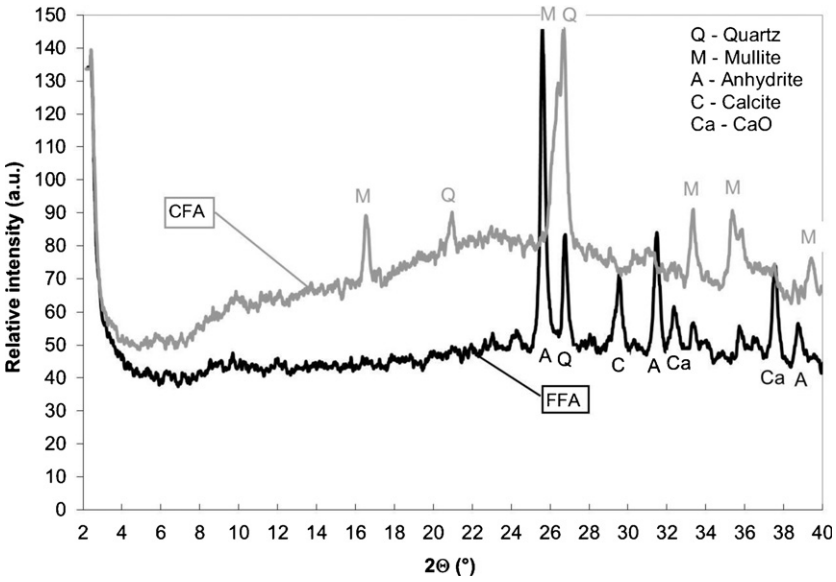

Fig. 1. Mineralogical composition of used CFA and FFA (X-ray diffraction).

fly ash with decomposition products of clay minerals, and by subsequent production of anorthite, which is accompanied by the increase of the body volume [15]. At the same time, the addition of fluidized fly ash must not negatively influence the mechanical physical properties of the body. In the frame of the experiment, the aim was to answer the following questions:

(1) Is the addition of fluidized fly ash able to eliminate firing shrinkage of a fly ash–clay body?
(2) What is the maximum possible amount of fluidized fly ash in the fly ash–clay mixture (clay and classical high-temperature fly ash) so that the parameters of a fired body correspond with the requirements of EN 14411 for ceramic tiles of the BIII group (water absorption 10–20%, bending strength min. 12 MPa)?
(3) How do the properties of a fly ash–clay body change depending on the fluidized ash additive in the raw material mixture, and based on the granulometry of the fly ashes (milling)?
(4) To what degree does the presence of fluidized ash in the raw material mixture increase the content of sulphur dioxide in flue gases during firing?

2. Materials and methods

2.1. Raw materials and their properties

Classic high-temperature brown coal fly ash CFA (from Melnik Thermal Power Plant) and fluidized fly ash FFA (from Hodonin Thermal Power Plant) were used as non-plastic components for the preparation of laboratory samples. The basic difference between CFA and FFA consists in the mineralogical composition (Fig. 1). CFA contain up to 80% glassy phase as the main component, and up to 20% mullite. SO_3 content is usually below 1%, because calcium sulphate decomposes at temperatures above 1150 °C. FFA are characterized by their higher SO_3 content (in the form of anhydrite $CaSO_4$), free calcium oxide CaO (up to 15%) and calcite $CaCO_3$. They do not contain either glass phase or mullite. The chemical composition of FFA therefore typically has a high content of CaO (Table 1). FFA shows usually hydraulic properties (they solidify and harden after mixing with water, without addition of any other components). Quartz is present in both types of fly ashes (Fig. 1). CFA, thanks to their higher firing temperature, form spherical grains (Fig. 2a), whereas FFA contains irregularly shaped sharp-edged grains (Fig. 2b).

Granulometry of the fly ashes used was determined based on the residue on a screen with a size of 63 μm (R63) – at the untreated fly ashes (R63-n) and after milling (R63-m) in a laboratory ball mill in dry conditions to around 5 wt.% residue on a screen of 63 μm (Table 2). This value is typical for the fineness of milling standard raw mixtures for the production of the dry pressed ceramic tiles of the BIII Group according to EN 14411 [16].

Kaolinic clay was applied as the plastic component in the raw material mixture, as it belongs in the group of refractory clays (refractoriness 1720 °C) with a good binding power (min. 70%) and sinterability (sintering temperature max. 1150 °C). It

Table 1
Chemical composition of used materials.

Raw material	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	LOI	S
Clay	48.6	33.5	2.7	0.8	0.1	0.3	2.2	2.2	1.8	0.0
CFA	55.9	29.3	4.7	1.7	2.2	1.4	1.6	0.1	1.2	0.1
FFA	27.4	15.2	6.9	0.5	31.4	4.3	0.6	<1.0	5.0	4.0

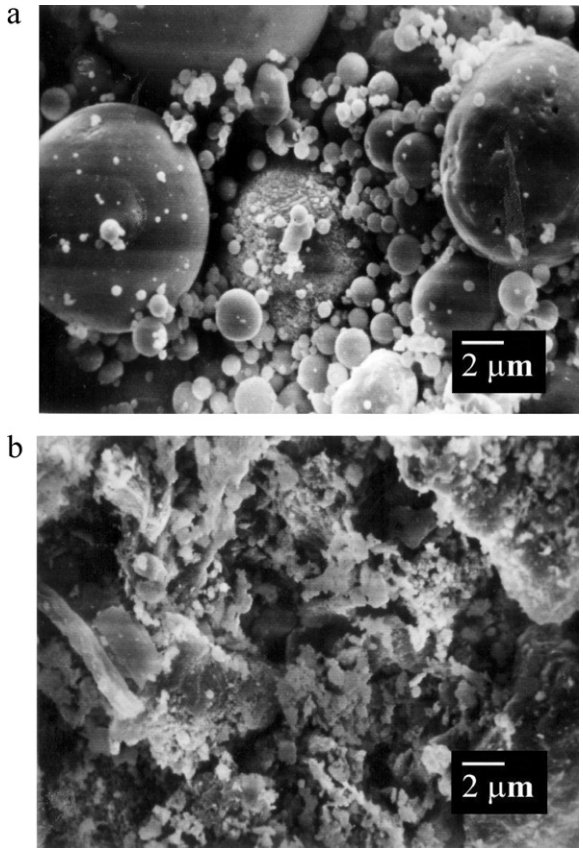

Fig. 2. Microstructure of fly ashes: (a) CFA (REM 1500×), (b) FFA (REM 1500×).

contains 85% of grains below 2 μm (sedimentation analysis). Mineralogical composition of used kaolinic clay is 65% kaolinite, 25% illite-hydromuskovite, 3% illite-montmorillonite and 5% quartz as the main mineralogical phase.

2.2. Preparation of test samples and test methods

The raw material mixtures for the production of test samples were prepared by mixing raw materials according to the given proportion, i.e. 60 wt.% fly ash from power plants (CFA and FFA in a determined ratio) and 40 wt.% clay in two stages. A set of samples was prepared in the 1st stage (Table 3), exclusively from milled fly ashes containing 0–60 wt.% of FFA to verify the influence of the FFA addition on the properties of the fly ash–clay body after firing and to find an optimum content of FFA in the raw material mixture.

The 2nd stage of the research involved assessment of the influence of milling the used fly ashes on the properties of fly ash–clay body containing 0 wt.% and 15 wt.% of FFA in the raw material mixture (Table 4) while maintaining the same ratio between the plastic and non-plastic components in the mixture as in the 1st stage of the research.

Table 2
Residue of used fly ashes grains on 63 μm sieve.

Fly ash	R63-n (wt.%)	R63-m (wt.%)
CFA	43.2	5.9
FFA	25.9	5.2

Table 3
Marking of test samples and their composition in the 1st stage.

Batch	Fly ash (wt.%)		Clay (wt.%)
	FFA	CFA	
FFA0m	0	60-milled	40
FFA10m	10-milled	50-milled	
FFA20m	20-milled	40-milled	
FFA30m	30-milled	30-milled	
FFA60m	60-milled	0	

The raw material mixtures (Tables 3 and 4) for the production of the test samples were dry-mixed for 24 h in the homogenizer. The mixture was then moistened at the pressure moisture 12% (0.2 wt.% of pentasodium triphosphate as a deflocculant was dissolved into this water) and the moistened mixture was pressed through the 1 mm sieve. Granulate was thus prepared and subsequently mixed for 24 h in the closed vase of the homogenizer to reach a homogenous moisture. Testing samples with a green body size of 100 × 50 × 8 mm were unaxially pressed at 20 MPa.

The green bodies were fired in electric laboratory furnace at temperatures of 1080 °C with heating rate 10 °C/min and 10 min soaking time at the maximum temperature. The subsequent cooling proceeded spontaneously following the natural cooling rate of the furnace. The applied firing process corresponds with its thermal output to the industrial fast firing of dry pressed ceramic tiles of the BIII Group according to EN 14411 in a roller kiln - determined with use of standard temperature identification tools - Bullers Rings [17]. The sulphur dioxide SO_2 content in the flue gases was assessed continually during the firing process by use of the TESTO M-I 300 flue gas analyzer, with a maximum measurable limit of 4000 ppm.

After firing, the body properties were defined according to the official testing standard EN ISO 10545 (water absorption WA, bulk density ρ_v, apparent porosity P, apparent density ρ_a and flexural strength σ). Firing shrinkage FS was calculated according to the following formula:

$$\mathrm{FS} = \frac{(l_f - l_d) \times 100}{l_d}\ [\%]$$

where l_d is the length of dried test samples (mm) and l_f is the length of fired test samples (mm).

Table 4
Marking of test samples and their composition in the 2nd stage.

Batch	Fly ash (wt.%)		Clay (wt.%)
	FFA	CFA	
FFA0m	0	60-milled	40
FFA15m	15-milled	45-milled	
FFA0n	0	60-not milled	
FFA15n	15-not milled	45-not milled	

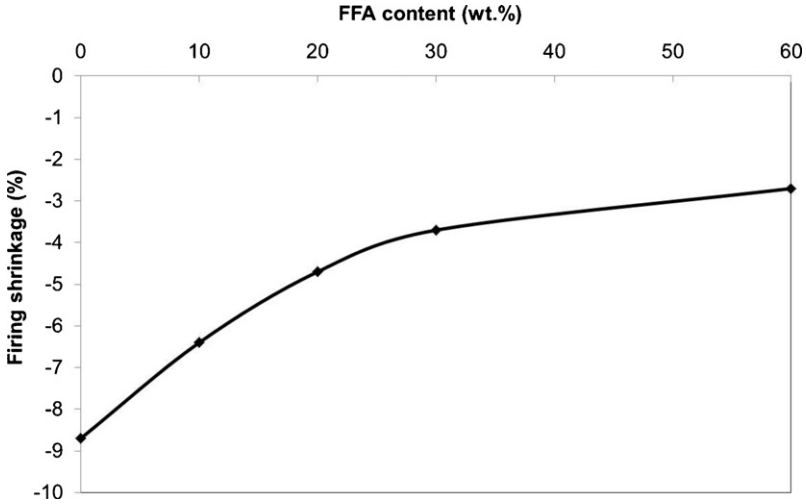

Fig. 3. Firing shrinkage of test samples depending on the FFA content.

To allow for comparison, samples were also prepared from industrially made spray granulate used for the production of dry pressed ceramic tiles of the BIII Group according to EN 144111 (marked with Ref).

3. Results and discussion

3.1. Determination of optimal fluidized fly ash content

Addition of FFA in the fly ash–clay mixture decreases the firing shrinkage of the test samples (Fig. 3), which, however, also in case of maximum content of FFA in the raw material mixture (mixture FFA60m), was greater than the firing shrinkage of the Ref reference body (firing shrinkage FS = −1.2%), based on a standard raw material mixture. With an increased content of FFA in the raw material mixture the porosity of the fired body increases as well - its water absorption and apparent porosity increased, and bulk density and bending strength decreased (Table 5).

In order to attain the required properties of the fired fly ash–clay body, from the point of view of water absorption (10–20%) and bending strength (min. 15 MPa), it is possible to use a maximum of 20 wt.% FFA in the raw material mixture, where the body shows a firing shrinkage of 4.7%. This is less by 46% than the fly ash–clay body in which FFA is not used. The subsequent tests in the 2nd stage involved preparation of mixtures and test samples containing 15 wt.% of fluidized fly ash FFA, which is an amount assuring creation of a fly ash–clay body with almost identical properties as shown by the Ref reference body (Table 5).

Table 5
Properties of fired fly ash–clay bodies (1st stage).

Batch	σ (MPa)	WA (%)	ρ_v (kg m^{-3})	ρ_a (kg m^{-3})	P (%)
FFA0m	25.9	12.5	1972	2655	25.0
FFA10m	21.1	16.1	1827	2640	30.8
FFA20m	15.5	17.9	1771	2591	31.6
FFA30m	13.0	22.9	1619	2575	37.1
FFA60m	8.9	30.3	1436	2680	44.4
Ref	17.8	16.9	1788	2562	30.2

3.2. Effect of fly ash milling

3.2.1. Properties of dried green samples

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. By the addition of FFA, the bending strength σ_g of dried samples slightly increases, but only in cases when milled fly ash is used, and the bulk density ρ_{vg} of dried samples increases with the addition of FFA as well (Table 6). Non-milled FFA, on the contrary, decreases the bending strength σ_g of dried samples, as well as their bulk density ρ_{vg}. Remarkably the highest bending strength of the dried green samples was shown by the fly ash–clay body which contained only non-milled CFA (FFA0n). All mixtures may be used for production of fly ash–clay dry pressed bodies because they can reach a bending strength higher than 1.5 MPa of green samples after drying.

3.2.2. Properties of fired samples

A major favorable effect of fluidized fly ash using in the fly ash–clay mixtures is the reduction of length changes (shrinkage) of the body after firing; however, this is at the expense of an increase in porosity of the body and its lower

Table 6
Bending strength σ_g and bulk density ρ_{vg} of dried green samples.

Batch	σ_g (MPa)	ρ_{vg} (kg m^{-3})
FFA0m	1.6	1522
FFA15m	1.8	1571
FFA0n	2.8	1546
FFA15n	1.7	1407

Table 7
Properties of fired fly ash–clay bodies (2nd stage).

Sample	σ (MPa)	ρ_v (kg m^{-3})	WA (%)	FS (%)	P (%)	ρ_{av} (kg m^{-3})
FFA0m	25.9	1972	12.5	−8.7	25.0	2655
FFA15m	18.9	1833	16.9	−5.6	30.9	2653
FFA0n	21.5	1835	13.3	−5.8	22.6	2369
FFA15n	9.0	1573	23.2	−4.3	36.1	2466

strength. Addition of FFA in the raw material mixture contributes to a higher porosity of the fired body, especially due to the decomposition of calcium carbonate and anhydride. This phenomenon is much more apparent with non-milled FFA as the properties of a FFA15n body (Table 7) do not meet the requirements for water absorption (23.2% - 10–20% required) and bending strength (9.0–12 MPa minimum required) for the body of the ceramic tiles of the BIII Group according to EN 14411.

From the point of view of the properties of the fired body, the FFA0n mixture without addition of FFA appears to be the most suitable variant. Instead of 15 wt.% of milled FFA in the raw material mixture with 45 wt.% of milled CFA (non-plastic component of the mixture FFA15m), 60 wt.% of non-milled CFA may be advantageously used (mixture FFA0n). Thereafter, this body shows similar firing shrinkage as the FFA15n body, but higher bending strength and lower water absorption, and without the economically more costly additional milling of fly ashes (Table 7).

Fluidized fly ash in the raw material mixture also changes significantly the mineralogical composition of the fired body (Fig. 4) – by adding FFA, the mineral anorthite is created in body during firing, which decreases firing shrinkage of the body.

Addition of FFA in the raw material mixture increases thermal expansion coefficient α (within temperature interval 20–500 °C) of the fly ash–clay body (Table 8). This fact does not correspond completely with the described creation of anorthite in bodies containing FFA. The thermal expansion coefficient of crystalline anorthite is low (about 40×10^{-7} K^{-1}) [18]. Fly ash bodies, also in the case of use of 15 wt.% of FPA in the raw material mixture, have a thermal expansion coefficient lower than the Ref reference body from porous ceramics tiles of the BIII Group, produced from a standard basic mixture from natural resources (clays, quartz, limestone, kaolin).

Table 8
Thermal expansion coefficients σ of test samples.

Sample	σ_{20-500} °C ($\times 10^{-7}$ K^{-1})
Ref	76.3
FFA0m	51.8
FFA15m	66.5
FFA0n	52.4
FFA15n	61.1

Firing bodies which are made of fly ashes brings a risk of increased concentration of sulphur dioxide in flue gases, especially in mixtures with a fluidized fly ash content which contains a considerable amount of anhydrite ($CaSO_4$). Sulphur dioxide appears in flue gases already from temperatures around 860 °C (Fig. 5) due to the decomposition of anhydrite $CaSO_4$. Sulphur oxide content in flue gases, created during the firing of fly ash–clay bodies, is generally higher in samples where FFA has been added. Milling fly ash speeds up the decomposition of anhydrite during firing - SO_2 begins to be released at lower temperatures (by about 50 °C

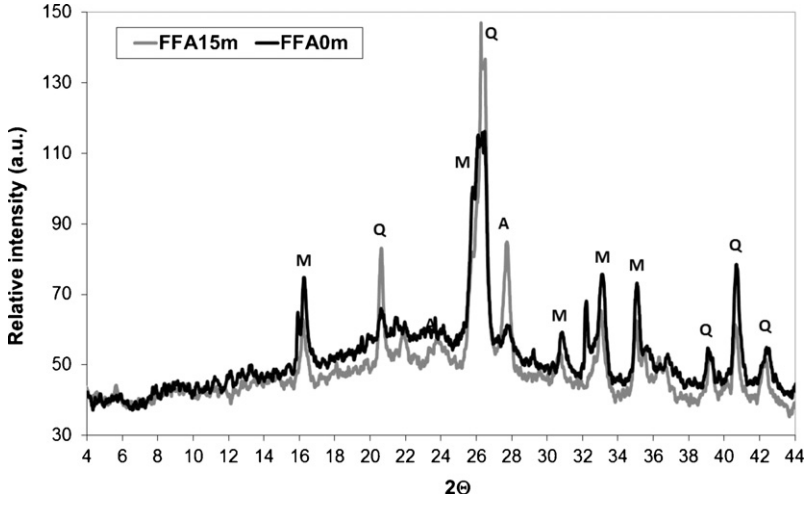

Fig. 4. Mineralogical composition of fired test samples: Q-quartz, M-mullite, A-anorthite (X-ray diffraction).

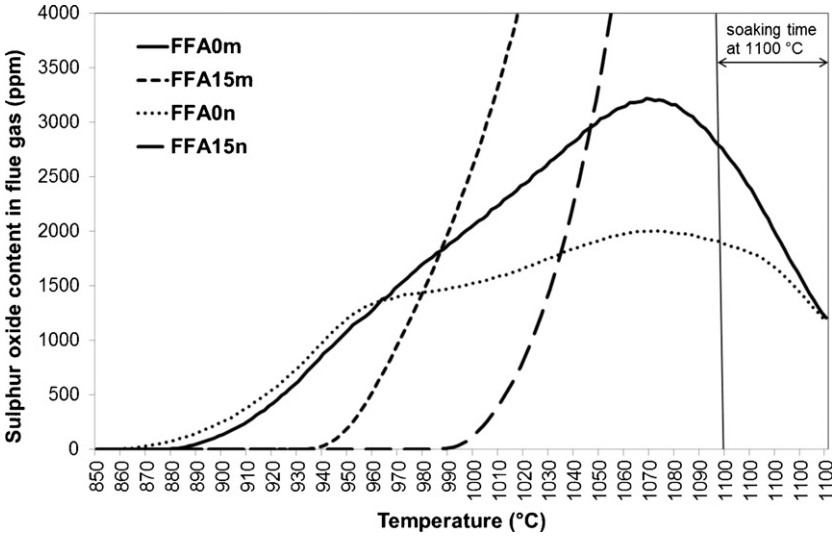

Fig. 5. Sulphur oxide content in flue gas during firing of tested fly ash–clay samples.

in the case of mixtures with FFA, and by 20 °C in mixtures without FFA). A classical high-temperature fly ash also represents a source of sulphur dioxide in flue gases, but less marked in comparison with FFA. The release of sulphur dioxide begins in bodies only containing CFA at lower temperatures than in the bodies based on the mixture of both types of fly ashes, CFA and FFA. In CFA, the granulometry influences SO_2 content in flue gases – if non-milled CFA is used, the maximum value is 2000 ppm; milling increases this content up to 3200 ppm.

Examining the microstructure of fired bodies (Fig. 6) proves a higher volume of pores in bodies with FFA content. In the bodies based on non-milled fly ashes, the spherical grains of the CFA used are very clearly visible.

4. Conclusion

It is possible to modify the fly ash–clay raw material mixture with FFA so that the firing shrinkage of a body due to sintering is compensated due to creation of anorthite during firing. However, at the expense of the increase of porosity of the body, decrease of bending strength and increase of sulphur dioxide content in flue gases. The maximum amount of FFA that can be used in the raw material mixture composed of high-temperature fly ash CFA and kaolinic clay, so that the monitored parameters of fired body correspond with the BIII Group of dry pressed ceramic tiles, is 20 wt.%. A more advantageous solution is the use of a mixture based exclusively on classical high temperature fly ash CFA in non-milled form, i.e. the FFA0n

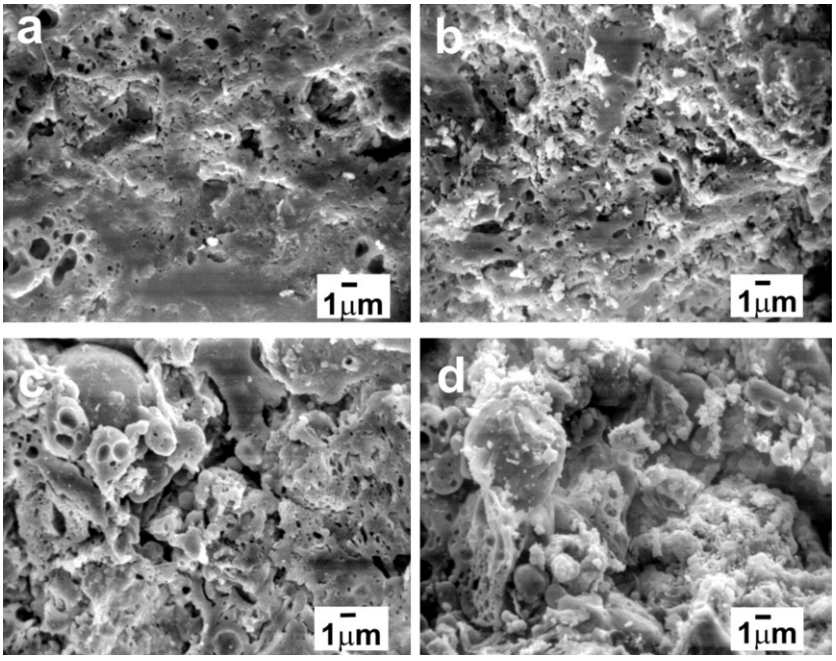

Fig. 6. Microstructure of fired test samples (REM 1000×): (a) FFA0m; (b) FFA15m; (c) FFA0n; (d) FFA15n.

mixture, which also provides the highest bending strength of the dried green sample, e.g. for the manufacture of larger formats of dry pressed ceramics tiles of the BIII Group.

Acknowledgement

This Research project was financed with Czech Ministry of Education, Youth and Sports MSM 0021630511 ''Progressive Building Materials with Utilization of Secondary Raw Materials and their Impact on Structures Durability''

References

[1] R. Sokolar, L. Smetanova, Dry pressed ceramic tiles based on fly ash–clay body: influence of fly ash granulometry and pentasodium triphosphate addition, Ceramic International 36 (1) (2010) 215–221.
[2] I. Queralt, X. Querol, A. López-Soler, F. Plana, Use of coal fly ash for ceramics: a case study for a large Spanish power station, Fuel 76 (8) (1997) 787–791.
[3] A. Zimmer, C.P. Bergmann, Fly ash of mineral coal as ceramic tiles raw material, Waste Management 27 (1) (2007) 59–68.
[4] Z. Haiying, Z. Youcai, Q. Jingyu, Study on use of MSWI fly ash in ceramic tile, Journal of Hazardous Materials 141 (1) (2007) 106–114.
[5] K. Dana, J. Dey, S.K. Das, Synergistic effect of fly ash and blast furnace slag and the mechanical strength of traditional porcelain tiles, Ceramic International 31 (1) (2005) 147–152.
[6] N. Chandra, P. Sharma, G. Pashkov, L. Voskresenskaya, E.N. Amritphale, S.S.N.S. Baghel, Coal fly ash utilization: low temperature sintering of wall tiles, Waste management 28 (10) (2008) 1993–2002.
[7] E. Furlani, S. Brückner, D. Minichelli, S. Maschio, Synthesis and characterization of ceramics from coal fly ash and incinerated paper mill sludge, Ceramic International 34 (8) (2008) 2137–2142.
[8] A. Olgun, Y. Erdogan, Y. Ayhan, B. Zeybek, Development of ceramic tiles form coal fly ash and tincal ore waste, Ceramic International 31 (1) (2005) 153–158.
[9] N. Chandra, N. Agnihotri, S. Bhasin, A.F. Khan, Effect of addition of talc on the sintering characteristics of fly ash based ceramic tiles, Journal of the European Ceramic Society 25 (1) (2005) 81–88.
[10] M. Little, R. Adell, V. Boccaccini, A.R.C.R. Cheeseman, Production of novel ceramic materials from coal fly ash and metal finishing wastes, Resources, Conservation and Recycling 52 (11) (2008) 1329–1335.
[11] M. Erol, A. Genç, M. Öveçolu, L. Yücelen, E. Küçükbayrak, S.Y. Taptik, Characterization of a glass–ceramic produced from thermal power plant fly ashes, Journal of the European Ceramic Society 20 (12) (2000) 2209–2214.
[12] L. Barbieri, I. Lancellotti, T. Manfredini, I. Queralt, J. Rincon, Ma.M. Romero, Design, obtainment and properties of glasses and glass–ceramics from coal fly ash, Fuel 78 (2) (1999) 271–276.
[13] M. Erol, S. Küçükbayrak, A. Ersoy-Meriçboyu, Characterization of sintered coal fly ashes, Fuel 87 (7) (2008) 1334–1340.
[14] M. Ilic, Ch. Cheeseman, Ch. Sollars, J. Knight, Mineralogy and microstructure of sintered lignite coal fly ash, Fuel 82 (3) (2003) 331–336.
[15] M.U. Taskiran, N. Demirkol, A. Capoglu, A new porcelainised stoneware material based on anorthite, Journal of the European Ceramic Society 25 (4) (2005) 293–300.
[16] G. Biffi, Book for the Production of Ceramic Tiles, Gruppo Editoriale Faenza Editrice S.p.A., Faenza, 2003.
[17] R. Sokolar, Methodology of laboratory and industrial firing equivalence determination, Keramicky zpravodaj 26 (4) (2010) 5–9.
[18] B. Ryu, I. Yasui, Sintering and crystallization behaviour of a glass powder and block with a composition of anorthite and the microstructure dependence of its thermal expansion, Journal of Materials Science 29 (1994) 3323–3328.