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INFLUENCE OF CLASS C FLY ASH ON THE PROPERTIES OF PLASTIC CLAY AND A FIRED BRICK BODY

VPLIV DIMNIŠKEGA PEPELA RAZREDA C NA LASTNOSTI PLASTIČNE GLINE IN ŽGANIH OPEK

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Class C fly ash (CCFA) was used, according to ASTM C618-12a, as an admixture (10 %/*w*) in calcareous brick clay to determine the difference (in comparison with pure clay) in the clay body plasticity (CCFA increases the water content, decreases the drying shrinkage, drying sensitivity and bulk density of a green body) and in the properties of a fired body (since CCFA acts as a pore-forming agent, we can expect a lower bulk density and better thermal insulation). Due to low firing temperatures of the brick body (850 °C and 1000 °C), there is no risk of an anhydrite decomposition as Class C fly ash does not increase the SO_2 content in flue gas during the firing and efflorescence.

Keywords: fly ash, brick body, sulphur-dioxide emissions, firing

Avtorji so uporabili dimniški pepel razreda C (CCFA), v skladu s standardom ASTM C618-12a, kot dodatek (10 % mas.) v karbonatno glino za opeke, da bi določili razlike, ki nastopajo v primerjavi z uporabo naravne (čiste) gline. Avtorji so pričakovali, da bo dodatek vplival tako na plastičnost surovcev (CCFA namreč poveča vsebnost vode, zmanjša skrček po sušenju, občutljivost in volumsko gostoto surovcev), kakor tudi na končno žgane opeke (sredstvo za tvorbo por namreč znižuje volumensko gostoto in poveča toplotno izolativnost). Zaradi nizkih temperatur žganja opeke (850 °C in 1000 °C) ni bilo nevarnosti za razpad anhidrita, saj dodatek dimniškega pepela razreda C ne povečuje vsebnosti SO_2 v dimnih plinih med žganjem in kristalizacijo.

Ključne besede: dimniški pepel, opeka, emisije žveplovega dioksida, žganje

1 INTRODUCTION

Class C fly ash (CCFA, fluidized fly ash) is a by-product obtained during the combustion of a coal-limestone finely milled mixture in a fluidized-bed boiler in thermal-power or heating plants at lower temperatures (about 800 °C). The term "fluidized fly ash" is not used in scientific literature – the type of fly ash is usually not specified. Fluidized fly ash is generally called Class C fly ash according to the American Standard ASTM C618-12a (Standard Specification of Coal Fly Ash and Raw Calcined Natural Pozzolan for Use in Concrete), which determines CCFA (**Table 1**).

Table 1: Classification of fly ashes according to ASTM C618-12a

Class	$\Sigma(SiO_2+Al_2O_3+Fe_2O_3)$	SO_3	LOI
C	min 50 %	max 5 %	max 6 %

In the Czech Republic, the total production of CCFA is about 1.4 million tons per year. Fluidized technology is one of the most popular methods for burning coal and other sorts of fuel in thermal-power plants in order to limit sulphur-dioxide emissions.

Fly ash/clay mixtures for the single-firing technology for 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 with this method show a high shrinkage after firing, often even in the reduction cores, in comparison with the standard bodies based on natural-raw materials. We can use CCFA for glass-ceramic materials development.[3,4] Here, CCFA shows a poorer sinterability (higher water absorption, porosity) than in ceramic bodies.[5] Milling of fly-ash mixtures improves the sintering activity.[1,6] The recycling of three different fly ashes (CCFAs with different CaO contents of 6.76–37.80 %) obtained from the coal thermal-power plants was studied for the glass materials.[7]

Fly ash from the coal power plant (CCFA with 14.3 % of CaO and 3.6 % of SO_3 – quartz, calcite, hematite) was used for the production of bricks in the local brick factory (0–25 % of clay) as fly ash decreases the compressive strength of bricks due to a high porosity (firing at 800 °C); as a result, a low efflorescence was observed in the bricks incorporating fly ash.[8] Environmentally friendly bricks containing clay, fly ash (FA) and bottom ash (BA) were developed. An increase in the FA content leads to an increase in the apparent porosity and water absorption; however, it decreases the bulk density

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Table 2: Chemical compositions (in mass fractions, *w*/ %) of used raw materials – fly ash CCFA (Tisova) and brick clay (Novosedly)

Material	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO	K_2O	Na_2O	SO_3	LOI
clay	56.4	12.7	4.4	0.1	9.8	3.3	0.1	3.0	1.7	0.6	12.2
CCFA	35.0	23.3	5.5	5.4	21.5	1.6	0.1	0.5	0.1	2.5	4.5

and thermal conductivity of bricks. The BA content does not have any significant influence on the properties of bricks.

All heavy metals were immobilized in the structures of fired bricks.[9] Brick clay, sewage sludge and fly ash (CFFA – 2.33 CaO, 0.3 SO_3) were successfully used for the production of brick fired at two different temperatures (900 °C and 1050 °C).[10] Municipal solid waste incineration (MSWI) fly ash (36,7 % of CaO as free CaO, $Ca(OH)_2$, calcite, quartz) was re-utilized for eco-friendly dry-pressed ceramic-brick production (fired at 1000 °C).[11] The fly ashes (CFFA – 2.26 % of CaO and 0,03 % of SO_3) from the co-combustion of coal and pet coke were used as raw materials to replace clay to make dry-pressed fired (800, 900, 1000) °C bricks. These bricks do not present environmental problems according to a leaching study.[12] Dry-pressed (at 26 MPa) bricks based on pure-lignite fly ash with different granulometries were developed and reported in[13] – their production included a compressive strength of 27–57 MPa and water absorption of 19–25 % depending on the firing temperature in a range of 900–1050 °C.

The aim of the article is to define:

- The CFFA influence on the properties of a plastic and green body (interaction of brick clay and CFFA) – drying sensitivity, drying shrinkage, working water.
- The effect of CFFA in a raw-material mixture used for clay masonry bricks on sulphur oxide SO_2 emissions included in flue gas during the firing (up to 1000 °C and with the soaking time at 1000 °C).
- The CFFA influence on the properties of a fired body (at 850–1000 °C, the maximum firing temperatures for bricks) – water absorption, bulk density, firing shrinkage, flexural strength and efflorescence.

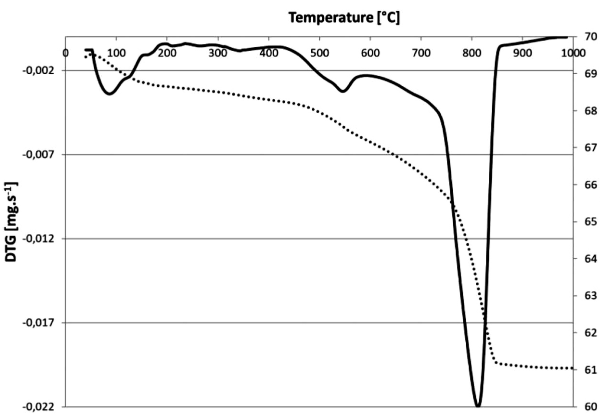

Figure 1: TG (solid line) and DTG (dashed line) of brick clay (heating at 10 °C/min). The initial mass of the sample for TG was 69.4548 mg

2 MATERIALS, SAMPLES AND METHODS

Fluidized fly ash CCFA from the thermal-power plant (Tisova-CEZ Group, Czech Republic) and typical brick clay for the THERM clay-masonry-unit (EN 771-1) production (Novosedly-Wienerberger Group, Czech Republic) were used for the preparation of laboratory samples. The chemical compositions of both used materials (**Table 2**) are typical and correspond to their mineralogical compositions (**Figures 3** and **4**). CFFA is characterized by a high SO_3 content (in the form of anhydrite $CaSO_4$), quartz, calcium oxide CaO and calcite $CaCO_3$ (**Table 3**). Brick clay can be characterized by its calcareous nature (the content of calcite is about 12 *w*/%. according to the thermal analysis – TG, DTG, Mettler Toledo TGA/DSC1 device – the decomposition of calcite in a temperature range of 720–850 °C (**Figure 1**), and the presence of several clay minerals (kaolinite, illite and montmorillonite), quartz and orthoclase (**Figure 3**). The mineralogical composition was identified using an X-ray diffraction analysis (XRD; PANALYTICAL Empyrean) with Cu-K_α as the radiation source, an accelerating voltage of 45 kV, beam current of 40 mA, diffraction angle 2θ in a range of 5–80° and step scan of 0.01°.

Granulometry of the used materials was determined using the residue on a screen with a size of 63 µm (R_{63}) (**Table 3**). According to granulometry (**Figure 2**), brick clay, suitable for the production of thermal insulating masonry THERM units (EN 771-1) was used as the basic plastic material for the preparation of test samples from the plastic body. It contains about 28 % of grains below 2 µm (a sedimentation analysis).

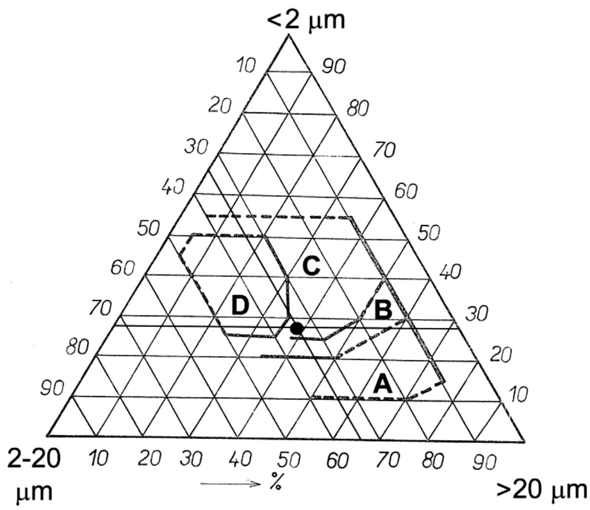

Figure 2: Grain-size classification of used brick clay (black point) according to Winkler's diagram:[14] common bricks, b) vertically perforated bricks, c) roofing tiles and masonry bricks, d) hollow products

Table 3: Residue of used fly-ash and brick-clay grains on a 63-μm sieve

Material	R_{63} (w/%)
clay	16.0
CCFA	25.9

For the preparation of test samples, the average sample of dried brick clay (60 °C) was ground in a laboratory pan mill to get a homogenous fineness of 0–1 mm. Two batches of brick clay and CCFA (0 %/w – N and 10 %/w – N10) were prepared for the experiments. The raw-material mixture (dry-milled clay and CCFA) was dry-mixed for 24 h in the homogenizer. The brick clay (N) and mixture brick clay/CCFA (N10) were moistened to achieve the plasticity that corresponds to the deformation ratio of 0.7 according to K. Pfefferkorn[15] (H_f/H_0 where H_0 is the initial height and H_f is the final height after the deformation on the Pfefferkorn apparatus). After 24-hour ageing of the plastic clay body, the samples were made by hand, the clay being churned into a metal form with dimensions of (100 × 50 × 20) mm.

The drying was conducted in the natural way in the laboratory at a temperature of about 21 °C; the samples were subsequently finally dried in the laboratory drier at a temperature of 110 °C. The established Bigot curve (**Figure 5**) was used to calculate the drying sensitivity index DSI-B[16]:

$$DSI-B = \frac{w_i - w_c}{100} \cdot DS \quad [-] \qquad (1)$$

where:

W_i is the initial water content of the plastic body during the preparation of test samples [%];

W_c is the critical water content of the test samples subtracted from the Bigot curve (**Figure 5**) (%);

DS is the drying shrinkage (%).

The samples were fired in the laboratory electric kiln at 850 °C and 1000 °C (3 °C.min^{-1} with 1-hour soaking time at the maximal temperature), which corresponds to the typical firing temperature interval for clay masonry bricks. The sulphur dioxide (SO_2) content in the flue gases was assessed continually during the firing process using a TESTO 340 flue-gas analyser.

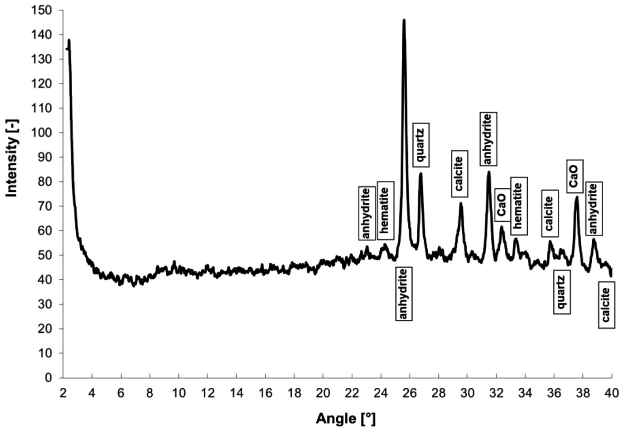

Figure 4: XRD diffraction of used CCFA

After the firing, the body properties (water absorption WA, bulk density B and flexural strength R) were defined in accordance with the official testing standard EN ISO 10545. Firing shrinkage FS was calculated with the following Equation (2):

$$FS = \frac{(l_f - l_d) \cdot 100}{l_d} \quad [\%] \qquad (2)$$

where:

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

The susceptibility to efflorescence was determined in accordance with ASTM C 67 – the test samples were immersed to a constant depth of 10 mm under water at one end. After 7 d, the water was allowed to dry (at 110 °C) in 24 h and observations relating to efflorescence were recorded.

3 RESULTS AND DISCUSSION

According to K. Pfefferkorn,[15] CCFA as an additive to a raw-material mixture increases the water content w_r (**Table 4**), achieving the plasticity of a clay body with a ratio of 0.7 by 4.3 % and, at the same time, reduces the

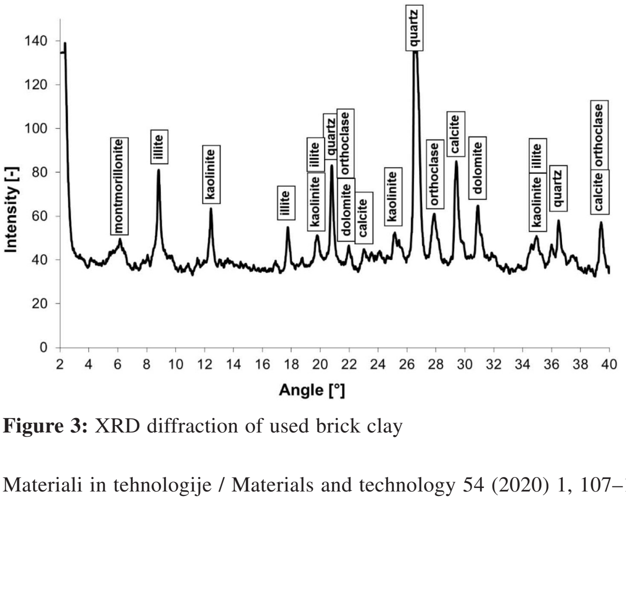

Figure 3: XRD diffraction of used brick clay

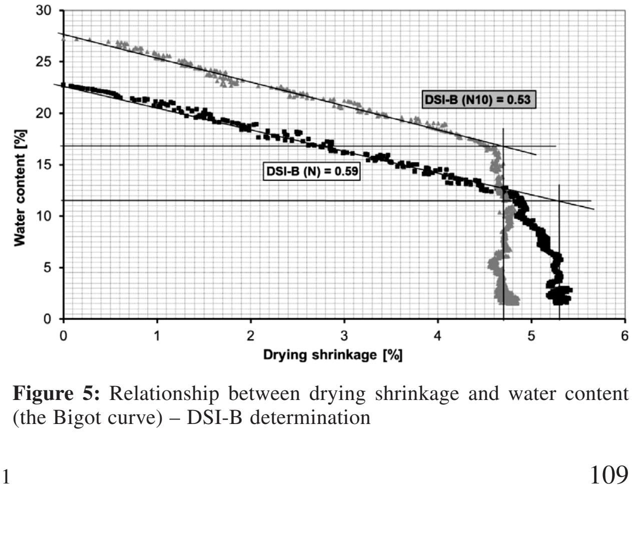

Figure 5: Relationship between drying shrinkage and water content (the Bigot curve) – DSI-B determination

drying shrinkage *DS*, resulting in a reduction in the bulk density *BG* of a dried green body (**Table 4**). The drying process of both compared plastic clay bodies (mixtures N and N10) is documented with the Bigot curve – according to Bigot DSI-B, CCFA causes a complete decrease of the clay-body shrinkage when reaching the critical water content and a slight decrease in the sensitivity to drying (**Figure 5**).

Table 4: Properties of the plastic body (w_r – water content, *DS* – drying shrinkage, *BG* – bulk density of a dried green body)

Mixture	w_r (%)	*DS* (%)	*BG* ($kg \cdot m^{-3}$)
N	22.7	–5.3	1430
N10	27.0	–4.7	1400

According to Equation (3):

$$2CaSO_4 \rightarrow 2CaO + 2SO_2 + O_2 \qquad (3)$$

decomposition of anhydrite $CaSO_4$ can be expected during the firing of a dry-pressed body based on pure CCFA when the temperature exceeds 1200 °C or about 1000 °C for dry-pressed clay/CCFA mixtures.[17] For this reason, there is a risk of sulphur dioxide leakage during the firing of the N10 samples at higher temperatures, but this was not confirmed (**Figure 6**). Conversely, the admixture of CCFA resulted in a slight reduction of the SO_2 content of the flue gas. This can be caused by the calcite content in CCFA, which was able to bind sulphur dioxide from the brick clay. The admixture of CCFA in brick clay slightly increases the shrinkage of the test samples during the firing (**Figure 7**) due to the sintering of body N10 in a range of 800–900 °C compared with body N. We can observe a higher volume increase for the fired body, when CCFA is used (mixture N10), in a temperature range of about 1000–1100 °C – this is typical of an anorthite creation during the firing.[18] CCFA is a source of a higher quantity of anorthite in the fired brick bodies due to the CaO content (**Table 2**).

The main effect of the CCFA addition to brick raw-material mixtures is in the pore-forming ability – there is an evident bulk-density (*B)* reduction and an increased water absorption (*WA)* of the body (**Table 5**) due to the decomposition of calcium carbonate and formation of anorthite, leading to a volume increase (**Figure 7**). Significantly better thermal-insulation properties of a fired brick body can be expected at both tested firing temperatures (850 °C and 1000 °C) in the case of a CCFA addition to the raw-material mixture (N10) – see the coefficient of thermal conductivity, λ in **Table 5**.

The efflorescence on the surface of brick specimens after a 7-day immersion in distilled water was documented. No marginal difference (N vs. N10) in the efflorescence was observed on the surface of the samples after drying at 110 °C (**Figure 8**).

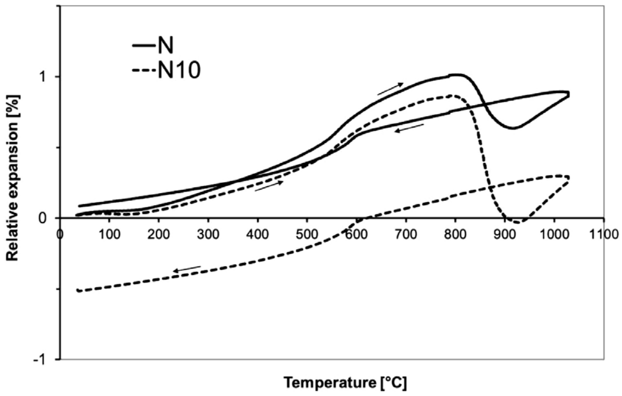

Figure 7: Dilatometric analysis during the firing (3 °C/min without the soaking time)

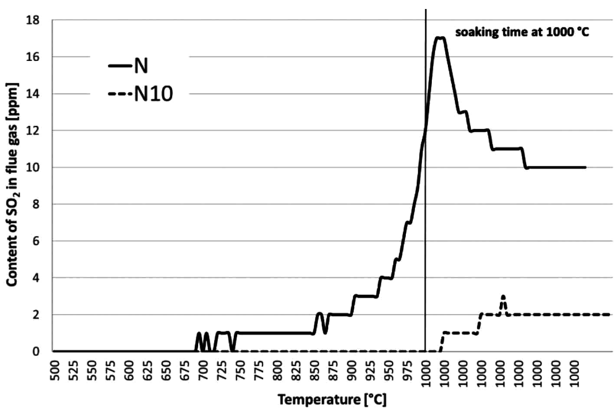

Figure 6: Content of sulphur dioxide (SO_2) in flue gas during the firing of test samples

Table 5: Properties of fired bodies (*R* – flexural strength, *B* – bulk density, *WA* – water absorption, *FS* – firing shrinkage) – the effect of the firing temperature

Sample	Firing (°C)	*R* (MPa)	*B* ($kg.m^{-3}$)	*WA* (%)	*FS* (%)	λ (W/mK)
N	850	15.9	1720	23.0	+ 1.5	0.5184
	1000	12.0	1700	28.3	– 0.1	0.6654
N10	850	12.5	1590	22.9	+ 0.3	0.4565
	1000	9.8	1560	28.0	– 0.6	0.4666

5 CONCLUSIONS

In the Czech Republic, about 1.4 million tons of Class C fly ash (CCFA) are produced per year that are not applied in the production of building materials. The aim of the paper was to verify the applicability of CCFA

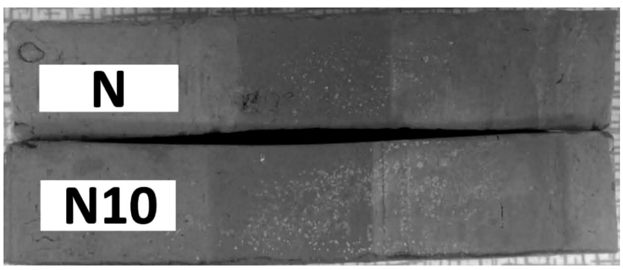

Figure 8: Fired samples after the efflorescence test

in the brickmaking industry. A mixture of typical calcareous (about 12 %/w/ of calcite) brick clay for the production of clay masonry bricks (Novosedly, Wienerberger Group, Czech Republic) and 10 %/w of CCFA (Tisova, CEZ Group, Czech Republic) was analysed and compared with a pure-clay brick. CCFA influences the properties of clay-body plasticity (increases the water content, decreases the drying shrinkage, drying sensitivity and bulk density of a green body) and a fired body (CCFA acts as a pore-forming agent – we can expect a lower bulk density and better thermal-insulation properties of fired bodies). Due to low firing temperatures in the brickmaking industry (in a range of 850–1000 °C) there is no risk of an anhydrite decomposition – Class C fly ash does not increase the SO_2 content in flue gas during the firing and efflorescence. As a source of CaO, CCFA contributes to a higher anorthite content in a fired body.

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