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The fly ash of class C for ceramic technology

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Abstract. The properties of different Czech fluidized fly ashes FFA (class C fly ash according to ASTM C618 12a with high content of CaO in the form of anhydrite primarily) and emissions of SO₂ in flue gas during the firing of FFA are discussed. The decomposition of anhydrite CaSO₄ was observed during the soaking time at 1200 °C during the firing of dry pressed bodies based on pure fluidized fly ash. The effect of fluidized fly ashes admixtures on the properties of ceramic bodies is as fluxing agent and the source of CaO for the creation of anorthite in the fired ceramic body. The properties of domestic fluidized fly ashes in connection with their utilization in ceramic technology are described.

1. Introduction

Fluidized fly ash FFA is a secondary raw material - energy by-product from the process of combustion of coal in fluidized bed boilers. Fluidized ash is produced by fluid combustion of finely ground coal together with limestone or dolomite at lower temperatures (about 850 °C) compared with traditional combustion of pure solid fuel (coal) at about 1400 °C – classical high-temperature fluid fly ash (CFA) is produced. The term "fluidized fly ash" is unknown in foreign scientific literature. Fluidized fly ash is generally called as "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 classifies fly ash based on the content of selected oxides and divides them into two basic groups. "Class F" – classical high temperature fly ash and "class C" - fluidized fly ash, see table 1.

Table 1. The classification of fly ashes according to ASTM C618.

Class	$\Sigma(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$	SO ₃	LOI
C	min 50 %	max 5 %	max 6 %
F	min 70 %	max 3 %	max 6 %

Total production of by-product energy products in the Czech Republic in 2014 was approximately 13.7 million tonnes. The total production of all types of fly ash was 9.3 million tonnes - high-temperature ash production about 7.9 million tonnes (85 %) and fluidized fly ash 1.4 million tonnes (15 %). The fluidized technology is one of the most popular 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]. 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 use of fluidized fly ash in concrete technology, geopolymers, solidification of dangerous substances, or stabilization of unstressed layers for roads is studied abroad especially. The studies about the application of FFA in ceramic technology are rare. The recycling of three different fly ashes (FFA) obtained from the coal fired thermal power plants has been studied for the glass materials [15]. There is evident that all used fly ashes are typ FFA (class C) according to their chemical composition. The significant difference in CaO content (6.76 – 37.80 %) is interesting (table 2).

Table 2. Chemical composition of used fly ashes [15].

Fly ash	SiO₂	Al₂O₃	CaO	MgO	Fe₂O₃	Na₂O	K₂O	SO₃	LOI
Cayirhan	41.53	17.77	12.52	4.46	9.93	2.57	2.43	7.25	0.68
Seyitomer	44.58	22.54	6.76	8.98	9.85	0.22	0.60	2.52	3.83
Afsin-Elbistan	18.11	7.63	37.80	3.50	5.23	0.22	0.60	18.22	8.40

All presented results of scientific research of FFA utilization in ceramic (fired) materials did not solve the problem of sulfur dioxide emissions – this is the aim of Czech Science Foundation project GACR 18-02815S Elimination of Sulphur oxide emission during the firing of ceramic bodies based on fly ashes of class C (2018 – 2020). The aim of the article is an evaluation of properties of Czech fluidized fly ashes (mineralogical and chemical composition, granulometry, morphology of grains) compared with traditional classic high-temperature fly ash. The problem of sulphur oxide SO₂ emissions in flue gas during the firing of pure FFA and pure stoneware clay dry pressed bodies is discussed. Main goal of the research is to define conditions when the FFA can be used in ceramic technology as a unexpensive source of CaO – necessary in the modern production of porous wall tiles (group BIII according to EN 14411) for example.

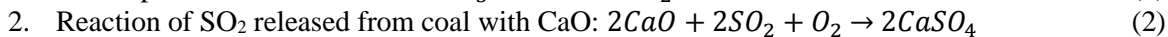
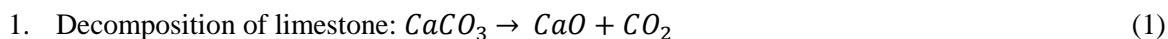
2. Properties of fluid fly ash (FFA)

Three Czech fluidized fly ashes FFA (from Hodonin, Tisova and Ledvice Thermal Power Plant) compared with classical high-temperature fly ash CFA (from Melnik Thermal Power Plant) as non-plastic raw materials for the preparation of laboratory samples were used.

2.1. Chemical and mineralogical composition

The basic difference between CFA and FFA consists in the mineralogical composition (figure 1). CFA contain up to 80 % glassy phase as the main component, and up to 20 % mullite. SO₃ content is usually below 1 %, because calcium sulphate decomposes at temperatures above 1150 °C. FFA are characterized by their higher SO₃ content (in the form of anhydrite CaSO₄), free calcium oxide CaO (up to 15 %) and calcite CaCO₃. Fluidized fly ashes do not contain either glass phase or mullite. The chemical composition of FFA therefore typically has a high content of CaO (table 3). FFA shows usually hydraulic properties (they solidify and harden after the mixing with water, without addition of any other components). Quartz is presented in both types of fly ashes (figure 1). A comparison of the

mineralogical composition of high temperature and fluid fly ash is shown in figure 1 (powder X-Ray diffraction). The creation of anhydrite in FFA during the combustion of the milled coal and limestone mixture inside the fluidized boiler we can described according to chemical equations:



The following table (table 3) shows the chemical composition of the typical Czech class C fly ashes from three thermal power plants in Hodonin, Ledvice and Tisova, as well as the classical high temperature fly ash from the Mělník power plant. The chemical composition of all fluidized fly ashes is very similar with slightly higher amount of calcium oxide (over 20 %) and a lower amount of alumina and SiO₂. On the other hand, classical high-temperature fly ash from the Mělník plant contains only 2.2 % CaO and higher content of Al₂O₃ and SiO₂.

Table 3. Chemical composition of different Czech fluid class C fly ashes (Hodonin, Tisova, Ledvice) compared with traditional high temperature fly ash (Melnik).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	MnO	K ₂ O	Na ₂ O	SO ₃	LOI
Hodonin	32.5	16.0	6.7	0.6	24.5	3.4	0.1	0.8	0.1	4.0	4.5
Tisova	35.0	23.3	5.5	5.4	21.5	1.6	0.1	0.5	0.1	2.5	4.5
Ledvice	35.7	25.4	6.5	1.8	20.5	1.1	0.1	1.5	0.3	3.3	3.8
Melnik	57.3	29.3	5.1	1.7	2.2	1.4	0.0	1.6	0.1	0.1	1.2

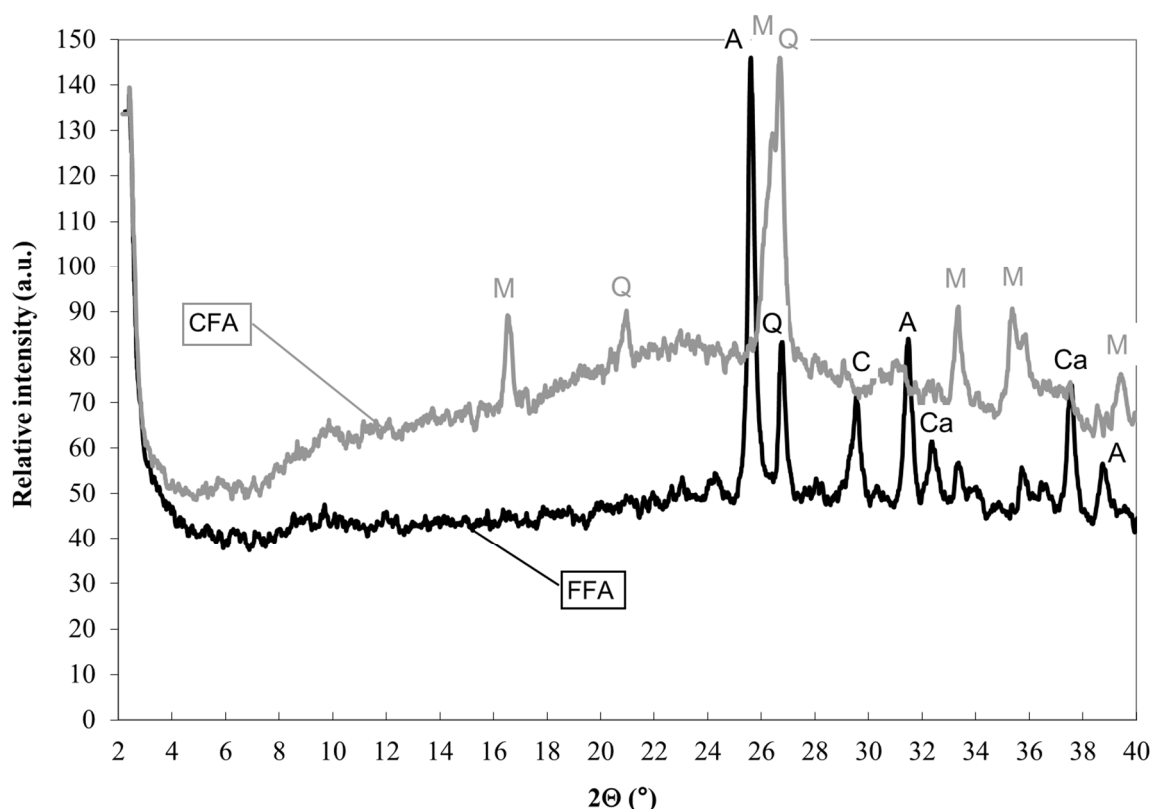


Figure 1. X-Ray diffraction of different types of fly ash – CFA and FFA: M-mullite, Q-quartz, A-anorthite, C-calcite, Ca-CaO.

2.2. Granulometry

The difference in morphology between classical high temperature fly ash CFA (left) and fluidized fly ash (right) in the images from the scanning electron microscope SEM is evident (figure 4). High-temperature of combustion creates spherical shape of CFA grains with different diameters. Grains of fluidized fly ash are irregular shaped with sharp edges due to lower temperature of combustion.

Granulometry of the fly ashes used was determined according to the residue on a screen with a size of 63 μm (R63). From the granulometric point of view, the fluidized fly ash from the Ledvice power plant differs. It contains the highest proportion of grains above 63 μm which is approximately twice number compared to the other analysed FFA. The grain size comparison is shown in table 4.

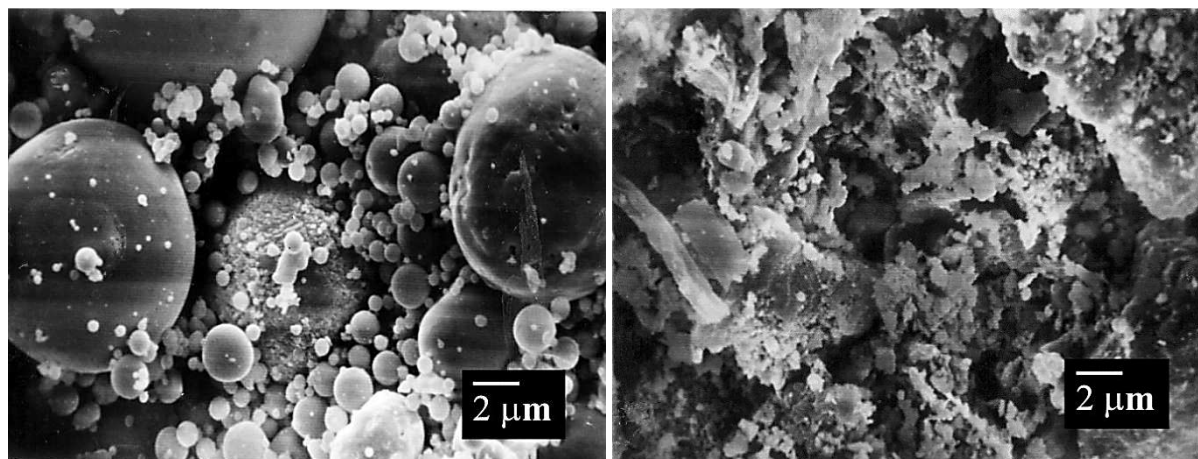


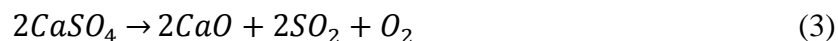
Figure 2. Morphology of classical high-temperature fly ash CFA (left) and fluidized fly ash – class C FFA (right), SEM 1500 \times .

Table 4. Granulometry of the fly ashes according to the residue on a screen with a size of 63 μm - R₆₃.

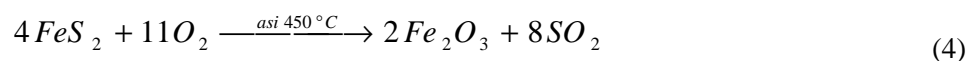
FFA	Hodonin	Ledvice	Tisova
R ₆₃ [%]	32.2	54.2	25.1

2.3. SO₂ emissions during the firing

Dry pressed body based on pure FFA (Hodonin) has been fired with continual analysing of flue gas (content of SO₂) by use of the TESTO M-I 300 flue gas analyzer, with a maximum measurable limit of 4000 ppm. Decomposition of anhydrite during the soaking time at 1200 °C (figure 3) produces calcium oxide, sulfur dioxide gas and oxygen very intensively according to the equation (reverse reaction (2):



The same decomposition we can observe during the firing of pure ceramic clays (for example stoneware clay MM – figure 4.), but from the lower temperatures (about 700 °C). The source of SO₂ in fuel gas during the firing of ceramic bodies is content of pyrite (marcasite) in clays – the decomposition of pyrite (marcasite) is evident about the temperature of 450 °C (figure 4) via equation (4):



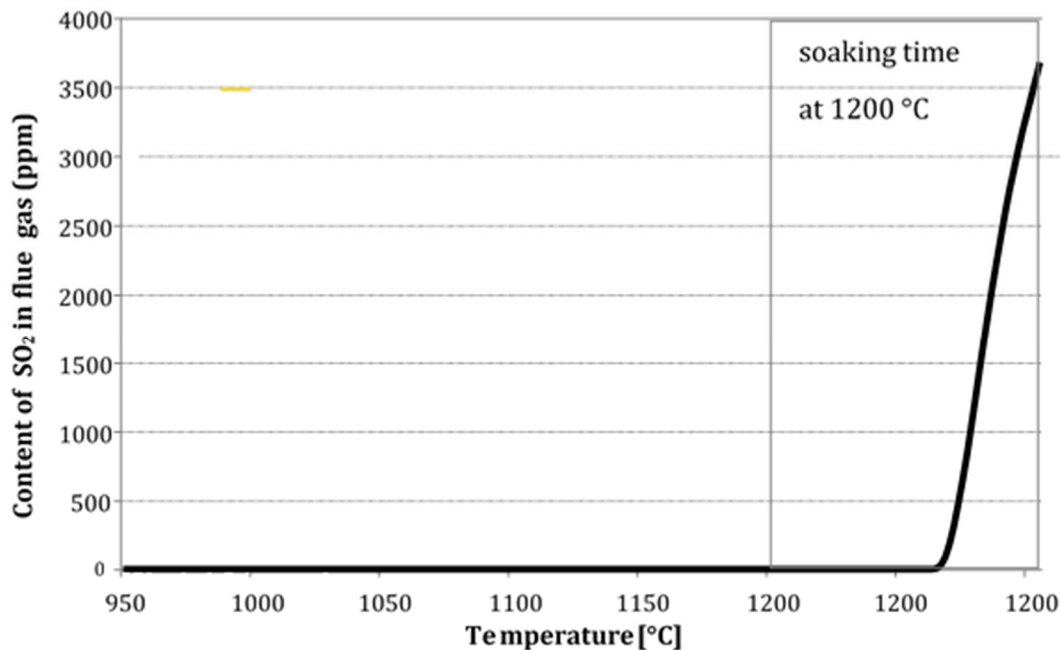


Figure 3. The content of sulfur dioxide in flue gas during the firing of class C fly ash (FFA – Hodonin).

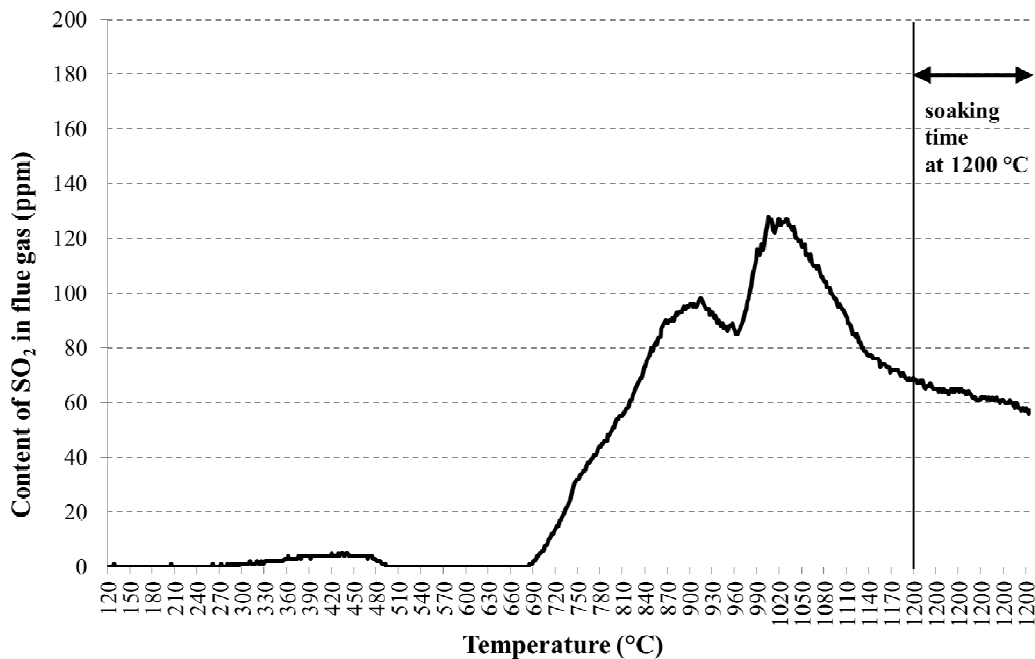


Figure 4. The content of sulphur oxide in flue gas during the firing of stoneware clay (MM).

3. Conclusion

The aim of the paper was to have a think about the possibility of application of fluidized fly ash (class C fly ash according to ASTM C618 12a) in the production of fired (ceramic) materials as a source of CaO in raw materials mixture. Fluidized and classical high-temperature fly ash were compared in terms of mineralogical and chemical composition, grain morphology and granulometry and their different firing behavior.

Every year about 1.5 million tonnes of fluidized fly ash are produced in Czech Republic but there has not been found a wider application of FFA for example in the production of fired building materials because the decomposition of anhydrite and thus releasing the emissions of sulfur dioxide have not been solved.

The aim of research within the Czech Science Foundation (via acknowledgement) solution is to define the temperature interval in which the anhydrite decomposes, the determination of the SO₂ content in the flue gas and the design of the treatment of the raw material mixture for the binding of SO₂ into the ceramic body without emissions.

Acknowledgement

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