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# Application of fly ashes from fluid bed coal combustion within refractory materials

J Kotrla<sup>1</sup>, F Šoukal<sup>1</sup>, J Másilko<sup>1</sup>, J Švec<sup>1</sup> and M Janča<sup>1</sup>

<sup>1</sup> Brno university of technology, Faculty of Chemistry, Materials Research Centre, Purkyňova 464/118, Brno Cz-612 00, Czech Republic

Email: xckotrla@fch.vut.cz

**Abstract.** The study deals with the possibility of utilization of fly ashes from coal combustion in refractory materials and its influence on resulting properties of the material. The effect of bed and filter ash addition on the properties of the droplet and the resulting mechanical properties, bulk density, shrinkage and firing temperature of stove fireclay. The subject of this study is also reduction of SO<sub>2</sub> emissions evolved burning of fireclay containing fluid ash rich of anhydrite. Emissions of SO<sub>2</sub> were observed by TG-DTA method. Characterization of prepared samples and study of heat treatment processes were based on XRD and TG-DTA.

## 1. Introduction

With technological advances of mankind, the demand for energy is growing. Today, the main source of energy is coal. In recent years, the trend of energy-saving and non-waste economy has grown. For this reason, it is important to look for a new and efficient use of energy industry byproducts [1].

Chemical, physical and mineralogical properties of the energy products, depends on a type of coal and a type of combustion process [2], [3]. A main type of the combustion process today is high-temperature and fluidized bed combustion [4]. Fluidized bed combustion is increasingly being applied, the advantage of it is that the desulfurization process is situated in a boiler and desulphurization stations are not needed [5]. Limestone is added directly to the boiler, where it reacts with SO<sub>2</sub> to form CaSO<sub>4</sub>. The main difference between high-temperature fly ash and fluid fly ash is a higher content of SO<sub>3</sub> and CaO in the fluid fly ash [6]. Fluid bed combustion takes place at a lower temperature and therefore it differs from high-temperature fly ash by chemical properties and content of amorphous phase [5].

Because of the high content of CaO, fluid fly ashes should not be used as an additive to concrete. There are some studies that deal with the possible use of fluid fly ash. Mostly fluid fly ash was used in smaller quantities as a replacement for high-temperature fly ash [7]–[9].

Fluid fly ash also contains a certain amount of anhydrite produced in the reactor during the desulfurization process. The presence of anhydrite in the fly ash is undesirable from an ecological point of view because during the firing process SO<sub>2</sub> is emerging to the atmosphere. One way to prevent SO<sub>2</sub> escaping to the atmosphere is to bond it to thermostable compounds such as hauyne. Hauyne is a tectosilicate mineral with endmember formula Na<sub>3</sub>Ca(Si<sub>3</sub>Al<sub>3</sub>)O<sub>12</sub>(SO<sub>4</sub>) and it is formed at higher temperature and pressure, so naturally it could be found in volcanic rocks [10]. Bo Wei et al. [11] dealt with the processes occurring between SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and CaSO<sub>4</sub> at high temperature. Bo Wei used fly ash to remove sodium ions which induces severe fouling and slagging in pulverized coal furnaces and found out that optimal temperature for hauyne formation is 1 050°C.



## 2. Experimental

### 2.1. Material

Fireclay samples were prepared for the measurements where the primary raw materials were partially replaced by fluid fly ash. For the preparation of samples was used fluid fly ash from the power plant Tisová and stove fireclay materials (BX shale, fireclay, and clay TPU) comes from P-D refractories CZ a.s. As a source of sodium ions, sodium water glass (Na<sub>2</sub>O 16.15%) was used, which is important for the formation of thermally stable phases. This premise was based on the work of Vodová [10].

The chemical composition of the used ashes was determined by ICP-OES and the values are in Table 1. The content of free lime in fly ashes was determined by the saccharate method and values are given in Table 2.

**Table 1.** The chemical composition of used ashes.

Major oxides [%]	Tisová	
	Filter ash	Bed ash
SiO <sub>2</sub>	32.2	24.5
Al <sub>2</sub> O <sub>3</sub>	25.4	16.1
CaO	10.5	24.5
K <sub>2</sub> O	5.1	5.8
MgO	0.4	0.4
SO <sub>3</sub>	7.7	14.8
TiO <sub>2</sub>	5.7	3.4
Fe <sub>2</sub> O <sub>3</sub>	7.0	7.5

**Table 2.** The content of free lime in used ashes.

	Tisová	
	Filter ash	Bed ash
Content of free lime [wt.%]	4.29	18.20

### 2.2. Sample preparation

Sample preparation consisted of mixing the ceramic mixture, pressing, drying and firing. The homogenization of the mixture was carried out in a planetary mixer. The pressing was carried out by one-sided compression in a 55 mm diameter steel cylindrical form on a hydraulic press BetonSystem DESTTEST 3310. Compression pressure was 25 MPa, acting on the body for 50 seconds. After pressing, the samples were dried at 105°C to a constant weight. Thereafter, the samples were placed in the Classic 7013L muffle furnace. The temperature mode consisted of a temperature ramp of 2 °C/min to 1 100 °C/min, a two hours isotherm and a ramp 2 °C/min to 500°C. The weights of raw materials for preparation of test samples are shown in Table 3.

**Table 3.** The composition of samples.

<b>Filter ash</b>							
<b>Sample</b>	<b>[g]</b>						
<b>identification</b>	<b>0%</b>	<b>1%</b>	<b>2%</b>	<b>5%</b>	<b>10%</b>	<b>20%</b>	<b>30%</b>
Fireclay	34.6	41.3	40.9	39.7	37.6	33.4	29.3
BX shale	103.3	123.9	122.5	118.8	112.5	100	87.5
TPU clay	68.6	82.4	81.6	79.1	74.9	66.6	58.3
Ash	0	2.5	5	12.5	25	50	75
Water	25	25	25	27	30	34	40

<b>Bed ash</b>							
<b>Sample</b>	<b>[g]</b>						
<b>identification</b>	<b>0%</b>	<b>1%</b>	<b>2%</b>	<b>5%</b>	<b>10%</b>	<b>20%</b>	<b>30%</b>
Fireclay	34.6	41.3	40.9	39.7	37.6	33.4	29.3
BX shale	103.3	123.9	122.5	118.8	112.5	100	87.5
TPU clay	68.6	82.4	81.6	79.1	74.9	66.6	58.3
Ash	0	2.5	5	12.5	25	50	75
Water	25	25	25	27	30	30	30

### 2.3. Methods

Mechanical properties, compressive strength, were measured on the complex device for strength test on building materials Betonsystem DESTTEST 3310. Compressive strength was measured on each testing body, which dimensions were 55 × 50 mm. Bulk density and shrinkage of samples were determined by dimensional and weight measurements.

Saccharate method was used to determine a content of free lime in ashes, according to ČSN P 72 2080 standard. The content of free lime (Table 2) was calculated according to the formula:

$$\% CaO = \frac{c \cdot V \cdot M}{m \cdot \nu} \quad (1)$$

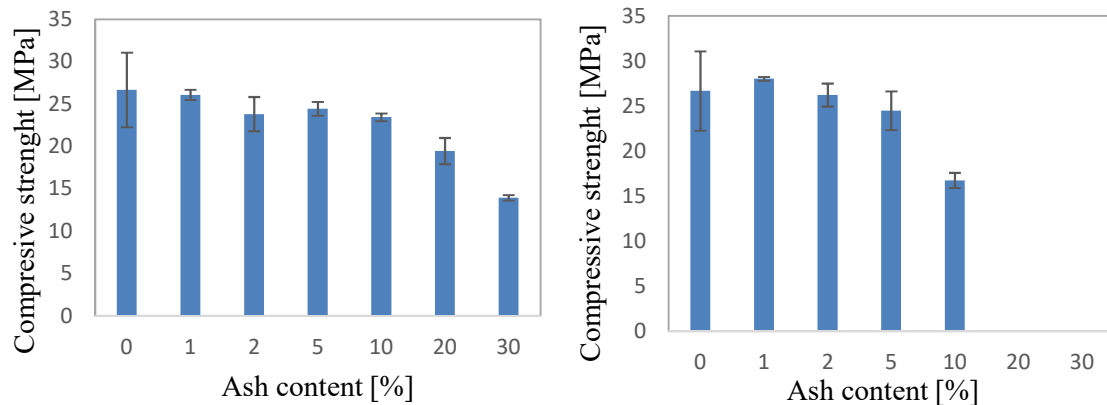
where  $c$  is a concentration of hydrochloric acid solution,  $V$  is the volume of the hydrochloric acid solution,  $M$  is the molar weight of CaO,  $m$  is the weight of the sample of ash and  $\nu$  is the stoichiometric ratio of reaction.

The TG-DTA was used to determine the behavior of the ceramic mixture. Measurements were performed on the TA INSTRUMENTS SDT Q600. The measurement started at 30°C, the heating rate was 10°C per minute to 1 350°C in the air atmosphere.

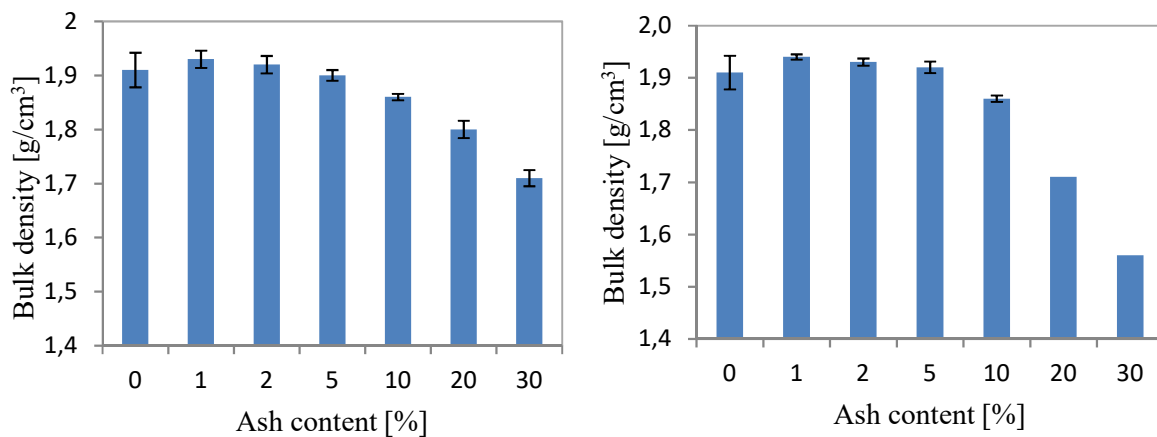
The XRD method was used to find out the occurrence of the hauyne crystalline phase. For observation, XRD Empyrea from Panalytical was used measured by referencing the intensity ratio method. For the measurement, the copper anode was used, voltage was 40 kV and the current was 30 mA.

### 3. Results and discussion

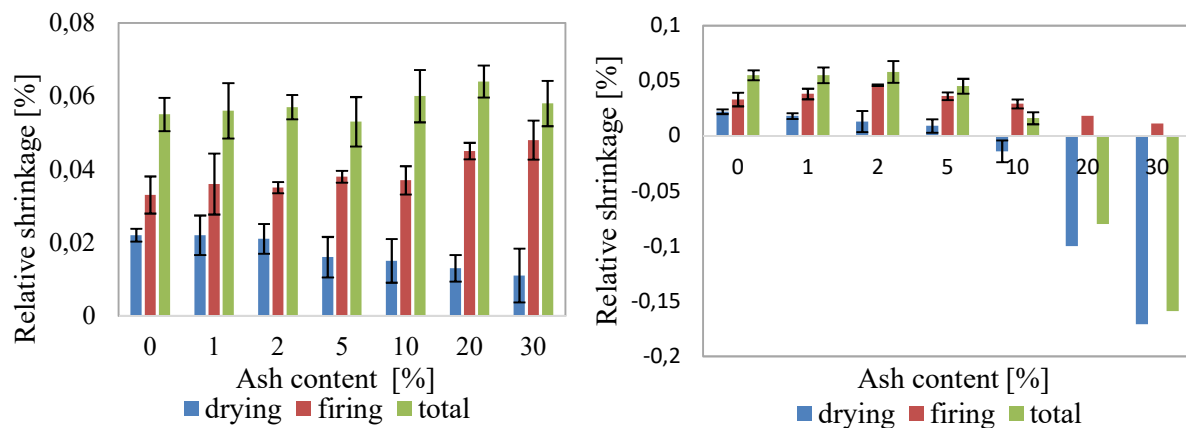
The influence of filter and bed fluid fly ash on compressive strength, bulk density and shrinkage are shown in Figure 1, 2 and 3.



**Figure 1.** Influence of filter (left) and bed (right) ash on compressive strength.



**Figure 2.** Influence of filter (left) and bed (right) ash on bulk density.



**Figure 3.** Influence of filter (left) and bed (right) ash on shrinkage.

From the measured values, it is evident, that the addition of filter ash, up to 10 wt. %, and bed ash, up to 5 wt. %, does not have a significant effect on the resulting mechanical properties. Higher addition of fluid fly ashes, cause a decrease in compressive strength due to hydration of CaO and anhydrite. When there is a change in volume and the formation of micro-cracks. For samples with higher bed fly

ash content, a large number of cracks occurred and it was not possible to determine their compressive strength.

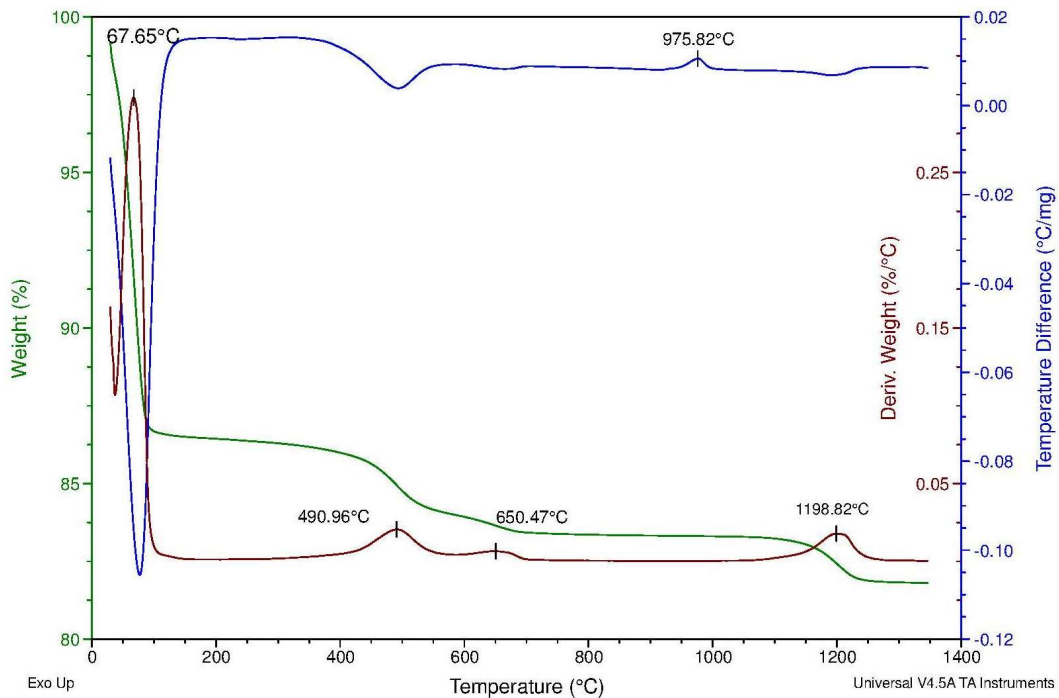
Keršnerová et al. [12] found that bulk density decreases with the increasing addition of fluid fly ash. This trend has been also observed, but only with higher additions (over 2–5 wt. %). The addition of fluid fly ash up to 2–5 wt. % increased the bulk density, due to filling the space between coarse fractions in the sample.

There was also observed shrinkage which occurred during drying and firing. From Figure 3 it is apparent that the addition of fluid filter ash reduces shrinkage during drying. However, this contraction is compensated by higher shrinkage during firing, so the addition of filter ash does not have the effect to the overall shrinkage. Higher fluid bed ash additives did not cause shrinkage during drying, but on the contrary to their expansion and cracking, due to CaO hydration. Cracks were evident in all samples containing bed ash (Figure 4).



**Figure 4.** Samples with a fluid bed fly ash (top left: 1, 2 and 5 wt. %, bottom left: 10, 20 and 30 wt. %).

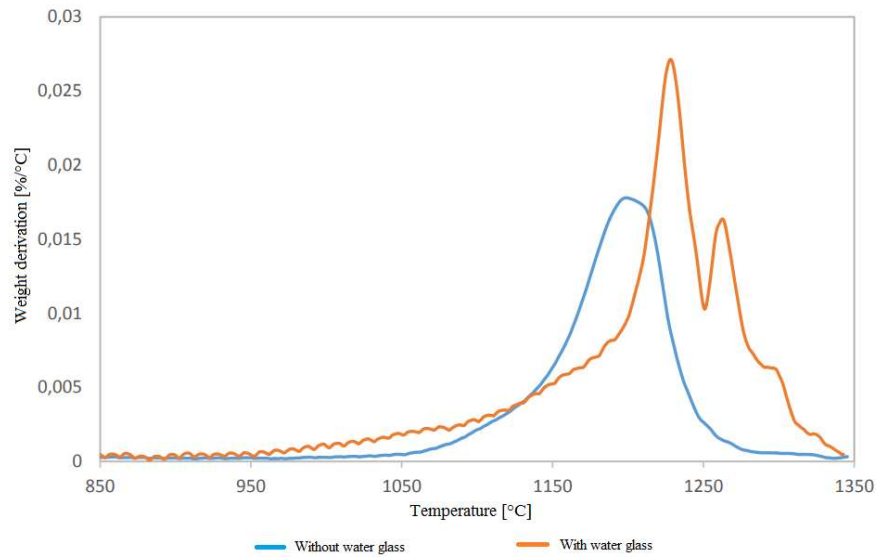
TG-DTA analysis was used to determine the chemical processes occurring during firing. Figure 5 shows the TG-DTA curve of the ceramic mixture with the addition of filter ash.



**Figure 5.** TG-DTA curve of ceramic mixture with filter ash (30 wt.%).

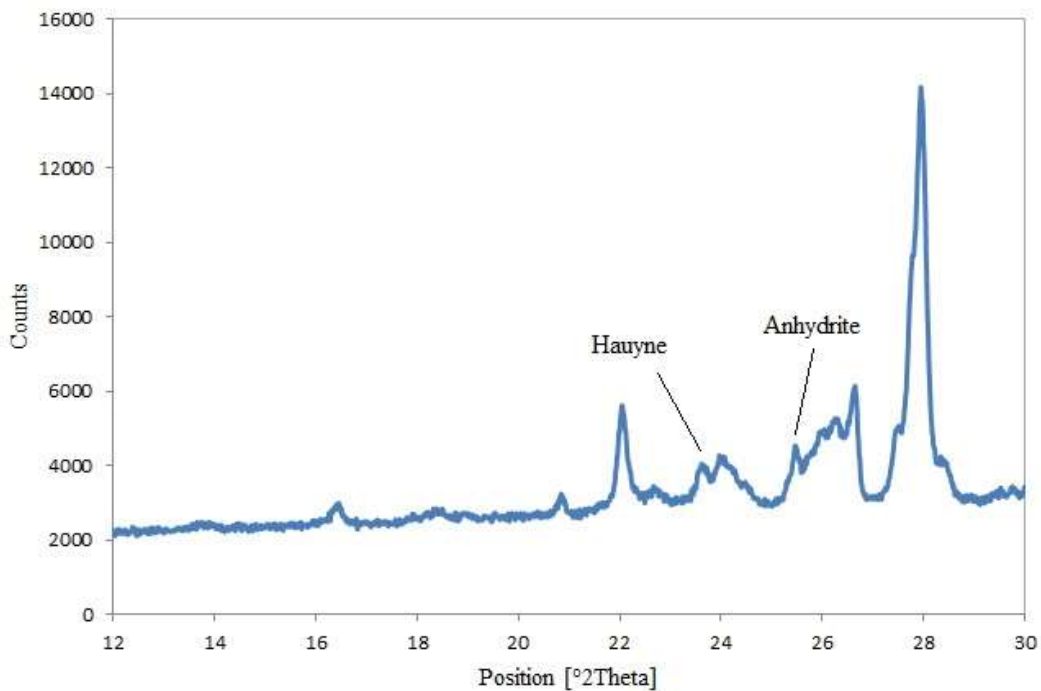
During the firing of the ceramic mixture with filter ash addition, the evaporation of water occurs to 68°C. Next weight loss is due to the dehydroxylation of clay minerals at about 491°C contained in TPU and decarbonization of carbonates in fly ash at about 650°C. At 976°C there is an exothermic reaction, which is the crystallization of the defective spinel [13]. Furthermore, from 1 070°C, mass loss occurs, which is associated with the decomposition of anhydrite and released SO<sub>2</sub>.

To reduce SO<sub>2</sub> emissions sodium water glass was added to the ceramic mixture with ash, which, according to dissertation [10], should provide sodium ions to react with anhydrite and form a heat-resistant compound (hauyne). In the Figure 6 are DTG curves of two samples with 30 wt. % filter ash, where one of the sample being enriched with 12 wt. % of sodium water glass (water glass was calculated on the weight of fly ash). The addition of water glass has caused that SO<sub>2</sub> release in two steps. The first release was from anhydrite decomposition and the second was from heat-resistant hauyne. It has been demonstrated [10] that the use of 12 wt. % of water glass reduce the SO<sub>2</sub> content in flue gas. This quantity proved to be inadequate because part of anhydrite remained in the sample.



**Figure 6.** DTG curves of samples with and without sodium water glass.

Created hauyne was observed by XRD analysis. However, demonstrable presence was less than in the dissertation of Vodová [10]. Samples with 30 wt. % of water glass were also observed (Figure 7). Anhydrite was still present in the sample, which signifies that the firing time was insufficient.



**Figure 7.** XRD analysis of sample with 30 wt. % of filter ash and 30 wt. % of water glass.

#### 4. Conclusion

The work was focused on the utilization of filter and bed fluid fly ash in refractory materials. From experimental observations, the highest values of pressure strength were measured on samples containing 1 to 10 wt. % of filter fly ash and 1 to 5 wt. % bed fly ash. However, samples with bed fly ash contained

cracks. This has shown that ash with a high content of CaO is unsuitable for the preparation of refractory materials.

The use of filter ash reduces shrinkage during drying, but this is compensated by bigger firing shrinkage and resulting shrinkage corresponds with the reference sample. The use of bed fly ash significantly influences the dimensions of the prepared samples due to the high content of CaO.

The use of fluidized fly ash in low additions (up to 10 wt. %) increases the bulk density, but the higher fly ash additions decrease the bulk density.

In the mixture, with the addition of sodium water glass, the heat-resistant compound was identified by XRD after firing. However, the firing time or addition of the water glass was not sufficient to react with all the present anhydrite.

The study has shown that fluid fly ash with a lower content of free lime could be serving as a partial replacement of primary raw materials.

### Acknowledgements

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