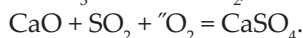


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## Preliminary Studies of Content of Unburned Carbon in Fly Ash from Coal-Fired Fluidized Bed Combustion\*\*

### 1. Introduction

Environmental requirements for reduced emissions from power plants have led to the development of new and modified coal combustion technologies. Application of fluidized bed combustion (FBC) technology gives opportunities for use of low-class solid fuels, particularly high-sulphur and high ash content fuels. Generally, this technology characterized low level of emission of sulphur and nitrogen oxides in combustion gases. Problem poses solid waste produced in process of fluidized bed combustion, which differ in form and chemical composition from ashes of conventional (PCC) [1]. FBC ashes are produced at a significantly lower temperature (800–950°C) than of PCC ashes (1200–1400°C) and sulphur removal process takes place in furnace. About 50% of the mass of waste is calcium components CaO and CaSO<sub>4</sub>, arisen from limestone or dolomite use as a sorbent for sulphur dioxide SO<sub>2</sub> released during coal combustion. The limestone is calcinated to CaO in the furnace, where it reacts with SO<sub>2</sub> and O<sub>2</sub> to form CaSO<sub>4</sub>:



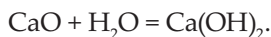
The level of reaction doesn't exceed 30%, it forces to use threefold excess of sorbent to achieve over 80% efficiency of desulphurization exhaust gases. In connection with this the amounts of Ca to S molar ratios 2,5 to 3 is necessary. The presence of calcium compounds in FBC ashes causes chemically active properties of these by-products [2].

First calcium oxide in contact with water, whether in liquid or vapour form converts to calcium hydroxide:

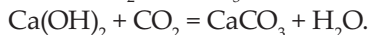
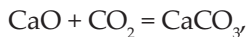
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Contact with the air leads to carbonization of calcium oxide [2–5].



Beside of those components silicon dioxide  $\text{SiO}_2$ , silicates, calcium aluminates and hematite ( $\alpha - \text{Fe}_2\text{O}_3$ ) are present in FBC ashes. Structural constituents and particle size distribution depend on kinds of sorbent, fuel and waste rock. In the case of incorrect combustion can be occurred sulfides, CaS.

One of the most characteristic properties of FBC fly ashes concerning possibilities of utilization is their chemical activity, especially after mixing contact with water. In contact with water solid product of combustion is setting due to presence of calcium oxide and anhydrite, turn into structure with low permeability and high compressive strength [3-5]. The physical and chemical properties of coal fly ashes, their large quantity and environmental reasons enable to use them in many industrial branches. If the content of unburned carbon is below 5 wt% fly ash may be a aluable raw material for the construction industry [6, 7]. Fly ashes with higher levels of unburned carbon content are unsuitable for concrete mixtures. Concrete mixtures containing such ashes require increased amounts of costly air-entraining agents to achieve a given level of air entrainment [8-10]. The control of the residue of unburned carbon in fly ash has constantly been an up-to-date problem in exploitation of coal power plants, because of the need for the optimization of the combustion process, protection of environment and the use of ash in industry.

## 2. Unburned Carbon Content

The loss-on-ignition (LOI) test according to American standard ASTM D 3278 and Polish standard PN – 77/G-04528/02 is the standard method for determination of the carbon content of fly ash from coal fired boilers. Fly ash sampled from the exhaust of a combustor is dried and weighted before being placed in a muffle furnace for several hours at 715°C in American standard, 815°C in Polish standard. The sample is then reweighted and the loss in weight is assumed to be due to the carbon initially present in the sample. The basic problem with the application of a standard method (LOI) is the influence of other components of the ash on the unburned carbon results. In particular this is important for hydrated sulfates, calcium hydroxide and carbonates. Interferences occurring in matrix of fly ashes from fluidized bed combustion:  $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$ ,  $\text{CaSO}_4 \times 2\text{H}_2\text{O}$  cause overestimate results of LOI method [11–15].

Accordingly, the error  $S_{\%}$  in the LOI test can be calculated by the equation (1).

$$s_{\%} = \frac{m_I}{m_C} \cdot 100\% \quad (1)$$

where:

$m_I$  – weight loss of sample due to interferences,

$m_C$  – weight loss of sample due to carbon oxidation.

Term “loss-on-ignition” in the case application of LOI test in analysis of fly ashes from fluidized bed combustion should be treated as it calls.

### 3. Experimental

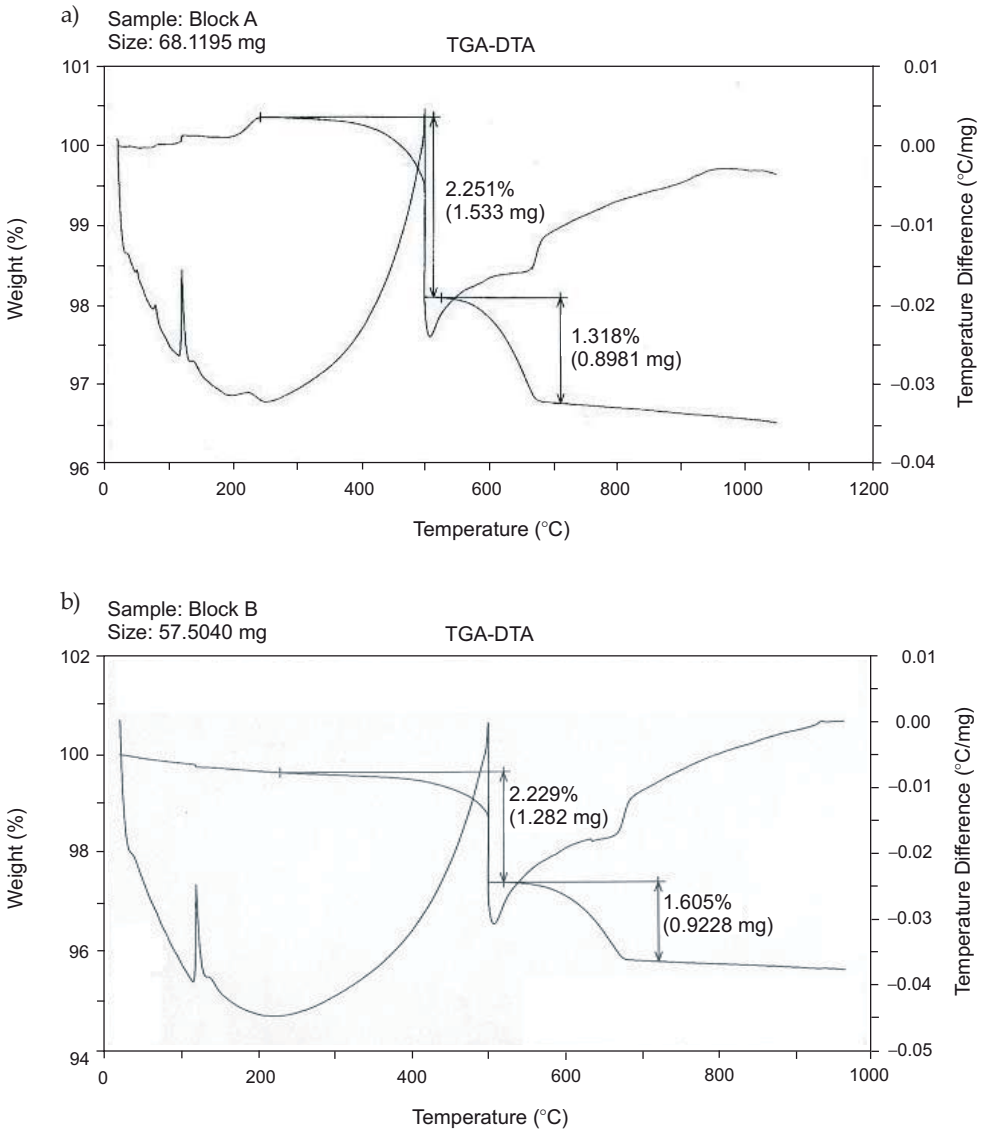
The goal of the study was to assess the application of “gradual roasting” for the measurements of unburned carbon content in FBC fly ashes. This method could be used in power plants which do not apply thermogravimetric method for determination of unburned carbon in FBC fly ashes. Moreover it could be used as a comparative method for industrial analyzer [16–18]. In “gradual roasting” method sample is heating in muffle furnace (PLM 7/2,5; temp max 1150°C) in three stages. In the first stage sample is dried to constant mass in temperature 150°C. for few hours. In the second stage is carrying out burn of unburned carbon present in sample through very slow heating in temperature 500°C for two hours (4°C/min) and leaved sample for next two hours in this temperature. Slow heating of sample in the second stage is of great importance to limit the sudden growth of temperature connected with sudden burning of unburned carbon in sample and emission of significant amount of heat. In the third stage sample is heated in 800°C in order to perform calcination of carbonates. “Gradually roasting” method was applied to two fly ash fractions obtained from sieved (63 µm sieve): fraction of lower granularity (<63 µm sieve) and fraction of higher granularity (> 63 µm sieve).

Thermogravimetric method TG and Differential Thermal Analysis TGA (Derivatograph Simultaneous TGA-DTA type SDT 2960, TA Instruments) was applied to the assessment of results obtained by “gradually roasting” method. TG-DTA curves provide data concerning transformations connected with change of mass sample (growth or loss) during heating and temperature range of transformations.

The fly ash samples used in the experiment originated from A and B energetic blocks of Siersza Power Plant, with circulating fluidized bed combustion (CFBC), 336 MWt. Ash samples were taken from the I fields of electrofilters of A and B energetic blocks.

### 4. Results and Discussion

TGA-DTA curves for the analyzed fly ash samples from A and B energetic blocks are shown in Figure 1. On the basis of TGA-DTA curves can be specified three main temperature ranges of weight loss in examined samples.



**Fig. 1.** TGA-DTA curves for fly ash sample from: a) A energetic block; b) B energetic block

The first range from 20°C to 120°C is due to the loss of water. The second range of 500°C illustrates oxidation of unburned carbon, connected with exothermic peak on the DTA curves. In the last range of heating, in 600–700°C the weight loss is caused by the calcinations of carbonates. Comparison of the results obtained by TGA-DTA method and “gradual roasting” test is shown in Table 1.

**Table 1.** The weight loss (weight %) in the specified temperature ranges obtained by TGA-DTA method and “gradual roasting” test

		A Block			B Block		
		weight loss in 500°C oxidation of unburned carbon	weight loss in 700°C calcination of carbonates	total weight loss	weight loss in 500°C oxidation of unburned carbon	weight loss in 700°C calcination of carbonates	total weight loss
		weight %					
„Gradual roasting” test <i>n</i> = 5	1	1,96	1,54		1,88	1,82	
	2	1,97	1,51		1,91	1,84	
	3	2,03	1,48		1,99	1,70	
	4	1,99	1,49		1,87	1,88	
	5	1,96	1,48		1,89	1,88	
	Average	1,98	1,50	3,48	1,89	1,86	3,74
SD	0,03	0,02		0,01	0,03		
TGA		2,25	1,32	3,57	2,23	1,60	3,83

SD – standard deviation

Mean values of the results in “gradual roasting” test were obtained on the basis of five single samples. Total weight losses were obtained on the basis of means in selected temperature. Results obtained in “gradual roasting” test and thermogravimetric method are in good agreement. Differences in the mass sample examined by thermogravimetric method of the order of tens milligrams and mass sample analyzed in laboratory muffle furnace of the order of 1 gram probably caused differences in results. More over it caused different conditions of oxide flow in thermogravimetric furnace and in laboratory muffle furnace. Results show in Table 2 the weight loss in temperature 500 and 700°C for two fractions of fly ashes, fraction of lower granularity (< 63 μm sieve) and fraction of higher granularity (> 63 μm sieve). Based on the results obtained for fly ash fractions one may conclude that the unburned carbon occurs in fly ash fraction of lower granularity (< 63 μm sieve). Whereas calcium carbonate occurs in both fractions. Fly ash fraction of lower granularity (< 63 μm sieve) shows higher content of carbonates then fraction of higher granularity. Occurring of unburned carbon in fraction of lower granularity facilitates carbon oxidation process in proposed temperature 500°C. Study of fly ashes with thermogravimetric method and “gradual roasting” test allowed to determine error  $S_{\%}$  due to the presence of carbonates in matrix of fly ashes from fluidized bed combustion.

**Table 2.** The weight loss (weight %) in the specified temperature ranges obtained in “gradual roasting” test for two fractions of fly ash, fraction of lower granularity (< 63  $\mu\text{m}$  sieve) and fraction of higher granularity (> 63  $\mu\text{m}$  sieve)

Fractions	A Block		B Block	
	weight loss in 500°C oxidation of unburned carbon	weight loss in 700°C calcination of carbonates	weight loss in 500°C oxidation of unburned carbon	weight loss in 700°C calcination of carbonates
	weight %			
> 63 $\mu\text{m}$	0	1,58	0	1,47
< 63 $\mu\text{m}$	2,75	4,05	2,68	4,34

Values of the error  $S_{\%}$  were calculated according to the equation (1). Value of the error for the sample from A block amounts to 58,7% and for sample from B block is 71,8%. For fly ashes with higher amount of interferences error  $S_{\%}$  turns to be larger.

## 5. Conclusions

The content of unburned carbon in fly ash is one of the important factors in power plants exploitation, because of the optimization of combustion process and utility of fly ashes in industry. Application of LOI standard method for fly ashes from fluidized bed combustion is limited because of the presence of some components which mass vary during the heating. Analysis of FBC fly ash samples in accordance with LOI standard method in temperature above 700°C is not possible, for the reason of overestimation results of unburned carbon content and following error of measurements. Thermogravimetric method was applied to assess of “gradual roasting” test. On the basis of preliminary studies one may conclude that it can be use as a measurement method of unburned carbon in fly ash from fluidized bed combustion.

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