



# Effect of the temperature of different combustion zones in the boiler grate on changes in physical and chemical parameters of bituminous coal and slags



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## ABSTRACT

This paper presents the results of a study on the influence of the temperature of characteristic zones of coal combustion in a stoker fired boiler (drying, degassing, and burn-out), on changes in physical and chemical parameters of bituminous coal and slags. This information is important as it helps identify the impact of coal properties on the accumulation of trace elements, primarily mercury, in combustion waste. The study is the continuation of research work on the impact of mercury compounds accumulated in combustion waste on the natural environment (mercury from landfills of slag, and fly ash). Studies were undertaken because no in-depth analysis of the impact of the temperature of particular zones of stoker fired boilers on the physical and chemical parameters of the post-process slag, including mercury content, had been reported in literature. Both of the coals examined, classified as bituminous coal according to the International Classification of Seam Coals and of type 32.1 according to the PN-G-97002:1982 standard, showed an average mercury content of 0.0849  $\mu\text{g/g}$ . In the chemical composition determined for the ash derived from burnt coal, the dominance of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  over other oxides was found. This feature results in the increase of the softening temperature and ash melting and, therefore, during the combustion of coal tested in a stoker fired boiler, only ash was subjected to the sintering process. Mercury content in the other examined samples taken from various locations of the stoker fired boiler (drying – 32–1050  $^\circ\text{C}$ , degassing – 1050–1020  $^\circ\text{C}$ , and burn-out – 1020–400  $^\circ\text{C}$ ) varied from 0.0668 to 0.0009  $\mu\text{g/g}$  and was determined with the use of a LECO atomic absorption spectrometer. The analyses of the elemental composition, performed with the application of XRF spectrometry, for ash obtained from samples collected from different sampling points of the stoker fired boiler showed that the largest concentration of trace elements was observed for the ash derived from the samples collected in the degassing zone (temperature range 1050–850  $^\circ\text{C}$ ).

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## 1. Introduction

Global coal consumption in the energy sector is expected to gradually increase by 1.3% per annum according to the forecasts of the U.S. Department of Energy ([International Energy Outlook, 2013](#)).

Hard coal, as a sedimentary rock of organic origin, consists of three basic components: organic matter, composed of a few basic chemical elements, such as carbon, hydrogen, oxygen, nitrogen, sulfur and phosphorus; mineral matter, forming non-organic compounds, and water ([Ali, Tuzen, & Kazi, 2016](#)). Coal properties

are typical in complex colloidal systems. Hard coal is a multi-phase, microheterogeneous solid solution which is organosol, organogel or xerogel. The type of solid solution depends on the coal rank ([Jasieñka, 1995](#)).

In Poland over 90% of total electricity production is based on coal combustion. In 2015, the balance resources of hard coal in Poland amounted to 24.933 million Mg ([Polish Geological Institute, 2015; Smoliński, 2007, 2011](#)).

The combustion process in a stoker fired boiler is performed in three main zones with varying temperatures: zone of drying, degassing and burn-out ([Karolczuk, 1998; Kruczek, 2001; Roga, 1954](#)).

Therefore, during combustion in grate boilers hard coal passes through three phases: drying, degassing and burn-out of the produced coke.

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In the first section of a grate, coal is heated up by absorbing heat from the combustion chamber walls, already burning coal and air passing through the coal layer on a grate. The drying phase lasts until coal reaches a temperature of 100 °C. After releasing the moisture, the coal temperature further increases and the degassing phase takes place, during which volatile organic compounds, primarily hydrocarbons, are released. At a temperature of 350–500 °C, a release of volatile matter from successive layers of fuel and partial conversion of the produced carbon dioxide into carbon monoxide takes place. The degassing product is a coke breeze composed of carbon and mineral matter (Karolczuk, 1998; Kruczek, 2001; Roga, 1954; Szlęk, 2008). The coke breeze burns out very slowly, because of its internal structure. Therefore, the burn-out phase of coke breeze determines the time needed to burn coal.

The time of coke breeze combustion depends on the coal caking properties; the stronger the sintering, the more compact the resultant coke breeze is.

According to the Agency for Toxic Substances and Disease Registry (ATSDR, 2015), the most poisonous compounds are: arsenic, lead and mercury. This is why the question of mercury compound release in to the environment from coal combustion processes is considered to be so important.

Worldwide research carried out by UNEP (the United Nations Environment Programme) (UNEP, 2013) has shown that approximately 50% of global mercury emissions are of anthropogenic origin (stoker fired boilers and pulverized coal boilers operated in heat and power plants) (Zarzycki & Wichliński, 2014).

Mercury contained in coal is usually present in inorganic compounds, and is often associated with pyrite, in particular coarse pyrite of epigenetic origin (Ali et al., 2016; Ali, Tuzen, & Kazi, 2016). Mercury is also found in organic compounds as well as micro intrusions of metallic mercury (Dziok, Strugała, Rozwadowski, Macherzyński, & Ziomber, 2015; Kłojzy-Karczmarczyk & Mazurek, 2014; Róg, 1998; Zarzycki & Wichliński, 2014).

The impact of the combustion temperature together with the qualitative and quantitative impact of gases present in the coal combustion chamber on the rate of mercury compounds release in to the atmosphere has been described previously (Dziok, Strugała, Rozwadowski, & Okońska, 2014; Gostomczyk, Jędrusik, & Świerczok, 2010; Hławiczka, Kubica, & Zielonka, 2003; Yudovich & Ketris, 2005a, 2005b). It has been found that the emission of mercury compounds from fuels takes place immediately after putting a sample into the test furnace, at temperatures of

200–300 °C and at a temperature (300–500 °C) that corresponds with the degassing phase (Wichliński, Kobytecki, & Bis, 2011). It has been also shown that the most important parameters affecting the degree of mercury compound removal from hard coal include: the final combustion temperature, the heating rate, as well as the type and flow rate of the carrier gas. The increased gas flow rate and low heating rate enhance the release of mercury compounds from a fuel. It has been also found that mercury release is most effective in a reducing atmosphere (Dziok et al., 2014).

During the storage of solid combustion waste (slag, fly ash), water erosion takes place causing leaching of mercury compounds from combustion waste and its migration to water. The thermally processed waste has a particularly high potential for the release of toxic substances, including mercury, into the water and soil environment. Mercury may also be transported with particulate matter in the atmosphere (Ali et al., 2016; Feng, Sommar, Lindqvist, & Hong, 2002; Glodek & Pacyna, 2009; Hower, Eble, & Quick, 2005; Kostova, Hower, Mastalerz, & Vassilev, 2011; Niedźwiecki, Meller, Malinowski, & Sammel, 2007; Nowak, 2014; Pacyna et al., 2010; Sushil & Batra, 2006; Vejahati, Xu, & Gupta, 2010; Wichliński, Kobytecki, & Bis, 2012; Zhang, Zhao, Ding, Zeng, & Zheng, 2007).

Nevertheless, no in-depth analysis of the impact of the temperature of particular zones of stoker fired boilers on the physical and chemical parameters of the post-process slag, including mercury content, has been reported in literature.

The aim of this study was therefore to identify the changes in physical and chemical parameters of bituminous coal and slags during the combustion process in different zones of a boiler grate, and in particular the changes in mercury content, as well as the temperature effect on these changes. The study is considered to be important for identifying the impact of coal properties on the accumulation of mercury in combustion waste.

## 2. Materials and methods

Samples of coal and combustion waste were collected from different parts of a boiler grate, type WR10. Places of sample collection are presented in Fig. 1.

Tests were carried out on the stoker fired boiler WR10. This boiler is equipped with a vertical lifting fire door and a movable grate. The grate movement speed was: 1 m/6 min. The total residence time of coal on the movable grate was about 30 min (from the front section to the end of zone V). Samples were collected in

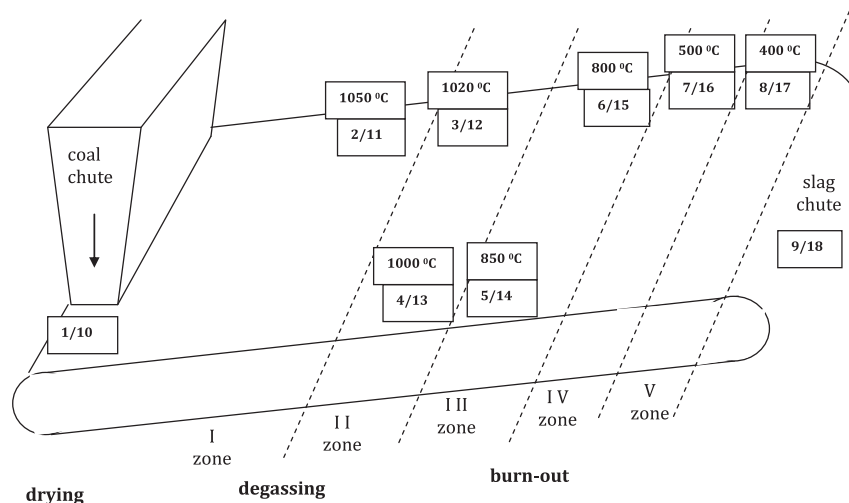


Fig. 1. Diagram of sampling points along the grate of the boiler.

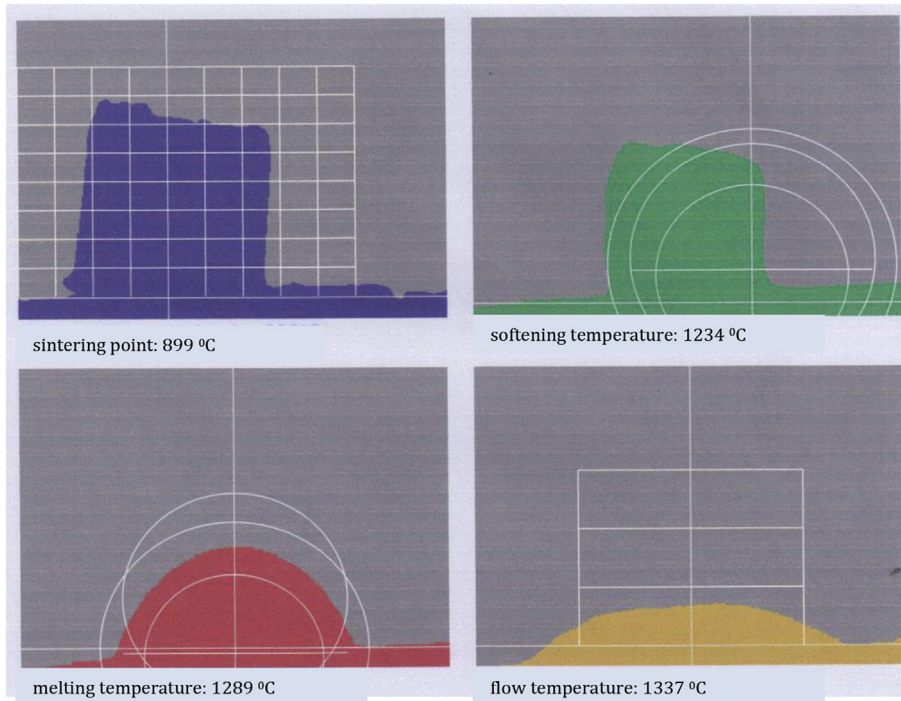


Fig. 2. Characteristic melting temperature of the ash for sample No. 1, reducing atmosphere.

two stages. In each of the stages, a sample of coal was collected from the front section of the grate (sample No. 1 in series I and sample No. 10 in series II), and next, when the coal was moved to the first combustion zone, a sample of burning coal was collected (sample No. 2 in series I and sample No. 11 in series II). Two samples were also collected from both sides of the grate in the second combustion zone (sample No. 3 and 4 in series I and sample No. 12

and 13 in series II). Then, following the same pattern, samples from 5/14 to 8/17 were collected in subsequent combustion zones: III, IV and V. Samples were collected directly from the hot grate. In addition, a sample of slag was collected from the waste outlet (sample No. 9 in series I, and sample No. 18 in series II).

The physical and chemical properties were determined for all of the samples of bituminous coals and slags, including: analytical

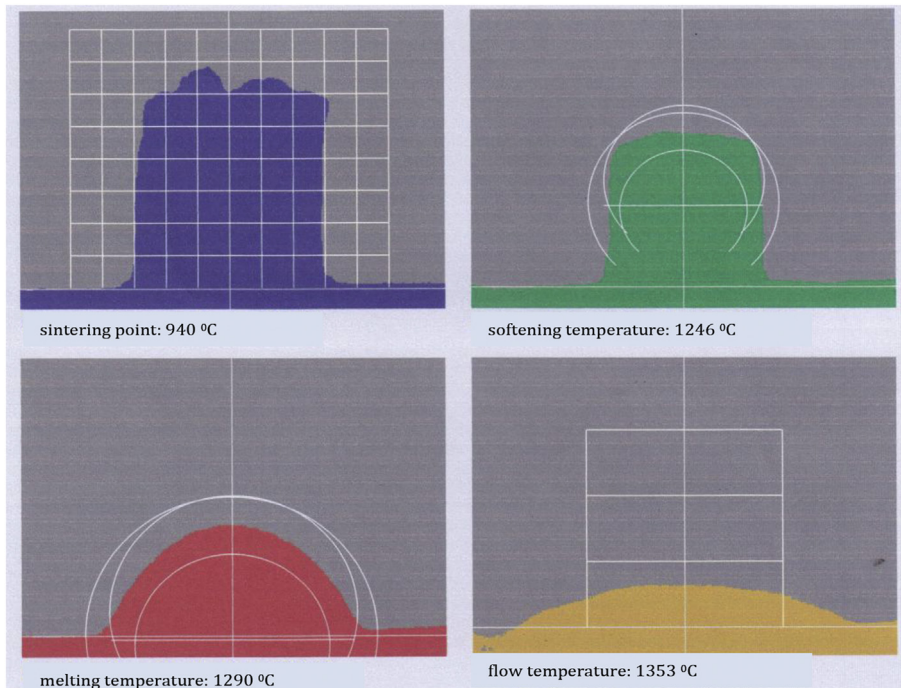


Fig. 3. Characteristic melting temperature of ash for sample No. 10, reducing atmosphere.

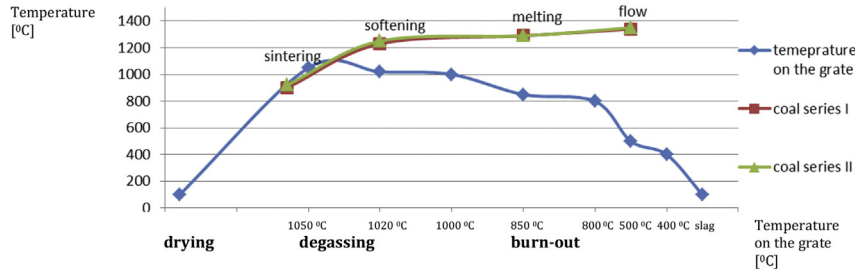


Fig. 4. Characteristic melting temperatures of burnt coal ash vs temperatures along the grate.

Table 1

Physical and chemical properties of burnt coals.

Coal	Sample no.	Vitrinite reflectance index, $R_0$	Mercury, Hg [ $\mu\text{g/g}$ ]	Volatiles matter, $V^{\text{daf}}$ [%]	Ash, $A^a$ [%]	Calorific value, $Q_i^f$ [J/g]	Carbon, $C_t^a$ [%]	Total sulfur, $S_t^a$ [%]	Pyritic sulfur, $S_p^a$ [%]	Sulfur in ash, $S_A$ [%]	Combustible sulfur, $S_c^a$ [%]	Roga index, RI
Series I	1	$0.70 \pm 0.02$	$0.10 \pm 0.02$	$35.37 \pm 0.33$	$16.16 \pm 0.44$	$24860 \pm 189$	$63.08 \pm 0.86$	$0.70 \pm 0.04$	$0.35 \pm 0.03$	$0.29 \pm 0.03$	$0.41 \pm 0.03$	$16 \pm 3$
Series II	10	$0.67 \pm 0.02$	$0.07 \pm 0.02$	$34.03 \pm 0.32$	$15.71 \pm 0.44$	$24959 \pm 190$	$63.30 \pm 0.86$	$0.68 \pm 0.04$	$0.36 \pm 0.03$	$0.31 \pm 0.03$	$0.37 \pm 0.03$	$16 \pm 3$

moisture content and ash according to PN-G-04560:1998, carbon content according to standard PN-G-04571:1998, total sulfur content according to PN-G-04584:2001, pyritic sulfur content according to PN-G-04582:1997, ash sulfur content according to PN-G-04584:2001, heat of combustion according to standard PN-G-04513:1981, and the mercury content according to our own procedure based on the standard PN-G-04562:1994. In addition, characteristic temperatures of ash melting in a reducing atmosphere were determined for two samples of burnt bituminous coal according to PN-G-04535:1982, the content of volatile matter in accordance with PN-G-04516:1998, vitrinite reflectance according to PN-ISO 7404–5:2002, and the type of coal according to PN-G-97002:1982.

These analyses were performed in the Department of Solid Fuels Quality Assessment of the Central Mining Institute. The moisture and ash content were determined with a LECO thermogravimetric analyzer (St. Joseph, MI, USA). Carbon content and total sulfur content were determined by use of high-temperature combustion with the infrared detector technique, using LECO and the Tele and Radio Research Institute apparatus (Warsaw, Poland). Pyritic sulfur content was determined by the chemical method. The heat of combustion was determined with a LECO calorimeter. In order to determine the characteristic melting temperature of ash, apparatus from the Tele and Radio Institute was used. Mercury content was determined with the use of a LECO atomic absorption spectrometer.

In the next stage, ash from the collected samples was heated in laboratory conditions in a furnace at a temperature of 815 °C. The resulting ash was tested for trace element content in the Department of Environmental Monitoring of the Central Mining Institute by means of XRF spectrometry using a RIGAKU, ZSX Prymus II spectrometer (Ettlingen, Germany). Tablets for testing were prepared from ash through compression with graphite. Then 3 g of sample ash, 1.5 g of cellulose and 0.45 g of graphite were dried at a temperature of 105 °C for about 2 h. This was mixed for 1 min, then

transferred to a HERZOG HSM 100A grinding mill (Midland, ON, Canada). The mixture was ground at a high speed of 1.500 rpm for 1 min to obtain pellets suitable for the X-ray Fluorescence technique. The ground sample was pressed in a HTT40 hydraulic press (Bursa, Turkey) under a pressure of 20 kN.

All of the analyzers were operated under standard laboratory conditions.

### 3. Results and discussion

#### 3.1. Characteristic temperatures of ash melting

Figs. 2 and 3 show the results of typical ash melting temperature, in a reducing atmosphere for two burnt samples of bituminous coal.

On the basis of the characteristic temperature of ash melting, determined under a reducing atmosphere, and on the basis of temperature measurements at sampling points along the grate (Fig. 1), the zones in which the coal ash is subjected to transformation of: sintering, softening, melting and flow, can be determined.

Due to the fact that the highest temperature identified along the grate was 1050 °C (Fig. 4), ash from burnt coal was only subjected to the sintering process. Other characteristic temperatures, i.e.: softening, melting and flow temperatures, were higher than the maximum temperature found along the grate.

#### 3.2. Qualitative characteristics of burnt bituminous coal

Table 1 shows the physical and chemical parameters of the bituminous tested coal.

On the basis of the values of the vitrinite reflectance, the content of volatiles and the sintering ability RI (Table 1), burnt fine coal was classified as a bituminous coal (International Classification of Seam

Table 2

The oxide composition of ash from coal.

Sample	Oxides (% weight)											
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Mn <sub>3</sub> O <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>
1	$52.16 \pm 3.13$	$23.40 \pm 2.81$	$7.94 \pm 0.64$	$4.38 \pm 0.35$	$2.78 \pm 0.50$	$0.99 \pm 0.23$	$2.45 \pm 0.25$	$3.85 \pm 0.69$	$0.99 \pm 0.12$	$0.36 \pm 0.06$	–	–
10	$51.41 \pm 3.08$	$23.85 \pm 2.86$	$7.99 \pm 0.64$	$4.57 \pm 0.37$	$2.85 \pm 0.51$	$0.97 \pm 0.23$	$2.42 \pm 0.24$	$3.90 \pm 0.70$	$1.04 \pm 0.12$	$0.37 \pm 0.06$	–	–

**Table 3**  
The content of trace elements in the ash from coal.

Sample	Trace elements (µg/g)																
	Ag	As	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Rb	Sb	Sn	Sr	V	Zn
1	<2 ± 1	48 ± 10	1284 ± 257	3 ± 1	41 ± 8	533 ± 107	98 ± 20	751 ± 150	3 ± 1	275 ± 55	107 ± 21	156 ± 31	<2 ± 1	<2 ± 1	859 ± 172	213 ± 43	209 ± 42
10	< ± 1	57 ± 11	1293 ± 259	<2 ± 1	30 ± 6	311 ± 62	100 ± 20	789 ± 158	2 ± 1	189 ± 38	130 ± 26	152 ± 30	<2 ± 1	<2 ± 1	842 ± 168	221 ± 44	212 ± 42

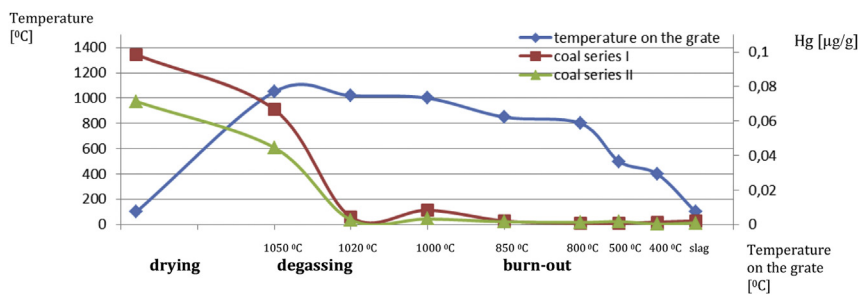
**Table 4**  
Values of the determined parameters for the collected samples.

Series	Sample no.	Mercury, Hg [µg/g]	Ash, A <sup>a</sup> [%]	Heat of combustion, Q <sub>s</sub> <sup>a</sup> [J/g]	Carbon, C <sub>t</sub> <sup>a</sup> [%]	Total sulfur, S <sub>t</sub> <sup>a</sup> [%]	Pyritic sulfur, S <sub>p</sub> <sup>a</sup> [%]	Sulfur in ash, S <sub>A</sub> [%]	Combustible sulfur, S <sub>C</sub> [%]	
I	2	0.07 ± 0.02	23.30 ± 0.28	23,996 ± 182	61.88 ± 0.86	0.78 ± 0.04	0.41 ± 0.04	0.33 ± 0.03	0.45 ± 0.01	
	3	0.004 ± 0.007	29.82 ± 0.28	22,425 ± 170	60.12 ± 0.86	0.53 ± 0.04	0.06 ± 0.01	0.39 ± 0.04	0.14 ± 0.01	
	4	0.008 ± 0.007	35.00 ± 0.28	20,708 ± 157	59.39 ± 0.78	0.65 ± 0.04	0.12 ± 0.01	0.39 ± 0.04	0.26 ± 0.01	
	5	0.002 ± 0.007	67.48 ± 0.28	9456 ± 97	37.26 ± 0.78	0.39 ± 0.04	0.08 ± 0.01	0.29 ± 0.03	0.10 ± 0.01	
	6	0.001 ± 0.007	64.99 ± 0.28	6520 ± 67	32.61 ± 0.78	0.29 ± 0.04	0.06 ± 0.01	0.27 ± 0.02	0.02 ± 0.01	
	7	0.001 ± 0.007	74.07 ± 0.28	5463 ± 56	24.63 ± 0.78	0.26 ± 0.04	0.04 ± 0.01	0.23 ± 0.02	0.03 ± 0.01	
	8	0.001 ± 0.007	78.94 ± 0.28	3832 ± 39	21.86 ± 0.78	0.27 ± 0.04	0.08 ± 0.01	0.26 ± 0.02	0.01 ± 0.01	
	Waste	9	0.002 ± 0.007	78.52 ± 0.28	3928 ± 40	21.20 ± 0.78	0.22 ± 0.04	0.07 ± 0.01	0.21 ± 0.02	0.01 ± 0.01
II	11	0.05 ± 0.02	18.00 ± 0.28	25,744 ± 196	62.15 ± 0.86	0.66 ± 0.04	0.18 ± 0.01	0.39 ± 0.04	0.27 ± 0.01	
	12	0.003 ± 0.007	32.49 ± 0.28	22,556 ± 171	60.36 ± 0.86	0.51 ± 0.04	0.04 ± 0.01	0.41 ± 0.04	0.10 ± 0.01	
	13	0.003 ± 0.007	42.68 ± 0.28	16,350 ± 124	55.66 ± 0.78	0.67 ± 0.04	0.09 ± 0.01	0.29 ± 0.03	0.38 ± 0.01	
	14	0.002 ± 0.007	81.09 ± 0.28	3200 ± 33	16.85 ± 0.78	0.25 ± 0.04	0.08 ± 0.01	0.22 ± 0.02	0.03 ± 0.01	
	15	0.001 ± 0.007	72.99 ± 0.28	4737 ± 48	26.84 ± 0.78	0.23 ± 0.04	0.05 ± 0.01	0.19 ± 0.02	0.04 ± 0.01	
	16	0.007 ± 0.007	78.63 ± 0.28	3649 ± 37	20.44 ± 0.78	0.25 ± 0.04	0.06 ± 0.01	0.22 ± 0.02	0.03 ± 0.01	
	17	0.001 ± 0.007	83.50 ± 0.28	2625 ± 27	15.22 ± 0.78	0.28 ± 0.04	0.06 ± 0.01	0.28 ± 0.03	0.00 ± 0.01	
	Waste	18	0.001 ± 0.007	78.87 ± 0.28	4093 ± 42	20.35 ± 0.78	0.25 ± 0.04	0.08 ± 0.01	0.19 ± 0.02	0.06 ± 0.01

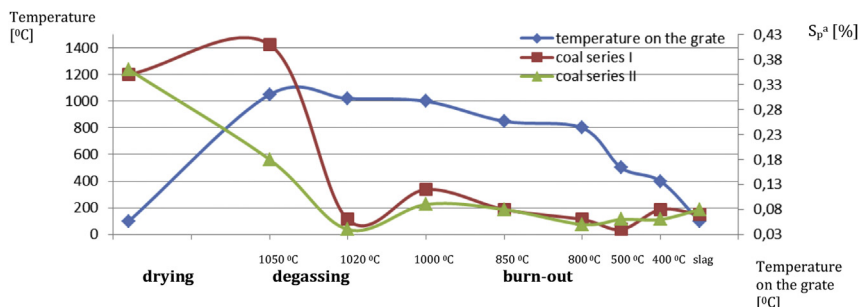
Coals, 1995) of type 32.1 (PN-G-97002:1982 standard). This was a gas-flame type coal, with a high concentration of volatiles and weak sintering properties. These types of coal burn for a long time and with a highly luminous flame. Ash content (A<sup>a</sup>) in both types of coal was similar, about 16%. This implied a good calorific value (Q<sub>f</sub><sup>a</sup>), which for both types of coal was almost 25,000 J/g. Total sulfur content (S<sub>t</sub><sup>a</sup>) was not high, 0.70% for sample No. 1, and 0.68% for sample No. 10. A very small part of the total sulfur content was pyritic sulfur: 0.35% for sample No. 1, and 0.36% for coal samples

from series II. The remaining part of the sulfur included sulfate sulfur and organic sulfur.

The burnt coal differed significantly in terms of mercury content. In coal samples from series I the mercury content was 0.0985 µg/g and for coal samples from series II it was 0.0714 µg/g. The average mercury content in coal from the USC (Upper Silesian Coal Basin) reported in literature is 0.063 µg/g (Okulski, 2007). The mercury content range was from 0.001 µg/g to 0.758 µg/g, and therefore the average value was lower than the value observed for



**Fig. 5.** Mercury content [Hg] in coal and its combustion products depending on the combustion temperature on the grate.



**Fig. 6.** Pyritic sulfur content [S<sub>p</sub><sup>a</sup>] in coal and its combustion products depending on the temperature of combustion on the grate.

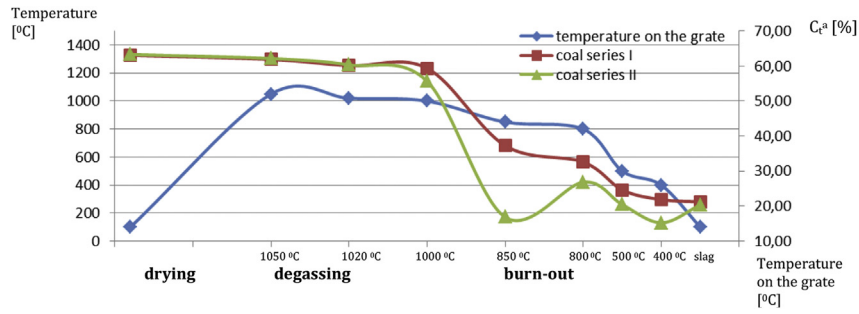


Fig. 7. Total carbon content [C<sub>a</sub><sup>2</sup>] in coal and its combustion products depending on the temperature of combustion on the grate.

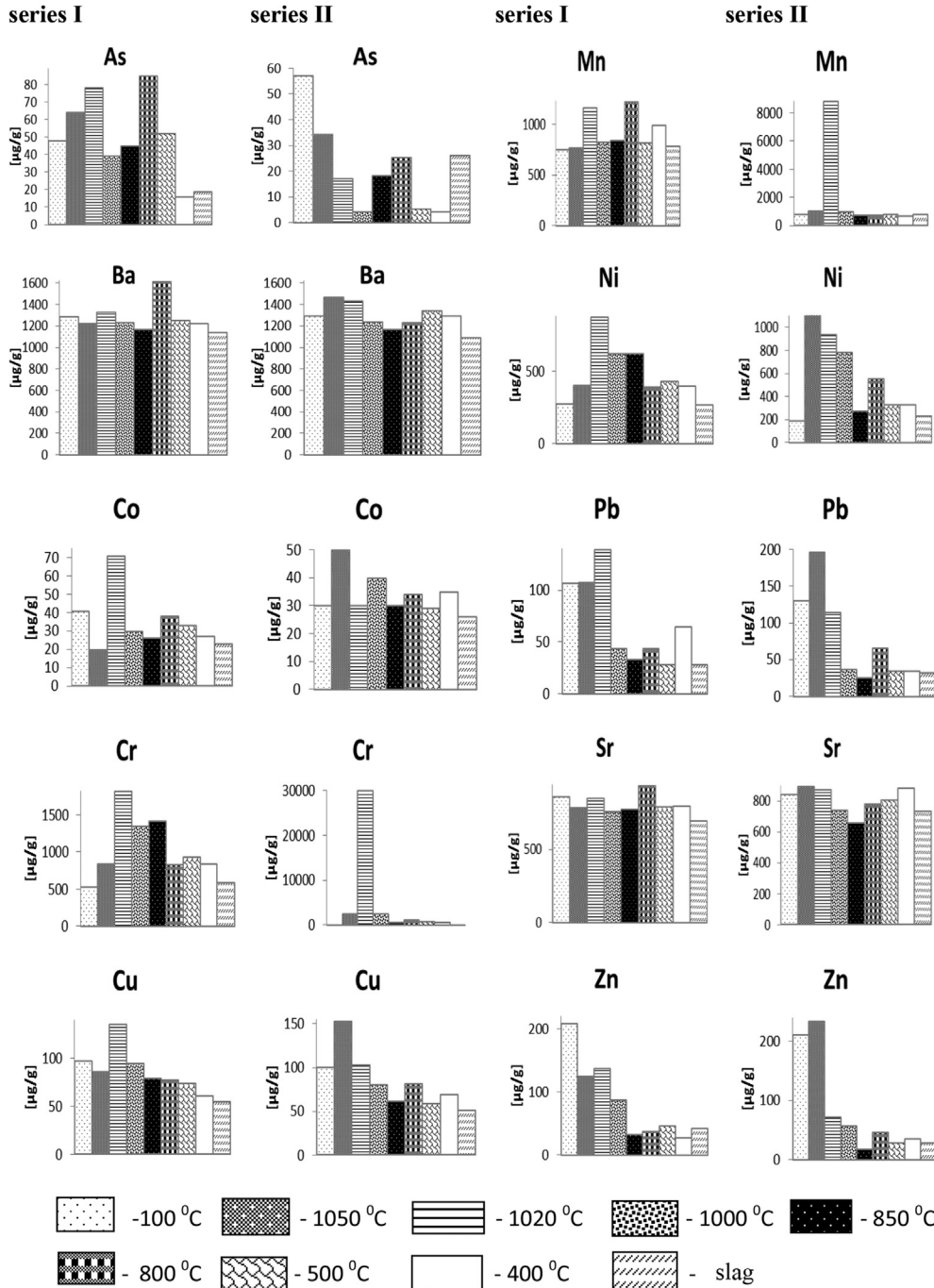


Fig. 8. Variations in trace element content in coal and its combustion products depending on the temperature on the grate for series I and II.

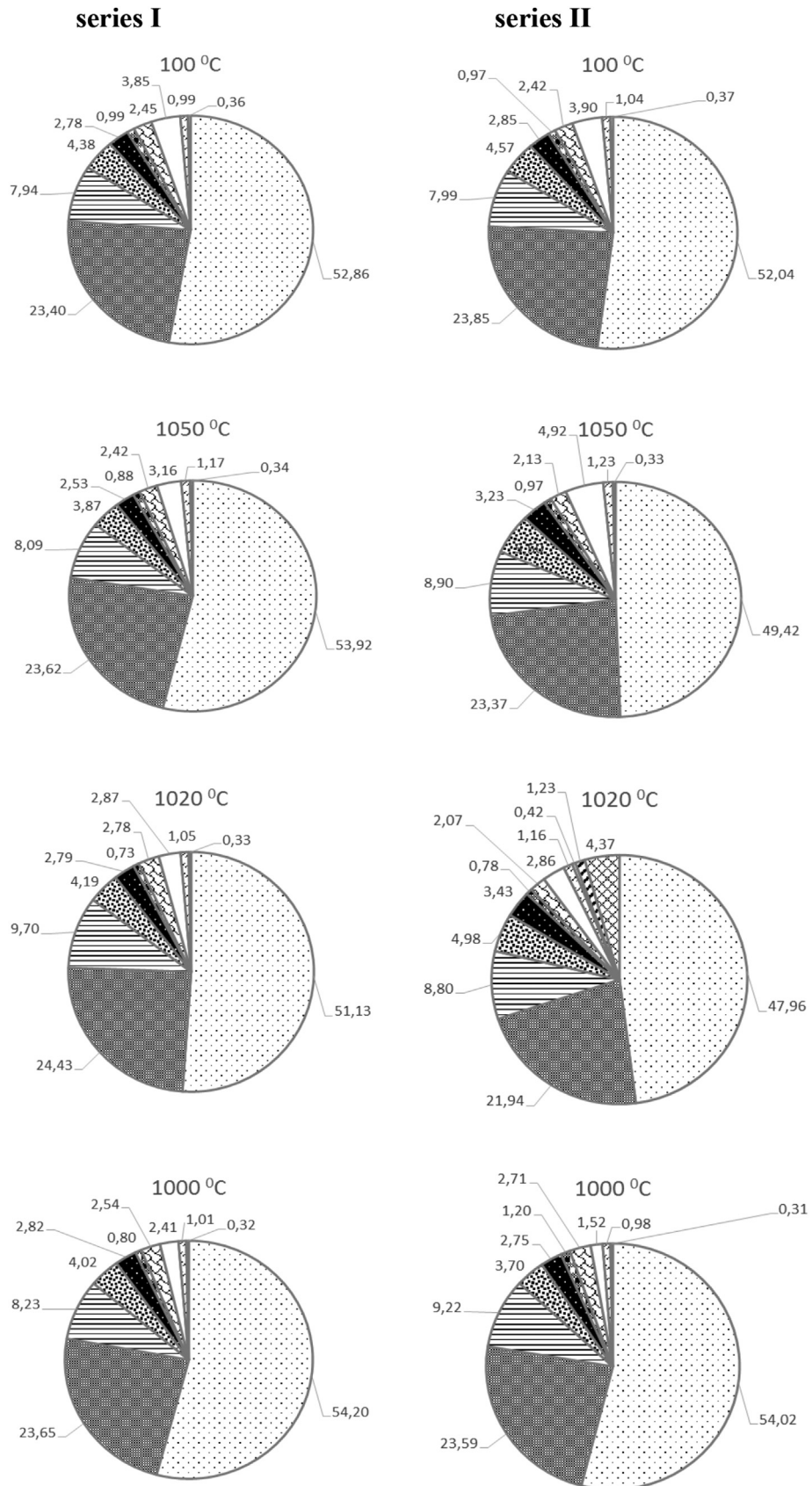


Fig. 9. Variations in the chemical composition of coal ash and its combustion products depending on the temperature on the grate for series I and II.

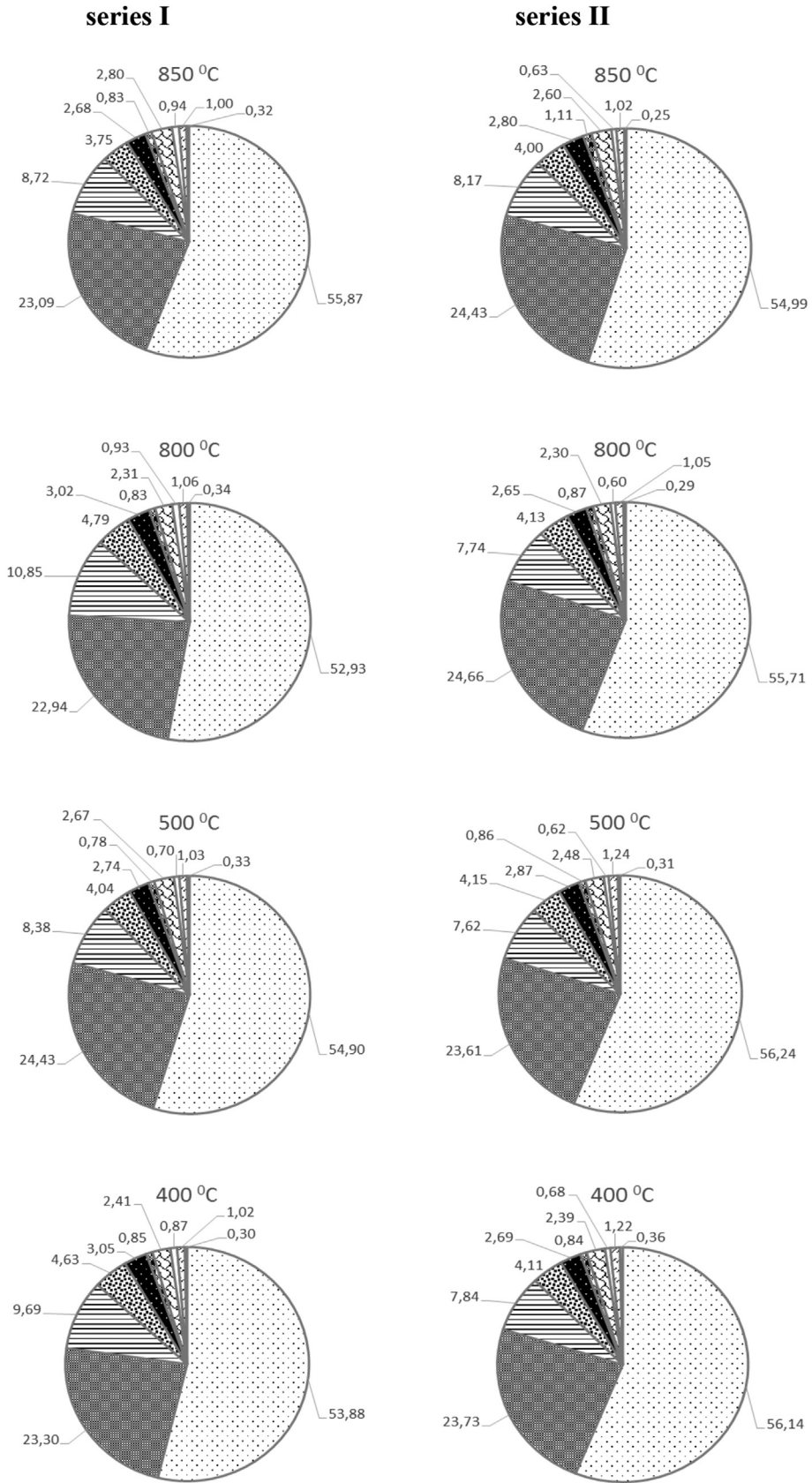


Fig. 9. (continued).



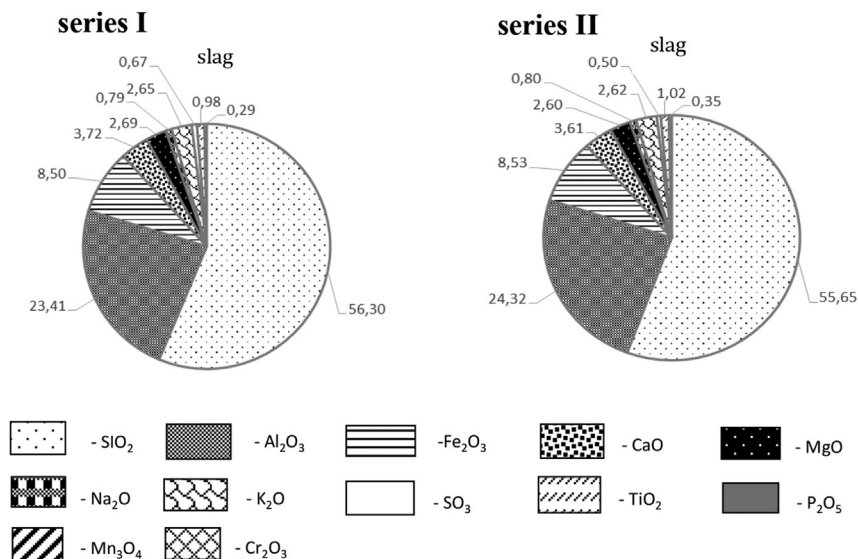


Fig. 9. (continued).

burnt coals. In comparison, the average mercury content reported for coals from LZW (Lublin Coal Basin) is  $0.105 \mu\text{g/g}$  and varies from  $0.018 \mu\text{g/g}$  to  $0.561 \mu\text{g/g}$ . In contrast, the mercury content in the coal globally is about  $0.10 \mu\text{g/g}$  (Ketris & Yudovich, 2009).

### 3.3. Geochemical characteristics of burnt coal ash

Tables 2 and 3 show the contents of trace elements and the oxide composition of ash obtained from the tested coal.

The dominant components of the burnt coal were  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (Table 2), which are beneficial for the combustion process, because having a high content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  has a very positive impact on the softening or melting temperature of ash, raising its value (Hamala & Róg, 2004; Róg, 2003).

It is worth noting that the content of Ag, Ba, Cr, Mn, Ni and Pb in the burnt coal ash was significantly higher, the content of As, Co, Cu, R, Sr, V and Zn was comparable, and the content of Cd, Mo, Sb and Sn was significantly lower (see Table 3) than the respective values reported for world coals (Ketris & Yudovich, 2009).

### 3.4. Changes in physical and chemical properties of coal in the combustion process

The physical and chemical properties determined for samples collected from various sampling points of the boiler grate (Fig. 1) showed a change in the qualitative characteristics of burnt coal (Table 4), depending on the temperature in different zones of the grate (Figs. 5–7).

The temperature in the boiler rises along the grate from the drying zone (approximately  $100^\circ\text{C}$ ) to  $1050^\circ\text{C}$  in the degassing zone and decreases with the burn-out zone of coke breeze.

The mercury content in samples collected directly from the hot grate was very low and ranged from  $0.0003$  up to  $0.008 \mu\text{g/g}$ . It confirmed the findings that the majority of mercury emissions take place in the first phase of coal combustion (degassing phase), as reported previously in the literature (Wichliński et al., 2011).

The low mercury content, made it impossible to employ the X-ray Diffraction (XRD) and Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS-Energy Dispersive X-ray Spectroscopy) for the qualitative assessment of mercury compounds present in coals and furnace waste (slags).

According to previous studies (Rompalski et al., 2016), it could

be expected that no mercury minerals would be identified in the fine coal and combustion waste samples studied. In fine coal, mercury in alumina silicates and in solid solutions in minerals could probably be detected, while in combustion waste, mercury could be present in hauyne  $\text{Na}_3\text{Ca}(\text{Si}_3\text{Al}_3)\text{O}_{12}(\text{SO}_4)$  and in an amorphous component (mineral glass).

It should be noted that in previous studies the EDS spectra of studied pure coal grains did not show the emission lines of mercury.

Mercury content in coal is strongly associated with the presence of pyritic sulfur (Dziok et al., 2015). Figs. 5 and 6 show the changes of the mercury and pyritic sulfur content depending on the temperature along the grate. As can be seen from the graphs, the course of these changes is very similar for both parameters. The greatest loss of mercury occurred in the temperature range of  $1020$ – $1050^\circ\text{C}$  (Fig. 5), that is in the initial part of the degassing zone. A similar situation occurred in the case of pyritic sulfur content (Fig. 6). The total sulfur also decreased along the grate. Its largest loss was found for the temperature decrease from  $1000$  to  $850^\circ\text{C}$ . The combustion heat of the products decreased regularly in various parts of the grate. For the sample of slag 9 from series I, it was  $3928 \text{ J/g}$  and for the sample of slag 18 from series II –  $4093 \text{ J/g}$ . A significant value of the heat of combustion for the two samples of the slag may be the result of the incomplete combustion of the organic substance of coal, which is indicated by a carbon content of  $21.20\%$  in sample No. 9 and  $20.35\%$  in sample No. 18.

The largest decrease in carbon content occurred in the degassing zone, that is in the temperature range  $1050$ – $850^\circ\text{C}$  (Fig. 7). Then the carbon content gradually decreased in the coke combustion zone, reaching a level of about  $21\%$  in the slag. This regularity was observed for both types of the burnt coal.

### 3.5. Changes in trace element contents and oxide composition

Fig. 8 shows the changes in trace element content for the samples collected in different parts of the grate, whereas Fig. 9 shows the variations in the oxide composition of these samples.

The analysis of trace elements of the samples (Fig. 8) proves that in the case of samples from series I: the highest concentration of Co, Cr, Cu, Ni and Pb was reported for ash obtained from samples collected at the temperature of  $1020^\circ\text{C}$ , and of As, Ba, Mn and Sr for ash obtained from samples collected at  $800^\circ\text{C}$ .

For series II, the highest concentration of trace elements, such as e.g. Ba, Co, Cu, Ni, Pb was reported for ash obtained from samples collected at the temperature of 1050 °C. It was also observed that concentrations of some elements in the ash, such as e.g. Zn, decreased with the decrease in temperature along the grate. This relationship is apparent in both series I and II.

It should be emphasized, however, that sample No. 12 was the only one which showed high chromium (2.9920 µg/g) and manganese (8.828 µg/g) content, and hence, the presence of Mn<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> was found in it. This may be due to the contamination of the sample with metal during sampling.

The oxide composition of ash (Fig. 9), obtained from samples collected at various temperatures along the grate was similar for all samples. However, the content of SO<sub>3</sub> in ash for both series decreased with decreasing temperature along the grate.

#### 4. Conclusions

During the combustion process, bituminous coal passes through the characteristic combustion zones of drying, degassing and burn-out. Both examined coals were of type 32.1 and showed an average mercury content at a level of 0.0849 µg/g. In the chemical composition determined for the ash derived from burnt coal, the dominance of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> over other oxides was found. This feature results in the increase of the softening temperature and ash melting, and therefore, during the combustion of tested coal in a stoker fired boiler, at the maximum temperature in the combustion chamber of 1050 °C, only ash was subjected to the sintering process.

Mercury content in the other examined samples taken from various locations of the stoker fired boiler varied from 0.0668 to 0.0009 µg/g. The greatest release of mercury took place in the degassing zone. At the same time, in the temperature range 1050–850 °C, the greatest loss of carbon, pyritic sulfur and total sulfur was reported.

The analysis of the elemental composition of the ash obtained from samples collected from different sampling points of the stoker fired boiler showed that the largest concentration of trace elements was observed for the ash derived from the samples collected in the degassing zone (temperature range 1050–850 °C).

It could also be seen that the concentrations of some trace elements (e.g. Zn), and some oxides (e.g. SO<sub>3</sub>) in the ash obtained from the samples tested decreased with decreasing temperature.

A possibility to modify the capacity to accumulate mercury compounds in furnace waste originating from a stoker fired boiler is likely in the degassing zone. A very high correlation of mercury content with sulfur content, and the content of carbon may suggest the possibility of using, for example, fly ash of mesoporous structure to capture mercury compounds. Simultaneously, fly ash, rich in oxygen and halogen groups, also tends to capture mercury compounds more efficiently (Hławiczka & Fudala, 2008; Mercedes Maroto-Valer, Zhang, Granite, Tang, & Pennline, 2005). It is associated with the adverse impact of an oxidizing atmosphere on the release of mercury compounds from fine coal (Mercedes Maroto-Valer et al., 2005; Dziok et al., 2014).

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