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# Assessment of the possibility of mercury removal from the organic and the mineral matter of hard coals in the process of thermal pretreatment

T Dziok<sup>1,2\*</sup>, A Strugała<sup>1</sup> and J Górecki<sup>1</sup>

<sup>1</sup> AGH University of Science and Technology, Faculty of Energy and Fuels, Mickiewicza Av. 30, 30-059 Krakow, Poland

<sup>2</sup> AGH University of Science and Technology, AGH Centre of Energy, ul. Czarnowiejska 36, 30-054 Krakow, Poland

E-mail: [tadeusz.dziok@agh.edu.pl](mailto:tadeusz.dziok@agh.edu.pl)

**Abstract.** One of the methods which enable a reduction of mercury emission from the energochemical coal conversion processes is the usage of low-mercury coal. The availability of such coals is limited. This necessitates the use of technological operations which allow for the removal of mercury from coal before its conversion (the precombustion methods). The effectiveness of these methods is strongly dependent on the mode of mercury occurrence in coal. It is common knowledge that mercury can occur in coal in both the organic and the mineral matter. Therefore, a universal method should allow for the removal of mercury from the mineral matter as well as from the organic matter of coal. The coal cleaning technologies currently used (dry and wet) enable the removal of only a portion of mercury occurring in the mineral matter of coal. In the case of the thermal pretreatment process, there is a conspicuous lack of knowledge concerning its effectiveness in terms of mercury removal from the organic and the mineral matter of coal. This issue was considered in the presented paper.

To achieve the goal, samples of clean coals and rejects derived from the hard coal cleaning process were investigated in the thermal pretreatment process at the temperature of 300 °C. The examined clean coals were characterized by a relatively high content of the organic matter and a low content of the mineral matter. The rejects, by contrast, contained mainly the mineral matter.

The thermal pretreatment process allowed for the removal of mercury from clean coals within the range from 13.0 to 45.2%. In the case of the rejects, the effectiveness of mercury removal was 33.3% and 34.5%. On this basis, it could be assumed that the thermal pretreatment process enables a partial mercury removal from both the organic and the mineral matter of hard coal.

## 1. Introduction

Nowadays, under the Minamata Convention [1], actions allowing for a reduction of the anthropogenic mercury emission are taken worldwide. Great emphasis is placed on reducing the mercury emission from the processes of energochemical coal conversion, which were the source of 37% of global anthropogenic mercury emission in the year 2000 [2]. It is predicted that until the year 2035, the processes utilizing coal will still be a main source of this emission [2].



One of the methods which enable a reduction of mercury emission from the energochemical coal conversion processes is the usage of low-mercury coal. However, it should be noted that the availability of such coals is limited. For example, the mercury content in Polish sub-bituminous coals varies from 18 to 518  $\mu\text{g/kg}$ , with the average at the level of 104  $\mu\text{g/kg}$  [3]. This necessitates the use of technological operations which allow for the removal of mercury from coal before its conversion (the precombustion methods). Currently, on an industrial scale, the coal cleaning processes are widely used [4, 5], but the thermal pretreatment process (mild pyrolysis) is also applied [6].

The coal cleaning processes allow for the removal of the impurities of gangue in the form of the rejects from a raw coal. For Polish hard coals such rejects are characterized by a mercury content in the range from 55 to 249  $\mu\text{g/kg}$  [7]. Thus, the removal of rejects allows for a decrease in the amount of mercury in coal which is used in the combustion, gasification as well as coking processes. In turn, the thermal pretreatment of coal is the process of coal heating up to the temperature in the range from 200 to 400  $^{\circ}\text{C}$ . At that temperature, a portion of mercury occurring in the coal organic matter as well as in some inorganic constituents characterized by a relatively low temperature of mercury release is removed [8]. It should be mentioned that the thermal pretreatment process may be applied in the case of coals used in the combustion and gasification processes and also in some cases for decreasing the mercury content in a coal blend used in coke production [9, 10].

The effectiveness of mercury removal in the methods of coal cleaning and thermal pretreatment is strongly diversified [9], which is related to the mode of mercury occurrence in coal. It is common knowledge that mercury can occur in coal in both the organic and the mineral matter, most frequently combined with sulfur [11, 12]. Therefore, a universal method should allow for the removal of mercury from the mineral matter as well as from the organic matter of coal. The currently used coal cleaning technologies (dry and wet) enable the removal of only a portion of mercury occurring in the mineral matter of coal. In the case of the thermal pretreatment process, there is a conspicuous lack of knowledge concerning its effectiveness in terms of mercury removal from the organic and the mineral matter of coal. This issue was considered in the presented paper.

## 2. Aim and scope of research

The aim of the paper was to determine the effectiveness of mercury removal from the organic and the mineral matter of coal in the process of its thermal pretreatment. To achieve the goal, the samples of clean coals and rejects derived from the hard coal washing process were investigated in the thermal pretreatment process at the temperature of 300  $^{\circ}\text{C}$ . The examined clean coals were characterized by a relatively high content of the organic matter and a low content of the mineral matter. The rejects, by contrast, contained mainly the mineral matter. The effectiveness of mercury removal was determined on the basis of changes in mercury content in rejects and clean coals before and after thermal pretreatment.

## 3. Experimental and analytical procedure

### 3.1. Analyzed samples

Five samples of clean coals and two samples of rejects derived from the hard coal washing process were analyzed. The characteristics of the examined samples are presented in Table 1. In the examined samples the contents of moisture, ash, mercury and particular forms of sulfur (total, pyritic, sulfate and organic) were determined. The content of mercury was analyzed with the use of the mercury analyzer DMA-80 (Milestone) based on the sample thermal decomposition, mercury amalgamation and atomic absorption detection. The total sulfur content was determined by the high temperature combustion method using CHS 580 (ELTRA). The pyritic and sulfate sulfur content was determined by the gravimetric method according to the Polish Standard PN-G-04582:1997P. The organic sulfur content was estimated as a difference between the total sulfur content and the sum of contents of the pyritic and sulfate sulfur.

**Table 1.** Characteristics of examined samples.

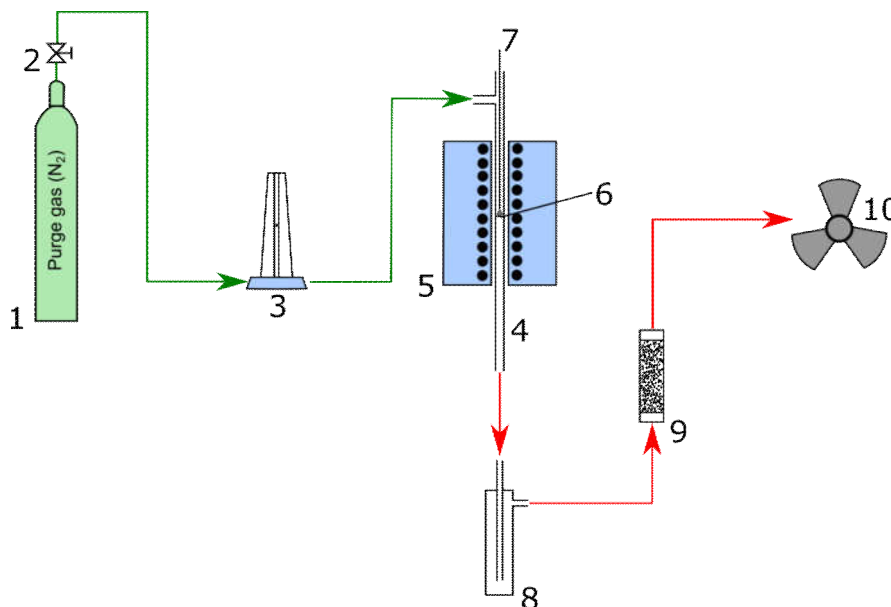
	Type of sample	M <sup>ad</sup> (%)	A <sup>ad</sup> (%)	S <sub>t</sub> <sup>d</sup> (%)	S <sub>p</sub> <sup>d</sup> (%)	S <sub>SO<sub>4</sub></sub> <sup>d</sup> (%)	S <sub>o</sub> <sup>d</sup> (%)	Hg <sub>t</sub> <sup>d</sup> (µg/kg)
<b>C1</b>	clean coal	1.4	6.3	0.45	0.14	0.03	0.28	42
<b>C2</b>		1.5	5.8	0.59	0.06	0.03	0.50	90
<b>C3</b>		1.6	5.8	0.61	0.12	0.03	0.46	118
<b>C4</b>		1.5	5.4	0.93	0.57	0.03	0.33	108
<b>C5</b>		1.3	7.2	0.74	0.27	0.03	0.44	185
<b>R1</b>	rejects	1.8	77.8	0.95	0.87	0.08	0.00	293
<b>R2</b>		1.7	79.2	0.34	0.33	0.01	0.00	87

### 3.2. Procedure of thermal pretreatment (mild pyrolysis)

The thermal pretreatment process was conducted with the use of the laboratory equipment presented in Figure 1. The purge gas (nitrogen) was dosed from a gas cylinder (1). The purge gas flow velocity was set using a gas reducer with a control valve (2) and was controlled online with a rotameter (3). A downstream quartz reactor (4) placed in a vertical tube furnace (5) was used. In the middle of the reactor a grid with the sample (6) was placed. In the sample, a furnace control thermocouple (7) was put.

The mass of the sample was 5g with the grain size below 3.15 mm. The sample was heated from the ambient temperature up to 300 °C with the heating rate of 8 °C/min. After reaching 300 °C, the sample was further kept in that temperature with the residence time of 5 minutes. The purge gas flow was 50 cm<sup>3</sup>/min. The processing gases leaving the reactor were cooled in a cooler (8) and, after cleaning on an active carbon bed (9), were released to the exhaust (10).

After the completion of the process, the reactor was pulled out of the tube furnace and cooled down to the ambient temperature in the purge gas flow. Process parameters based on our previous studies were selected [13]. The effectiveness of mercury removal was determined on the basis of the measured contents of mercury in the analyzed samples before and after thermal pretreatment.



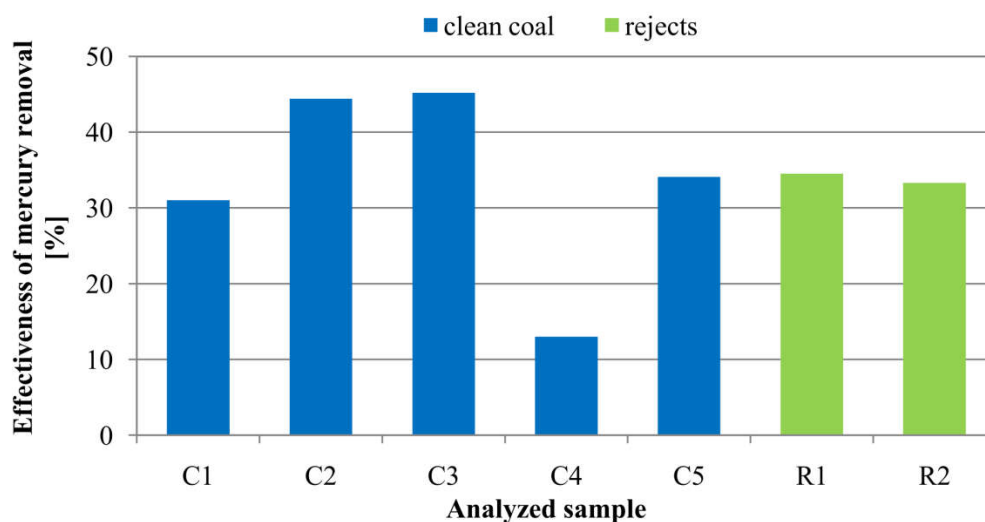
**Figure 1.** Laboratory equipment for the thermal pretreatment of coal (1 – purge gas cylinder, 2 – gas reducer with control valve, 3 – rotameter, 4 – quartz reactor, 5 – tube furnace, 6 – grid with sample, 7 – furnace control thermocouple, 8 – cooler, 9 – active carbon bed, 10 – exhaust).

#### 4. Results and discussion

In Figure 2, the determined effectiveness of mercury removal from the analyzed samples in the process of thermal pretreatment at the temperature of 300 °C was presented. The results show the possibilities of mercury removal from both clean coals and rejects. For the clean coals, the average effectiveness of mercury removal was at the level of 33.5% (from 13.0 to 45.2 %) and for the rejects 33.9% (from 33.3 to 34.5 %).

The removal of mercury from the clean coals indicates the possibilities of mercury removal from the organic matter and from a part of the mineral matter which is closely associated with the organic matter (the so-called inherent inorganic constituents) [14, 15]. It is believed that mercury which occurs in the organic matter of coal is mainly bound with sulfur in thiol groups [11]. For the analyzed clean coal C4, the low effectiveness of mercury removal could be explained by the occurrence of a significant amount of mercury in pyrite in the inherent inorganic constituents. The clean coal C4 was characterized by the highest content of the pyritic sulfur among all the analyzed clean coals (0.57 %). According to the paper [8], in the thermal pretreatment process the mercury occurring in pyrite is much more difficult to remove than the mercury associated with the organic matter.

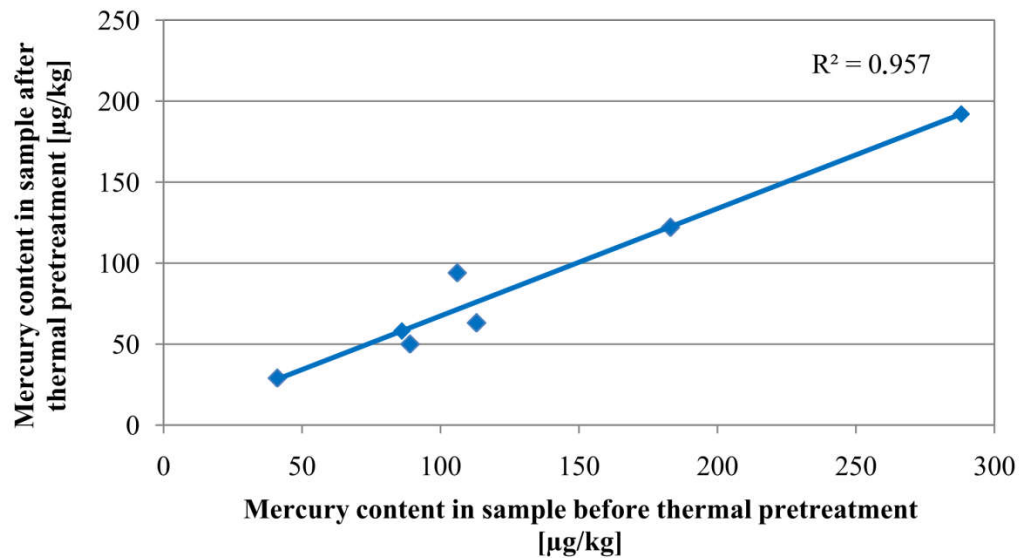
The results obtained for rejects indicate the possibilities of mercury removal from the mineral matter (adventitious inorganic constituents). In the light of literature data, the removal of mercury may concern its part released from chlorides, oxides, sulfates as well as from carbonates and silicates [8, 16, 17]. A diversified influence of the pyrite occurrence in the rejects on the effectiveness of mercury removal was noticed. For the analyzed samples of the rejects, a similar effectiveness of mercury removal and also a significant difference between the content of pyritic sulfur (0.87 and 0.33%) were simultaneously obtained. It may indicate the possibilities of mercury occurrence also in other inorganic constituents.



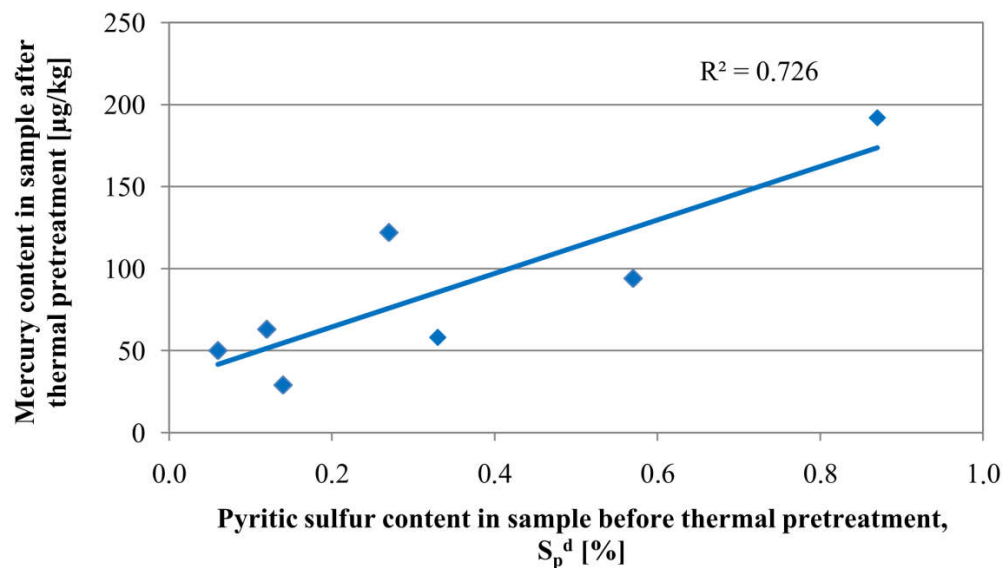
**Figure 2.** Effectiveness of mercury removal from analyzed samples.

It was noticed that for the analyzed samples the content of mercury before thermal pretreatment was a main parameter which determined the mercury content in the samples after thermal pretreatment – Figure 3. For that relationship, a significant determination coefficient equal to 0.957 was obtained. A significant correlation was also noticed between the content of mercury in the analyzed samples after thermal pretreatment and the contents of pyritic sulfur and total sulfur in the samples before thermal pretreatment. The determination coefficients were 0.726 (Figure 4) and 0.623 (Figure 5), respectively. A similar correlation was not found in relation to the contents of sulfate sulfur and ash in the analyzed

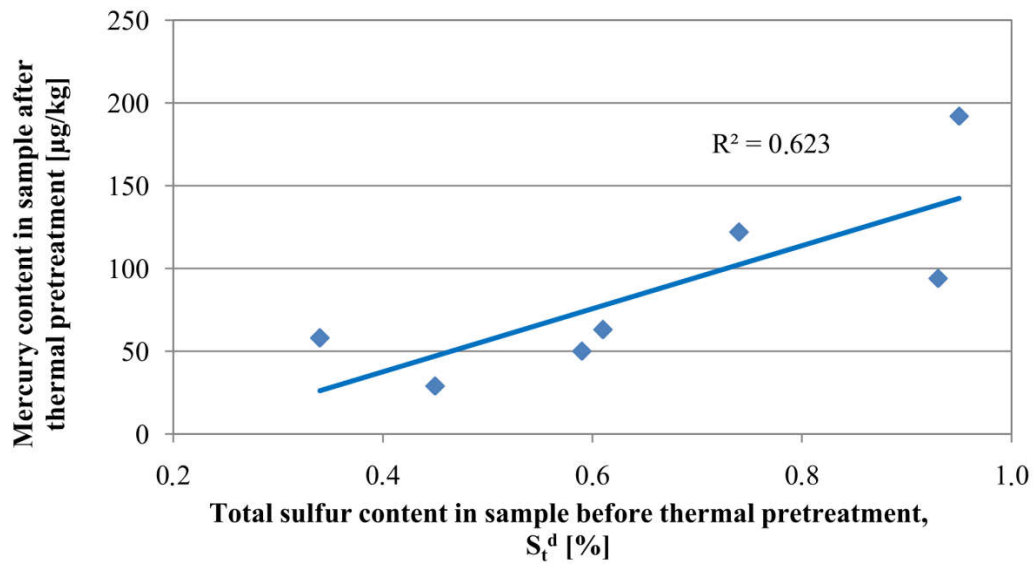
sample before thermal pretreatment. The significance of determination coefficients was verified statistically using the F-Snedecor test at the significance level of 0.05.



**Figure 3.** Relationship between mercury content in analyzed samples before and after thermal pretreatment.

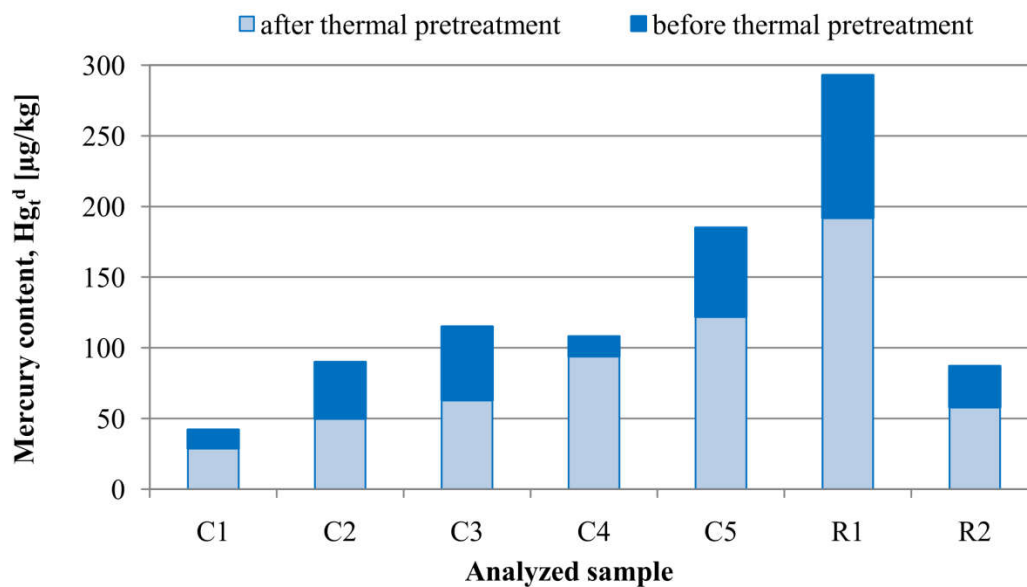


**Figure 4.** Relationship between pyritic sulfur content in analyzed samples before thermal pretreatment and mercury content in analyzed samples after thermal pretreatment.



**Figure 5.** Relationship between pyritic sulfur content in analyzed samples before thermal pretreatment and mercury content in analyzed samples after thermal pretreatment.

In the light of the obtained results, the process of thermal coal pretreatment can be included in the group of universal methods which allow for the removal of a portion of mercury from both the organic and the mineral matter of coal. An additional advantage of this process is a lower mercury content in each coal after thermal pretreatment, which does not always take place in the case of the cleaning processes [18]. A comparison of mercury content in the analyzed samples before and after thermal pretreatment is given in Figure 6.



**Figure 6.** Comparison of mercury content in analyzed samples before and after thermal pretreatment.

## 5. Conclusions

The thermal pretreatment process allows for the removal of a portion of mercury from the clean coals and the rejects. That indicates the possibilities of mercury removal from both the organic and the mineral matter of coal. The effectiveness of mercury removal from clean coal was in the range from 13.0 to 45.2% and from the rejects it was 33.3% and 34.5%.

As expected, the main parameter determining the content of mercury in the sample after thermal pretreatment was the content of mercury in the sample before thermal pretreatment. A significant correlation was also noticed between the content of mercury in the analyzed samples after thermal pretreatment and the contents of pyritic sulfur and total sulfur in the samples before thermal pretreatment.

The process of thermal coal pretreatment can be included in the group of universal methods which allow for the removal of a portion of mercury from the organic matter as well as from the mineral matter of coal. However, it should be mentioned that the effectiveness of mercury removal can be diversified for various coals.

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