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The ability of Polish coals to release mercury in the process of thermal treatment

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ABSTRACT

Coal combustion for energy production is the main source of mercury emission in Poland and several other countries. One of the pre-combustion methods to reduce mercury emission is coal cleaning by mild pyrolysis. Eighteen steam coals from the Upper Silesian Coal Basin in Poland have been used to study the thermal treatment in a developed system, based on the common MA-2 mercury analyser.
Three groups of mercury compounds, sequentially decomposing during thermal treatment, were defined. The total mercury removal from the steam coals was in the range from 28% to 97% at 375 °C. The significant differences in the coals' ability to release mercury in the thermal treatment process were demonstrated. The best coals for thermal cleaning should contain compound with a low decomposing temperature (like $HgCl_2$). There was no significant correlation found between basic parameters of coals (content of volatile matter, ash, sulphur and chlorine) and the amount of thermally removed mercury. The obtained data imply the need for careful selection of coals for the mild pyrolysis process.

1. Introduction

According to literature 30–75% of the mercury content in coal is released to the atmosphere during combustion processes [1–3]. There are three forms of mercury emitted from coal-fired power plants: elemental (Hg^0), oxidized (Hg^{2+}) and particulate-bound (Hg_p) [4]. Hg^0 emission has a significant impact on global contamination, because it is insoluble in water and can be transported for long distances. Hg^{2+} and Hg^0 after oxidation may reach the water reservoirs with rain. Due to the methylation process in aqueous environments mercury could be transformed into the most toxic organic forms, which are bioavailable [5] and after biomagnification may reach the hazardous level for living species. The toxicity of mercury was the reason why considerable efforts are taken to reduce its emissions. The Minamata Convention [6] of 2013 has already been signed by 97 countries. It regulates the use of mercury in order to reduce its negative impact on the environment. The convention is the result of many years' efforts to work out a global agreement which would prevent the global environmental poisoning by mercury. The convention pushes the scientists towards effective methods to reduce emission of this hazardous air pollutant.

One of the sources of mercury emission to the air is the combustion of fossil fuels in coal-fired power plants [7–9]. One estimates that anthropogenic mercury emission is at the level of 2500 tons per year [10]. In 2012 and 2013 approximately 84% of energy in Poland came from hard coal and lignite combustion [11]. The industry was responsible for emission of 10.4 tons of mercury whereas about 5.8 tons was emitted from the energy sector [12,13]. The amount of mercury emitted in Poland remains stable in recent years. Thus, special care should be taken to limit the emission of mercury. Several methods of reducing mercury emission from coal combustion have been described. One of them is mild pyrolysis [2,3,14,15]. The heating of coal in an atmosphere of inert gas at 350–400 °C is one of the pre-combustion methods in which coal is cleaned before utilization (combustion). The first step in the mild pyrolysis method should be the selection of suitable coals ensuring effective and low-cost reductions of mercury. According to the literature data the process of mild pyrolysis allows up to 90% of mercury from coal [10]. Different factors such as type of reactor, residence time, size of grains, heating ratio or type of carrier gas have an influence on the effectivity of mild pyrolysis process. Wang et al. [15] reported that up to 80% of mercury was removed from coal at 400 °C, whereas Guffey et al. [16] removed 70–80% at 290 °C from low-ranked coals. Mild pyrolysis conducted in a fluidized bed reactor by Wichliński et al. [10] showed efficiency of 90% at 380 °C. Presented examples indicate that the process of thermal treatment conducted in inert atmosphere may be applied to decrease total mercury concentration in coal.

The purpose of this paper is to show and explain the differences in the ability of Polish coals to release mercury during thermal treatment.

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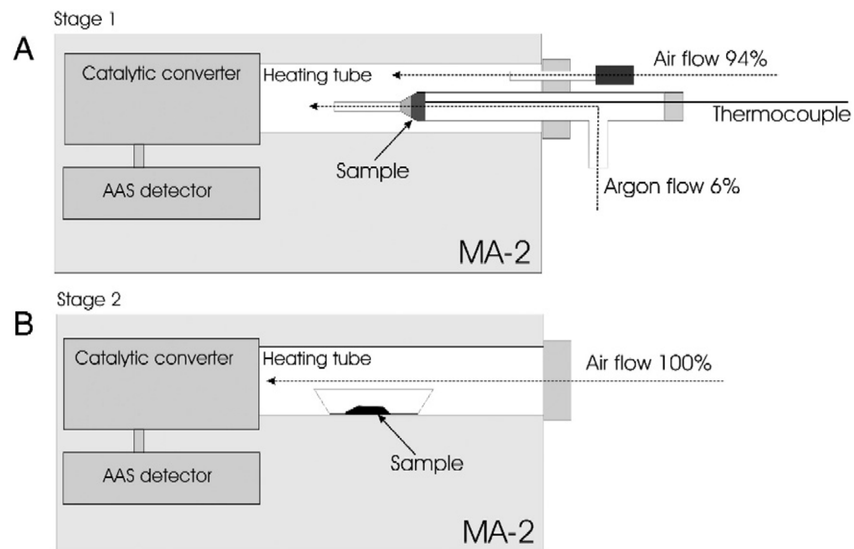

Fig. 1. Scheme of developed mercury thermal speciation system.

2. Materials and methods

2.1. Origin and characteristics of samples

To study the mercury release in the mild pyrolysis process, eighteen Polish hard coals were thermally treated. Coal samples were obtained from coal mines located in the region of the Upper Silesian Coal Basin in Poland. Samples were collected and prepared for analysis in accordance with PN-ISO 13909-4:2005 regulations. The particle size of the analytical samples was less than 0.2 mm. Such a grain size (typical for Hg measurement with an MA-2 mercury analyser) enables one to compare the results of coal thermal treatment with the results of Hg determination with the MA-2 analyser. Before thermal treatment, coal samples were analysed to determine basic parameters such as content of: moisture, ash and volatiles. Additionally, elemental analysis was conducted to measure the content of carbon, sulphur, hydrogen, chlorine and mercury.

2.2. Apparatus

To examine a large number of samples, a new approach to study the processes of releasing mercury, during low-temperature thermal treatment, was proposed. The new system for thermal mercury treatment designed and prepared for the purpose of this study is shown in Fig. 1A. The mercury determination unit was a common MA-2 mercury analyser (NIC, Japan). To release mercury from coal sample, during thermal treatment, the analyser was equipped with a thermal treatment module. Thermal treatment module was a glass reactor, placed inside the ceramic heating tube of MA-2 analyser. The reactor was a glass pipe (inner diameter of 12 mm) tapered at the tip. Argon, at a flow of 30 ml/min, was used as a carrier gas and removed Hg from thermal treatment module to the analyser ceramic heating tube. Argon provides a gas flow of 6% of total gas flow. The rest (94%) was air passing through the by-pass equipped with a charcoal filter. The air was mixed with post-process gases from thermal treatment module and enabled the stable work of the MA-2 detection system.

To determine mercury residue in the sample (after heating sample up to 375 °C) the MA-2 system with boat (Fig. 1B) was used.

Other elements of the thermal treatment system were a flowmeter and a thermocouple equipped with a CHY thermometer. A 2 mm thermocouple was used to measure the temperature inside the coal sample. Fig. 2 presents a sample placed inside the thermal treatment module. Additive B (used during MA-2 measurements) is a mixture of calcium hydroxide and sodium carbonate. This additive protects the amalgamation unit against the acidic products of sample decomposition.

The MA-3000 (NIC, Japan) automatic mercury analyser was used to determine the total mercury concentration in the coals.

To determine moisture, ash and volatile matter content the Thermostep (Eltra, Germany) automatic analyser was used. Measurements of carbon, sulphur and hydrogen contents were conducted with the CHS-580 (Eltra, Germany) automatic analyser.

2.3. Procedures

2.3.1. Procedure for the thermal mercury treatment of coals

Thermal mercury treatment method consisted of two main stages. Stage 1: Hg is released in ten temperature steps (up to 375 °C). Stage 2: Hg is determined in the coal sample residue with the MA-2 analyser.

Before the thermal treatment of coal sample, the glass reactor (Fig. 2) was heated up to 450 °C inside the MA-2 analyser heating tube.

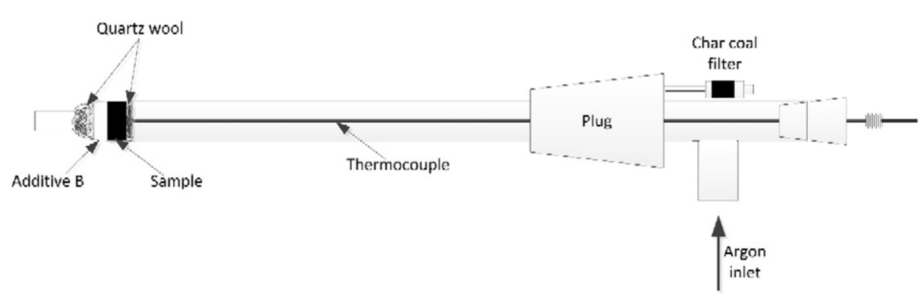

Fig. 2. Glass reactor loaded with the coal sample.