RESEARCH

Thermal desorption of mercury from lignite in a high-temperature furnace and in power plant mills

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Abstract

In this article, the binding forms of two lignite samples are determined by thermal desorption using a high-temperature furnace. Each mercury compound, such as $HgCl_2$, has a specific binding strength whose decomposition requires a certain thermal energy. Hence, the release of mercury from pure substances and lignite samples was analyzed in a high-temperature furnace. The released mercury is determined with a Mercury Vapor Monitor. The obtained characteristic temperature range and peak of the mercury release were compared between lignite samples and mercury pure substances. For the lignite samples investigated, the binding form of mercury was then identified as Humic Acid. These organic compounds vaporize at lower temperatures. About half of the mercury bound in the lignite was already released at 350 °C. Furthermore, the question arises whether mercury is already released during the grinding-drying process in the coal mill of a power plant. At two power plants, lignite samples were taken simultaneously at the feeder before entering the coal mill and at the dust line afterwards. The samples were analyzed for mercury concentration. The results show that up to one third of the mercury was already released in the coal mill. The vaporized mercury enters the combustion chamber detached from the lignite. The stated analysis methods and the results presented in this article contribute to the understanding of the mercury binding forms in lignite. It also shows the potential of thermal coal pretreatment as a favorable alternative mercury separation technology to others such as activated carbon dosing.

Keywords Mercury binding forms · Thermal desorption · Mercury release · Coal mill · Coal pretreatment

1 Introduction

Mercury removal from flue gas in power plants remains an important topic in Germany and worldwide, particularly due to the decreasing limits for mercury emissions. The demand for more efficient and less expensive separation technologies are increasing. The difficulty is that the reactions of mercury that take place during coal combustion are not fully understood yet. The separation technologies must be selected on a power plant-specific basis and do not yet provide a guarantee of separation efficiency. The efficiency of mercury removal from flue gas depends on the fuel used, the plant design, the operating conditions and the behavior of mercury.

Due to the high combustion temperatures, mercury is initially present in its elemental form. During cooling of the flue gas, heterogeneous and homogeneous reactions can take place, producing mercury bound to ash particles and oxidized mercury. Knowledge about the influencing variables on these reactions and their effects is now quite extensive. Zhao et al. (2019) provides a summary overview in their article. Nevertheless, many research results are poorly transferable due to the diversity of power plants with the used coal, structure and process conditions.

Oxidized mercury is the preferred mercury species, because its good water solubility allows it to be effectively separated (by means of precipitants) via wet flue gas desulfurization plant (FGD). The addition of halogen salts to the combustion process has proven to be a method of mercury reduction. The homogeneous gas-phase reaction with chlorine, iodine or bromine can increase the mercury oxidation degree. The effectiveness has to be investigated power

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plant-specifically with consideration of special operating conditions and plant peculiarities. In hard coal-fired power plants, the denitrification system SCR (selective catalytic reduction) shows a co-benefit as it catalytically oxidizes elemental mercury. In lignite-fired power plants, less nitrogen oxides are produced due to the lower combustion temperatures, which means that denitrification systems (SNCR – selective non-catalytic reduction, SCR) are not necessary. Thus, the positive catalytic effect of SCR does not exist for most lignite-fired power plants.

If mercury binds to ash particles, it can be separated using filters such as electrostatic precipitators (ESP). However, in lignite-fired power plants, the content of unburned carbon is very low for adsorptive processes. A certain amount of mercury is neither particle-bound nor oxidized. This elemental mercury cannot be separated from the flue gas either via the FGD or ESP and leads to mercury emissions from the power plant.

In German lignite-fired power plants, adsorptive mercury reduction has become established using (doped) activated carbon. In this process, mercury binds to the activated carbon and is separated with the fly ash via the ESP. The mass ratio between mercury in the flue gas and the activated carbon is extremely high. In addition, there are high operating costs due to the activated carbon itself (Sloss 2008). The production of activated carbon of any origin (lignite, biochar, coconut shell, etc.) and the associated transport costs should be viewed in a differentiated manner. While this separation technology is very effective for mercury, it is also expensive and ecologically questionable. Against the background of decreasing mercury emission limits, alternative cheap and efficient mercury separation technologies are needed not only in Germany but worldwide.

Another possibility is to separate mercury from the coal before the combustion process. In coal pretreatment, a distinction is made between coal washing with solvents, hydrothermal and thermal pretreatment (pyrolysis) (Chang et al. 2019. Zhao et al. (2019) describe different chemical and thermal pretreatment methods in their review. The authors are not aware of any coal-fired power plant in Germany that uses coal pretreatment as a mercury reduction technology. Dronen et al. (2004), Dziok et al. (2019a), Luo et al. (2011) show that inorganically bound mercury can be removed by coal washing. Since inorganically bound mercury (e.g. pyrite bound) is primarily present in hard coals, mercury can be removed by coal washing as well as magnetic separation. Pyrolysis as thermal coal pretreatment is particularly suitable for lignite due to the predominantly organic binding forms with the low temperatures of release (Schwieger et al. 2020). It has long been known that mercury can be released during the thermal treatment of coal (Mashyanov et al. 2017; Luo et al. 2011; Lusilao-Makiese et al. 2012;

Uruski et al. 2015). The release behavior of mercury from coal depends on the binding forms of the mercury and thus the binding strength. South African bituminous coals were studied by Mathebula et al. (2020). This showed that 76% of the coals released mercury in the low temperature range of 20–180 °C and 180–360 °C. It should be noted that pyrolysis for mercury removal is particularly dependent on reaction temperature and residence time (Merdes et al. 1998). The flow rate of the purge gas and the mercury binding form are also important (Zhao et al. 2019).

In summary, there are many different technologies to avoid mercury emissions in coal-fired power plants. Nevertheless, the technologies are often not efficient enough, partly due to unknown influencing parameters. For example, the high mercury oxidation degrees achieved by adding calcium bromide in American power plants, as described by Berry et al. (2007), often cannot be achieved in German lignite-fired power plants. Other separation technologies can also be expensive (e.g. activated carbon injection) or retrofitting a technology is not feasible (e.g. SCR at lignite-fired power plants). To improve mercury separation technologies and understand the behavior of mercury in the power plant, the entire pathway of mercury from coal to emission must be considered. Most efforts have focused on studying mercury from the time coal enters the combustion chamber until it is captured or emitted. However, earlier attention must be paid to when and under what conditions mercury enters the gas phase. Therefore, this article examines the binding forms and the release of mercury from the coal.

In this article, two German lignite are used to investigate how mercury is bound in the lignite and how the release behavior depends on this. There are several methods for determining mercury binding forms. In Schwieger et al. (2020) and Zhao et al. (2019) physical (e.g. sink-float analysis), chemical (e.g. sequential leaching) and thermal methods are described. Due to the low mercury concentrations, the often-fine distribution in the coal and the different binding partners (organic, inorganic), it is very complex to detect the binding form. Often the methods have to be combined and are not comparable with other literature data, because there are no standardized methods. Thermal desorption for the determination of mercury compounds was already used for sediment samples in the 1990s (Biester and Scholz 1997; Zimmer 1996). In the meantime, this method is also used for coal samples and is described in Zhao et al. (2019) as the favored method to determine mercury binding forms. For this reason, lignite samples are investigated using thermal desorption in this study. The binding forms of mercury are distinguished by their specific release behavior from the coal into the gaseous aggregate state. The various mercury compounds have specific binding strengths that require different amounts of energy to break down. The obtained

Table 1 Comparison of literature data on mercury release from pure substances

Mercury species	Source	Temperature range of release (°C)	Peak temperature of release (°C)
Hg^0	Biester and Scholz (1997)	30–160	120
Hg^0	Luo et al. (2011)	< 150	not specified
HgI_2	Rumayor et al. (2013)	60–180	100 ± 12
HgI_2	Klöfer et al. (2021)	50–160	130
$HgBr_2$	Rumayor et al. (2013)	60–220	110 ± 9
$HgBr_2$	Klöfer et al. (2021)	40–160	90
$HgCl_2$	Biester and Scholz (1997)	60–400	200
$HgCl_2$	Luo et al. (2011)	150–250	not specified
$HgCl_2$	Reis et al. (2012)	125–225	190
$HgCl_2$	Rumayor et al. (2013)	90–350	138 ± 4
$HgCl_2$	Rumayor et al. (2015)	not specified	135 ± 5
$HgCl_2$	Klöfer et al. (2021)	50–150	120
Hg_2Cl_2	Rumayor et al. (2013)	60–250	119 ± 9
Hg_2Cl_2	Klöfer et al. (2021)	70–190	150
$Hg-FeS_2$	Luo et al. (2011)	400–600	not specified
$Hg-FeS_2$	Rumayor et al. (2015)	not specified	169 ± 5
Hg-Humic Acid	Reis et al. (2012)	100–240	150
Hg-Humic Acid	Biester and Scholz (1997)	190–340	270
HgS	Rumayor et al. (2015)	not specified	303 ± 13
HgS	Rumayor et al. (2013)	210–340	305 ± 12
HgS	Reis et al. (2012)	225–325	290
HgS	Luo et al. (2011)	250–400	not specified
HgS	Biester and Scholz (1997)	230–350	310
HgS	Klöfer et al. (2021)	200–340	280
HgO	Rumayor et al. (2015)	not specified	310 ± 5; 462 ± 9
HgO red	Rumayor et al. (2013)	200–360, 370–530	308 ± 1, 471 ± 5
HgO yellow	Rumayor et al. (2013)	190–380, 320–540	284 ± 7, 469 ± 6
$HgSO_4$	Rumayor et al. (2015)	not specified	580 ± 19
$HgSO_4$	Rumayor et al. (2013)	500–600	583 ± 8
$HgSO_4$	Klöfer et al. (2021)	420–610	520, 570

curves can be compared with those of a coal sample by means of characteristic temperature range and peak of the release. However, this method is highly dependent on the specific test setup, reaction gas used, particle sizes, heating rate and profile. There is also no standardized procedure for this method. The thermal decomposition has to be analyzed with mercury pure substances for each experimental setup. The results of a literature study show the differences between mercury pure substances and the temperature range and peak of mercury release in Table 1. Some of the data were taken from diagrams and are therefore estimated. For these reasons, the binding forms of mercury in lignite samples were investigated in this article by thermal desorption using a high-temperature furnace.

The binding form of the mercury determines the release behavior. Therefore, the release of mercury from the lignite samples studied with thermal desorption were also investigated at two German lignite-fired power plants. It should be examined whether the conditions during the grinding-drying process in the coal mill are sufficient to release mercury from the coal.

The stated analysis methods and the results presented in this article contribute to the understanding of the mercury binding forms in lignite. The article shows that the comparative evaluation of mercury binding forms by means of thermal desorption can only be done under the same experimental conditions. The results of the thermal desorption indicates that thermal coal pretreatment could be a suitable technology for mercury removal. Further investigation of the release behavior of mercury from lignite in coal mills of two power plants extends the statements of this study and gives a good practical reference. For modeling and understanding the effect of oxidants and catalysts to increase the mercury oxidation degree, the experiments can contribute.

2 Materials and methods

2.1 Determination of mercury binding forms by thermal desorption

The thermal decomposition of mercury compounds and lignite samples was carried out in a high-temperature furnace (HTL 10/17 Thermoconcept), see Fig. 1. A temperature heating profile with four different heating rates and holding times up to a maximum temperature of 1750 °C could be set.

The furnace can be operated with different reaction gases like nitrogen or air. The reaction gas is not preheated. The flow of the reaction gas is controlled by a variable area flow meter. For the tests, compressed air with a flow rate of 120 NL/h was selected. It was decided to use an oxygen-containing gas in order to reflect the oxygen-containing atmosphere in power plants.

Before starting the experiments, the gas outlet at the furnace was already heated to 180 °C to avoid condensation of mercury-containing compounds. Approximately 80 NL/h of the exhaust gas was extracted via a heating hose at 185 °C. Since the Mercury Vapor Monitor VM-3000 (Mercury Instruments GmbH) measures elemental mercury by means of CV-AAS (cold vapor atomic absorption spectrometry), oxidized mercury compounds must first be reduced. For this purpose, a heated reduction unit with a solid catalytic bed (HovaMerc by IAS GmbH) is connected upstream
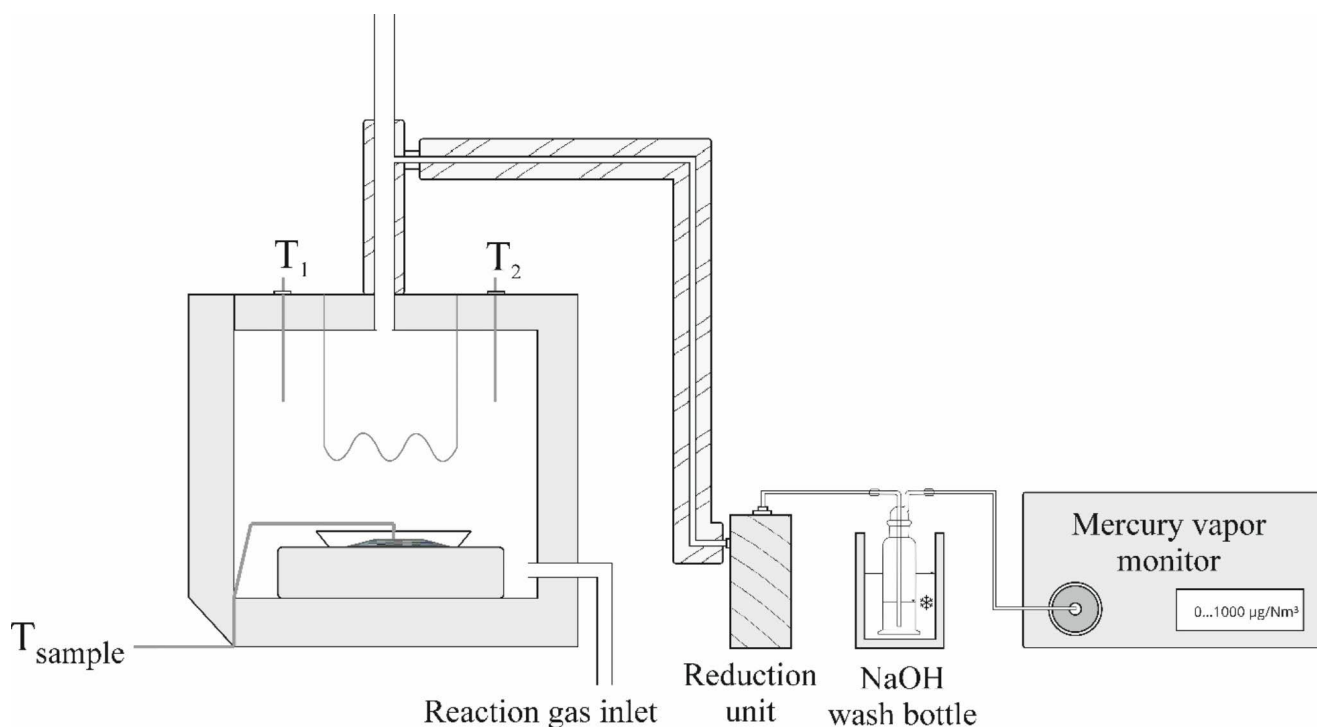
Fig. 1 Schematic high-temperature furnace for mercury release tests

of the Mercury Vapor Monitor. The maximum flow through the reduction unit corresponds to the flow through the Mercury Vapor Monitor. No significant delays or influences on the measuring signal are to be expected. The catalytic bed material (metal compounds) does not consume. It can only be inactivated by chlorine-containing sample gas. The bed material would be consumed at a loading of 60 g HCl. Before the tests, new bed material was filled into the reduction unit. Due to the small sample quantities of chlorine-containing pure substances ($HgCl_2$) and the lignite samples, saturation of the bed material was not achieved and the complete reduction of oxidized to metallic mercury was ensured. This was verified by computational balancing.

After reduction, the exhaust gas is passed through a wash bottle with 5% NaOH cooled at 3.5 °C. This caustic solution absorbs sulfur and HCl contained in the exhaust gas to protect the Mercury Vapor Monitor and to avoid cross sensitivities. At the same time, the exhaust gas is cooled to the necessary measuring temperature of < 65 °C. During the experiments, the temperatures in the furnace and in the sample were monitored.

First, the mercury pure substances were tested in the test rig under the same conditions as the lignite samples to be tested. Typical mercury compounds in coal should be analyzed as reference materials for the determination of the mercury binding forms in lignite. The required sample quantity of the pure substances is very small. The pure substances were weighed into alumina crucibles (70 μL) and

then were placed in the center of a larger porcelain dish (ϕ 120 mm). The mercury pure substances HgO, $HgCl_2$, HgS, Hg-Acetate and $HgSO_4$ were purchased from Sigma-Aldrich and Alfa Aesar. Humic Acids were obtained by Sequential Leaching of lignite performed to Schwieger et al. (2020).

The lignite samples (Lignite A and Lignite B) are Central German lignite from different opencast mines, but the geological formation history of the coal seams is equal. The samples were ground and sieved to a particle size fraction of $> 0.08 < 0.2$ mm. Two grams of the sample were weighed directly into a porcelain dish (ϕ 120 mm). The height of the sample fill is smaller than 0.5 cm. This ensures relatively uniform and simultaneous heating of the sample and supports clear delineation of the release of mercury from various mercury pure substances. The heating rate is 5 K/min up to a maximum temperature of 900 °C. The maximum temperature is held for fifteen minutes. Data acquisition for temperature and mercury concentration was carried out every second. The Mercury Vapor Monitor was calibrated once hourly. The experiments were performed as duplicate determinations.

2.2 Investigation of mercury release from lignite in power plant mills

At two power plants, lignite samples (Lignite A and Lignite B) were taken simultaneously at the feeder before entering the coal mill and from the dust line after the coal mill.

Fig. 2 Schematic beater wheel mill with measuring points
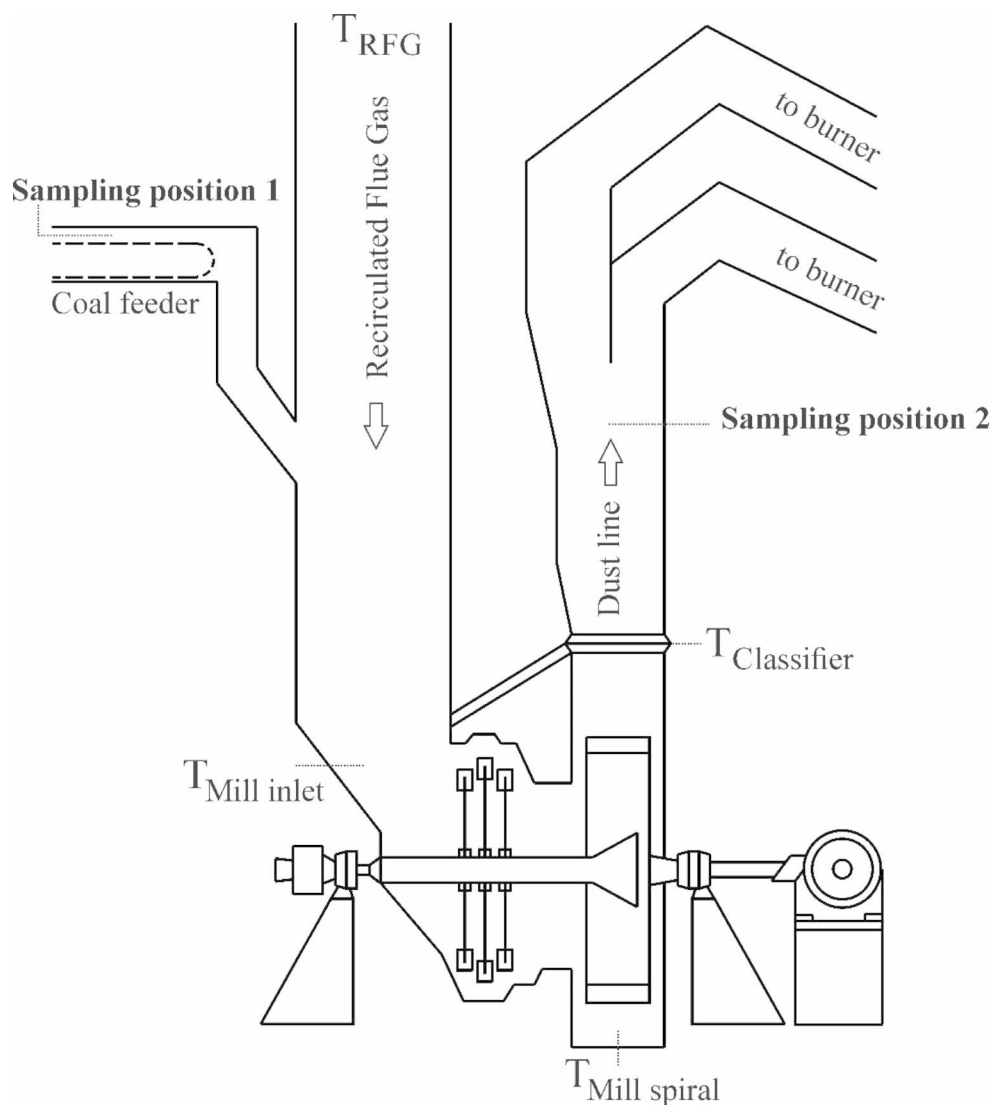
Afterwards, the raw lignite and the ground lignite were analyzed for mercury concentration. A statement could be made about the release of mercury under the given circumstances during the grinding-drying process.

The power plants are almost identical in construction. The coal mills are beater wheel mills in both power plants. The tests were carried out under full and part load of a mill. The Fig. 2 shows a schematic beater wheel mill, which is to be applied to both power plants. The corresponding measuring points for sampling and temperatures are marked. At both mills, a gravity deflection classifier is used to separate lignite particles. The raw lignite samples were directly taken at the coal feeder (sampling position 1). The sampling in the dust line (sampling position 2) was carried out isokinetically as a network measurement after checking the reproducibility according to DIN EN 13284-1: 2018-02 (2018) and DIN - VDI 2066 (2006). The measurement took an average of 30 min. From the samples collected during this time from sampling position 1 and sampling position 2, mixed samples were prepared in each case and these were used for mercury analysis.

2.3 Analytical methods

2.3.1 Elemental analysis

The elemental amount of carbon, hydrogen, nitrogen, sulfur and oxygen (difference) of the lignite samples was determined by chromatography with purge and trap chromatography with Elementar Vario EL (Germany).

All lignite samples taken from sampling position 1 were air dried at 38 °C to a constant mass. Then they were ground. The proximate and ultimate analyses of the samples are listed in Table 2.

Table 2 Proximate and ultimate analyses of the lignite samples

Sample	Proximate analysis w_{dry} (%)				Ultimate analysis w_{dry} (%)				
	Moisture	Ash	Volatile	Fixed Carbon	C	H	O	N	S
Lignite A	8.55	17.83	45.44	27.88	57.05	4.30	15.30	0.56	3.23
Lignite B	8.12	11.58	50.32	29.98	60.95	4.85	18.07	0.60	2.93

Fig. 3 Mercury release from pure substances and Lignite A by means of high-temperature furnace
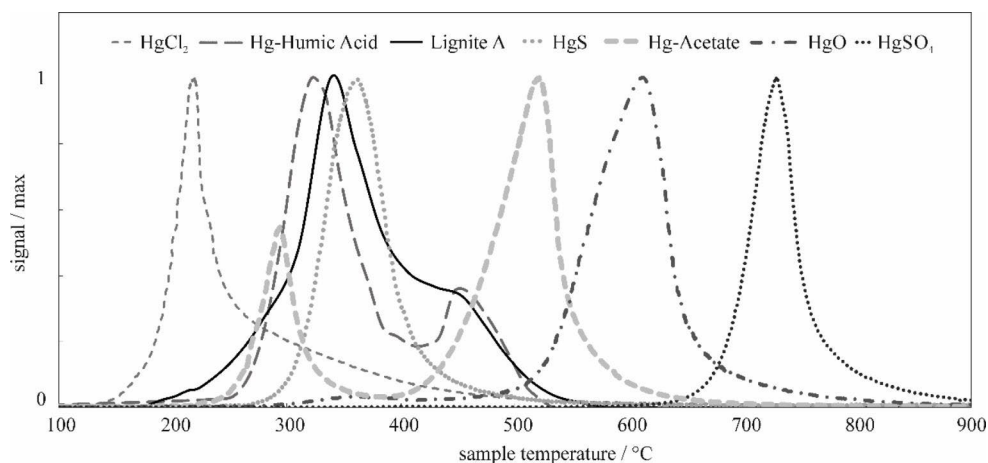
Fig. 4 Mercury release from pure substances and Lignite B by means of high-temperature furnace
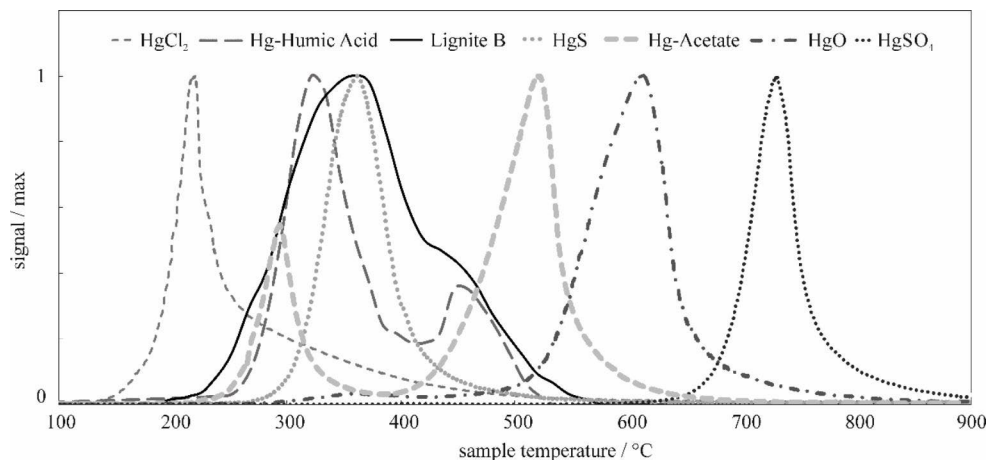
Table 3 Sample temperature at peaks of mercury release of pure substances and lignite (°C)

Sample	HgCl$_2$	Hg-Humic Acid	HgS	Hg-Acetate	HgO	HgSO$_4$	Lignite A	Lignite B
Peak 1	219	322	362	293	363	729	338	356
Peak 2	–	447	–	520	613	–	453	436

2.3.2 Mercury analysis in solid samples

Mercury in solid was analyzed as total mercury with CV-AAS (cold vapor atomic absorption) by PSA Merlin Plus (P S Analytical). The solid samples were chemically digested in triplicate (DIN EN 13,657) and the measured values were averaged. The averaged standard deviation of all mercury analyses is about 0.002 mg/kg (in dry).

3 Results and discussion

3.1 Mercury concentration in gas at laboratory test rig

The results of mercury release by thermal desorption from mercury pure substances are compared to Lignite A in Fig. 3 and to Lignite B in Fig. 4. Table 3 summarizes the corresponding peak temperatures of the mercury pure substances and the lignite samples.

The diagrams show, that HgCl$_2$ is released at lowest temperature and HgSO$_4$ at highest temperature. Thus, the

Table 4 Experimental conditions during lignite sampling at two lignite power plants

Plant A	Feeder speed (%)	T_{RFG} (°C)	$T_{Mill\ inlet}$ (°C)	$T_{Classifier}$ (°C)	Drying degree (%)	Mercury release w_{dry} (%)
Mill 1	94	812	524	171	75	26
Mill 2	73	761	544	164	75	8
Plant B	Feeder speed (%)	T_{RFG} (°C)	$T_{Mill\ inlet}$ (°C)	$T_{Classifier}$ (°C)	Drying degree (%)	Mercury release w_{dry} (%)
Mill 3	102	938	165	149	79	16
Mill 3	75	920	158	152	73	25
Mill 4	105	924	237	149	81	31
Mill 4	77	824	290	154	77	33

binding strength is therefore lowest (HgCl$_2$) and highest (HgSO$_4$), respectively. Hg-Acetate and Hg-Humic Acid show a bimodal characteristic with two peaks of mercury release. HgO also shows two peaks, but the first at 363 °C is very weak compared to the second peak at 619 °C. The literature data from Table 1 also show two peaks for HgO. The peak temperatures of the pure substances in Table 2 are very different from the literature data in Table 1. However, this should not be misinterpreted. This shows that a comparison of own experimental results of the mercury binding forms with literature data is not possible. The results are only comparable as long as the same experimental setup and the same method are used. Accordingly, the results cannot be classified in literature data or a statement about the correctness of results could derived.

Lignite A and Lignite B have a similar mercury release curve with two peaks, where the second peak has no strong characteristic, but only influences the gradient of the curves. The mercury release starts at about 170 °C and ends at 550 °C. The bimodal characteristic can be caused by a mercury pure substance with bimodal characteristic or by superposition of pure substances with one or two peaks. In case of Lignite A and Lignite B, the curves have strong similarity to the mercury bound to Humic Acid. It can be assumed that most or all of the mercury is organically bound to Humic Acid. The deviations of the measurement signal between the curve of the lignite samples and the pure substance Hg-Humic Acid could be explained by radial and vertical heat and mass transfer barrier. The lignite particles behave according to the shrinking core model (e.g., Zhang et al. 2021) when temperature increases. The size reduction of the particles is based on the diffusion of the surrounding flow and desorption of volatile components from the coal particle. This effect can lead to delays or deviations in the mercury measurement signal even though the height of the sample fill in the dish is very low (compare Sect. 2.1 and Fig. 1).

In summary, the organic binding form of mercury was demonstrated in the lignite samples studied. Further, it is clear that about half of the mercury bound in the coal was released in the temperature range between 170 and 350 °C under the experimental conditions.

3.2 Mercury release in coal mills of lignite power plants

The test conditions for the lignite sampling at coal mills at the power plants A and B are listed in Table 4. Tests were carried out at different load conditions (feeder speed of lignite). By comparing the mercury concentration of the lignite samples from the feeder (sampling position 1) and the dust line (sampling position 2) of one coal mill, the percentage mercury release is determined for each test point in relation to the mercury concentration of the raw lignite (sampling position 1).

On average, the raw lignite at both power plants had a water content of between 49% and 53%. The moisture content of the ground lignite in the dust line was between 9.4% and 17.4%. The resulted drying degree of the lignite for each coal mill is included in Table 4. As the test results in Table 4 show, up to one third of the lignite-bound mercury was released into the vapor while grinding-drying process in the coal mill. This means that the vaporized mercury enters the combustion chamber detached from the lignite. The mercury remaining in the lignite is then released in the combustion chamber. A direct correlation between load condition and release behavior could not be determined. However, a dependence of the mercury release on the temperature in the coal mills in Plant B may be postulated. The higher the temperature in the mill ($T_{Mill\ spiral}$), the more mercury is released. Here, the release of mercury during the grinding-drying process depends on the temperature profile of drying, the load-dependent residence time and the influence of the composition of the recirculated flue gas. Processes of heat and mass transfer also play a significant role. The release of the mercury also depends on the initial size of the raw lignite. The smaller the size of the lignite before the coal mill, the more the hot recirculated flue gas heats the lignite and thus more mercury is released.

3.3 Discussion

Against the background of the results in this study, three specific aspects arise that should be considered further. Firstly, thermal coal pretreatment as a mercury separation

technology should be taken into account especially for coal-fired power plants still in the planning stage. Mercury removal by thermal coal pretreatment leads to lower emissions (e.g. mercury, sulfur, etc.) and quality improvement of the coal (e.g. higher calorific value). Concepts for dry lignite firing have already been investigated and are possible to implement in principle. The pressure-charged steam fluidized bed drying as coal pretreatment was researched in the last decades (Merzsch et al. 2015; Porsche et al. 2009). For Germany, these developments are of minor importance due to the coal phase-out. Worldwide, however, coal-fired power generation is a current topic and many new coal-fired power plants are being built particularly in Asia. Dziok et al. (2019b) also confirm the benefits of thermal pretreatment for mercury removal and that technical implementation is certainly topical. Chmielniak et al. (2017) state that the cost of thermal coal pretreatment for mercury removal is quite competitive and does not exceed the cost of other separation technologies like activated carbon dosing. However, a plant concept for thermal pretreatment must always be carried out on the basis of the coal under consideration and cannot be generalized. The study by Merriam (1993) shows very high mercury separation efficiencies up to 70%–80% in hard coal and lignite using a fluidized bed reactor (thermal treatment 150–290 °C). Schwieger et al. (2020), on the other hand, were able to achieve as high as 87% reduction in mercury content in the coal sample for thermal treatment at 200 °C of central German lignite in a fixed bed with a slow heating rate in air. There is thus a high dependence of the efficiency of mercury reduction on the reactor type, temperature profile, process gas, residence time, binding forms of mercury in the coal, etc. This must be taken into account in a thermal coal pretreatment concept.

The second point describes the influence of the release of mercury on the separation technologies for enhancing the oxidation of the mercury by halogen salt addition like calcium bromide. The results in Sect. 3.2 show that even before combustion, a certain amount of mercury is present in the gas phase and detached from the coal. Thus, the timing of the release of mercury and the halogen for the homogeneous gas-phase reaction is different. Calcium bromide, for example, decomposes in an oxygen-containing atmosphere between 600 and 900 °C and thus only in the combustion chamber of a power plant (Paulik et al. 1979; Schwieger et al. 2018). By this time, a significant amount of mercury may have already been released. This raises questions about the probability of the two reaction partners getting together. Hot flue gas moves viscously due to the high temperatures in the combustion chamber. In power plants with unfavorable flue gas flow distribution or mixing, this could reduce the probability of the reactants colliding. This is particularly

important due to the very low concentrations of mercury and additives such as calcium bromide.

Finally, if mercury is released from the coal at such a low temperature, the production of activated carbon from lignite or hard coal should also be considered more closely. In the pyrolysis and thermal activation, the coal is heated to temperatures up to 1000 °C (Gazda-Grzywacz et al. 2021). All bound mercury evaporates at such high temperatures. A life cycle assessment is required to determine whether the vaporized mercury from the process is emitted into the environment or is separated from the exhaust gas of the activated carbon plant using suitable separation technologies.

4 Conclusions

In this work, mercury release from lignite in a high-temperature furnace and in power plant mills were examined. The investigation of the mercury binding forms of two lignite samples by thermal desorption shows the release of mercury from approx. 170 °C onwards. By analysis of the mercury pure substances at the high-temperature furnace, the results indicate that the released mercury was primarily bound to Humic Acid in the two lignite samples. That means that low temperature exposure leads to the release of organically bound mercury. The hypothesis that mercury could be released into the vapor prior to combustion under the conditions of the grinding-drying process was subsequently investigated. By means of simultaneously sampling of lignite samples prior to coal mill and after it, conclusions about mercury release could be make. Mercury was released into vapor up to one third while grinding-drying process and enters the combustion chamber separated from the coal grain. These results highlight the potential of thermal coal pretreatment as a mercury removal technology.

Author contribution Anne-Christin Kropp: Conceptualization, Methodology, Investigation, Visualization, Writing - Original Draft. Kathrin Gebauer: Resources, Writing - Review & Editing. Michael Beckmann: Project administration, Supervision, Writing - Review & Editing.

Declarations

Conflict of interest All the authors of this manuscript have approved the article's submission for publication, and there are no conflicts of interest to declare. This paper has not been published elsewhere and is not under consideration by another journal.

References

Berry M, Dombrowksi K, Richardson C, Chang R, Borders E, Vosteen B (2007) Mercury Control evaluation of calcium bromide injection into a PRB-fired furnace with an SCR. Air Quality VI Conference. Arlington/Washington DC, Crystal Gateway Marriott

Biester H, Scholz C (1997) Determination of Mercury Binding Forms in Contaminated Soils: Mercury Pyrolysis versus Sequential Extractions. Environ Sci Technol 31:233–239. https://doi.org/10.1021/es960369h

Chang H, Zhang Z, Qiang L, Gao T, Lan T, Sun M, Xu L, Ma XX (2019) Study on the Pyrolysis Characteristics of a Typical Low Rank Coal with Hydrothermal Pretreatment. Energy Fuels 33:3871–3880. https://doi.org/10.1021/acs.energyfuels.8b04312

Chmielniak T, Słowik K, Sajdak M (2017) Mercury removal by mild thermal treatment of coal. Fuel 195:290–298. https://doi.org/10.1016/j.fuel.2017.01.073

DIN - VDI 2066 Blatt 1 (2006) Messen von Partikeln - Staubmessungen in strömenden Gasen - Gravimetrische Bestimmung der Staubbeladung. Particulate matter measurement - Dust measurement in flowing gases - Gravimetric determination of dust load 2006

DIN EN 13284-1:2018-02 (2018) Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method 2018

Dronen LC, Moore AE, Kozliak EI, Seames WS (2004) An assessment of acid wash and bioleaching pre-treating options to remove mercury from coal. Fuel 83:181–186. https://doi.org/10.1016/S0016-2361(03)00251-5

Dziok T, Strugała A, Włodek A (2019a) Studies on mercury occurrence in inorganic constituents of Polish coking coals. Environ Sci Pollut Res Int 26:8371–8382. https://doi.org/10.1007/s11356-018-1667-1

Dziok T, Strugała A, Górecki J (2019b) Assessment of the possibility of mercury removal from the organic and the mineral matter of hard coals in the process of thermal pretreatment. IOP Conf Ser : Earth Environ Sci 214:012028. https://doi.org/10.1088/1755-1315/214/1/012028

Gazda-Grzywacz M, Winconek Ł, Burmistrz P (2021) Carbon Footprint for Mercury Capture from Coal-Fired Boiler Flue Gas. Energies 14:3844. https://doi.org/10.3390/en14133844

Klöfer I, Bittig M, Bathen D (2021) Speciation of Inorganic Mercury Compounds in Solid Samples via Thermo-desorption Experiments. Chem Eng Technol 44:788–796. https://doi.org/10.1002/ceat.202000444

Luo G, Yao H, Xu M, Gupta R, Xu Z (2011) Identifying modes of occurrence of mercury in coal by temperature programmed pyrolysis. Proc Combust Inst 33:2763–2769. https://doi.org/10.1016/j.proci.2010.06.108

Lusilao-Makiese J, Tessier E, Amouroux D, Tutu H, Chimuka L, Cukrowska EM (2012) Speciation of mercury in South African coals. Toxicol Environ Chem 94:1688–1706. https://doi.org/10.1080/02772248.2012.728604

Mashyanov NR, Pogarev SE, Panova EG, Panichev N, Ryzhov V (2017) Determination of mercury thermospecies in coal. Fuel 203:973–980. https://doi.org/10.1016/j.fuel.2017.03.085

Mathebula MW, Panichev N, Mandiwana K (2020) Determination of mercury thermospecies in South African coals in the enhancement of mercury removal by pre-combustion technologies. Sci Rep 10:19282. https://doi.org/10.1038/s41598-020-76453-z

Merdes AC, Keener TC, Khang S-J, Jenkins RG (1998) Investigation into the fate of mercury in bituminous coal during mild pyrolysis. Fuel 77:1783–1792. https://doi.org/10.1016/S0016-2361(98)00087-8

Merriam NW (1993) Removal of mercury from powder river basin coal by low-temperature thermal treatment. https://doi.org/10.2172/10189789

Merzsch M, Posselt J, Wiedemann P, Krautz H-J (2015) Die Druckaufgeladene Dampfwirbelschicht-Trocknung von Braunkohlen (DDWT). In: Schulz D (ed) Nachhaltige Energieversorgung und Integration von Speichern. Springer Fachmedien Wiesbaden, Wiesbaden, pp 160–165. https://doi.org/10.1007/978-3-658-10958-5_25

Paulik F, Paulik J, Buzágh-Gere É, Arnold M (1979) Examination of the decomposition of $CaBr_2$ with the method of simultaneous TG, DTG, DTA and EGA. J Therm Anal 15:271–277. https://doi.org/10.1007/BF01903650

Porsche T, Thannhäuser L, Höhne O, Martin JS (2009) First test results of the pilot plant for the pressure loaded vapour loaded fluidized bed drying process (DDWT) of brown coals, A pilot plant for 5 t/h dry coal and till 6 bar dryer pressure. In: VDI-Gesellschaft Energietechnik. 24 th German flame day, Combustion and furnaces (ed), Düsseldorf, pp 337–342

Reis AT, Coelho JP, Rodrigues SM, Rocha R, Davidson CM, Duarte AC, Pereira E (2012) Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments. Talanta 99:363–368. https://doi.org/10.1016/j.talanta.2012.05.065

Rumayor M, Diaz-Somoano M, Lopez-Anton MA, Martinez-Tarazona MR (2013) Mercury compounds characterization by thermal desorption. Talanta 114:318–322. https://doi.org/10.1016/j.talanta.2013.05.059

Rumayor M, Lopez-Anton MA, Díaz-Somoano M, Martínez-Tarazona MR (2015) A new approach to mercury speciation in solids using a thermal desorption technique. Fuel 160:525–530. https://doi.org/10.1016/j.fuel.2015.08.028

Schwieger A-C, Gebauer K, Ohle A, Beckmann M (2020) Determination of mercury binding forms in humic substances of lignite. Fuel 274:117800. https://doi.org/10.1016/j.fuel.2020.117800

Schwieger A-C, Ohle A, Beckmann M (2018) Oxidationsverhalten von Quecksilber bei der Kohleverbrennung. In: Beckmann M (ed) Emissionsminderung in Kraftwerken 2018. Emission reduction in power plants, SAXONIA Standortentwicklungs- und verwaltungsgesellschaft mbH, Freiberg, pp 45–54

Sloss LL (2008) Economics of mercury control. https://doi.org/10.13140/RG.2.2.15055.84648. CCC/134

Uruski L, Gorecki J, Macherzynski M, Dziok T, Golas J (2015) The ability of Polish coals to release mercury in the process of thermal treatment. Fuel Process. Technol. 140:12–20. https://doi.org/10.1016/j.fuproc.2015.08.005

Zhang X, Zhu Z, Wen G, Lang L, Wang M (2021) Study on gas desorption and diffusion kinetic behavior in coal matrix using a modified shrinking core model. J Pet Sci Eng 204:108701. https://doi.org/10.1016/j.petrol.2021.108701

Zhao S, Pudasainee D, Duan Y, Gupta R, Liu M, Lu J (2019) A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. Prog Energy Combust Sci 73:26–64. https://doi.org/10.1016/j.pecs.2019.02.001

Zimmer H (1996) Immobilisierung von Quecksilber in kontaminierten Böden mittels schwefelhaltiger Reagenzien. Diploma Thesis, Ruprecht-Karls-Universität Heidelberg

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