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Hg occurrence in coal and its removal before coal utilization

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ABSTRACT

Mercury emission control technology in the combustion flue gas of coal-fired power plants has been under intensive development, but none has been implemented commercially because of the high cost. Treatment of coal before combustion provides an alternative option for Hg emission control. In this study, samples of one anthracite, one lignite and three bituminous coals were investigated to determine the feasibility of pre-combustion Hg emission control. Density separation, temperature-programmed pyrolysis, HNO_3 extraction and sequential selective extraction (SSE) were used to determine the occurrence and speciation of mercury in the different types of coal. The results showed that the characteristic temperature range for Hg release is <150 °C for Hg^0, 150–250 °C for $HgCl_2$/organic-bound Hg, 250–400 °C for HgS/silicate-bound Hg, and 400–600 °C for pyrite-bound Hg. HNO_3 extraction and sink-float were found to be effective for the removal of pyrite-bound Hg and then the coal can be pyrolysed at 400 °C to remove other forms of Hg.

1. Introduction

The high-level health risks of Hg emission from anthropogenic activities are a worldwide concern [1]. Although the concentration of Hg in coal is only 0.1 mg/kg [2,3], coal combustion is a major source of Hg emission due to the huge consumption of coal in coal-fired power plants without any form of emission control [4]. In the USA, 33% of the anthropogenic emission of Hg was estimated to come from coal combustion [5]. In the past few decades, especially in recent years, both academics and industry have made great efforts to understand mercury emissions and to develop Hg emission control technology for coal-fired power plants. Most of these efforts have been focused on the removal of Hg from flue gases of coal combustion.

All forms of Hg in coal vaporize and are converted to elemental Hg at the temperature of coal combustion. As the flue gas cools, elemental Hg can be oxidized under the appropriate conditions. Some of the Hg can be adsorbed onto fly ash. Thus, there are three principal forms of Hg in post-combustion flue gases: particulate bound Hg (Hg_p), gas phase elemental Hg (Hg^0) and gas phase oxidized Hg (Hg^{2+}) [6]. Hg_p can be captured easily by air pollution control devices (APCDs); e.g. an electrostatic precipitator (ESP) [7–10] or fabric filter (FF) [8]. Hg^{2+} is water-soluble and can be captured by a wet scrubber [9–11]. However, Hg^0 can easily pass through these conventional APCDs, releasing Hg into the atmosphere where it has a life-span of 0.5–2 years [12].

In order to control Hg^0 emission from coal combustion, a variety of Hg control technologies have been under intensive development. One approach is to inject strong oxidants such as Br_2 [13], Cl_2 [14] and O_3 [15] into the flue gas, which enhance the transformation of Hg^0 to Hg^{2+}. However, this approach is prone to equipment corrosion and may cause secondary pollution. Various types of sorbents can capture and solidify Hg but this approach is very costly. Due to the ultra low concentration of Hg in flue gas, the sorbent/Hg ratio needs to be kept at a relatively high level to attain a satisfactory Hg removal efficiency. In addition, the collection of Hg-containing spent sorbent by particulate control devices would cause contamination of fly ash by Hg and sorbent materials, such as carbon, limiting the utilization of fly ash [16].

Due to these adverse aspects of post-combustion technologies, pre-combustion technologies are being developed. The idea of pre-combustion technologies is to find a way to reduce Hg content and make coal "clean" before its combustion. Unfortunately, only a few studies on the pre-combustion removal of Hg (including physical, chemical, and thermal methods) from coal have been reported. Conventional physical methods for cleaning coal, including density separation and froth flotation, etc., are usually used to remove inorganic minerals and render coal suitable for transportation and commerce. The sink-float tests have been widely used in the laboratory to separate coal from mineral matter on the basis of differences in density. The sink-float tests are

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effective for removing excluded minerals but cannot remove included mineral without losing associated organic matter [17]. Therefore, the efficiency of Hg removal from coal by density-based method depends on the form of Hg present.

Originally, selective sequential extraction (SSE) was used to determine the form of Hg in contaminated soils and sediments [18]. Several SSE studies have been devoted to determination of the form of Hg in coal [19–21]. It has been difficult to reach consensus by different extraction procedures. Specific reagents are known to be efficient for specific coals, which depends on the selectivity of the reagent and the form of Hg in the coal. Insufficient selectivity of the leachants and/or inadequate extraction time might be the reason for limited success in distinguishing specific Hg compounds. Acids such as HCl [22,23] and HNO_3 [24], chelate-forming reagents [25], subcritical water [26], etc. have been used as reagents to extract Hg from coal. Some leachants, such as strong oxidant acids, might change the state of Hg during the extraction. The low Hg content in coal makes it difficult to achieve comparable and conclusive results. There has been little research into Hg removal by SSE.

Pyrolysis technology was designed to study the release of Hg from solid samples and to determine the form of Hg in soil and biological samples. Hg removal from coal by mild pyrolysis before combustion was originally proposed by Merriam et al. [27], and further studied in other laboratories [28–33]. The influence of temperature, residence time, volatile matter content, etc. on Hg removal efficiency was considered. However, there are only a few reports relating Hg occurrence to its removal efficiency.

In summary, the technology for identification of Hg species in coal needs further development. The efficiency of various Hg removal techniques (sink-float, pyrolysis and extraction) is affected by the forms of Hg in coal and/or the association of Hg with mineral/organic phases. Understanding the form of Hg in coal is of crucial importance for its removal. The aim of this study was to determine the form of Hg in coal by pyrolysis, sequential extraction and sink-float tests and to link this information to the potential removal by single/hybrid methods.

2. Experimental

2.1. Preparation and characterization of coal samples

The properties of the five test samples of coal named V, Y, Z, L and H and the reference coal 1632c used in this study are given in Table 1. The test samples belonged to three major groups: coal V is lignite from Australia with a very low ash content and high Hg content; coal Y is anthracite; and coals Z, L and H are bituminous coals from China. Coal 1632c is a standard reference coal used for calibrating trace element analysis and was purchased from the National Institute of Standards and Technology (NIST). Before the experiment, all the test coal samples were dried and ground to a particle size of less than 200 μm.

Low-temperature ash (LTA) of the coal samples was obtained <150 °C with a low-temperature asher (LTA, EMITECH K1050X). X-ray diffraction (XRD) patterns of LTA samples were obtained using a Rigaku X-ray diffractometer equipped with a Geigerflex 2173 vertical goniometer, running 2θ from 5° to 90° at 0.05°/step and 3°/min scan rate.

The Hg content in coal was determined using EPA method 7473 and a direct Hg analyser (Milestone DMA-80).

2.2. Sink-float test

The major constituents of the mineral matter in coal include quartz (2.65 g/cm^3), pyrite (5.00 g/cm^3), calcite (2.71 g/cm^3), and clay (2.90 g/cm^3) [34]. The density of organic matter in coal is <1.4 g/cm^3, which is much less than the density of the minerals. Separation of minerals of different density by the sink-float separation process is in widespread use. In this study, heavy liquids of specific gravity (SG) of 1.4, 1.5, 1.6 and 1.8 were used to separate coal samples into five density fractions of <1.4, 1.4–1.5, 1.5–1.6, 1.6–1.8 and >1.8 g/cm^3. To prepare the heavy liquids of required specific gravity, carbon tetrachloride (CCl_4), bromoform ($CHBr_3$), benzene (C_6H_6) and their binary mixtures were used.

The sink-float separation was done as follows: a 10 g coal sample was placed into a centrifuge tube containing 200 mL of heavy liquid and stirred for 1 h. The mixture was centrifuged in a bench top centrifuge for 15 min at 3000 rpm to enhance gravimetric separation. The low-density fraction floating in the upper part of the suspension was skimmed off and dried at 55 °C in a vacuum oven to collect the solid of lower density than the liquid, which was stored in a sealed sample bottle. The solids of higher density than the liquid sank to the bottom of the centrifuge tube and were collected and dried for use in the next round of the sink-float separation process using the next heavier liquid.

2.3. Extraction

The sequential selective extraction method described by Bloom et al. [35] was used with slight modifications. The fractions obtained with corresponding sequential leaching reagents were coded as follow: F1 (3 M HCl), F2 (1 M KOH), F3 (2 M HNO_3), F4 (5 M HCl + 5 M HF) and F5 (residue). In a single-step extraction test, 2 M HNO_3 was used as the leaching reagent. For both methods, a 1 g sample was added to 10 mL of reagent solution. The sequential selective extraction was done at room temperature for 18 h for each step. The single-step extraction was done at 80 °C for 2 h.

2.4. Pyrolysis

All pyrolysis experiments were done with a custom-built apparatus consisting of a quartz tube (4 mm i.d.) reactor within a programmable electric furnace (Thermolyne 79300 Tube Furnace), as shown in Fig. 1. To avoid adsorption/deposition of Hg compounds

Table 1
Proximate and ultimate analysis of coal samples used in this study.

Coal sample	Proximate analysis (wt.%, ad)				Ultimate analysis (wt.%, daf)				
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	Hg[a]
Y	1.42	22.65	8.91	67.02	68.32	2.38	0.76	1.95	201.0
V	19.67	2.00	40.90	37.43	57.59	6.17	0.52	0.47	2765.0
Z	1.20	23.10	10.00	65.70	66.10	2.20	0.60	6.30	188.0
L	2.09	26.64	22.40	48.86	57.33	3.89	1.22	2.67	157.0
H	2.45	49.58	14.61	33.36	35.16	2.28	0.53	5.47	552.0
1632c									93.8

[a] Unit of Hg is ng/g.