

# Behavior of mercury release during thermal decomposition of coals

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**Abstract**—The mercury release behavior during thermal decomposition of three Chinese coals with different types was studied under nitrogen, carbon dioxide and air at temperatures of 800, 900, 1,000 and 1,100 °C. The thermal treatment experiments were carried out in a quartz tube reactor. Results showed that the release ratio of total mercury during thermal decomposition of coals increases with the increasing temperature. The order of the amount of mercury released under the three atmospheres is nitrogen<carbon dioxide<air for all three coals during thermal decomposition. This indicates that air and carbon dioxide can promote the mercury release due to their reactivity with coal. However, the order of amount of elemental mercury released under the three atmospheres is nitrogen>carbon dioxide>air for all three coals. The release behavior of the total mercury under air is independent of the coal type. Under the other two atmospheres the release behavior is distinguished by the coal type.

Key words: Mercury Release, Coal, Thermal Decomposition

## INTRODUCTION

Mercury (Hg) is a volatile and toxic metal. Although it exists in coal in low levels, Hg emission from coal processing is one of the major sources of anthropogenic discharge due to the high volatility of Hg and the huge amount of coal used in consumption. It can strongly affect the environment and human health because of its persistence and bioaccumulation character [1,2].

The existence of Hg in coal is usually associated with pyrite (FeS<sub>2</sub>) and cinnabar (HgS) or organically bound to the coal macerals [3]. Mercury released from coal combustion can be in elemental or oxidized forms [4-6]. Elemental Hg and oxidized Hg have different characteristics and migration abilities in the environment. Oxidized Hg is soluble and has a tendency to associate with particulates. Therefore, oxidized mercury can be efficiently captured by an air control system such as a wet flue gas de-sulfuring scrubber or electrostatic precipitator. Elemental Hg, however, cannot be removed through conventional air control devices due to its high volatility, stability and water-insolubility [7]. The estimated lifetime of elemental Hg in the atmosphere can be up to 2 years, and it can migrate over trans-continental distances. Therefore, elemental Hg emission is harder to control than oxidized Hg [8].

To protect the environment from the Hg pollution, it is important to control Hg emission from coal. It is necessary to understand the behavior of Hg in coal during thermal decomposition, which occurs in most coal conversion processes.

Many studies on behavior of Hg release in coal combustion and pyrolysis have been reported in recent years [9-17]. However, the

knowledge on Hg release during thermal decomposition is still limited, especially the information on the Hg emission during thermal decomposition of coal with different types. Gaining such information is worthwhile not only to science but also to development of Hg control technology. The objective of this study is to reveal the fate of Hg emission from three Chinese coals with different types during thermal decomposition under nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and air atmospheres at temperatures of 800, 900, 1,000 and 1,100 °C.

## EXPERIMENTAL

### 1. Coal Samples

Three Chinese coals with different types, Jincheng (JC, anthracite), Datong (DT, bituminous) and Huolinhe (HLH, lignite), were studied. The coals were crushed and sieved to 0.16-0.27 mm and dried prior to use. Proximate and ultimate analyses of the dried coals were made following Chinese national standards, GB/T 212-2001 and GB/T 476-2001, and the results are shown in Table 1. The contents of Hg are also shown in Table 1.

### 2. Thermal Decomposition Experiments

The thermal decomposition experiments were conducted in a

**Table 1. Proximate and ultimate analyses of the coals**

Coal sample	Hg <sup>b</sup>	Proximate analysis, wt%			Ultimate analysis, wt% daf				
		V <sub>daf</sub>	A <sub>as</sub>	M <sub>as</sub>	C	H	N	S	O <sup>a</sup>
JC	282	9.50	21.60	1.80	90.7	3.5	1.2	0.5	4.1
DT	214	31.00	13.74	0.26	82.8	5.0	0.8	2.4	9.0
HLH	161	48.85	24.70	2.17	76.6	4.6	1.5	0.7	16.6

as: as received; daf: dry and ash free; a: by difference; b: ng/g

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fixed bed quartz tube reactor under a flow of N<sub>2</sub>, CO<sub>2</sub> or air (300 cm<sup>3</sup>/min) at temperatures of 800, 900, 1,000 or 1,100 °C. A quartz boat with about 0.5 grams of coal sample was quickly placed into the reactor at a predetermined temperature. The sample reached the predetermined temperature in less than 1 minute. The samples were kept at this temperature for 5 minutes. Then the quartz boat with char was moved quickly to a cold end of the reactor and cooled under a N<sub>2</sub> flow. The fixed-bed quartz tube reactor was directly connected to an on-line atomic fluorescence spectrometer (AFS), which is sensitive only to elemental Hg. The volatile products during thermal decomposition of coal were swept into the AFS detector by specified gas flow. The weights of the sample before and after the thermal decomposition were recorded, and the chars were analyzed for total Hg content.

### 3. Determination of Mercury

The content of Hg in the coals and the chars was determined following the Chinese national standard, GB/T 16659-1996. Mercury in the sample is dissolved in HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> solution as Hg<sup>2+</sup> in the presence of V<sub>2</sub>O<sub>5</sub>. Then the Hg<sup>2+</sup> is reduced to elemental Hg with the potassium borohydride (KBH<sub>4</sub>) and measured directly by AFS. The detection limit by this method is 0.05 ng/L. The elemental Hg release profiles from the thermal decomposed coals were obtained by an on-line AFS.

Release ratio of elemental mercury (RRE) is used to quantify the amount of elemental Hg released from coal and defined as:

$$\text{RRE}(\%) = \frac{\text{Elemental Hg released}}{\text{Total Hg in coal}} \times 100(\%) \quad (1)$$

Release ratio of total Hg (RRT) is used to quantify the amount of total mercury released from coal and defined as:

$$\text{RRT}(\%) = \frac{\text{Hg concentration in coal} - \text{Hg concentration in char} \times \text{char yield}}{\text{Hg concentration in coal}} \times 100(\%) \quad (2)$$

Volatile yield (VY) is used to evaluate the quantity of volatile matters (tar+gas) released during the thermal decomposition process and defined as:

$$\text{VY}(\%) = 100 - \frac{\text{Char mass}}{\text{Coal mass}} \times 100(\%) \quad (3)$$

## RESULTS AND DISCUSSION

### 1. The Mercury Released During Thermal Decomposition of Coals

The release ratio of total Hg (RRT) and the volatile yield (VY) of JC anthracite during thermal decomposition under N<sub>2</sub>, CO<sub>2</sub> and air atmospheres are presented in Fig. 1. It shows that the RRT and the VY of the JC coal increase with increasing temperature under the atmospheres tested. Generally, the RRT is in the order of air >> CO<sub>2</sub> > N<sub>2</sub>, which is similar to the order of VY. The RRT under N<sub>2</sub> and CO<sub>2</sub> is significantly lower than that under air; the RRT under CO<sub>2</sub> is slightly higher than that under N<sub>2</sub> atmosphere at temperature range studied. Similar to the RRT, the VY under N<sub>2</sub> and CO<sub>2</sub> is also distinctly lower than that under air; the VY under CO<sub>2</sub> is also slightly higher than that under N<sub>2</sub>. This indicates that Hg release from coal could relate to the volatile release. However, the RRT is much higher

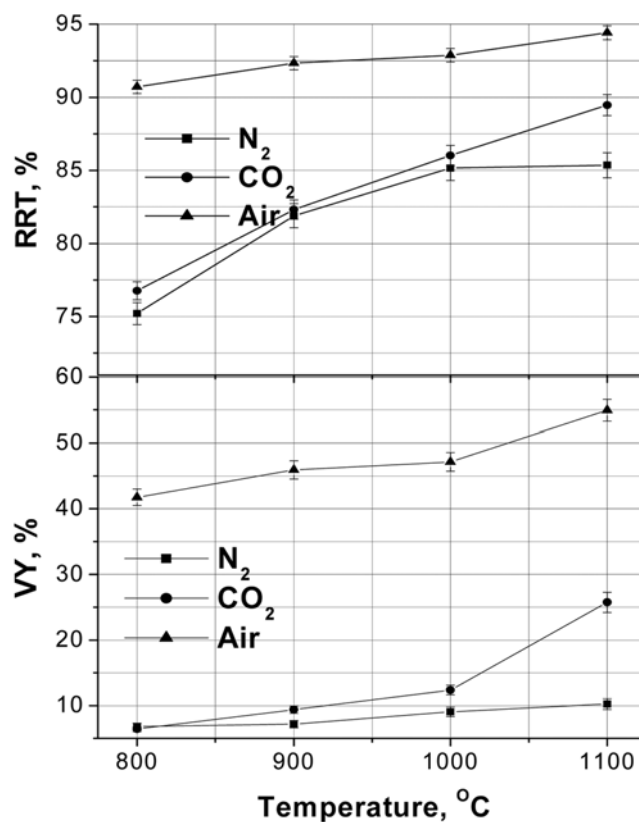


Fig. 1. The RRT and VY of JC anthracite under N<sub>2</sub>, CO<sub>2</sub> and air atmospheres.

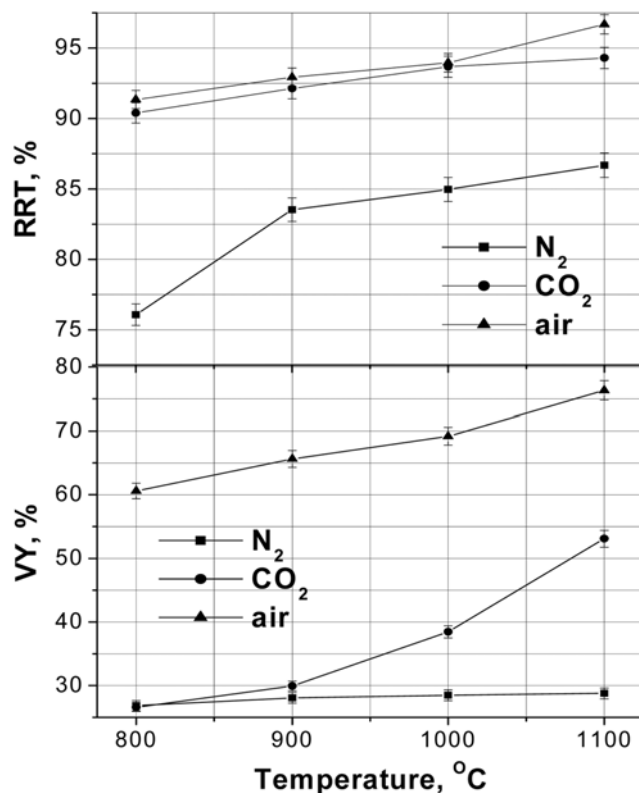


Fig. 2. The RRT and VY of DT bituminous coal under N<sub>2</sub>, CO<sub>2</sub> and air atmospheres.

than the corresponding VY at the same conditions. For example, the RRT is higher than 75% at 800 °C under  $N_2$  and  $CO_2$  while the VY is less than 10%. This may imply that the Hg release is not only affected by volatiles.

Fig. 2 shows the RRT and the VY of DT bituminous coal during thermal decomposition under  $N_2$ ,  $CO_2$  and air atmospheres. Similar to JC anthracite, the RRT and the VY of the DT coal increase with the increasing temperature under the three atmospheres. Generally, the amount of mercury release and the volatile release is in the order of  $air > CO_2 > N_2$ . Compared to the RRT and VY of JC anthracite, the RRT and the VY of DT bituminous coal is generally higher. This may result from the bituminous coal having higher volatility than anthracite. However, it should be noted that at 1,100 °C, the RRT of the two coals has no distinct difference under the three atmospheres, although the VY of DT bituminous coal is much higher than that of JC anthracite. This indicates that the effects of coal type on Hg release can be eliminated at higher temperature.

Fig. 3 shows the RRT and the VY of HLH lignite during thermal decomposition under  $N_2$ ,  $CO_2$  and air atmospheres. It also shows that the RRT and the VY of the HLH coal increase with increasing temperature. In comparison with the effect of the atmospheres for three coals, both RRT and VY are generally in a similar order:  $air > CO_2 > N_2$ . In comparison with the effect of coal types, the VY of HLH lignite is significantly higher than that of JC and DT coals, as shown in Fig. 1 and Fig. 2, respectively. However, the RRT of these coals do not have a similar relationship.

From the RRT shown in Figs. 1-3, it can be seen that the RRT of the coals studied are higher than 75%. In addition, the RRT under air is always the highest at the same temperature. The release behavior of the total Hg under air is independent of the coal type. It

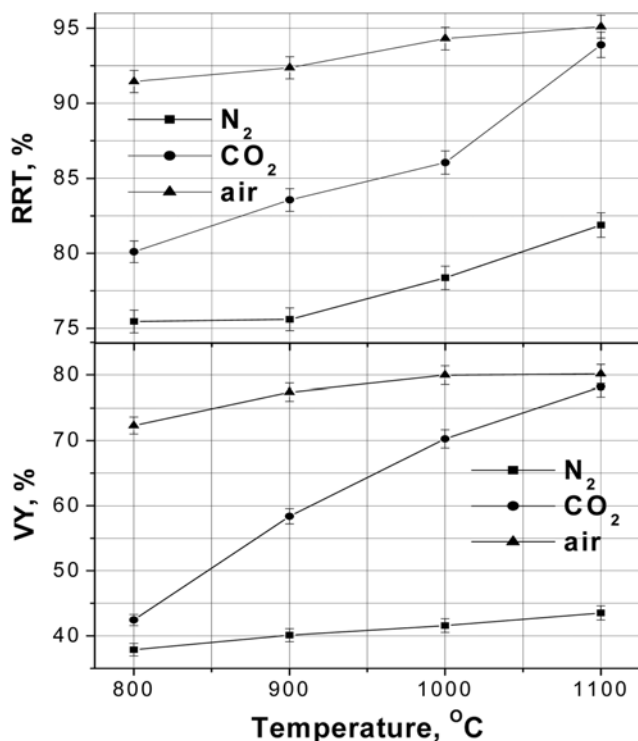


Fig. 3. The RRT and VY of HLH lignite under  $N_2$ ,  $CO_2$  and air atmospheres.

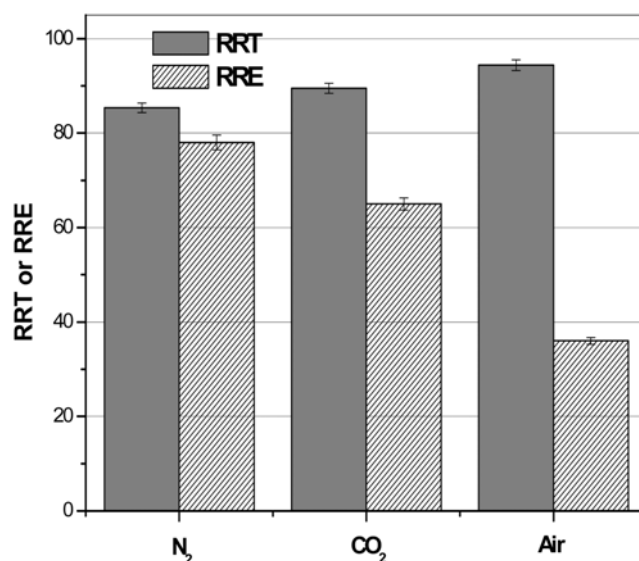


Fig. 4. Comparison of RRT and RRE of JC anthracite under  $N_2$ ,  $CO_2$  and air atmospheres.

implies a maximum Hg release value from coals at the experimental conditions. Under the other two atmospheres the release behavior varies with the coal type. Nevertheless more than 75% of Hg was released during coal decomposition at the temperature higher than 800 °C. It can be concluded that the Hg release behavior during thermal decomposition of coals is mainly affected by atmosphere and temperature. Most of the mercury in coals (no matter the type of coal used) was released during combustion or gasification at a temperature higher than 800 °C.

## 2. The Comparison of RRT and RRE During Thermal Decomposition of Coals

Fig. 4 shows a comparison of RRT and RRE of JC anthracite under  $N_2$ ,  $CO_2$  and air atmosphere at 1,100 °C. It clearly shows that the RRE is less than the RRT for all the cases. This indicates that the Hg with a form other than the elemental Hg must exist in the total released Hg during thermal decomposition of coal. The difference between the RRT and RRE depends on the atmosphere used. In addition, similar results can be found when JC anthracite was combusted at 800, 900 and 1,000 °C. The similar results can also be found for DT and HLH coals. It is understandable that the highly oxidized atmosphere should convert more Hg to oxidized Hg.

## CONCLUSIONS

An attempt was made to understand the release of Hg from different coals under different atmospheres during thermal decomposition. It was found that the release behavior of Hg during thermal decomposition of coals is mainly affected by atmosphere and temperature. The release behavior of the total mercury under air is independent of the coal type. It is a maximum amount of mercury that can be released from coals at the experimental temperatures. Under the other two atmospheres the release behavior is distinguished by the coal types. Nevertheless more than 75% of mercury was released during coal decomposition at the temperatures higher than 800 °C for all the cases studied.

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