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Article

The Effect of Atmosphere on Elemental Mercury Release During Thermal Treatment of Two Bituminous Coals

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The dynamic release behavior of elemental Hg (Hg^0) during thermal treatment of two bituminous coals was studied under N_2, CO_2 and air atmospheres. The results show that the profiles of Hg^0 released present several peaks during thermal treatment of two bituminous coals. The Hg peak profiles for the same coal are different with the different atmosphere used. The amount of Hg^0 released from the coals is about 92-94, 73-74 and 31-33% under N_2, CO_2 and air atmosphere, respectively. This indicates that the Hg^0 is the dominant form during thermal treatment of the coals under N_2 atmosphere whereas part of Hg^0 is converted into the oxidized Hg during thermal treatment of the coals under CO_2 and air atmosphere. The total Hg released is promoted by the volatile matter release to some extent while the Hg^0 released is mainly affected by the atmospheres used.

Keywords: bituminous coal, dynamic release behavior, elemental Hg, thermal treatment

Introduction

Mercury (Hg) is a toxic trace element in coal with a high volatility.[1] Because of the tremendous amount of coal used each year, its utilization has been one of the main sources of anthropogenic discharge of Hg.[2] Hg has the persistence and bioaccumulation character, which can strongly affect the environment as well as the human health.[3,4] Therefore, more and more attention has been paid to the Hg emission control from coal-fired power plants.[5-9] Also, a series of strict policies for controlling Hg emissions have been established, including the emission standard of air pollutants for coal-fired power plant in China. To satisfy the emission standard of Hg, effective Hg control technology should be introduced to reduce the Hg emission. Consequently, it is important to develop effective Hg control technologies.

Generally, Hg released presents mainly in two forms (Hg^{2+} and Hg^0) during coal combustion. The two forms of Hg show different characteristics and have different migration abilities in environment. The Hg^{2+} is a local pollutant, which is water-soluble and can fall from the atmosphere quickly.[10,11] However, the Hg^0 is a global pollutant, which is low water solubility with high vapor pressure and can present 3 to 24 months of residence time in environment atmosphere with a wide dispersion range.[12-14] Therefore, the emission control of Hg^0 is harder than that of Hg^{2+} and it becomes the main concern for Hg pollution control.

To develop an effective Hg controlling technology, it is necessary to understand the release behavior of Hg during coal thermal treatment because it happens in most coal conversion processes. In recent years, extensive studies have been focused on the Hg release during coal combustion and pyrolysis.[14-24] However, the information about the effect of atmosphere on Hg^0 release during thermal treatment of bituminous coal is still limited. In the present paper, the effect of atmosphere on Hg^0 release from two bituminous coals during thermal treatment has been studied.

Experimental

Coal samples

Two Chinese bituminous coals were used, which were labeled as 1 and 2. The coals were crushed and sieved to 0.16-0.27 mm and dried before use. Proximate and ultimate analyses of the two coals and the concentration of Hg contents in the coals are shown in Table 1. The major mineral elements of the two coals detected by X-ray fluorescence analysis are shown in Table 2.

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Table 1. Proximate and ultimate analyses of the coals

Coal sample	Hg in coal / (ng g^{-1})	Proximate analysis / (wt.%)			Ultimate analysis (daf) / (wt.%)				
		V_{daf}	A_{as}	M_{as}	C	H	N	S	O^a
1	132	41.69	20.29	1.81	80.16	4.34	0.85	2.37	12.28
2	169	44.82	12.15	0.87	81.32	5.22	1.20	3.97	8.29

[a]By difference; V: volatile; A: ash; M: moisture; as: as received; daf: dry and ash free.

Table 2. Major mineral elements in the coals[a]

Coal sample	Ash analysis / (g 100 g^{-1})									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
1	9.42	3.91	2.83	1.20	0.84	0.27	1.04	0.41	0.28	0.09
2	3.97	1.75	2.77	1.83	0.18	0.08	1.36	0.06	0.11	0.04

[a]Dry basis.

Thermal treatment experiments

The thermal treatment process was carried out under N_2, CO_2 and air atmosphere with a flow rate of 300 cm^3 min^{-1} in a fixed bed quartz tube reactor from room temperature to 1200 °C at a heating rate of 20 °C min^{-1}. 1 g (the precision is 0.0002 g) of coal sample was charged into a quartz boat. Then, the quartz boat with the coal sample was pushed into the constant temperature zone of the reactor. A thermocouple was placed in the center of the coal sample to measure the temperature. Before thermal treatment of coal, 10 min purge time for the reactor was used to assure the atmosphere (N_2, CO_2 or air) purity. The release of Hg^0 from the thermal treatment of the coals was analyzed dynamically by coupling a temperature-programmed decomposition (TPD) unit with an on-line atomic fluorescence spectrometer (AFS) detector. The volatile products from the thermal treatment of the coals were swept into the AFS detector by purging gas continuously and the Hg^0 intensity is recorded by a computer. In this way, a dynamic Hg^0 release profile during coal thermal treatment can be obtained.[25] The detection limit of Hg in this system is 100 ng N m^{-3}. The on-line mass spectrometry (MS) (Balzers QMS422) was used to monitor the volatile matter release during the thermal treatment of the coals. At the temperature of 1200 °C, the boat with sample was moved quickly to the cold end of the reactor and cooled down under N_2 flow. The weights of the sample were weighed and recorded. The Hg contents in chars were analyzed.

Release ratio of elemental mercury is used to quantify the amount of Hg^0 released from coal, which is abbreviated as RRE and defined as:

$$\text{RRE}\ (\%) = \frac{\text{elemental Hg released}}{\text{total Hg in coal}} \times 100\ (\%) \qquad (1)$$

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

$$\text{RRT}(\%) = \frac{\left(\begin{array}{c}\text{Hg concentration}\\ \text{in coal}\end{array}\right) - \left(\begin{array}{c}\text{Hg concentration}\\ \text{in char}\end{array}\right) \times \text{ char yield}}{\text{Hg concentration in coal}} \times 100\ (\%) \qquad (2)$$

Volatile yield (VY) is used to evaluate the quantity of volatile matters released during the coal thermal treatment, defined as:

$$\text{VY}\ (\%) = 100 - \frac{\text{char mass}}{\text{coal massl}} \times 100\ (\%) \qquad (3)$$

Determination of mercury

The contents of Hg in the two coals and the chars were determined following the Chinese national standard (GB/T 16659-2008). Firstly, mercury in the coal sample was dissolved in HNO_3-H_2SO_4 solution and converted into Hg^{2+} in the presence of V_2O_5. Then, the Hg^{2+} is reduced to Hg^0 with the solution of KBH_4. Finally, Hg^0 was detected by the atomic fluorescence spectrometer with the detection limit of 0.05 ng L^{-1}. The Hg^0 release profiles during the thermal treatment of the coals were obtained by the on-line AFS.

Results and Discussion

Dynamic release behavior of Hg^0 during thermal treatment of two coals under N_2

The dynamic Hg^0 release profiles *versus* the increase of temperature for these two coals were measured using TPD-AFS technique and the results are shown in Figure 1, which the intensity of all the profiles is normalized for easy comparison.

Figure 1 shows that the initial Hg^0 release from the two coals is around 150 ºC and most of the Hg^0 releases at temperatures below 600 ºC. It indicates that pyrolysis is an effective method to remove Hg from coals, which somewhat agrees with the Hg release behavior reported in the literature.[18-21] Generally, the profiles of Hg released present two or three well-resolved peaks and most of them are broad and overlapped, indicating the diversity of modes of occurrence of Hg in the coals.[25-29] Note that the profiles present the Hg peaks at similar temperature range for these two coals. For example, two typical peaks can be observed for the two coals. One peak was located in the range of 150 to 400 ºC and the other peak was located in the range of 500 to 600 ºC. It indicates the similar modes of occurrence of Hg in the coals, which possibly are organic-bound and pyrite-bound Hg in coal.[30] However, the minor peak at 800-900 ºC is only shown for coal 1, while it is not shown for 2. This result indicates the existence of different modes of occurrence of Hg in the coals.

Generally, the N_2 is an inert gas and cannot react with coal or other gas. Therefore, the Hg released profiles under N_2 shown in Figure 1 can be regarded as the thermal stability of the mercury in the coals. Actually, the most known Hg compounds are thermally unstable above 700 °C.[31-33] However, Figure 1 shows the Hg released peak at 800-900 ºC for coal 1. According to Guo *et al.*[30] the Hg released above 700 °C should be silicate-bound Hg in coal. In addition, the major mineral elements in the coals listed in Table 2 shows that 1 has higher content of SiO_2 and Al_2O_3 than coal 2. Therefore, the Hg peak at 800-900 ºC for coal 1 is probably due to the influence of silicates or aluminosilicates.[34]

The amount of Hg released after TPD process for the two coals is listed in Table 3, in which the amount of Hg released as Hg^0 (RRE) was calculated based on AFS profile[25] and the amount of total Hg released (RRT) was calculated by comparing the mercury content in raw coal and char at 1200 ºC. The result shows that higher than 92% of total Hg in the coals releases in Hg^0 form under N_2. Meanwhile, approximately 94-95% of total Hg in the coals releases out during thermal treatment under N_2. Because the RRE is nearly equal to the RRT for the two coals used, it may be concluded that the Hg^0 is dominant form of Hg released from the coals during thermal treatment under N_2.[35]

The previous study reported that the modes of occurrence of Hg in the coals can be characterized based on the profiles in Figure 1 and the detailed discussions were given in the literature.[30] The Hg in coal can be separated

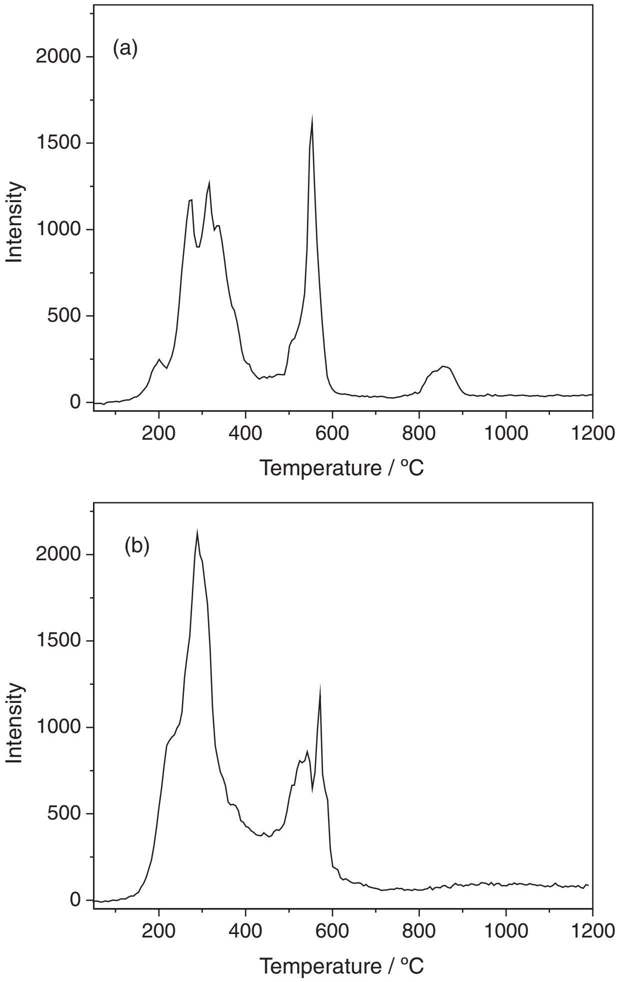

Figure 1. Dynamic release behavior of Hg^0 during thermal treatment of two coals under N_2, (a) 1; (b) 2.

Table 3. The amount of Hg released and VY during thermal treatment of two coals

Coal	Under N_2 / %			Under CO_2 / %			Under air / %		
Sample	RRE[a]	RRT[b]	VY[c]	RRE[a]	RRT[b]	VY[c]	RRE[a]	RRT[b]	VY[c]
1	92.1	94.3	30.84	73.6	97.3	77.97	31.1	98.5	80.70
2	93.5	94.2	36.85	73.4	96.5	81.94	32.6	99.4	88.94

[a]Based on the AFS profile; [b]according to the mercury content in raw coal and char; [c]according to the mass of raw coal and char; RRE: release ratio of elemental mercury; RRT: amount of total Hg released; VY: volatile yield.

into four modes of occurrence of Hg: the organic-bound Hg, the silicate-bound Hg, the pyrite-bound Hg and the HCl-soluble Hg.[30] For coal 1, it contains all the four modes of occurrence of Hg whereas coal 2 contains three modes of occurrence of Hg without the silicate-bound released in the temperature range > 750 °C.[30]

Dynamic release behavior of Hg^0 during thermal treatment of two coals under CO_2

The dynamic Hg^0 release profiles *versus* the increase of temperature for two coals under CO_2 atmosphere are shown in Figure 2. Also, the intensity of the profiles is normalized.

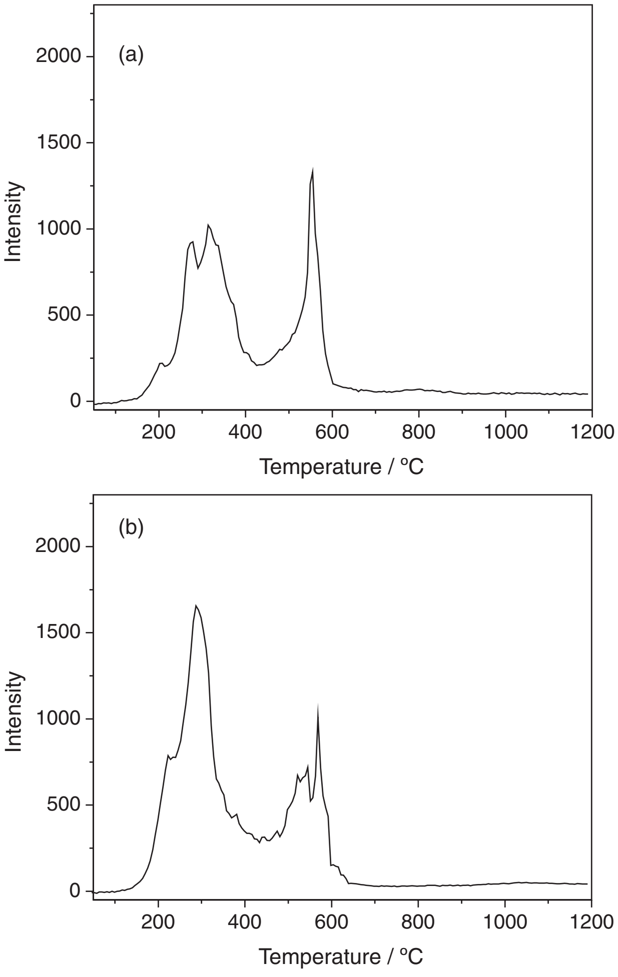

Figure 2. Dynamic release behavior of Hg^0 during thermal treatment of two coals under CO_2, (a) 1; (b) 2.

Similar to the release behavior of Hg^0 under N_2, the profiles also show several peaks and the Hg^0 starts to release at about 150 ºC. Note that the shape of the peaks < 600 ºC under CO_2 is similar to that under N_2 except that the intensity of the corresponding peaks under CO_2 is slightly lower than that under N_2. However, the peaks at 800-900 ºC under N_2 for coal 1 almost disappear after the thermal treatment under CO_2.

The RRE and RRT under CO_2 are listed in Table 3. It shows that the amount of Hg^0 released under CO_2 counts for 73-74% of Hg in the coals, which is lower than that under N_2. However, the amount of total Hg released counts for 96-98% of Hg in the coals and higher than that under N_2 at temperature range studied. It indicates that CO_2 atmosphere restrains the Hg^0 release and promotes the total Hg release to some extent.[36]

In fact, the thermal treatment of the coals under CO_2 < 800 °C is the process of pyrolysis due to the gasification of the coals that cannot occur at lower temperature range. Therefore, the behavior of Hg^0 release is similar to that under N_2 at lower temperature range. Generally, CO_2 can be produced as part of volatile matter during coal pyrolysis.[37,38] Also, the result of MS verifies the production of CO_2 during pyrolysis of the coals. The CO_2 release behavior during thermal treatment of two coals under N_2 is shown in Figure 3. Theoretically, coal pyrolysis is a complex chemical reaction and CO_2 gas is part of the reaction product.[37] When the additional CO_2 is introduced into the reaction system, it inhibits the reaction to a certain degree according to the theory of chemical reaction balance, leading to the decrease of the volatile matter produced during coal pyrolysis. Consequently, Hg^0 as part of volatile matter or reaction product during coal pyrolysis is also inhibited, resulting in a lower Hg peaks than that under N_2.

The thermal treatment of coal under CO_2 > 800 °C is a process of coal gasification because coal can react with CO_2 at high temperature.[39,40] And the coal gasification promotes the volatile matter release, leading to a dramatic increase of VY for both coals (see Table 3). It seems that the Hg^0 release should be promoted by the coal gasification because the coal matrix is destroyed and the Hg in it can easy release out during the coal gasification. However, contrary to what we suspect, the Hg^0 release even decreases. It might be caused by CO_2. For example, CO_2 can react with C ($C + CO_2 = 2CO$) during coal gasification.[40] Similarly, CO_2 could react with Hg^0 during coal gasification, resulting in a decrease of Hg^0 release.[41]

It should be pointed out that the VY for the two coals at temperature < 800 °C under CO_2 is less than that under N_2 whereas the VY at temperature > 800 °C under CO_2 is higher than that under N_2. For example, the VY for coal 1 at 700 and 1200 ºC under N_2 is 25.38 and 30.84%, respectively, while that under CO_2 is 24.27 and 77.97%, respectively. This implies that the CO_2 atmosphere restrains the volatile matter release < 800 °C and promotes the volatile matter release > 800 °C.

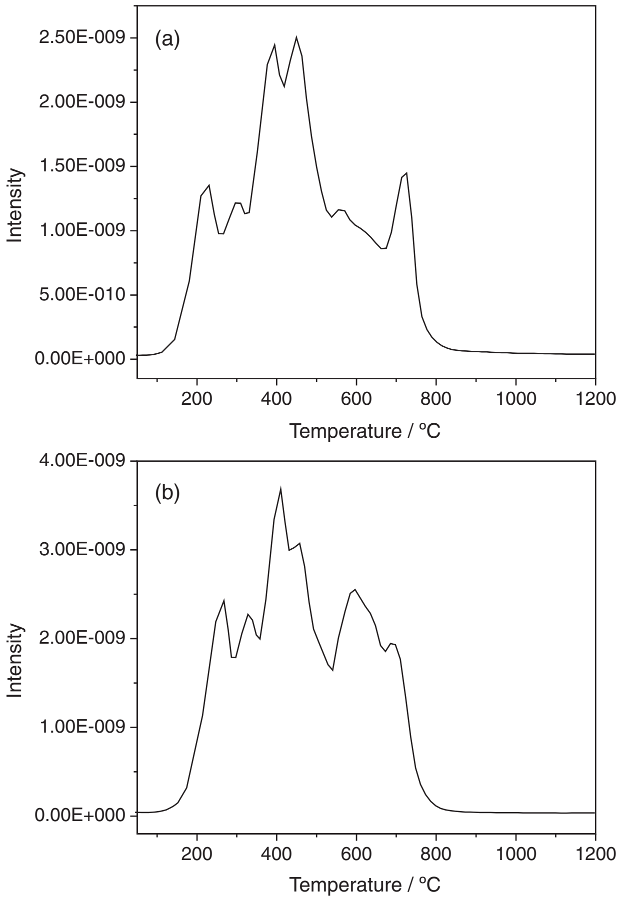

Figure 3. Release behavior of CO_2 during thermal treatment of two coals under N_2, (a) 1; (b) 2.

Dynamic release behavior of Hg^0 during thermal treatment of two coals under air

The dynamic Hg^0 release profiles *versus* the increase of temperature for two coals under air are shown in Figure 4. The intensity of the profiles is also normalized.

Figure 4 shows that the profile of the peaks is different with that under N_2 and CO_2 atmosphere. In addition, the peak intensity under air is distinctly lower than that under N_2 and CO_2 atmosphere, which indicates a lower Hg^0 release under air. Note that the peaks in Figure 4 show similar profiles at 200-500 °C for both coals, possibly attributing to the similar modes of occurrence of Hg in the coals. However, the peaks at temperature > 500 °C under N_2 and CO_2 for these two coals almost disappear after the thermal treatment under air. This result implies that the Hg released at temperature > 500 °C under air is mainly oxidized Hg.

The RRE and RRT under air (in Table 3) show that the amount of Hg^0 released under air counts for 31-33% of Hg in coal and is distinctly less than that under N_2 and CO_2. However, the amount of total Hg released is higher than that under N_2 and CO_2. This result indicates that a large part of Hg^0 has been converted into oxidation state of Hg by the oxygen in the air.[42] Table 3 shows that the VY under air is higher than that under N_2 and CO_2. However, the higher VY under air does not promote the Hg^0 release because of the formation of the oxidized Hg during thermal treatment of the two coals under air.[42]

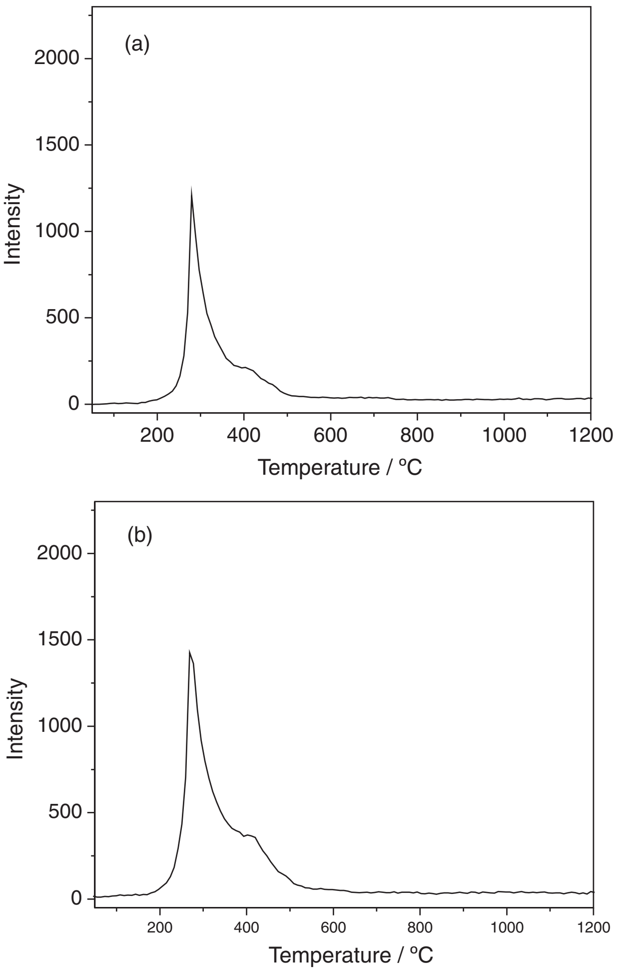

Figure 4. Dynamic release behavior of Hg^0 during thermal treatment of two coals under air, (a) 1; (b) 2.

Conclusions

A study was made to understand the release behavior of Hg^0 from two bituminous coals under different atmospheres during thermal treatment. The profiles of Hg^0 released present several peaks during thermal treatment of these two coals. With the different atmosphere used, the profiles are also different for the same coal, which indicates that the release behavior of Hg^0 is affected by the atmosphere used. Generally, the RRE is in the order of $N_2 > CO_2 >$ air. The RRE for both coals is higher than 92% under N_2, which is nearly equal to the RRT under N_2 atmosphere. This result indicates that the Hg^0 released is the dominant form during thermal treatment of these two coals under N_2. The RRE is approximately 73-74 and 31-33% under CO_2 and air atmosphere, respectively, which is less than the corresponding RRT. This indicates that a part of Hg^0 has been converted into the oxidized Hg during thermal treatment of these two coals under CO_2 and air atmosphere.

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