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Volatility and Speciation of Mercury during Pyrolysis and Gasification of Five Chinese Coals

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ABSTRACT: The fate of mercury in coal gasification systems is closely relevant to its transformation in fuel gases and subsequent release into the environment. This paper presents a study of the volatility and speciation of mercury during pyrolysis and gasification of five typical Chinese coals commonly used in gasification stations. Experiments were conducted on a bench-scale fixed bed under atmospheric pressure at final temperatures from 400 to 1200 °C, in 200 °C increments. The mercury concentration in coals ranged from 0.259 to 8.339 μg/g. The gas-phase mercury was analyzed by an atomic fluorescence mercury analyzer according to the Ontario Hydro Method. It was observed that mercury volatility increased monotonically with temperature over 30 min. $Hg^0(g)$ was the dominant species at most of the temperatures and holding times examined. It was also observed that high temperatures and long times enhanced mercury oxidation. With the temperature increasing from 800 to 1200 °C, $Hg^{2+}(g)$ increased from 5% to 35% during pyrolysis, and from 20% to 60% during gasification. The ratio of Hg^{2+}/Hg^T reached its minimum at 800 °C for one coal (GZA) during pyrolysis, whereas for two other coals (BS and SF) the maximum value of that ratio was higher than the other coals and occurred during high temperature steam gasification at 1200 °C, respectively. The maximum value of the ratio of Hg^{2+}/Hg^T was achieved during the high temperature steam gasification. Comparative studies on mercury emission under different conditions indicated that the volatility and speciation of mercury may correlate with the halogen concentration in the coals. However, no obvious correlation between Hg^{2+}/Hg^T and basic oxides or acidic oxides in the ash was observed.

1. INTRODUCTION

The global emission of mercury (Hg) due to anthropogenic activities is estimated to be between 2000 and 6000 tons per year.[1] Regulations exist to control the industrial and commercial use and emission of mercury worldwide because of mercury's high toxicity to human health.[2−5] According to the EPA Mercury Study Report, coal utilization in combustion or gasification is an important source of mercury emissions to the atmosphere.[6] The effective control of mercury emissions requires an understanding of their fate through the various coal conversion processes and downstream pollution control systems.

In many coals commonly used in China, the mercury concentration is well above the world average.[7] For example, in Guizhou province, the average mercury concentration is 0.22 μg/g but reaches 7.2, 10.5, or 45 μg/g in some samples.[8,9] It has been reported that Hg can be volatilized from coals at temperatures as low as 150 °C.[2] All forms of Hg in coal vaporize at high temperatures and are released into the air in three principal forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate mercury (Hg_p).[2] Hg_p has a short atmospheric lifetime and can be easily removed by particulate control devices. Hg^{2+} compounds (such as $HgCl_2(g)$, $HgO(s,g)$, and $HgSO_4(s)$) can be effectively captured by conventional air pollution control devices (APCDs) because they are water-soluble and can be absorbed.[10] Hg^0, which is extremely volatile and insoluble in water, not only has a long atmospheric residence time and hence travels long distances, but also has a high vapor pressure at the typical operation temperatures of APCDs and therefore is difficult to control by any WFGD[11] or particle collection devices (PCDs).[12]

The emission of trace elements poses a potential problem for coal gasification processes because their volatile form can cause deposition and corrosion damage to the gas turbine after passing through the hot gas cleaning systems.[13−17] As a coal-based power generation technology, gasification makes coal a more amenable and acceptable alternative fossil fuel.[18] Pyrolysis is a common stage in gasification and liquefaction and it is considered as a prethermal technology for mercury removal.[19−23] In recent decades, the integrated gasification combined cycle (IGCC) system has been developed because of its high efficiency and significantly low emissions of NO_x, SO_2, and particulates. The emission and transformation of mercury in coals have been studied by examining the partitioning of mercury during the combustion and gasification processes. In coal gasification processes, Hg^0 is released from coal and is oxidized by halogen in flue gases, while Hg^{2+} compounds may undergo reduction to form Hg^0 through reactions with CO, SO_2, or iron-bearing minerals in the cooler regions.[13,24] The emission of Hg^0 is also influenced by many other factors such as coal type, gasifier operating parameters, and the temperature in hot gas filters.[25] Thermochemical equilibrium models have been developed to study transformation mechanisms of Hg and to predict the physicochemical forms of Hg as a function of temperature, pressure, and total composition in various coal combustion and gasification systems.[26−30] Thermodynamic models indicated that Hg is generally more volatile under the reducing conditions of gasification than in oxidizing environments, possibly because volatile gaseous compounds, such as chlorides, sulfides, and hydroxides, are more stable in reducing atmospheres.[31] At high temperatures, Hg^0 was found to be the only stable species of the gas-phase Hg, a finding that has been supported by both modeling and experimental studies.[17]

Table 1. Proximate Analysis, Ultimate Analysis, and Mercury Content in Coals

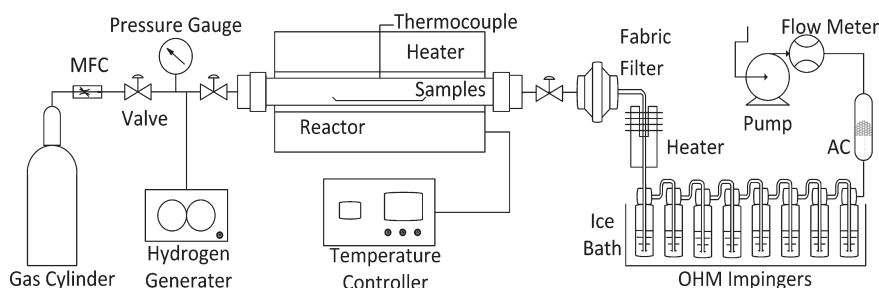| coal	proximate analysis/w_{ad}%				ultimate analysis/w_{ad} %					Hg (μg/g)	Cl (μg/g)	F (μg/g)
	M	A	V	FC	C	H	O	N	S			
BS	2.67	12.54	37.78	47.01	64.85	4.57	12.01	0.91	2.42	0.282	296.83	71.57
SF	10.19	7.24	31.10	51.48	66.5	3.96	11.05	0.73	0.33	0.259	239.99	76.29
HN	1.39	18.57	35.27	44.77	67.33	4.86	6.27	0.35	1.23	0.361	108.12	260.33
GZ	0.84	24.16	23.08	51.92	64.26	4.40	1.55	3.79	0.99	0.265	191.3	271.21
GZA	1.05	52.13	9.21	37.61	35.24	0.73	1.42	0.37	9.06	8.339	173.46	810.72

Figure 1. Schematic of the fixed bed apparatus.

Hg speciation chemistry is complex, for it involves numerous homogeneous and heterogeneous reactions.[27]

Mercury control technologies have been developed involving injecting strong oxidants (Br_2, Cl_2, O_3, etc.) into flue gas or using various sorbents to remove Hg by APCDs.[32] There are many experimental papers describing the use of carbon-based sorbents (e.g., activated carbon), calcium-/iron-/aluminum-based sorbents, fly ash, or noncarbon based minerals for Hg removal.[33−35] Also, chlorine and bromine have been reported to enhance the Hg sorption on carbon.[36] The disadvantages of the aforementioned approaches include (1) high cost, (2) equipment corrosion, (3) secondary pollution, or (4) deterioration of the quality of fly ash, and so on. Accordingly, no postcombustion technology is financially and technically feasible for injection upstream of hot side ESPs or in hot gas cleanup streams in gasification systems.

To achieve effective mercury emission control for gasifiers, it is important to investigate mercury volatility and chemical interactions between Hg and other species during pyrolysis and gasification at high temperatures, using typical coals which are used in the field. Despite the aforementioned previous work, experimental data regarding Hg behavior under gasification conditions are still limited because the measurements of trace elements in the gasification off-gas were either not validated by mass balance, or not published for commercial reasons.[37] This paper aims to identify how the volatility and chemical transformation of mercury are impacted by the following factors: reaction temperature, holding time, atmosphere, and the ash components of coal. This work is part of a large research project that investigates the development of mercury during gasification of pulverized coal.

2. EXPERIMENTAL METHODS

2.1. Samples. The five parent coals described below include four bituminous coals (BS, SF, HN, GZ) from different districts of China and one anthracite (GZA) from southwest China with high toxic trace elements. The four selected bituminous coals were obtained from gasification stations in China. The coal samples were sieved to under 74 μm (200 mesh). Ultimate and proximate analyses for the coal samples under air-dry basis as well as Hg/Cl/F concentration are present in Table 1. The selected coal samples were dried again before each test under vacuum of 93.3−98.6 kPa at 110 °C for 10 min, with a nitrogen purge to minimize the moisture. It should be noted that BS was a high volatile bituminous coal with high sulfur content; HN was a high volatile bituminous coal with a high ash fusion point; SF had the lowest ash-fusion point among the four bituminous coals; GZ coal contained the most trace elements among the four bituminous coals; GZA coal was a particular anthracite with high toxic trace elements (As, F, Hg, etc.) and a high ash yield, in which the Hg concentration was 8.339 μg/g, and the fluorine concentration was 810.72 μg/g.

2.2. Experimental Apparatus. To study mercury volatility and species during coal utilization, fixed bed experiments were conducted. Samples weighing 2 g each were spread on quartz containers (80 mm long, 20 mm wide) in the packed bed. The temperature of quartz reactor (42 mm O.D., 38 mm I.D., and 1200 mm long) was controlled by a programmed temperature controller (model KSY-6D-16). The gas entrained into the reactor was nitrogen (N_2) in the case of high-temperature pyrolysis (HTP), carbon dioxide (CO_2) in the case of high temperature gasification (HTCG), or steam (H_2O) carried by N_2 (HTSG). Gas flow rate was maintained at 0.5 L/min (at ambient temperature of 20 °C) by a calibrated mass flow controller (MFC), which was checked and verified in each experiment. Comparative tests showed that the optimal volume of steam should be maintained between 80 and 85 mL during gasification processes in order to obtain the maximum carbon conversion. The experiment ending temperature was increased from 400 to 1200 °C with a 200 °C increment. The holding times which were held at final temperatures were set 0, 30, and 60 min, respectively. The reactor was heated at a rate of 10 °C/min from the ambient temperature, and meanwhile the exit gas passed through the impingers during the entire heating period. Pressure drop across the fixed bed was monitored continuously from a pressure gauge so as to ensure

Table 2. Mass Balances and Species Distribution of Hg

atmosphere	temperature (°C)	time (min)	BS				SF				HN				GZ				GZA			
			Hg_{char}	Hg^0	Hg^{2+}	M	Hg_{char}	Hg^0	Hg^{2+}	M	Hg_{char}	Hg^0	Hg^{2+}	M	Hg_{char}	Hg^0	Hg^{2+}	M	Hg_{char}	Hg^0	Hg^{2+}	M
P	400	30	0.227	0.168	0.070	82.37	0.402	0.048	0.008	88.38	0.307	0.306	0.025	88.31	0.183	0.280	0.029	92.71	4.218	9.954	0.434	87.58
P	600	30	0.153	0.198	0.090	78.23	0.232	0.166	0.041	84.59	0.194	0.388	0.042	86.37	0.143	0.420	0.065	118.38	3.558	13.637	1.003	109.11
P	800	30	0.142	0.218	0.121	85.17	0.180	0.219	0.071	90.75	0.069	0.532	0.105	97.76	0.106	0.405	0.093	114.04	0.980	10.888	1.313	79.03
P	1000	30	0.111	0.183	0.110	71.49	0.151	0.211	0.085	86.42	0.063	0.493	0.087	89.15	0.067	0.260	0.057	72.33	0.991	11.690	1.492	84.98
GC	800	30	0.068	0.209	0.230	89.74	0.127	0.230	0.205	108.45	0.215	0.562	0.143	127.33	0.098	0.332	0.046	89.60	2.833	9.973	1.598	86.37
GC	1000	30	0.022	0.194	0.266	85.36	0.029	0.158	0.213	77.14	0.108	0.341	0.118	78.60	0.090	0.398	0.068	104.88	2.843	10.015	2.282	90.78
GC	1200	30	0.021	0.189	0.309	92.15	0.052	0.233	0.358	124.17	0.133	0.400	0.212	103.32	0.051	0.339	0.082	89.01	1.901	9.657	4.103	93.91
GH	800	30	0.071	0.208	0.262	95.87	0.121	0.229	0.219	109.90	0.086	0.357	0.116	77.37	0.083	0.279	0.102	87.58	1.566	9.837	1.551	77.67
GH	1000	30	0.016	0.166	0.243	75.28	0.031	0.170	0.252	87.56	0.094	0.321	0.115	73.29	0.055	0.364	0.163	109.71	1.143	10.415	2.875	86.54
GH	1200	30	0.025	0.216	0.422	117.43	0.024	0.140	0.249	79.82	0.064	0.381	0.165	84.53	0.032	0.347	0.179	105.38	0.369	9.252	5.124	88.41

there was no leak in the system. The sampling gas went through the filter system, which was maintained at 150 °C so as to prevent particulate Hg from attaching onto the sampling tubing. Details are shown in Figure 1.

The gaseous mercury released from coal was trapped by impingers that were immerged in an ice bath, as instructed by Ontario Hydro Method (OHM).[38] The first three impingers, which contained potassium chloride solution (KCl, 1 mol/L), were intended to absorb oxidized mercury (Hg^{2+}). The fourth impinger which contained acidified hydrogen peroxide (5% V/V HNO_3–10% V/V H_2O_2) was used to oxidize and absorb elemental mercury in the organomercury compounds. Subsequently, elemental mercury was mainly reduced and captured in the following three impingers which contained acidified potassium permanganate (4% W/V $KMnO_4$–10% V/V H_2SO_4). The last one was filled with silica gel for dehydrating the gas. A fabric filter was installed to collect particulate matter. After each test, the reactors were cleaned by acid solutions to remove the Hg attached on the wall with small amount of coke at lower temperatures. All the solutions were then digested and Hg was detected as discussed in the next section. An exhaust filter that contained activated carbon was installed in the outlet. Verification procedures were performed by means of an Hg generation system with or without a fabric filter, at ambient temperature and 1000 °C. One can conclude that the empty reactor, tubing, and fabric filter did not adsorb gaseous mercury.

2.3. Analysis. The OHM solution samples were recovered and digested according to the OHM standard chemical digestion procedure. The digestion of Hg in parent coals was carried out according to microwave-assisted acidified digestion (GB/T 16659-1996, HNO_3–H_2SO_4–V_2O_5 Method) using Milestone ETHOS E Microwave Accelerated Reaction System.[39] The mercury in all digestion solutions and OHM solutions was determined by Atomic Fluorescence Spectrometry (AFS) using QM201 Mercury Analyzer (detection limit: 0.001 μg/L). The content of Hg in coal char/ash was detected by a Teledyne Leeman Laboratories Hydra-C Mercury Analyzer according to EPA method 7473. The fluorine and chlorine content in coals was analyzed by Dionex Ion Chromatography System (ICS-90) using Eschka Reagents (GB/T 3558-1996; GB/T 4633-1997).[39]

The mercury volatility, denoted by R_v, was defined as follows:

$$R_v(\%) = \frac{Hg^0 + Hg^{2+}}{Hg_{coal}} \times 100\% \qquad (1)$$

where Hg^0 (μg/g) denotes the quantity of element mercury in gas phase, Hg^{2+} (μg/g) denotes the quantity of oxidized mercury in the gas phase, and Hg_{coal} (μg/g) is the total amount of mercury in coal.

Table 2 presents the average mass balance for all the experiments investigated in our study. The average mass balance of each sample, denoted by M, was given by

$$M(\%) = \frac{Hg^T}{Hg_{coal}} \times 100\%$$

$$= \frac{Hg_P + Hg^0 + Hg^{2+} + Hg_{char}}{Hg_{coal}} \times 100\% \qquad (2)$$

where Hg_{char} (μg/g) denotes the mercury content in char, and Hg_P denotes the mercury content in particle matters collected by fabric filter. The average values (at least three repeated trials under the same conditions) of the mass balance ranged 70–130%.
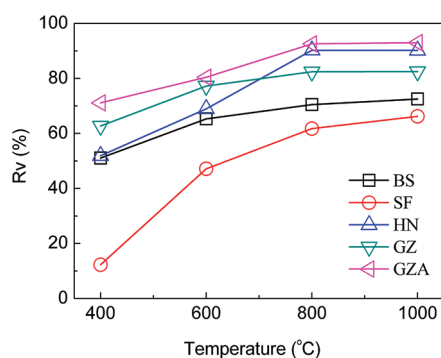
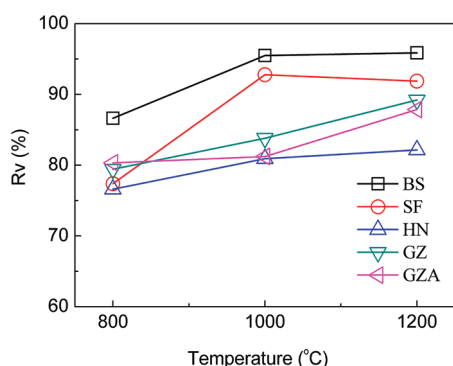**Figure 2.** Mercury volatility during coal pyrolysis from 400 to 1000 °C.

Figure 4. Mercury volatility during coal gasification (H_2O) at 800—1200 °C.

Figure 3. Mercury volatility during coal gasification (CO_2) at 800—1200 °C.

In most practical conditions, the amount of collected particulate matter (Hg_P) was negligible except for the lower temperatures pyrolysis process. We were not able to detect any Hg in the digestion solution for most conditions. So Hg_{char} in Table 2 represents the content of solid-phase Hg (in both collected particles and coal char).

3. RESULTS AND DISCUSSION

3.1. Mercury Volatility under Different Conditions. *3.1.1. Mercury Volatility during High Temperature Pyrolysis.* Mercury volatility increased monotonically with the increasing temperature during high temperature coal pyrolysis (HTP) at ending temperatures ranging from 400 to 1000 °C, as shown in Figure 2 (HTP is abbreviated to P in the figures). Previous experiments showed that temperature was the dominant factor for mercury volatility during pyrolysis and gasification, and that the release of mercury began at temperatures below 180 °C.[37] It was also found by research that only a marginal improvement in mercury volatility, form 72% to 80%, was achieved when pyrolysis temperature increased from 400 to 600 °C.[40] In our experiments, although the mercury volatility reached its maximum at 1000 °C, most of the release took place in the range of 400—800 °C. With an ending temperature of 1000 °C, the SF coal yielded the lowest R_v value (61.76%), compared with 70.48% (BS coal), 82.42% (GZ coal), 90.25% (HN coal), and 92.57% (GZA coal). Mercury released with the volatile matter in the coal during HTP. The difference in the mercury volatility among the five coals is attributed to the different occurrence of mercury in these coals. Whereas mercury-bearing minerals in coals transformed during heating,
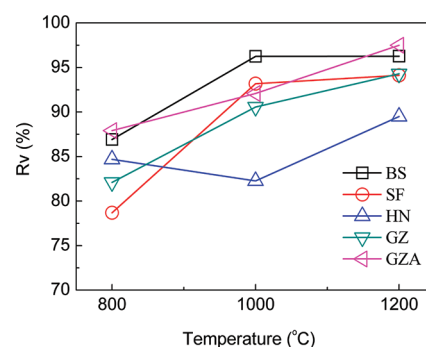
part of the volatile matter evolved during pyrolysis formed tars, which condensed on the char, consequently reducing the surface area of the coal char and closing pores during the char solidification.[41] Also, at high temperatures (1100—1500 °C), the carbon conversion was hindered by amorphous mineral matter (mainly alumino-silicates melts), which covered the surface and blocked the pores of coal particles.[42] Although mercury was expected to vaporize completely during the thermal process, there was still mercury in the largest ash particles that could be interpreted as indicative of limited vaporization.[30] It is worth mentioning that there was still a slight proportion of mercury trapped by chars when the temperature was above 800 °C. This phenomenon could have been due to two reasons: (1) mercury was absorbed by fixed carbons that acted as actived carbons at low temperatures and (2) mercury was confined by the closure of pores in coal chars.

Figure 3 shows the mercury volatility during high temperature CO_2 gasification (HTCG is abbreviated to GC in the figures) with the temperatures ranging 800—1200 °C. For all types of coals, R_v was observed to increase monotonically with the temperature, while the rate of increase with temperature varied for each coal type. The mercury volatility reached its maximum at 1200 °C: 82.15% (HN coal), 87.86% (GZA coal), and 89.21% (GZ coal); the maximum value was slightly higher in the SF coal (92.51%) and the BS coal (95.87%). R_v during HTCG was higher than that during HTP.

Figure 4 shows the mercury volatility during high temperature steam gasification (HTSG is abbreviated to GH in the figures), with the temperature ranging 800—1200 °C. Comparing Figure 4 with Figure 3, one may see that R_v during HTSG atmosphere was slightly higher than that during HTCG. For example, the volatility was around 95% for all coals except the HN coal at the ending temperature of 1200 °C. The reason was that the steam in gas enhanced the gasification reactions at high temperatures, and consequently reduced the fixed carbon in char and accelerated the release of mercury that remained in the chars.

3.1.2. Effect of Temperature on Mercury Volatility. Comparing the average value of R_v under three different atmospheres (HTP, HTCG and HTSG, all with a holding time of 30 min), one may conclude that temperature was the dominant factor on R_v (the volatility of mercury) in both coal pyrolysis and gasification. It is obvious that the R_v depends on the temperature, i.e., the higher the temperature, the higher the R_v will be. In the case of HN and GZA coals, R_v was extremely high during HTP at 800 °C. The R_v was 90.18% for HN coal during HTP, and 80.92% and 82.27% during HTCG and HTSG, respectively. For BS and SF coals, R_v was higher during gasification than during pyrolysis
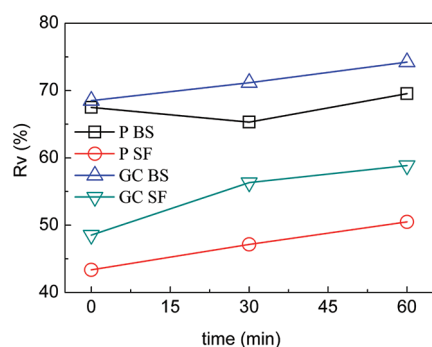
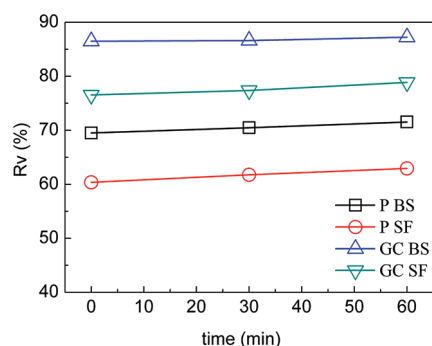**Figure 5.** Mercury volatility versus holding time at 600 °C.

Figure 6. Mercury volatility versus holding time at 800 °C.

Figure 7. Distribution of Hg(g) during pyrolysis and gasification at 800 °C.

Figure 8. Distribution of Hg(g) during pyrolysis and gasification at 1000 °C.

(at the same temperature). For example, at 1000 °C, R_v was 72.5% for BS coal during HTP, and 92.78% and 93.18% during HTCG and HTSG, respectively. For each coal, the difference between the minimum and maximum of its R_v is given as follows: 23.75% (BS coal), 26.29% (SF coal), 8.07% (GZ coal), 9.26% (HN coal), and 11.79% (GAZ coal).

When the ending temperature was below 800 °C, the difference in Hg volatility between pyrolysis and gasification was negligible. Mercury was released with the volatile matter in coal during heating-up in inert atmosphere. The release of volatile matter was similar at temperatures lower than 800 °C under inert and reducing atmosphere.

3.1.3. Effect of Holding Time on Mercury Volatility. Experiments were conducted to investigate the effect of holding time on R_v at 600 and 800 °C, regarding the BS and SF coals. The holding times examined were 0, 30, and 60 min, respectively. Figures 5 and 6 show that R_v was largely independent of the residence time, but closely relied on the reacting temperature. One probable explanation is that most of the mercury was released rapidly together with the volatile matter during the heating-up in a short period in the first pyrolysis stage. With the temperature ramp being 10 °C/min, it took a long time to reach the final reactor temperature and therefore the holding time did not influence the mercury volatility. In addition, the mercury volatility (R_v) was respectively low at 600 °C. The mercury was released slowly during heating-up because the reaction was relatively slow at the first stage under low temperatures in the reducing atmosphere. The mercury was released rapidly while the reaction rates increased during the whole process to the final temperatures.

To investigate the impact of heating, temperature ramps were varied between 5 and 15 °C/min. The results consistently indicated that the influence of heating rates was negligible.
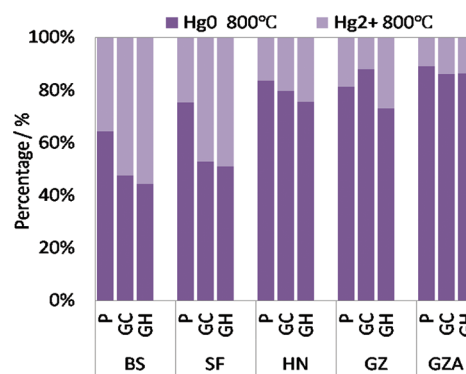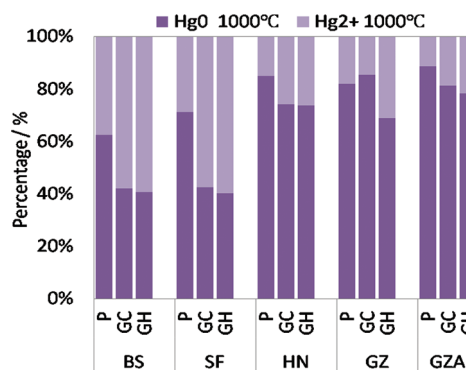
3.2. Mercury Speciation under Different Conditions. Elemental mercury is the dominant species of mercury existing in the gas phase, as shown in Figure 7; the observation is in accordance with thermodynamic equilibrium calculation.[30,37] At 1000 °C, the elemental mercury accounted for over 80% of the total gas-phase mercury for HN, GZ, and GZA coal, whereas this percentage was 62.5% for BS coal, the lowest among all coal samples. When the ending temperature increased, more gas-phase mercury was released in the oxidized form rather than the elemental form. Increasing temperatures consistently reduced the percentage of elemental mercury while increasing the percentage of oxidized mercury during HTCG.

The trend during HTSG was similar to that during HTCG from 800 to 1200 °C. Again, temperature increases consistently reduced the percentage of elemental mercury and increased the percentage of oxidized mercury. The percentage of Hg^0 in the total gas-phase mercury dropped from 83.64% to 33.71%, while the percentage of Hg^{2+} rose from 13.62% to 66.17%. Some observations regarding coal samples are worth mentioning. The ratio of Hg^0/Hg^T reached its maximum for GZA coal at 800 °C during HTP. The maximum value of the ratio of Hg^{2+}/Hg^T for BS and SF coal was much higher than the other three coals during HTSG, and occurred at 1200 °C, which were around 65%.

Figures 7 and 8 compare the distribution of Hg at 800 and 1000 °C (during both pyrolysis and gasification). The percentage of Hg^0 and Hg^{2+} in the total gas-phase mercury varied depending on coal samples and temperatures. The elemental mercury, Hg^0, constituted the majority of the gas-phase mercury in the gasification
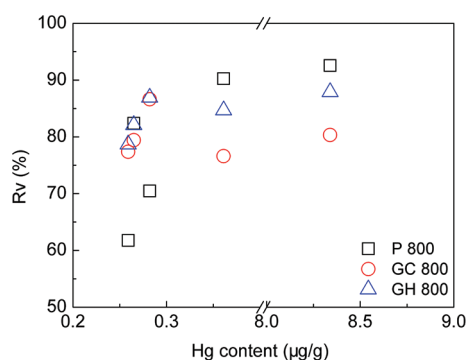
Figure 9. Correlation between mercury volatility (R_v) and Hg content.
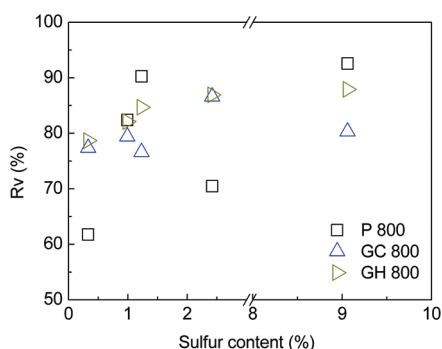

Figure 10. Correlation between mercury volatility (R_v) and sulfur content.

Figure 11. Correlation between mercury volatility (R_v) and halogen content.

Figure 12. Correlation between the ratio of Hg^{2+}/Hg^T and chlorine content at 800 °C.

process, and was prone to be oxidized during HTSG. We hypothesize that this was the effect of steam which promoted the oxidization of Hg^0 by inhibiting the generation of the halogen in the gas phase.

3.3. Effect of Coal Composition on Hg Volatility and Speciation. *3.3.1. Effect of Hg Content in Coals.* The five coals studied are from two coal ranks: BS is high sulfur content bituminous coal from northern China; HN is high ash melting point bituminous coal from eastern China; the ash melting point of SF bituminous coal from northwestern China is the lowest; GZ bituminous coal from southwestern China contains more trace elements as compared to the other three bituminous coals. GZA is an anthracite with particularly high concentrations of hazardous elements (As, F, Hg, etc.) and high ash yield from GZ province, southwestern China.

Figure 9 demonstrates that R_v increased with the increasing Hg content under most conditions. It is believed that the mode of occurrence for mercury in coal is in the forms of mercury sulfide (pyrite and sphalerite), metallic mercury, and organometallic compounds that are associated with the sulfide and selenide.[7,43] Hg is predicted to remain primarily in the vapor phase throughout an IGCC power cycle.[30] Thermodynamics models indicated that Hg was generally more volatile under the reducing conditions of gasification than in oxidizing environments, possibly because volatile gaseous compounds, such as chlorides, sulphides, and hydroxides, are more stable in reducing atmospheres.[31] However, it has been proved that the Hg volatility is attributed not to different coal properties but to the difference in the mode of occurrence of Hg in coals.[19] In BS coal, Hg is associated more with pyritic sulfur than with organic sulfur,[44] whereas in the GZ coal, Hg is mainly associated with pyrite or clay minerals.[45]
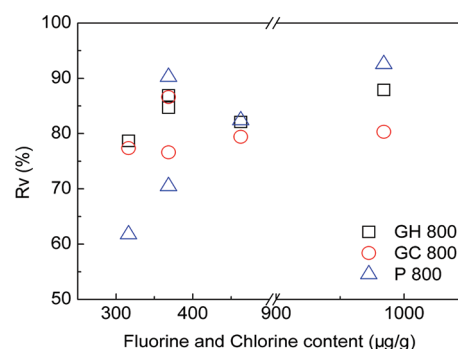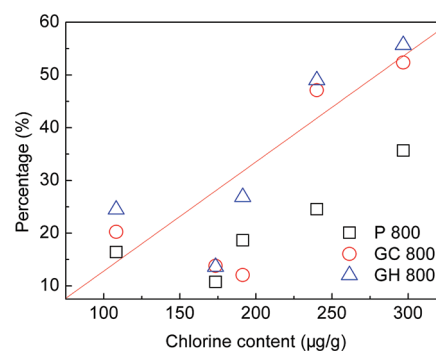
The mercury existing in pyrite and related minerals (hydrophobic and/or leaching-inaccessible circumstances) is hard to release, while the Hg that present in more hydrophilic minerals (carbonate, aluminosilicates, etc.) is easily released during mild pyrolysis.[46] As anthracites (GZA coal in our study, see Table 1) were shown to have the highest mercury concentrations, there appears to be a strong affinity for sulphide association with the mercury.[19] The emission of Hg^0 is also influenced by many other factors such as coal type, gasifier operating parameters, and the temperature in hot gas filters.[25]

3.3.2. Effect of Sulfur in Coals. As one of the main elements in coal, sulfur typically exists in pyrite form and organic forms in coals.[47] The occurrence of sulfur is associated with Hg and iron in coals.[44] The content of sulfur in the five coals is listed in Table 1, ranging from 0.39 to 6.5 wt %. H_2S is the primary species released with volatile matter during pyrolysis while some sulfur still remains in the organic compounds in coal tar.[45,48] H_2S released from coal chars reacts with minerals and thiophilic matter during heating process and consequently enhancs the transformation of Hg and other trace elements (speculations based on Figure 10).

No obvious correlation was observed between the proportions of oxidized mercury in the gas phase and the sulfur content in coals during pyrolysis and gasification at all temperatures. The low correlation indicated that sulfur was not the primary factor impacting the release of oxidized mercury.

3.3.3. Effect of Halogen in Coals. The fluorine concentration in GZA coal is extremely high (810.72 μg/g, see Table 1). Fluorine is released mainly as HF and SiF_4 into the gas phase.[49] Chlorine exists mainly as sodium chloride and potassium chloride in coals, and is released as species of hydrogen chloride (HCl)

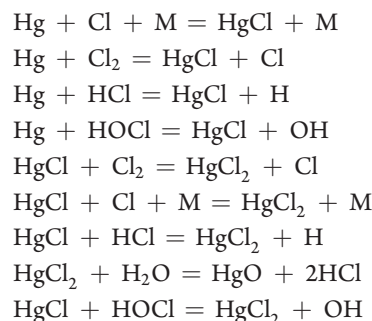**Table 3. Metal Contents in the Form of Oxides in Coal Ash (Wt %)**

coal	basic oxides					acidic oxides			basic/acidic
	Na$_2$O	K$_2$O	CaO	MgO	Fe$_2$O$_3$	Al$_2$O$_3$	SiO$_2$	TiO$_2$	
BS	0.21	0.44	12.65	1.59	24.01	15.23	37.12	0.6	0.735
SF	1.6	0.71	34.62	3.91	12.89	11.26	25.29	0.9	1.435
HN	0.46	0.54	2.15	0.68	3.83	33.5	55.6	1.41	0.085
GZ	0.86	0.52	7.42	1.38	21.43	20.78	43.05	1.26	0.486
GZA	0.6	4.39	0.37	0.73	7.91	28.26	53.99	2.79	0.165
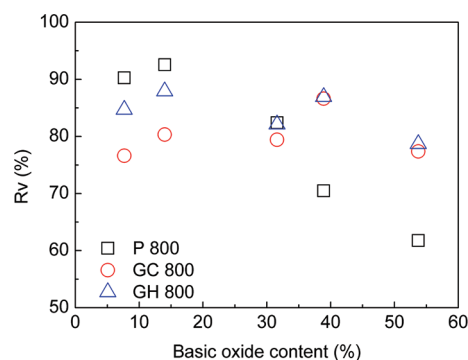
Figure 13. Correlation between mercury volatility (R_v) and basic oxide.
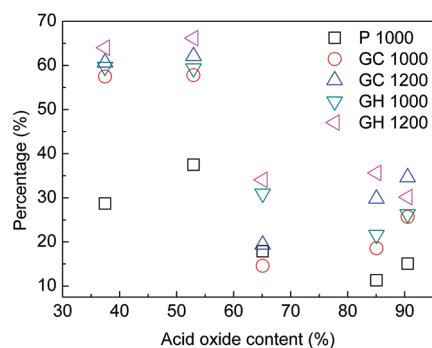
Figure 14. Correlation between the ratio of Hg^{2+}/Hg^T and acidic oxide at 1000−1200 °C.

during pyrolysis process. Figure 11 indicates that halogen enhanced R_v during HTP at 800 °C. Hg^0 was oxidized by halogen during volatilization and the subsequent gas cooling process before it entered the impingers. The percentage of Hg^{2+} in flue gas increased with the increased chlorine content in coal during HTP and HTSG at 800 °C (see Figure 12).

It has been observed in the literature that mercury in coal is oxidized by chlorine species via both homogeneous and heterogeneous reactions.[24,28] With the chlorine content in coal increasing from 100 to 300 μg/g, Hg^{2+} percentage in gas phase increased from 10% to 35% during HTP, and 20% to 65% during HTCG and HTSG. In acknowledged understanding, Hg^0 is the only thermodynamically stable species of mercury in gas phase at temperature above 750 °C, while HgCl$_2$(g) is the dominant species in a chlorine-bearing flue gas at temperatures below 430 °C.[17] In coal gasification processes, observations indicated Hg^0 was converted to Hg^{2+} by reacting with HCl or Cl$_2$ in gas-phase reaction in simulated coal gasification systems. The reaction was promoted only when either Cl$_2$ or HCl and COS were involved in the mixed gas stream at temperatures higher than 750 °C.[13,29] The reaction rate was high at high temperatures. The gas−solid (heterogeneous) oxidation also involved surface in mercury oxidation and subsequent binding with a chlorinated surface.[13,24,50] The possible gas phase reaction scheme under oxidizing conditions has been proposed as follows:[17,51]

$$Hg + Cl + M = HgCl + M$$
$$Hg + Cl_2 = HgCl + Cl$$
$$Hg + HCl = HgCl + H$$
$$Hg + HOCl = HgCl + OH$$
$$HgCl + Cl_2 = HgCl_2 + Cl$$
$$HgCl + Cl + M = HgCl_2 + M$$
$$HgCl + HCl = HgCl_2 + H$$
$$HgCl_2 + H_2O = HgO + 2HCl$$
$$HgCl + HOCl = HgCl_2 + OH$$

3.3.4. Effect of Ash Compositions in Coals. The ash compositions of the five coals investigated are shown in Table 3. The proportion of basic oxide in ash is 30−55 wt % in BS, SF, and HN coals. The proportion of acidic oxide was 65−90 wt % in GZ, HN, and GZA coal ashes. Alkali and alkaline earth metals oxides were 53.73 wt % in SF coal ashes, but only 7.66 wt % in HN coal. Alkali and alkaline earth catalysts as well as Group VIII metals are effective for gasification to overcome the slow reaction of carbon with CO$_2$.[52] As shown in Figure 13, R_v decreased with the increasing basic oxides content in coal ash during HTP at 800 °C, while it increased with the increasing acidic oxides content. However, no obvious correlation between Hg^{2+}/Hg^T and basic oxides or acidic oxides was observed, as shown in Figure 14.

For GZA, GZ, SF, and BS coal, Hg^{2+} increased during gasification at 1000 °C. The traces at different temperatures were also similar in pyrolysis, but not in gasification at 1200 °C. It has been found that the alkali and alkaline earth metals in coal reacted with HCl and Cl$_2$ in the gas phase, generating chloride and H$_2$O and thereby inhibiting mercury oxidation during combustion.[53] However, the reactions may go in the opposite direction within a reductive atmosphere at high temperatures. The poor correlation (see Figure 14) indicated that neither basic oxide nor acidic oxide was the primary impacting factor responsible for the release of oxidized mercury.

4. CONCLUSIONS

Mercury in gas phase during coal pyrolysis and gasification has been detected by the Ontario Hydro method. Laboratory-scale experiments were conducted to investigate the mercury volatility, speciation, and the following impacting factors: reaction temperatures, holding time, atmosphere, and compositions of coal such as halogen, sulfur, and ash compositions.

Temperature was the dominant factor on mercury volatility in both coal pyrolysis and gasification. The mercury volatility increased monotonically when the temperature increased. Among the three experimental conditions, (1) high temperature pyrolysis (HTP), (2) high temperature CO$_2$ gasification (HTCG), and (3) high temperature steam gasification (HTSG), the highest volatility of mercury during gasification was observed during HTSG, followed by HTCG and then HTP.

A longer holding time may also have promoted the mercury volatility but such impact was marginal compared with that of temperature. The release of mercury was slower under an inert atmosphere than under a reducing atmosphere because of the slow gasification reaction at the first stage under 800 °C.

Hg^0 was the dominant species of mercury existing in the gas phase. When the ending temperature increased, the proportion of Hg^0 decreased while the proportion of Hg^{2+} increased. Furthermore, Hg^0 was more prone to be oxidized in steam than in other atmospheres.

Regarding the influence of other major components (e.g., S) and minor components (F, Cl, Na, K, Ca, Mg, Fe, Al, Ti, and Si), it may be concluded that the increases in minor halogen concentrations enhanced the volatility of Hg; it was hypothesized that Hg was oxidized mainly by chlorine species via both homogeneous and heterogeneous reactions. In contrast, the effects of sulfur content and iron content were negligible. No evident correlation was observed between the minor components aforementioned and the volatility of mercury (or the oxidation of the gas-phase mercury), indicating a complicated mechanism that dictates the mercury release and the following oxidation reactions during coal pyrolysis and gasification at high temperatures.

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■ ACKNOWLEDGMENT

■ ABBREVIATIONS

AFS = atomic fluorescence spectrometry
APCDs = air pollution control devices
AQSIQ = General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China
BS = Beisu bituminous coal from northern China
EPA = Environmental Protection Agency
ESP = electrostatic precipitator
FF = fabric filter
FGD = flue-gas desulphurization
GZ = Guizhou bituminous coal from southwestern China
GZA = high arsenic anthracite from Guizhou Province, southwestern China
HN = Huainan bituminous coal from eastern China
HTP (P) = high temperature pyrolysis
HTCG (GC) = high temperature CO_2 gasification
HTHG (GH) = high temperature H_2O gasification
ICS = ion chromatography system
IGCC = integrated gasification combined cycle
MFC = mass flow controller
OHM = Ontario Hydro method

PCDs = particle collection devices
SF = Shenfu bituminous coal from northwestern China
WFGD = wet flue gas desulphurization

■ SCALARS

M = mass balance
R_v = the volatility of mercury
t = holding time
T = temperature
$Hg^0(g)$ = gaseous elemental mercury
$Hg^{2+}(g)$ = gaseous oxidized mercury
Hg_{coal} = mercury content in coal
Hg_p = particulate mercury
Hg^T = total mercury quantity
Hg^0/Hg^T = the percentage of gaseous elemental mercury in total mercury
Hg^{2+}/Hg^T = the percentage of gaseous oxidized mercury in total mercury

■ SUBSCRIPTS

ad = air-dried basis

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