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Investigation of mercury emission and its speciation from an oxy-fuel circulating fluidized bed combustor with recycled warm flue gas

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HIGHLIGHTS

- The oxy atmosphere was suitable for mercury oxidation.
- NO and SO_2 enhanced mercury oxidation under oxy-coal combustion.
- Larger H_2O concentration under the oxy atmosphere promoted mercury oxidation.

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ABSTRACT

This study evaluates mercury speciation and the effects of HCl, NO, steam and SO_2 on mercury emission and its speciation from the combustion of Chinese bituminous coal and American bituminous coal under O_2/CO_2 atmosphere especially with recycled warm flue gas in a 50 kW_{th} circulating fluidized bed. Compared to air coal combustion, higher gaseous mercury concentration and higher percentage of Hg^{2+} under oxy-coal combustion were observed. Moreover, HCl, NO, SO_2 and steam could cause the percentage of Hg^{2+} to increase. Compared to the air atmosphere, larger steam concentration under the oxy atmosphere played a significant role in promoting mercury oxidation. HCl promoted mercury oxidation via O and Cl radicals under oxy-combustion. These results are very significant for alternative methods of Hg removal under oxy-fuel combustion.

1. Introduction

China is going to decrease greenhouse gas emissions per unit of GDP in 2020 by 40–45% from its 2005 level [1]. Meanwhile, CO_2 is becoming a restricted discharge pollutant in the U.S. and Europe [2]. Many new technologies such as chemical-looping combustion, oxy-fuel combustion, and others are being developed to capture CO_2.

Oxy-fuel combustion is recognized as one of the most advanced technologies [3,4]. Some aspects of oxy-fuel combustion technology are not well understood, such as its operational parameters and its coal combustion characteristics [4,5]. The flue gas characteristics under oxy-combustion are different from those under air combustion such as higher SO_2 concentration, lower NO_X concentration [6] and different steam concentration [7]. Of course, the different recycled flue gas extracted location have different types of flue gas recirculation.

Oxy-fuel combustion has two main types of flue gas recirculation: cold-recycle and warm-recycle. Under cold-recycle flue gas condition, the recycled flue gas is extracted after the wet flue gas desulfurization scrubber, and the recycled flue gas contains only tiny amount of moisture [8]. Under warm-recycle flue gas condition, the recycled flue gas is taken before the bag filter and after the air heater, so water is not removed in the recycled flue gas [9,10]. There are few reports [11] regarding oxy-fuel circulating fluidized beds with recycled warm flue gas. During recycled warm flue gas [11], there are some difference from other types of recycle due to the higher moisture and SO_2 concentration in the recycle loop.

Mercury and its compounds are harmful to both the environment and the health of human beings [12]. Mercury also jeopardizes the CO_2 storage system for oxy-fuel combustion [13]. Elemental mercury can corrode the CO_2 processing units, such as brazed aluminum heat exchangers through an amalgamation process [14]. To enhance the safety of CO_2 capture and storage system in oxy-fuel circulating fluidized beds, mercury should be removed to levels below detectable limits [15,16]. Moreover, mercury form is very important for mercury removal.

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Nomenclature

CN	Chinese bituminous coal	FC_{ar}	fixed carbon
US	American bituminous coal	V_{ar}	volatile matter
CN air	Chinese bituminous coal under air combustion	A_{ar}	ash
CN oxy	Chinese bituminous coal under oxy combustion	M_{ar}	moisture
US air	American bituminous coal under air combustion	LOI	loss of incineration
US oxy	American bituminous coal under oxy combustion		

There are three speciations of mercury in flue gas [17]: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate mercury (Hg_p). Oxidized mercury and particulate-bound mercury are easy to control. Elemental mercury is difficult to remove due to its insolubility in water [18] and high volatility. It is essential to pay attention to mercury speciation under oxy-coal combustion [19].

There are few studies concerning mercury speciation during oxy-coal combustion. Achariya Suriyawong [20,21] reported that there are no differences in mercury speciation under air or O_2/CO_2 atmosphere. Some other authors [15,19,22,23] obtained data about mercury oxidation under oxy-fuel combustion. Other researchers [24,25] investigated mercury behavior under oxy-fuel combustion by simulation or equilibrium calculations. –Gharebaghi [24] tried to predict mercury oxidation under oxy-fuel conditions through a combined homogeneous-heterogeneous model. Contreras [25] used thermodynamical equilibrium calculation to evaluate the fate of trace metals under oxy coal combustion with biomass and coal/biomass blends.

However, little research about the fate of mercury under an oxy-fuel circulating fluidized bed combustor with recycled warm flue gas existing.

This paper reports experimental results exploring mercury speciation under air and oxy-coal combustion atmospheres. These experiments were conducted in a 50 kW_{th} oxy-fuel circulating fluidized bed combustor with recycled warm flue gas using Chinese bituminous coal and American bituminous coal. The effect of HCl, NO, steam and SO_2 on mercury emission and its speciation were also studied. All of the results reported under oxy-coal combustion were compared to those under air-coal combustion.

To the industry, the results about emissions of CO, CO_2, NO and temperature distribution are helpful for optimizing parameters of power plants and the results about mercury speciation are useful for mercury controlling under oxy-coal combustion.

2. Experimental

2.1. Feedstock

Chinese bituminous coal and American bituminous coal were chosen as the solid fuel with 0–6 mm particle sizes. Ultimate and proximate analyses of the coal are summarized in Table 1. The Ca-based sorbents used were limestone with 0–1 mm particle sizes. Table 2 shows the composition of the limestone.

The Ca/S molar ratio that was 2.5 under air combustion while Ca/S molar ratio was 4.0 under oxy-combustion with both Chinese bituminous coal and American bituminous coal. The reason the Ca/S molar ratio was increased from 2.5 to 4.0 was a limitation of our measurement conditions. If the Ca/S molar ratio was 2.5 under oxy-combustion, as it was under air combustion, the SO_2 concentration would exceed the acceptable range.

2.2. Experimental installation

The experiments were conducted in a 50 kW_{th} oxy-coal circulating fluidized bed combustor with recycled warm flue gas. The fluidized bed system was set up to study mercury speciation in oxy-coal combustion, as shown in Fig. 1. The height of the circulating fluidized bed body is 5200 mm with three sections. The dense zone is 1000 mm in height and 122 mm in inner diameter, the recycling zone is 200 mm, and the dilute zone is 4000 mm in height and 150 mm in inner diameter. The experimental system contained the coal feeding system, the gas mixing system, the fluidized bed body, the temperature control system, the exhaust cleaning system, and the warm recycle system. The temperature of the recycle flue gas was controlled to remain over 180 °C to avoid condensation of the vapor in the recycle loop [11]. Flue gas was sampled from the location between the outlet of furnace and the inlet of bag filter.

2.3. Determination of NO, SO_2 and H_2O

O_2, SO_2, NO, NO_2, CO and CO_2 were recorded on a dry basis by the J2KN online analyzer. The detection range and error for J2KN online analyzers are listed here: O_2 (Range: 0–21%; Accuracy: ±0.2%), CO (0–10,000 ppm; ±20 ppm), NO (0–5000 ppm; ±5 ppm), NO_2 (0–1000 ppm; ±5 ppm), SO_2 (0–5000 ppm; ±10 ppm), CO_2 (0–100%; ±0.2% measured). The MAC125 moisture sensor detected H_2O.

2.4. Determination of HCl

The HJ 548-2009 method recommended by the Ministry of Environmental Protection of China was used to determine hydrogen chloride concentration in flue gas.

2.5. Determination of Hg

The Ontario Hydro Method (OHM) recommend by the American Environmental Protection Agency was used to determine elemental mercury, oxidized mercury, particulate mercury and total gaseous mercury. The concentrations of Hg in coal, slag, and fly

Table 1
Ultimate and proximate analyses of Chinese coal and American coal.

Sample	Ultimate analysis (%)					Lower heating value	Proximate analysis (wt.%)				Mercury
	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	MJ Kg^{-1}	FC_{ar}	V_{ar}	A_{ar}	M_{ar}	μg kg^{-1}
Chinese coal	64.09	3.80	9.81	0.75	0.49	25.05	51.68	28.38	16.18	3.76	56.89
American coal	62.14	4.26	8.63	0.96	2.93	26.66	49.68	35.34	9.85	5.13	40.13

FC_{ar}: fixed carbon; V_{ar}: volatile matter; A_{ar}: ash; M_{ar}: moisture.