

Article

Homogeneous Mercury Oxidation under Simulated Flue Gas of Oxy-coal Combustion

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Abstract. This study investigated the effects of oxy-coal combustion on Hg-oxidation by HCl using simulated flue gas. Experiments were conducted with different carrier gases that one might find in oxy-coal combustion and conventional coal combustion. The extents of Hg-oxidation in pure CO₂, pure N₂ and air were also studied for comparison. Our experimental results demonstrated that CO₂ weakly assisted Hg-oxidation by HCl; however, its significance was outweighed by the presence of O₂. For all carrier gases, the presence of NO or H₂O inhibited Hg-oxidation. The inhibitory effects strongly depended on concentrations of NO, but not moisture content. The synergistic inhibitory effects were shown when both NO and H₂O were present together. The extents of Hg-oxidation were not significantly different for O₂-N₂, O₂-N₂-CO₂ and O₂-CO₂ gas mixtures for all conditions investigated in this study.

Keywords: Coal combustion, mercury emission, oxy-coal combustion, mercury speciation.

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1. Introduction

Global climate change is now an issue of great concern and strongly exacerbated by the rising levels of carbon dioxide (CO₂) in the atmosphere due to human activities, such as burning of fossil fuels and deforestation. Coal, the cheapest and most abundant fossil fuel, is currently one of the most widely used energy sources globally, and it will continue to be dominant for many decades. Capturing CO₂ from coal combustion exhaust has been receiving significant attention; however, the volume fraction of CO₂ in a conventional coal combustion system (with air) ranges between 13% - 15%, making it difficult to cost-effectively design these systems. One approach to overcome the limitation of low CO₂ concentration in the exhaust is oxy-coal combustion, where coal is combusted in an oxygen-enriched stream (with nitrogen removed) with recycled exhaust gas as a diluent. At steady state operation, such a configuration would result in a CO₂ concentration of 95% in the exhaust, making it more feasible to capture [1-4]. Many studies have reported other advantages of this combustion system, including reduction of volume of flue gas, elimination of thermal NO_x, and potential for increasing boiler thermal efficiency [5, 6].

While the benefits of the oxy-coal combustion are clear, changing the composition of the combustion gas mixture may have numerous effects on the pollutants associated with coal combustion, and subsequently the performance of pollution control devices. In our laboratory, we have previously investigated the effects oxy-coal combustion on the formation of submicrometer-sized particles and their capture by an electrostatic precipitator (ESP) [7, 8]. The submicrometer particle size distribution was shifted toward a smaller size when N₂ in air was replaced by CO₂ [7], and penetration of the particle through an ESP was 1-2 orders of magnitude higher in O₂-CO₂ environments than in O₂-N₂ environments [8]. Croiset and Thambimuthu (2001)[9] and Lui and Okazaki (2003)[6] observed a significant reduction in NO_x emissions from oxy-coal combustion. Croiset and Thambimuthu (2001)[9] also reported a decrease in the conversion of sulfur to sulfur dioxide (SO₂) from 91% to 75% when N₂ was replaced by CO₂, and to 64% when CO₂ came from the recycled flue gas.

Mercury is one of the most toxic environmental pollutants and highly bio-concentrated metals in the human food chain. Coal-fired utility plants are the largest anthropogenic source of mercury emission in the United States [10]. On March 15, 2005, the United States Environmental Protection Agency (US EPA) issued the Clean Air Mercury Rule (CAMR) to regulate Hg emissions from coal-fired power plants using a cap-and-trade approach. Mercury emission from coal-fired power plants would be reduced from 48 tons per year to 15 tons per year, a reduction of nearly 70% (US EPA, 2005). However, many states and organizations challenged the CAMR. On February 8, 2008, the U.S. Court of Appeals for the District of Columbia Circuit vacated the CAMR, and required the US EPA to reconsider the Mercury Rule (Edison Electric Institute, 2008). It is expected that mercury regulation will become more stringent and the power plants will be required to install Hg control devices. As a result, extensive research and development are in progress for control methodologies.

Like other pollutants, mercury capture methodology relies primarily on the knowledge of mercury speciation in flue gas. Mercury exists in three forms in coal-combustion flue gas: elemental mercury (Hg⁰), oxidized (Hg²⁺), and particulate-bound (Hg_(p)). During combustion, mercury is liberated from coal as Hg⁰. As the flue gas cools, some of the Hg⁰ is oxidized – presumably to HgCl₂ due to the presence of chlorine in coal. While Hg⁰ is insoluble in water and difficult to capture, HgCl₂ is water-soluble and readily captured in the pollution control devices, such as scrubbers. Several factors play an important role in the fate of mercury emission, including chlorine species, carbon monoxide (CO), moisture (H₂O), sulfur dioxide (SO₂), and nitrous oxide (NO). Chlorine species have been regarded as the key factor affecting mercury oxidation. Many studies indicated a strong correlation between chlorine content in coal and oxidized mercury in flue gas; high chlorine content typically resulted in more oxidized mercury in flue gas [11-14]. Extensive efforts have also been made in unraveling the reaction mechanism for homogeneous mercury oxidation through a sequence of elementary reactions. To date, it has been widely accepted that Hg⁰ was first oxidized into the intermediate HgCl, which further reacted with chlorinating species to form thermodynamically stable HgCl₂ [15-17]. The dominant mercury oxidizing species is atomic chlorine (Cl) and to a lesser extent of other chlorinating species, such as molecular chlorine (Cl₂), hypochlorite (HOCl) and hydrogen chloride (HCl) [11, 15, 18, 19]. Other constituents in flue gas and their concentrations also affect mercury oxidation. CO promotes mercury oxidation, while moisture and SO₂ impede the oxidation [19-23]. NO can either inhibit or promote mercury oxidation and HgCl₂ formation, depending on its concentration [18, 19].

In oxy-coal combustion, the constituents in flue gas are different than those generated in conventional (coal-air) combustion. In this context, the fate of mercury emission may be significantly affected. A few

research reported the fate of mercury under oxy-coal combustion [24, 25]. Font et al. (2012)[24] investigated fate of mercury and other trace elements in a coal fluidized bed oxy combustion pilot plant and reported that 7.5% of Hg existed in gaseous form and very high proportion was found in pollutant control devices, including cyclone and bag-filters. Wang et al. (2013)[25] compared speciation of mercury presence during air-coal and oxy-coal combustion. They reported that more Hg^0 and Hg^{2+} were released into gas-phase when coal was combusted in O_2 - CO_2 environment than that in air at $800^\circ C$; however, when coal was combusted at $850^\circ C$, less Hg^0 and Hg^{2+} were found in O_2 - CO_2 combustion environment than that in air. Coal-combustion is a complex process and several factors play important roles on the fate of mercury. Since selecting appropriate mercury control methodology relies primarily on the knowledge of mercury speciation in flue gas, systematically identifying the effects of influencing factors should be developed. This study aimed to establish the understanding of mercury oxidation under oxy-coal combustion using simulated flue gas. The influences of NO and H_2O on the oxidation are also reported. The results presented here will be beneficial to the current development of mercury control methodology, and will help to facilitate the transition of the technology when it is applied in oxy-coal combustion.

2. Experimental and Methods

2.1. Test Plan

The experimental plan is outlined in Table 1. Set I experiments evaluated the effects of carrier gases on Hg oxidation by HCl. Experiments were conducted at different temperatures, ranging between 500 to $900^\circ C$. The gas mixtures examined were chosen to mimic gas mixtures that one might find in oxy-coal and conventional (coal-air) combustions. Pure CO_2 , pure N_2 and air were also studied for comparison. Set II and Set III experiments were designed to independently evaluate the roles of H_2O and NO on the extent of Hg oxidation by HCl in different carrier gas. In these sets of experiments, concentrations of NO and H_2O were chosen based on the values typically reported in coal combustion systems. The concentration of HCl was held constant at 100 ppm_v, while concentrations of NO and H_2O were varied between 40 - 200 ppm_v and 0 - 20% by volume, respectively. Set IV experiments were conducted to examine the combined effects of H_2O and NO on Hg oxidation by HCl. In this set of experiments, the concentration of HCl and H_2O were held constant at 100 ppm_v and 7% by volume, respectively, while the selected concentrations of NO were 40 to 100 ppm_v.

Table 1. Summary of the experiments performed.

Set	Objective	Gas Composition						
		N_2 (%)	O_2 (%)	CO_2 (%)	H_2O (%)	NO (ppm _v)	Hg ($\mu g/m^3$)	HCl (ppm _v)
1	Investigate the role of carrier gas on Hg-oxidation by HCl	100	-	-	-	-	20	100
		-	-	100	-	-		
		90	10	-	-	-		
		-	10	90	-	-		
		-	10	14	-	-		
-	79	21	-	-	-			
2	Evaluate the effects of H_2O on Hg-oxidation by HCl in different carrier gas	balance	-	-	-	-	20	100
		-	-	balance	-	-		
		balance	10	-	0-20	-		
		-	10	balance	-	-		
		balance	10	14	-	-		
balance	21	-	-	-				
3	Evaluate the effects of NO on Hg-oxidation by HCl in different carrier gas	balance	-	-	-	-	20	100
		-	-	balance	-	-		
		balance	10	-	40-400	-		
		-	10	balance	-	-		
		balance	10	14	-	-		
balance	21	-	-	-				
4	Determine the combined effects of NO and H_2O on Hg-oxidation in different carrier gas	balance	-	-	-	-	20	100
		-	-	balance	7, 20	40, 100		
		balance	10	-	-	-		
		-	10	balance	-	-		
		balance	10	14	-	-		
balance	21	-	-	-				

2.2. Experimental Setup

The experimental setup, shown in Fig. 1, consisted of inlet manifolds, where Hg, carrier gases and other gases were introduced, a quartz tube reactor (50 cm long with an inner diameter of 2.54 cm), a furnace (1100°C laboratory tube furnace, Lindberg) to simulate a high temperature environment, and a mercury sampling train. Mercury vapor was introduced into the system by passing particle-free CO₂, N₂ or air above liquid mercury contained in a glass bottle at precisely controlled flow rates using a mass flow controller (MKS Mass-Flow Controller, MKS Instruments, Inc.). The bottle resided in a water-filled beaker with the bath temperature held constant at 40°C. To minimize mercury condensation, the tubing connecting the Hg feed bottle to the entrance of the furnace was wrapped with heating tape (Type 45500, Thermolyne), and set at 80°C. The carrier gases, either N₂, CO₂, or gas mixtures of O₂, N₂ and CO₂, and other constituents, including H₂O, HCl (2000 ppm-N₂, Wright Bothers) and NO (5000 ppm-N₂, Airgas), were introduced into the reactor via other inlet manifolds using mass flow controllers (MKS Mass-Flow Controller, MKS Instruments, Inc.). Water vapor (H₂O) was introduced into the reactor by bubbling N₂ or CO₂ through milli-Q water. The flow rates of N₂ or CO₂ were calibrated to establish the desired water vapor concentrations at the inlet of the reactor. The total flow rate through the reactor was 2.0 lpm, resulting in the residence time of 2 s inside the reactor at 800 °C. At the exit of the system, a mercury sampling train was connected downstream of the tubular reactor to determine oxidized and elemental mercury concentrations.

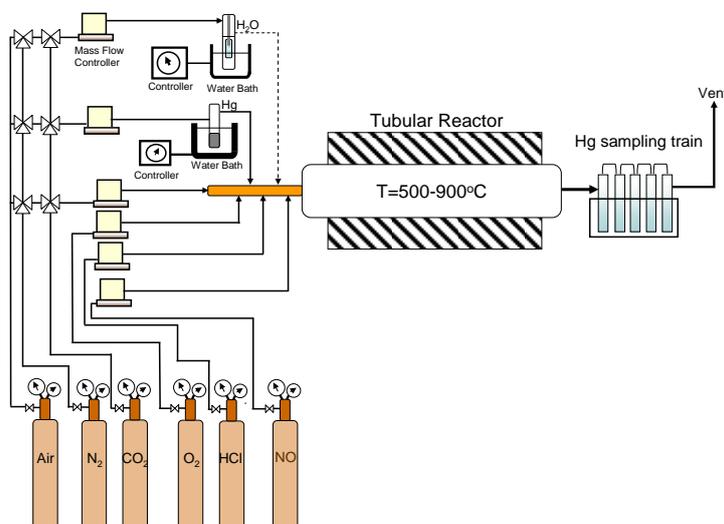


Fig. 1. Schematics of the experimental setup.

2.3. Mercury Measurement

The sampling train and technique used for gaseous mercury measurement was based on the method developed by Hedrick et al. (2001) [25]. The sampling train consisted of the following five impinger solutions: two impingers of 1.0 M tris-buffer and EDTA for capture of oxidized mercury, one impinger of 10% hydrogen peroxide and 2% nitric acid for oxidizing and capture of elemental mercury, and two impingers of 0.05 M potassium iodide and 2% hydrochloric acid for capture of elemental mercury. The impinger solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to determine the elemental and oxidized fractions of mercury in the exhaust gas. Due to the tendency of mercury to adsorb, extra precaution was exercised. To prevent cross-contamination between experimental runs, the reactor and all impingers were acid cleaned. The reactor was purged with particle-free carrier gases at the furnace temperature of 1100°C for 30 min before every run. The baseline mercury concentration was periodically verified during each set of experiments. At least four measurements were averaged for each run and the results are reported with standard deviation of all measurements. Since mercury was introduced as Hg⁰, the extent of Hg oxidation was calculated as follows:

$$\text{Hg}^0 \text{ oxidation (\%)} = \frac{\{[\text{Hg}^0]_{w/o \text{HCl}} - [\text{Hg}^0]_{w/\text{HCl}}\}}{[\text{Hg}^0]_{w/o \text{HCl}}} * 100 \quad (1)$$

3. Results and Discussion

The study evaluated the effects of flue gas constituents associated with oxy-coal combustion in post-combustion Hg-oxidation by HCl. The first part of this section discusses the influence of carrier gas on the extent of Hg-oxidation. The second and third parts focus on understanding the roles of moisture and NO on the oxidation. In the last part, the combined effects of carrier gases, moisture and NO on Hg-oxidation are discussed. It should be noted that no Hg-oxidation was observed in the absence of HCl for all conditions investigated in this study, and the measured Hg⁰ concentrations for each condition without adding HCl were used as a baseline to determine the extent of Hg-oxidation.

3.1. Role of Carrier Gas in Hg-oxidation

The first set of experiments was conducted to evaluate the effects of carrier gases on Hg-oxidation. The gas mixtures examined in the study, including 10%O₂-90%CO₂, 10%O₂-90%N₂, and 10%O₂-14%CO₂-76%N₂, were chosen to mimic flue gas constituents that would be in oxy-coal and conventional (coal-air) combustion. Pure CO₂, pure N₂ and air were also studied for comparison. The extents of mercury oxidation in different carrier gases at HCl concentration of 100 ppm_v are shown in Fig. 2. This HCl concentration represented the concentration in a typical combustion of bituminous and sub-bituminous coal with medium chlorine content [27, 28]. Our experimental results indicated that carrier gases evaluated in this study had significant effects on Hg-oxidation. The extent of Hg-oxidation, when it occurred at flue gas temperature of 800°C, was highest (32%) when air was a carrier gas and lowest (8%) when CO₂ was a carrier gas. No data were shown when N₂ was a carrier gas since no Hg-oxidation was observed for temperature evaluated in this set of experiments. For gas mixtures with the same O₂ concentration, the extent of Hg-oxidation was highest (28%) in a 10%O₂-90%CO₂ gas mixture, followed by a 10%O₂-14%CO₂-76%N₂ gas mixture (26%), and a 10%O₂-90%N₂ mixture (25%). The extent of Hg-oxidation increased with temperature for all carrier gases investigated in this study.

The differences in Hg-oxidation were attributed to the concentrations of the reactive Cl-species generating in air, N₂, CO₂ or gas mixtures. Since HCl has been at the reduced state and it cannot directly oxidize Hg⁰ [13], Hg-oxidation must occur via the reactive chlorine intermediates derived from HCl. Previous research has established the pathways for Hg⁰ oxidation, reaction 1-8 shown in Table 2 [15, 16, 19]. The reaction rate constant, *k*, suggested that only Cl can initiate Hg⁰ oxidation at a substantial rate, shown in reaction 1, Table 2. Roesler et al. (1995) and Mueller et al. (1998) reported that HCl can dissociate to Cl in the presence of oxygen (O), hydrogen (H) or hydroxyl (OH) radicals, shown in reactions 9, 10 and 11, Table 4.2 [29, 30]. Even though HCl dissociation via attack by OH radicals (reaction 11) would be the primary pathway for releasing Cl atoms into flue gas, for carrier gases investigated in this study, O radicals are the species initiating HCl dissociation reactions, and they must derive from O₂ or CO₂. The highest Hg-oxidation found in air, which contained the highest volume fraction of O₂ (air, 21%O₂-79%N₂), and the lowest found in pure CO₂, indicated that O₂ was the primary source of O. With the same volume fraction of O₂, slight differences in Hg-oxidation among the gas mixtures further verify that the volume fraction of O₂ controls the pool of Cl that is available to react with Hg⁰. These results are in agreement with Agarwal and Stenger (2006). Little effect of CO₂ on Hg-oxidation was observed in simulated flue gas of conventional coal combustion [31]. It should be also noted that N₂ did not assist dissociation of HCl as no Hg-oxidation was observed when N₂ was a carrier gas.

In oxy-coal combustion, concentration of O₂ would be higher than that in conventional coal combustion flue gas to maintain the same boiler temperature or to increase boiler thermal efficiency [7]. Our experimental results suggested that Hg-oxidation would be higher than that found in conventional coal combustion systems.

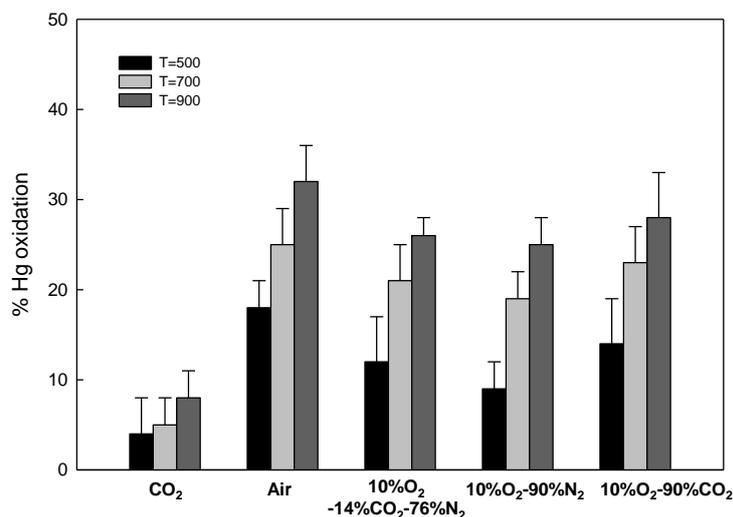


Fig. 2. Effects of carrier gas on Hg-oxidation by 100 ppm_v HCl.

Table 2. The pathways for Hg⁰ oxidation.

Reaction No.	Reactions	A (cm ³ /mol-s)	β	E _a Kcal/mol	Ref.
1	Hg+Cl+M → HgCl+M	2.4x10 ⁸	1.4	-14.4	20
2	Hg+Cl ₂ → HgCl+Cl	1.39x10 ¹⁴	0.0	34.0	20
3	HgCl+Cl ₂ → HgCl ₂ +M	1.39x10 ¹⁴	0.0	1.0	20
4	HgCl+Cl+M → HgCl ₂ +M	2.19x10 ¹⁸	0.0	3.1	20
5	Hg+HOCl → HgCl+OH	4.27x10 ¹³	0.0	19.0	20
6	Hg+HCl → HgCl+H	4.94x10 ¹⁴	0.0	79.3	20
7	HgCl+HCl → HgCl ₂ +H	4.94x10 ¹⁴	0.0	21.5	20
8	HgCl+HOCl → HgCl ₂ +OH	4.27x10 ¹³	0.0	1.0	20
9	HCl+O → OH+Cl	3.37x10 ³	0.0	3.51	27,28
10	HCl+H → H ₂ +Cl	1.69x10 ¹³	1.65	4.14	27,28
11	HCl+OH → H ₂ O+Cl	2.71x10 ⁷	2.87	-0.22	27,28
12	NO+O+M → NO ₂ +M	4.72x10 ²⁴	-2.87	1.55	28,35
13	NO+H+M → HNO+M	5.0x10 ¹⁹	-1.32	0.74	28,35
14	NO+OH+M → HONO+M	5.08x10 ²³	-2.51	-0.007	28,35
15	HONO+Cl → HCl+NO ₂	5.00x10 ¹³	0.0	0.0	28,35

Note: $k = AT^{\beta} \exp(-E_a/RT)$; M = any molecules acting as a third-body collision

3.2. Role of Moisture in Hg-oxidation

Several studies reported that H₂O is an important factor influencing the degree of Hg oxidation [19, 32]. In conventional coal combustion flue gas, moisture content ranges between 7 to 15% [25, 33]. Depending on flue gas recycled ratio, moisture content in oxy-coal combustion flue gas would range between that in conventional flue gas and that in the flue gas of coal combustion in pure oxygen (27%) (Sandia National Laboratories, 2009) [34]. In this set of experiments, the moisture content, ranging from 7% to 20%, was chosen to correspond to that in conventional and oxy-coal combustions. The effects of moisture on Hg-oxidation by 100 ppm_v HCl in different carrier gases are reported in Fig. 3. For all gas mixtures and air, the extent of the oxidation drastically decreased in the presence of H₂O; however, the effect of moisture content on the oxidation was not significant. For example, when air was a carrier gas, the extent of Hg-oxidation decreased from 32% without H₂O present to 25% with 7% H₂O added, but it decreased to 18%

when moisture content increased from 7% to 20%. The decrease in Hg-oxidation was attributed to the abundant supply of OH radicals that dissociated from H₂O and competed with Hg⁰ for Cl radicals to form less reactive chlorinating species, such as HOCl. In addition, high concentration of OH radicals substantially increased reduction rate of HgCl to form Hg⁰ and HOCl—thus, lowering Hg-oxidation [19]. In comparing gas mixtures and air, the effects of moisture in Hg-oxidation were not found significantly different. The extents of Hg-oxidation at 20% H₂O were 18% for air, ranging between 15%-16% for gas mixtures. This indicated that the impact of H₂O on Hg-oxidation outweighed that of O₂ concentrations demonstrated in Set I experiments.

When CO₂ and N₂ were carrier gases, in contrast to the gas mixtures, the presence of H₂O promoted Hg-oxidation at low moisture content (7%) and suppressed the oxidation when moisture content increased (15% and 20%). The former result suggested that OH radicals dissociated from H₂O initiated the formation of Cl radicals from HCl (shown in reaction 11, Table 4.2), which subsequently provided the channel towards Hg-oxidation. At high moisture content, the inhibitory effect on Hg-oxidation indicated that Cl radicals would mostly be consumed by OH radicals to form their respective oxidized products, or the reduction rate HgCl via attack by OH radicals substantially increased and it became a significant competing mechanism on Hg-oxidation. The results from this set of experiments clearly indicated the importance of flue gas constituents and their concentrations on Hg-oxidation.

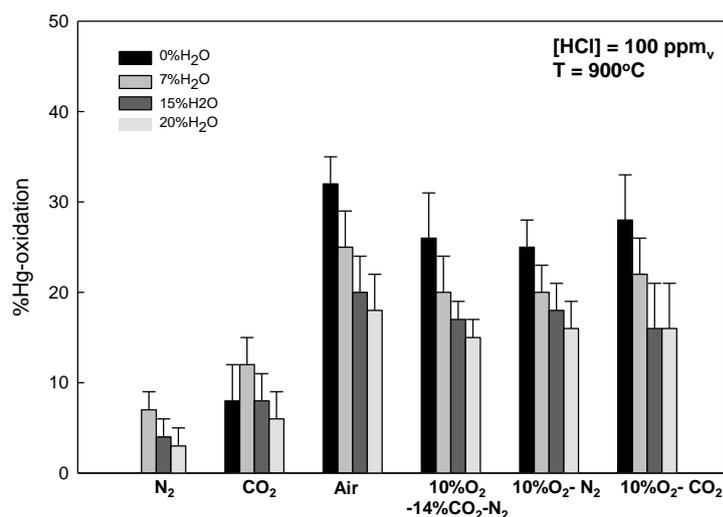


Fig. 3. Effects of H₂O on Hg-oxidation by 100 ppm_v HCl in different carrier gas.

3.3. Role of NO on Hg Oxidation

Besides moisture, the presence of NO in flue gas was reported to exert a strong impact on Hg-oxidation [19, 35]. Due to the absence of N₂ and a re-burn effect of the recycled flue gas in oxy-coal combustion, concentration of NO could be decreased to only 14% of conventional coal combustion [6]. In this set of experiments, the NO concentrations, ranging from 40 to 400 ppm_v, were selected to correspond to that in conventional and oxy-coal combustions. The effects of NO on Hg-oxidation by 100 ppm_v HCl in different carrier gases are reported in Fig. 4. No data were shown for N₂, since no Hg-oxidation was observed for all concentrations of NO evaluated in this set of experiments. It should be noted that Hg-oxidation by NO in the absence of HCl was negligible. The presence of NO strongly suppressed Hg-oxidation by HCl for all carrier gases. The effect was more pronounced when CO₂ was a carrier gas—the extent of Hg-oxidation was completely inhibited in the presence of NO. For gas mixtures with the same O₂ concentration, no Hg-oxidation was observed at NO concentrations above 200 ppm_v. When air was a carrier gas, the extent of the oxidation was completely suppressed at NO concentration of 400 ppm_v. The inhibitory effects were attributed to the consumption of O, H, and OH by NO. As shown in reaction 12, 13 and 14, Table 4.2, NO competed with HCl for O, H, OH [36], and subsequently impeded the formation of Cl radicals for Hg-oxidation. In pure CO₂, O radicals were much less available than those in gas mixtures. As a result, the complete inhibitory effect was exhibited at lower NO concentrations. When air was a carrier gas, O₂

concentration was highest (21%) and presumably so was the concentrations of radicals, specifically O. As a result, the complete inhibitory effect exhibited at higher NO concentration.

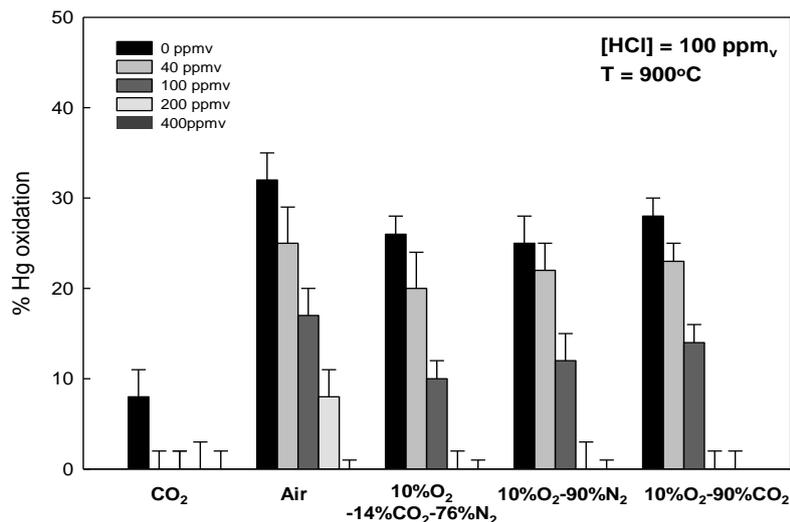


Fig. 4. Effects of NO on Hg-oxidation by 100 ppm_v HCl in different carrier gas.

3.4. Combined Effect of H₂O and NO

Set 4 experiments were designed to evaluate the extent of Hg-oxidation when moisture and NO were present together. The selected moisture content was 7% and 20% by volume and concentrations of NO were 40 and 100 ppm_v. Experimental results are reported in Fig. 5 (a) and Fig. 5 (b). For all gas mixtures, air and CO₂, the presence of H₂O and NO together exhibited stronger inhibitory effects on Hg-oxidation than those found when the individual compounds were present alone. For example, when air was a carrier gas, the extent of Hg-oxidation decreased from 32% without H₂O present to 25% with 7% H₂O added, it decreased from 32% without H₂O present to 25% when 40 ppm_v NO added, and when 7% H₂O and 40 ppm_v NO were present together, only 12% Hg-oxidation was observed. As previously described, the presence of H₂O and NO individually affects Hg-oxidation via controlling the pool of radicals, including Cl, H, OH, and O. This synergistic effect indicated that the availability of radicals decreased when H₂O and NO were together. Previous researchers had established that HONO formed when nitrogen species and OH radicals present together, shown in reaction 14, Table 2 [28,37]. With no activation energy required, HONO could directly scavenge Cl radicals to form HCl and H₂O, shown in reaction 15 in Table 4.2 [38,39]. This resulted in less Cl available for Hg-oxidation. In comparing all gas mixtures and air, the effects of coupling moisture and NO in Hg-oxidation were not found significantly different, 6% for air and ranging between 3% to 4% for gas mixtures at 7% moisture content and 100 ppm_v NO. This indicated that the impact of NO and H₂O on Hg-oxidation exceeded that of the carrier gases demonstrated in Set I experiments.

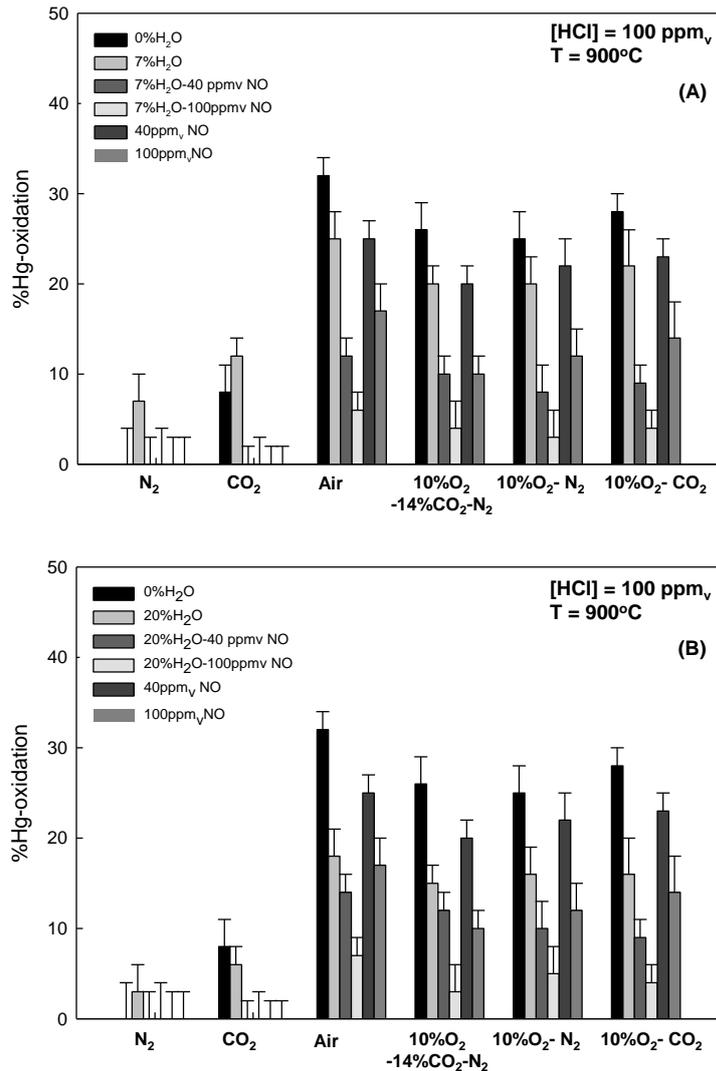


Fig. 5. The combined effect of NO and H_2O on Hg-oxidation by HCl in different carrier gas. (a) Hg-oxidation at 7% H_2O with 40 and 100 ppm_v NO, (b) Hg-oxidation at 20% H_2O with 40 and 100 ppm_v NO.

In comparing the influence of moisture content on the combined effects of H_2O and NO, the extents of Hg-oxidation slightly decreased when moisture content increased from 7% to 20% for all carrier gases. This indicated that OH radicals that dissociated from H_2O were abundant and that increasing moisture content did not significantly affect the pool of radicals, specifically Cl, and subsequently Hg-oxidation. In oxy-coal combustion, moisture content would be higher than that in conventional coal combustion, while concentration of NO would be lower than that in conventional coal combustion. Our experimental results suggested that Hg-oxidation in oxy-coal combustion would be higher than that found in conventional coal combustion systems.

4. Conclusion

This study explored the potential impact of oxy-coal combustion on homogeneous mercury oxidation. The experiments were systematically designed to identify the influence of each constituent and its concentration. Our experimental results demonstrated that CO_2 assisted Hg-oxidation by HCl; however, its influence was outweighed by the presence of O_2 . N_2 alone did not participate in the oxidation of Hg. The presence of NO and H_2O inhibited Hg-oxidation for all carrier gases investigated in this study. The inhibitory effects depended strongly on the concentration of NO, but not on moisture content. For all carrier gases, synergistic inhibitory effects were demonstrated when NO and H_2O were present together. These results were attributed to the impact of flue gas constituents on the pool of Cl that is available to react with Hg^0 .

Our experimental findings suggested that in oxy-coal combustion, while Hg-oxidation would not be critically affected by highly concentrated CO₂ in the flue gas, it would be impacted by other flue gas constituents, such as NO and H₂O, and their concentrations, which are influenced by oxy-coal combustion.

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