



Interactions between mercury and dry FGD ash in simulated post combustion conditions

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ABSTRACT

Two different flue gas desulfurization (FGD) ash samples were exposed to a simulated flue gas stream containing elemental mercury vapor to evaluate the interactions and determine the effects of gas components, dry FGD ash samples, and temperature on adsorption and heterogeneous oxidation of mercury. Both samples were characterized for surface area, unburned carbon content, element content, and mineralogical composition. Mercury speciation downstream from the sample was determined using Ontario Hydro Method. Results showed that higher levels of mercury oxidation were associated with higher levels of mercury capture. The NO_2 , HCl , and Cl_2 promoted mercury oxidation, while SO_2 and NO had inhibitory effects on mercury oxidation. Unburned carbon of dry FGD ash sample played an important role in mercury capture. Whether the surface area was caused by unburned carbon or by calcium-based sorbents might be more significant than the level of surface area. Extent of mercury oxidation and capture increased slightly and then decreased as the temperature rising due to the interaction of mass transfer and reaction rates control.

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1. Introduction

Anthropogenic emissions of mercury from coal-fired power plants have brought about tremendous pollution to the environment, and meanwhile, posed a potential threat to human health [1]. Mercury in coal exists in extremely low level (on the order of 1 mg/g) [2]. However, due to the huge coal consumption by coal-fired power plants, coal-fired utility boiler is identified as the largest source of mercury emission [3,4].

Recently, there is no single best technology that can be broadly applied for mercury emission control from power plants. Activated carbon injection is considered as the currently available technology, but it can be hardly promoted unless its costs are reduced to an affordable extent. Fortunately, almost all air pollution control devices (APCDs) show the capabilities on mercury emission control. The APCDs, such as fabric filter (FF) bag house, electrostatic precipitator (ESP), and wet flue gas desulfurization (FGD), can remove some particulate-bound and oxidized forms of mercury. Under such background, combined removal of mercury by APCDs is a practicable technology route. Besides wet FGD equipments, dry FGD also possesses the capacity on mercury removal.

The spray dryer system is a typical type of dry FGD technology used in coal-fired power plants with the electric power generation in the range of $10\text{--}500\text{ MW}$ [5]. The absorbers use an alkaline (typically lime) slurry to absorb SO_2 , and also absorb about 90% of the oxidized gaseous mercury. The mercury exiting a spray dryer system is primarily in elemental form, averaging 83% Hg^0 for FFs and 96% for ESPs, with less than 0.5% in particulate form [6]. Spray dryer systems equipped with an FF also remove a significant fraction of the Hg^0 entering at coal when chlorine contents are above 200 ppm [7]. A great deal of research work has been done to analyze coal combustion products, including fly ash and other fine particulate matter, in an attempt to quantify and determine the mode of disposition of trace elements. Dry FGD ash should be considered as sorbent for mercury capturing in combined process of mercury emission control with dry FGD absorbers. However, little is known about the characteristics of mercury adsorption on FGD ash or how flue gas components influence mercury capturing and heterogeneous oxidation by dry FGD ash.

This study focuses on the interactions between mercury and dry FGD ash by exposing the samples to a simulated flue gas stream in a fix-bed reactor. Factors affecting mercury adsorption on dry FGD ash were determined. In this regard, differences in the catalytic activities between various dry FGD ashes were being sought. An improved understanding to the roles of FGD ash on mercury chemistry may in turn help the development of the combined mercury removal technology with dry FGD devices.

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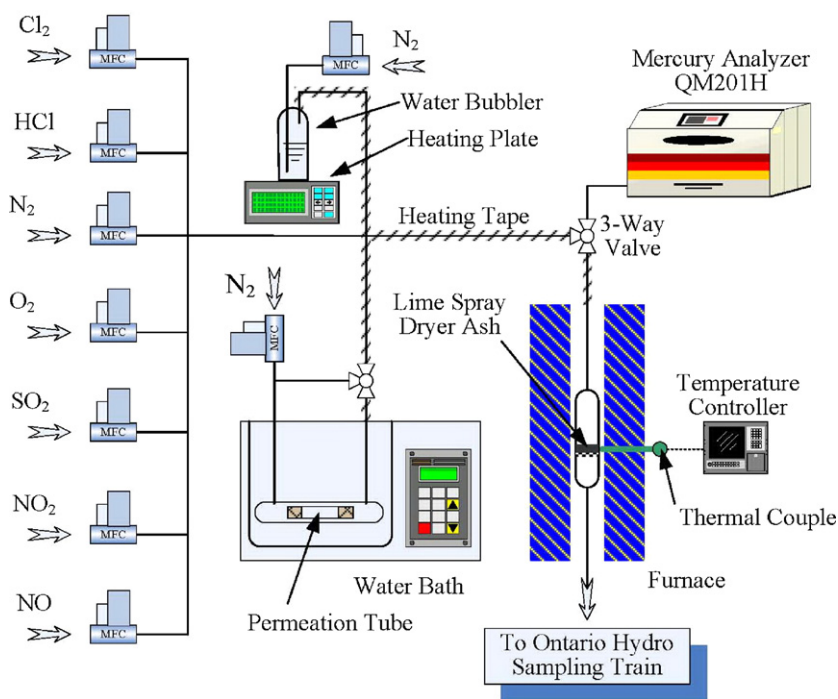


Fig. 1. Schematic of testing facility.

2. Experimental

2.1. Apparatus and procedure

The experiments described here were performed in a bench-scale system. A schematic of the system is shown in Fig. 1. The bench-scale system consists of an elemental mercury permeation device, a fixed-bed reactor placed in an electric furnace, a gas humidification device, a heated PTFE gas transport line, and various gas cylinders that contain different gas components at fixed and known concentrations. The Hg^0 vapor was generated using a VICI Metronics Inc. mercury permeation tube housed in a glass tube. A stream of N_2 flowed through a copper coil to be preheated before it flowed through the glass tube and carried the mercury vapor into the primary gas stream. Both the coil and the glass tube were maintained at 70°C by submersing them in a water bath with a precision of 0.1°C . Mass flow controllers (MFC, Sevenstar Electronics Co., Ltd. Mass Flow Meter Division, Beijing) were used to control the flow rates of the gas streams from cylinders. Water vapor was added to the gas matrix by passing a N_2 stream through a water bubbler placed on a heating plate.

All transport pipes were heated to about 363 K in order to prevent the adsorption of Hg vapor and the condensation of water vapor. Dry FGD ash samples were dispersed on a quartz filter in an oxidation reactor. The reactor was a quartz tube (with an outer diameter of 30 mm and inner diameter of 28 mm) surrounded by a tube furnace. A thermal couple was placed near the filter. A temperature controller with a precision of 1°C was employed to keep the adsorbent bed at desired temperature. The vapor-phase Hg^0 concentration was analyzed continuously upstream of the adsorbent bed using a QM201H (Greenalm Instruments Co., Ltd., China) before the streams flowed through the fixed-bed. QM201H is a cold vapor atomic fluorescence spectrophotometer (CVAFS), which can analyze only elemental mercury.

2.2. Dry FGD ash samples

Fixed-bed testing was performed with two types of dry FGD ash samples. Both samples were selected from the FGD devices in cogeneration plant of Sinopec Qilu Co., Ltd. The plant utilized eight 410 t/h pulverized coal boilers. One sample was from a novel integrated desulfurization (NID) system at No. 8 utility boiler. The NID system, following a fabric filter (FF), was designed by Alstom Power Inc. Quicklime was used as desulfurizer, and mixed with water to undergo a slaking process before it was injected into the desulfurization absorber. The other sample was from No. 6 utility boiler with a circulating fluidized bed FGD (CFB-FGD) absorber for flue gas cleaning. The CFB-FGD system following an FF, was designed by Tongfang Environment Co., Ltd. Lime slaking unit of the system was omitted, and hydrated lime was directly injected into the absorber. Both samples were collected near the circulating points. Samples subsequently were stored in sealed containers until experiments and other analyses were conducted.

2.3. Samples characterization

Various techniques were applied to characterize the NID and CFB-FGD ash samples in order to acquire information related to the effects on mercury adsorption and heterogeneous oxidation. X-ray fluorescence (PANalytical, AXIOS-PW 4400) was used to determine the element content. X-ray diffraction (XRD, Rigaku D/Max- $\alpha\beta$, Japan) was used to examine the mineralogical composition of the dry FGD samples. The surface area was calculated using the nitrogen Brunauer–Emmett–Teller (BET) isotherm equation. BET N_2 adsorption isotherms were obtained on both samples using a Micromeritics Instrument Corporation Accelerated Surface Area Porosimeter 2020. Unburned carbon contents were determined using a TGA (SDTA851e, Mettler-Toledo International Inc.).

Table 1
Flue gas mixtures for fixed-bed tests.

Baseline components		Testing components	
Gas	Composition	Gas	Composition
O ₂	5%	SO ₂	1200 ppm
CO ₂	14%	NO	600 ppm
H ₂ O	6%	NO ₂	20 ppm
Hg ⁰ vapor	93 μg/m ³	HCl	50 ppm
N ₂	Balance	Cl ₂	10 ppm

2.4. Testing approach

N₂ passed through all pipes for about 30 min to purify the lines and ensure the mercury permeating reached stable state. The mercury concentration in N₂ stream was first measured with QM201H. Once the stable state was obtained, simulated gas was switched to pass through the reactor at a desired flow rate. The total dry gas flow rate was 1 l/min. Mercury speciation measurement was performed by Ontario Hydro Method (OHM). Each test had a duration of 60 min, and all tests were performed at least in duplicate.

A continuous stream of Hg⁰ was passed over the dry FGD ash samples in the presence of different gas blends using a total dry gas flow rate of 1 l/min. This gas flow rate was selected because it is typical when sampling with the OHM, which is used to perform mercury speciation. Individual gas concentrations were listed in Table 1. The gas concentrations were designed to be within the range of typical coal-fired flue gas composition [8]. Typical ranges of main gas compositions for bituminous coal were as follows: 3–5% O₂, 14–15% CO₂, 500–2000 ppm SO₂, 400–800 ppm NO, 5–7% H₂O, and 20–120 ppm HCl. The baseline blend consisted of O₂, CO₂, H₂O, N₂ and Hg⁰ vapor. Other gases in Table 1 were considered as testing components that were mixed into the gas streams according to experiment design. The experiments were divided into two parts. In the first part, the testing components were added to baseline blend separately or in combination of two to constitute 15 gas streams. Tests of this part were performed for the purposes of investigating the effects of different gases on mercury adsorption and heterogeneous oxidation by two dry FGD ash samples. Weight of sample used in the first part was 3 g. In the other part, testing components were added to the baseline blend to constitute a full gas blend. Tests of the second part were intended to analyze the effects of temperature. Weight of samples used in this part was 2 g. Other sample loadings were also tried, but this two were selected since they provided good comparability among experimental results. Gas streams exiting the reactor were bubbled into a series of impingers to precipitate the mercury.

2.5. Mercury analysis

The OHM was used to determine the mercury speciation at the outlet of fixed-bed reactor. The OHM is a modified version of the EPA Method 29. It is an extractive technique specifically designed to isolate and capture various Hg species [9]. This method utilizes a condensing/absorbing system consisting of eight impingers connected in series and immersed in an ice bath. The first three impingers contain 1 N potassium chloride (KCl) solution, and the Hg²⁺ species is removed. The fourth impinger contains 5% nitric acid (HNO₃) and 10% hydrogen peroxide (H₂O₂), for the removal of any acid gases (such as SO₂) in the gas stream. The fifth through seventh impingers contain 10% sulfuric acid (H₂SO₄) and 4% potassium permanganate (KMnO₄) for the removal of Hg⁰. The last impinger contains silica gel to remove any moisture left in the gas stream. After processing the impinger solutions using a series of treatment steps, they were analyzed by cold vapor atomic absorption (CVAA) spectroscopy using a Leeman Hydra AA Automated Mercury Ana-

Table 2
XRF analysis of desulfurizer and desulfurization ash samples.

Elements	Desulfurizer (%)		Dry FGD ash (%)	
	NID	CFB-FGD	NID	CFB-FGD
Al	1.03	0.34	8.03	1.58
Br	ND ^a	ND	0.02	0.02
Ca	63.7	58.1	27.6	47.7
Cl	0.04	0.03	0.61	0.51
Fe	0.25	0.16	1.92	0.20
K	0.12	0.07	0.64	0.37
Mg	0.43	0.48	0.30	0.16
Mn	ND	ND	0.04	0.39
Na	0.07	0.05	0.24	0.11
O	32.7	40.1	40.2	40.9
P	0.01	0.00	0.09	0.02
S	0.12	0.12	9.70	6.00
Si	1.39	0.46	9.99	1.88
Sr	0.04	0.03	0.07	0.04
Ti	0.08	0.04	0.52	0.11
Zn	ND	ND	0.01	0.01
Zr	ND	0.01	0.03	0.01
Total	100	100	100	100

^a ND: not determined.

lyzer. Results of those analyses gave the mercury speciation for the tests.

Particulate form of mercury was measured using a DMA-80 Direct Mercury Analyzer (Milestone Inc.). Each measurement was executed with a parallel sample. Blank sample boat was used every two boats to avoid interference between different samples.

3. Results and discussion

3.1. Dry FGD ash characterization

Results of the XRF analyses are presented in Table 2. The XRF analyses of the samples indicated that the most abundant elements in desulfurizer and FGD ash samples were Ca and O. NID ash contained more S than CFB-FGD ash, which meant that the former contained more desulfurization products. It could be speculated that molar proportion between Ca(OH)₂ and sulfate or sulfite compounds was about 2.3 for NID ash and 6.4 for CFB-FGD ash, respectively. Analyzing of XRD results revealed that crystalline material in both samples contained primarily Ca(OH)₂ and CaSO₃·1/2H₂O. The XRD results also indicated that other crystalline material in the sample contained primarily mullite (Al₆Si₂O₁₃), quartz (SiO₂), magnetite (Fe₃O₄) and hematite (Fe₂O₃). Dry FGD ash was a mixture of fresh desulfurizer, unreacted desulfurizer, desulfurization products and fly ash. Fresh and unreacted desulfurizer were constituted mainly by Ca(OH)₂. Unreacted desulfurizer was sorbent that circulated in the reactor more than one circle, and still did not react with SO₂. Desulfurization products mainly referred to CaSO₃ and its crystalline hydrate. SiO₂ and Fe₂O₃ were mainly from coal-fired fly ash that escaped from the ESP.

Table 3 shows the unburned carbon contents and BET surface areas (S_{BET}) of dry FGD ash samples. The NID ash sample had approximately 0.69 wt.% unburned carbon, significantly higher than that of the CFB-FBD ash. All unburned carbon in the FGD ash samples was from coal-fired fly ash since there was no carbon-based material in desulfurizer. The reasons for this discrepancy

Table 3
Carbon contents and surfaces areas of dry FGD ash samples.

Samples	Unburned carbon (%)	BET surface area (m ² /g)
CFB-FGD ash	0.10	5.69
NID ash	0.69	2.12

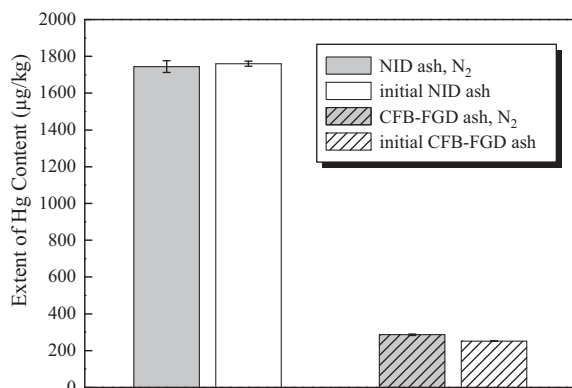


Fig. 2. Comparison of mercury contents of original and spent dry FGD samples. The spent samples were got by exposing the fresh samples to Hg⁰ vapor carried by a N₂ stream.

were complicated. It might result from different operation time or circulation ratios between two absorbers. S_{BET} of NID ash was 2.1 m²/g, while it was 5.7 m²/g CFB-FGD ash, more than twice of that of NID ash. BET surface area of activated carbon was about 500–1500 m²/g [10], much larger than that of lime, which was usually smaller than 10 m²/g [11]. Although unburned carbon content of NID ash was higher, its surface area was smaller than CFB-FGD ash. It could be speculated that larger surface area of CFB-FGD ash was not due to the carbon content of samples, but probably because of Ca-based materials in the FGD ash.

3.2. Effects of gas components

In the first series of fixed-bed experiments, both dry FGD ash samples were exposed to Hg⁰ vapor carried by a N₂ stream at temperature of 90 °C. Mercury contents of spent samples were measured and compared with fresh samples, as shown in Fig. 2. There were no significant differences on mercury contents between fresh and spent samples for both types of dry FGD ash. The results indicated that Hg⁰ vapor could hardly be captured by dry FGD ash, and revealed indirectly that mercury adsorbed on the surface of samples existed in Hg²⁺ form. In other fixed-bed experiments, samples were exposed to simulated flue gas with desired gas streams consisting of baseline blend and individual reactive gases or combinations of two.

Percentage of mercury captured (η_c , formula (1)) was the ratio of difference between Hg_{in} (mercury generated during the testing period) and Hg_{out} (total mercury measured using OHM) to Hg_{in}. Since mercury on spent ash samples was primarily in oxidized form, we considered percentage of mercury oxidized (η_o , formula (2)) as the ratio of difference between and Hg_{out}⁰ (elemental mercury measured using OHM) to Hg_{in}. The mass balance (η_b , formula (3)) was the ratio of the mercury measured, including Hg_p (on the ash) and Hg_{out} (in the flue gas), to the mercury generated. Table 4 presented the concentration of mercury on the spent ash and mass balance during the test. The maximum and minimum mass balances for all tests were 111.2% and 74%, respectively. This indicated that all tests were within an acceptable error range.

$$\eta_c = \frac{\text{Hg}_{\text{in}} - \text{Hg}_{\text{out}}}{\text{Hg}_{\text{in}}} \times 100\% \quad (1)$$

$$\eta_o = \frac{\text{Hg}_{\text{in}} - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}} \times 100\% \quad (2)$$

$$\eta_b = \frac{\text{Hg}_p + \text{Hg}_{\text{out}}}{\text{Hg}_{\text{in}}} \times 100\% \quad (3)$$

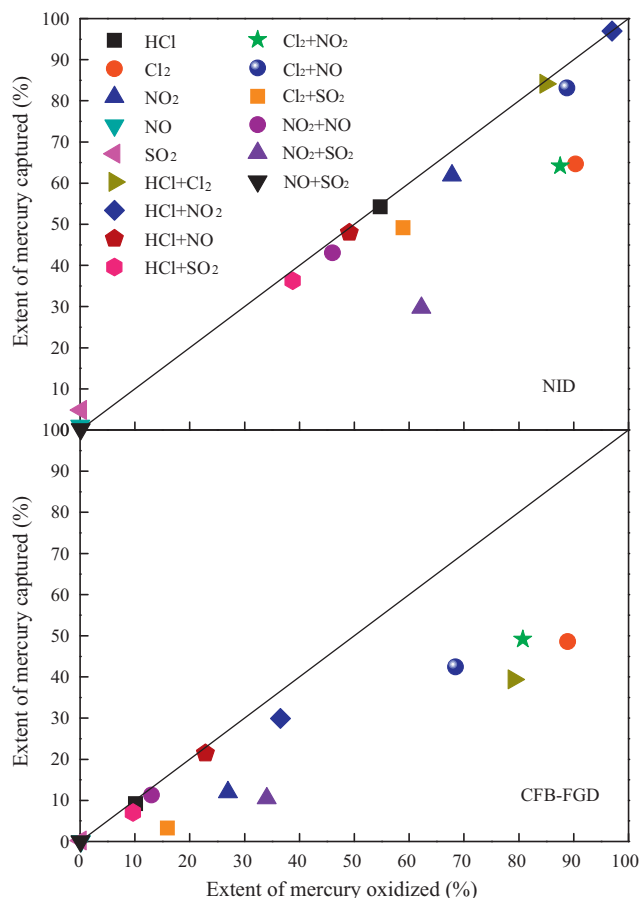


Fig. 3. Extent of Hg captured as a function of Hg oxidation. Straight line represents the conditions that extents of mercury captured equals to that of mercury oxidized.

Fig. 3 showed the extents of mercury captured versus extents of mercury oxidized. The results of this work indicated that higher levels of mercury oxidation were associated with higher levels of mercury capture. Dunham et al. [12] studied coal-fired fly ash samples in a fixed-bed experiment using simulated flue gas and got the similar relationship between mercury oxidation and capture. The effects of adding testing components individually to the gas matrices while using both dry FGD ash samples at 90 °C were shown in Figs. 4–8, respectively. Data of those histograms were extracted from Fig. 3 and shown separately to emphasize the effects of those components on mercury capture and oxidation. As can be seen from Figs. 4–6, the presence of HCl, Cl₂ and NO₂ greatly enhanced mercury capture and oxidation, and these gases could be considered as oxidative components. For most cases, mercury capture and catalytic oxidation by both dry FGD ash samples were promoted when adding another oxidative component to gas matrix. The results showed that mercury oxidation by the three oxidative components with the catalysis of FGD ash could be accumulated.

Several researchers have performed experimental work in attempts to explain the effects of various flue-gas components on the oxidation of elemental mercury (Hg⁰). HCl effectively oxidized Hg⁰ at higher temperature [13], whereas it was reported that Cl atom was the primary chlorine-containing species responsible for Hg⁰ oxidation and high temperature promoted Cl atom formation reactions [14]. Hall et al. [13,15] investigated mercury oxidation by NO₂ at a temperature of 340 °C. They observed 7.2% Hg oxidation when initial NO₂ concentration was 350 ppm. This indicated that Hg⁰ oxidized by NO₂ was significant only at high concentration. However, Cl atom formation reactions were less effective at the temperature in this work, and NO₂ concentration was also at a

Table 4

Hg contents of spent FGD ash samples and mass balance of each test. Particular mercury was determined using a DMA-80 Direct Mercury Analyzer.

No.	Testing components	NID ash		CFB-FGD ash	
		Mercury on spent ash ($\mu\text{g}/\text{kg}$)	Mass balance (%)	Mercury on spent ash ($\mu\text{g}/\text{kg}$)	Mass balance (%)
1	HCl	3210	128	443	105
2	Cl ₂	2531	80	624	74
3	NO ₂	2880	102	511	106
4	NO	1801	105	273	105
5	SO ₂	1774	99	246	103
6	HCl, Cl ₂	3898	135	1245	118
7	HCl, NO ₂	3562	103	626	94
8	HCl, NO	2703	106	550	98
9	HCl, SO ₂	2560	111	411	105
10	Cl ₂ , NO ₂	3070	110	1103	100
11	Cl ₂ , NO	3551	117	819	91
12	Cl ₂ , SO ₂	2907	116	360	106
13	NO ₂ , NO	2285	88	597	111
14	NO ₂ , SO ₂	2837	133	530	108
15	NO, SO ₂	1682	99	198	101

low level. Both conditions contributing to Hg oxidation mentioned above were not present in our tests, thus, the significant Hg⁰ oxidation by HCl and NO₂ was due to the catalysis of dry FGD ash samples.

Cl₂ substantially oxidized Hg⁰ even at room temperature via the following pathway [9]:

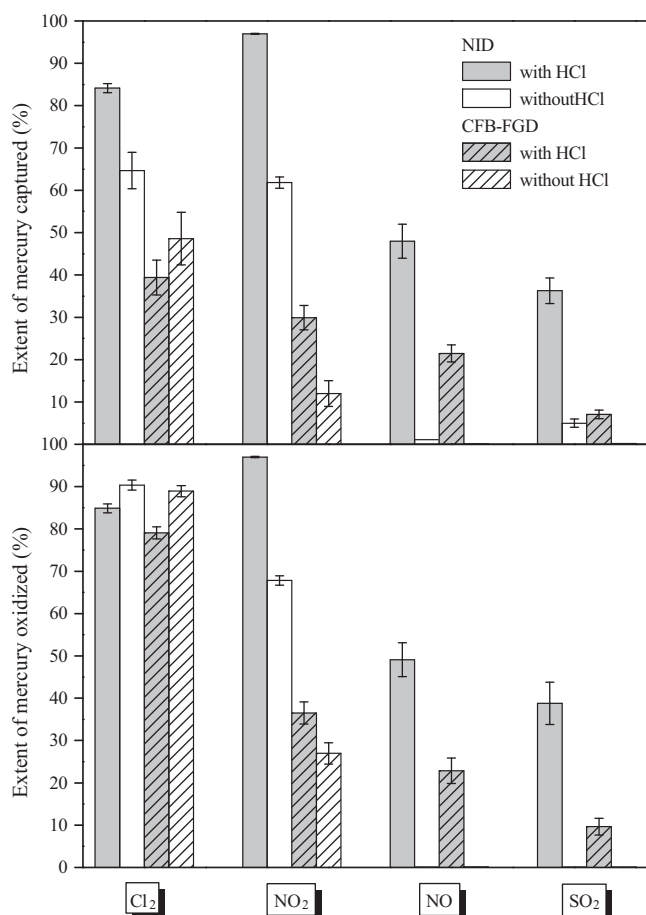
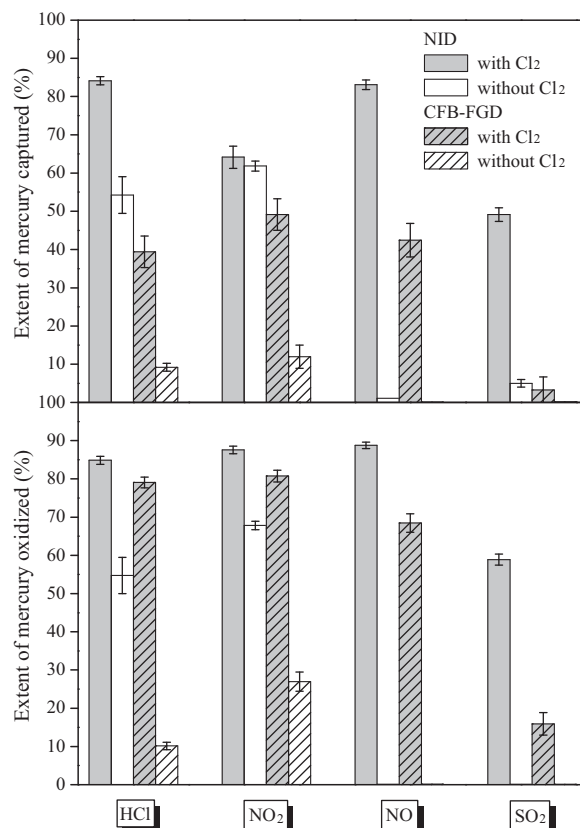


Therefore, both homogeneous and heterogeneous oxidation existed during the fixed-bed experiments while the gas streams contained Cl₂. It was observed that 10 ppm Cl₂ resulted in 90.4%

and 88.9% Hg oxidation for NID and CFB-FGD ash samples (Fig. 4), respectively. The addition of HCl or NO₂ did not promote the Hg oxidation, as shown in Figs. 4 and 6. It was likely that significant homogeneous oxidation suppressed the heterogeneous reactions between mercury and dry FGD ash samples.

Contrary to oxidative components, the presence of SO₂ and NO suppressed mercury capture and oxidation, as shown in Figs. 7 and 8, respectively. No data were shown for either SO₂ or NO alone and combination of two, since no significant mercury capture or oxidation was observed in these cases. Direct measure of mercury on spent samples using DMA-80 also supported the results.

SO₂ inhibited mercury capture and oxidation in all cases except for adding SO₂ to gas matrix contained NO₂, as shown in Fig. 7. The suppression of mercury oxidation by SO₂ was observed in all cases

**Fig. 4.** Effects of HCl on Hg captured and oxidized by dry FGD ash samples.**Fig. 5.** Effects of Cl₂ on Hg captured and oxidized by dry FGD ash samples.

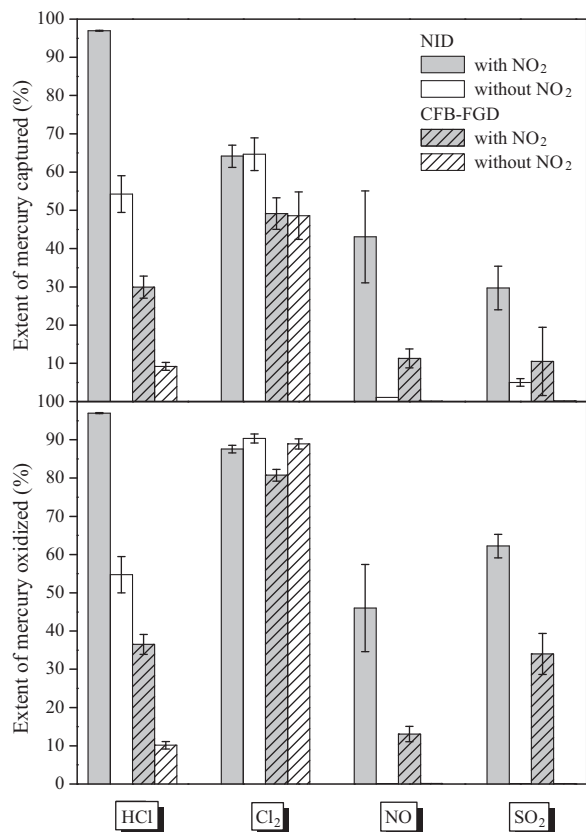


Fig. 6. Effects of NO₂ on Hg captured and oxidized by dry FGD ash samples.

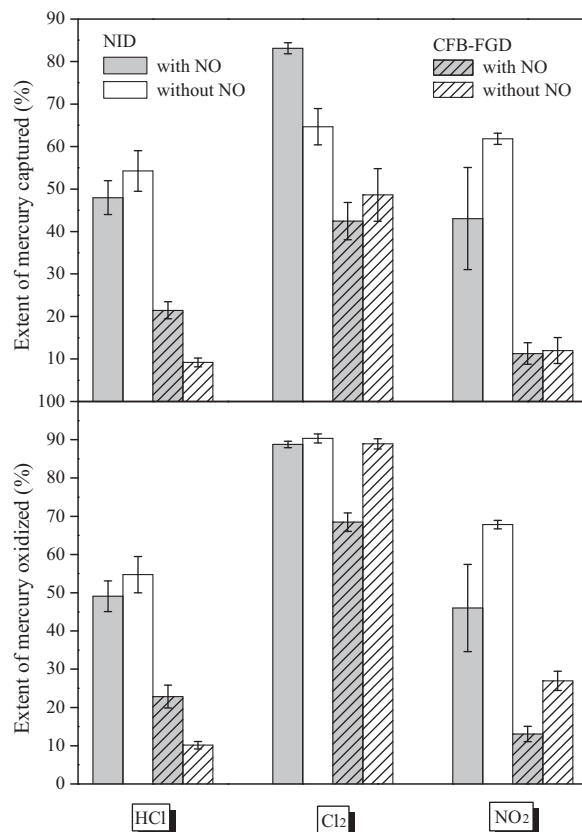


Fig. 8. Effects of NO on Hg captured and oxidized by dry FGD ash samples.

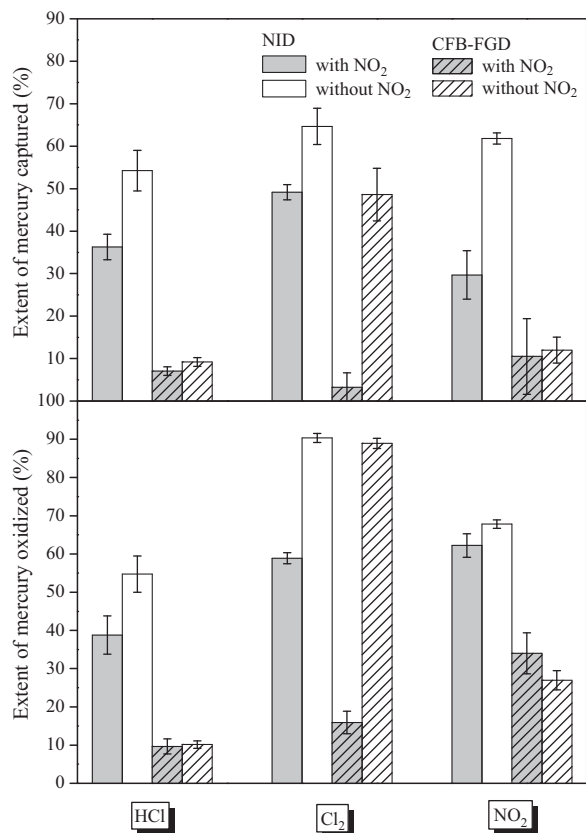


Fig. 7. Effects of SO₂ on Hg captured and oxidized by dry FGD ash samples.

in which significant amounts of mercury oxidation were observed in the absence of SO₂. For example, when only HCl was added to baseline blend, the amount of mercury capture by NID ash sample was about 54%. When SO₂ was also added, the amount of Hg⁰ capture by NID ash sample decreased to 36%. It has been reported that SO₂ competed with HCl for carbon sites on activated carbon and fly ash sorbents [16]. High concentrations of SO₂ were observed to inhibit mercury oxidation in simulated flue gases perhaps because of this competition for sites [17]. However, in some cases, SO₂ appeared to enhance oxidation [18] or have no effect [19,20].

Effects of NO on Hg capture and oxidation were similar to SO₂. The NO inhibited mercury capture and oxidation in most cases except for case adding NO to gas matrix contained HCl. Niksa et al. reported that NO either promoted or inhibited mercury oxidation, depending on the NO concentration [21]. They found that the impact of NO on homogeneous Hg⁰ oxidation was surprisingly strong, capable of inhibiting Hg⁰ from being oxidized through the elimination of OH radicals via reaction (5):



Other researchers postulated that a likely reaction between Hg⁰ and NO₂ produced HgO and NO via reaction (6) [13]:



If this is true, then adding NO to the gas stream contained NO₂ would tend to drive the reaction to the left and inhibit mercury oxidation by this mechanism. Therefore, effects of SO₂ and NO on mercury capture and oxidation were more complicated. Sorbents component and gas concentration might play important roles. However, in most cases, both SO₂ and NO inhibited mercury capture and oxidation.

3.3. Effects of dry FGD ash

Differences on trend of mercury capture in the same gas matrix indicated that dry FGD ash also played an important role in mercury oxidation chemistry. The greatest degree of mercury capture was observed when combination of HCl and NO₂ was added to the baseline blend for NID ash (Fig. 4), but for CFB-FGD ash, it was observed when combination of Cl₂ and NO₂ was present (Fig. 6). As can be seen from those histograms (Figs. 4–8), extents of mercury capture by NID ash samples were higher than by CFB-FGD ash samples in same conditions.

Dry FGD ash was the mixture of fresh desulfurizer, unreacted desulfurizer, desulfurization products and fly ash. Therefore, it should appear the characteristics of both calcium-based sorbent and fly ash during the fixed-bed tests for mercury adsorption. Component analysis of both samples (Tables 2 and 3) indicated that NID ash sample contained more fly ash, while CFB-FGD ash sample contained more calcium-based sorbent. It could be speculated that, during the fixed-bed tests, NID ash sample appeared more closed to fly ash compared to CFB-FGD ash sample, and the later showed more feature of calcium-based sorbent.

To date, most of the research in carbon-based catalysts had focused on fly ash, and this bias is likely coincidental [22]. Mercury oxidation on fly ash particles was believed to take place at carbon sites in the ash [23], hence more unburned carbon content resulted in more extent of mercury oxidation [24]. Since NID ash sample contained more unburned carbon than CFB-FGD ash sample, Hg capture and oxidation capabilities of the former were greater than the latter.

Iron and its oxides may catalyze Hg⁰ oxidation [1]. Ghorishi et al. [19] exposed simulated flue gas containing HCl to model fly ashes in a fixed-bed reactor and found that ash containing Fe₂O₃ achieved 90% oxidation of the incident Hg⁰ at 250 °C. Removing Fe₂O₃ from the model ash resulted in only a 10% conversion of Hg⁰ to Hg²⁺, suggesting that Fe₂O₃ catalyzed Hg⁰ oxidation in the Fe-containing ash. Fe content of NID ash was higher than that of CFB-FGD ash, which was beneficial for the former to show a better performance on mercury oxidation and capture. Mn and Ti may be useful as mercury catalysts under specific conditions [25,26], but effects of both elements could be neglected in our tests.

It should be noted that surface area of CFB-FGD ash sample was larger than that of NID ash sample. Several researchers suggested that the surface area of fly ash played an important role on mercury capture and catalytic oxidation [12,18]. However, it seems that the surface area of dry FGD ash was not a critical factor responsible for mercury capture. Whether the surface area was formed by unburned carbon or by calcium-based sorbent might be more significant than the level of surface area. More work still need to be done to determine the importance of desulfurization products on mercury oxidation.

3.4. Effects of temperature

Temperature plays an important role on mercury adsorption [12,18,27]. In this work, gas components in Table 1 except Cl₂ were mixed to simulate coal-fired flue gas. The results were shown in Fig. 9. In histograms of Fig. 9, sections filled with gray color and slash represented fraction of Hg^p. Sections filled with gray color but without slash represented oxidized mercury at outlet. The two together constituted the total oxidized mercury. When temperature increased, as shown in Fig. 9, extent of mercury capture increased slightly and then decreased.

The overall reaction rates of surface processes for both samples may be limited by either mass transfer from the bulk gas to the surface, or the rates of reactions occurring on the surface (e.g., chemisorption and oxidation). If mercury adsorption was mass

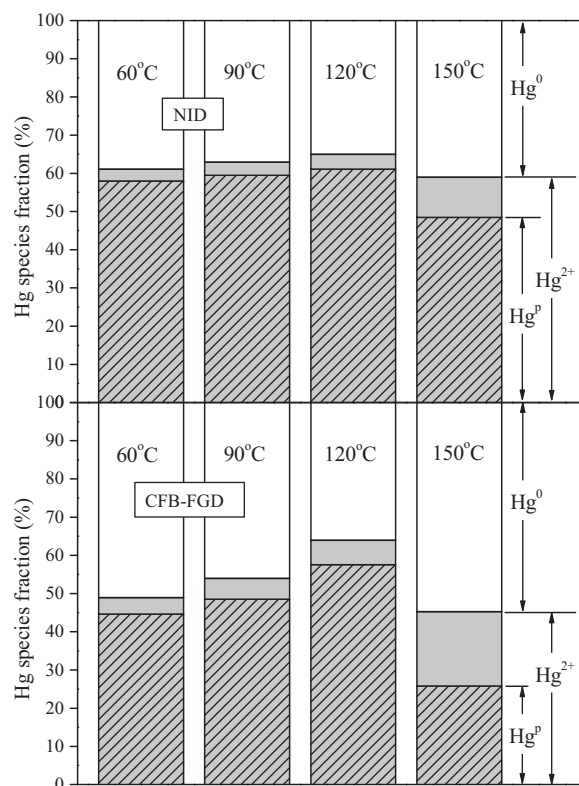


Fig. 9. Effects of temperature on mercury capture and oxidation.

transfer-limited, increasing temperature was a disadvantage for mercury adsorption. If mercury adsorption was kinetic limited, increasing temperature was an advantage for mercury adsorption. Ghorishi studied three types of calcium-based sorbents [28]. Increasing the temperature in the range of 65–100 °C caused an increase in the Hg⁰ capture by the two Ca-based sorbents. On the contrary, Dunham et al. [12] reported an inhibitory effect of increasing temperature on mercury capture by fly ash samples. The inverse effect of temperature on mercury oxidation and capture that had been widely observed suggested that physical adsorption was an important limiting step, since the rates of the subsequent surface reactions would be expected to increase with increasing temperature [1].

Dry FGD ash was the mixture of fresh desulfurizer, unreacted desulfurizer, desulfurization products and fly ash, so it showed features of both calcium- and carbon-based sorbents, depending on their fractions. Unburned carbon had strong catalytic ability, so gas phase transfer to carbon surface was the bottleneck of the overall reaction for mercury capture. This indicated that mercury capture by carbon-based sorbents was mass-transfer controlled. Decreasing temperature promoted the physical adsorption, however, since mercury capture capacity of Ca(OH)₂ was weaker than that of carbon-based sorbent, residence time might be not enough for reactions between Hg atoms and oxidative gas molecules on binding sites. As a result, mercury capture by calcium-based sorbents was kinetically controlled. The dry FGD ash contained both calcium- and carbon-based sorbents, and both types of sorbents effected the adsorption of mercury. Higher temperature inhibited mass transfer from the bulk gas to the surface, and mercury capture by dry FGD ash was mass-transfer controlled. Whereas lower temperature decreased the reaction rates for mercury capture, and mercury capture by dry FGD ash was kinetically controlled. Therefore, a specific equilibrium temperature existed. At this temperature, Hg atoms and oxidative gas molecules adsorbed on the surface were suffi-

cient, and reaction rates between them on binding sites were fast enough.

4. Conclusions

Samples from NID and CFB–FGD absorbers were tested in a fixed-bed reactor using elemental mercury in simulated flue gas mixtures. Both samples were characterized for surface area, unburned carbon, mineralogical composition, elements contents and original mercury contents. The results indicated that Hg⁰ vapor could hardly be captured by dry FGD ash if only N₂ and Hg⁰ vapor were present in the gas mixture. It could be speculated that mercury adsorbed on the surface of samples was mainly in oxidized form. The NO₂, HCl, and Cl₂ promoted mercury oxidation, and mercury oxidation by the three oxidative components with the catalysis of FGD ash could be accumulated in most cases. Significant homogeneous Hg oxidation by Cl₂ might suppress the catalysis between mercury and dry FGD ash samples. On the other hand, SO₂ and NO had inhibitory effects on mercury oxidation. Higher levels of mercury oxidation were associated with higher levels of mercury capture. However, more work is needed to determine the importance of desulfurization products on mercury oxidation. Unburned carbon in FGD ash samples also played important roles in mercury capture. Whether the surface area was caused by unburned carbon or by calcium-based sorbents might be more significant than the level of surface area. Mercury captured by carbon-based sorbents was mass-transfer controlled, while mercury captured by calcium-based sorbents was kinetically controlled. As both types of FGD ash samples contained carbon- and calcium-based sorbents, a specific equilibrium temperature existed, at which Hg atoms and oxidative gas molecules adsorbed on the surface were sufficient, and reaction rates between them on binding sites were fast enough.

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