

Enhanced Elemental Mercury Removal from Coal-Fired Flue Gas by Sulfur–Chlorine Compounds

NAI-QIANG YAN,^{†,‡} ZAN QU,^{†,‡} YAO CHI,[‡] SHAO-HUA QIAO,[‡] RAY L. DOD,[†] SHIH-GER CHANG,^{†,*} AND CHARLES MILLER[§]

Environmental Energy Technology Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, and National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15326

Received July 10, 2008. Revised manuscript received May 24, 2009. Accepted June 5, 2009.

Oxidation of Hg⁰ with any oxidant or converting it to a particle-bound form can facilitate its removal. Two sulfur–chlorine compounds, sulfur dichloride (SCl₂) and sulfur monochloride (S₂Cl₂), were investigated as oxidants for Hg⁰ by gas-phase reaction and by surface-involved reactions in the presence of flyash or activated carbon. The gas-phase reaction between Hg⁰ and SCl₂ is shown to be more rapid than the gas-phase reaction with chlorine, and the second order rate constant was $9.1(\pm 0.5) \times 10^{-18}$ mL·molecules⁻¹·s⁻¹ at 373 K. The presence of flyash or powdered activated carbon in flue gas can substantially accelerate the reaction. The predicted Hg⁰ removal is about 90% with 5 ppm SCl₂ or S₂Cl₂ and 40 g/m³ of flyash in flue gas. The combination of activated carbon and sulfur–chlorine compounds is an effective alternative. We estimate that co-injection of 3–5 ppm of SCl₂ (or S₂Cl₂) with 2–3 Lb/MMacf of untreated Darco-KB is comparable in efficiency to the injection of 2–3 Lb/MMacf Darco-Hg-LH. Extrapolation of kinetic results also indicates that 90% of Hg⁰ can be removed if 3 Lb/MMacf of Darco-KB pretreated with 3% of SCl₂ or S₂Cl₂ is used. Mercuric sulfide was identified as one of the principal products of the Hg⁰/SCl₂ or Hg⁰/S₂Cl₂ reactions. Additionally, about 8% of SCl₂ or S₂Cl₂ in aqueous solutions is converted to sulfide ions, which would precipitate mercuric ion from FGD solution.

Introduction

Mercury is emitted from coal-fired power plants in either oxidized form or as elemental mercury, Hg⁰, and either in the particulate or vapor phase, with the most difficult to control being vapor-phase Hg⁰, because of its high volatility and low solubility in water. Existing air pollution control devices (APCDs) have demonstrated that some degree of mercury control can be achieved as a co-benefit (1–5). However, the efficiency of mercury removal varies significantly depending on coal rank, flyash properties, and APCD

configurations. Particulate mercury can be easily removed by electrostatic precipitators or fabric filters (1), and vapor-phase oxidized mercury will usually deposit on particles in the gas stream and be removed with them. A high percentage of any gaseous oxidized mercury remaining in flue gas after particulate removal can be removed in a wet flue gas desulfurization (FGD) system.

Vapor phase Hg⁰, being highly volatile and insoluble in water, is not readily removed by existing APCDs. The challenge is to find a cost-effective method to convert the Hg⁰ to an oxidized or particle-bound form during its short residence time in the ducts before it encounters the APCDs. The Hg⁰ oxidation methods used for this include heterogeneous catalysis and homogeneous gas-phase oxidation (4–11). The catalysts used in selective catalytic reduction (SCR) of NO_x have shown significant success in mercury oxidation when the chlorine concentration in flue gas is high, such as is typically the case for bituminous coal combustion (4). The lower chlorine content of lower rank coals greatly reduces the efficiency of mercury oxidation by SCR catalysts (2, 5). Furthermore, for utilities without SCR apparatus installed, it is not obvious that installation for the sole purpose of removing elemental mercury would be cost-effective.

Injection of gaseous oxidants into the flue gas to oxidize Hg⁰ is relatively simple to implement. The challenge is the selection of the proper oxidants to be utilized (6–11). Given the short residence time of flue gas in the ducts and/or APCDs (typically less than 10 s), the reaction between Hg⁰ and the oxidant(s) needs to be rapid. In addition, the oxidation products need to be stable and environmentally benign. We report here investigation of multifunction oxidants which both oxidize and chemically stabilize the mercury.

Mercuric sulfide is one of the most stable and insoluble of mercury compounds, and thus any process that produces HgS would meet the product stability test. Elemental sulfur and H₂S, while readily available, were unable to efficiently oxidize Hg⁰ within the limited time available. We expected that a sulfur halide would be more active as an oxidant than elemental sulfur, and sulfur mono- and dichloride are widely used as sulfuring reagents in the rubber industry (12). Sulfur chlorides can be produced by mixing elemental sulfur and chlorine gas at about 373 K. The current market cost is \$0.4–0.5 per pound.

Based on the above considerations, we performed a series of experiments to determine the gas-phase reaction rate constants for the oxidation of Hg⁰ by sulfur chlorides, the effect on the reaction rate of the main components of flue gas (including flyash), and the main reaction products.

Experimental Section

Gas-Phase Reaction of Hg⁰. The reaction kinetics and removal efficiency for elemental mercury oxidation were studied with in situ monitoring of the concentration of Hg⁰ in the reactor as a function of time by a mercury cold vapor atomic absorption spectrophotometer (CVAAS) described previously (8, 9). A reference beam was added to minimize the noise in the monitoring signal, improving the sensitivity of the system.

Reactions Involving Particles. With a laboratory-scale system it is difficult to evenly disperse fine particles in the gas. Simulation can be achieved by coating the particles on the reactor wall (9), but this introduces a diffusion-limitation factor in processing. To minimize the diffusion-limitation factor, a new reactor was developed to test the reaction in the presence of particles (flyash or activated carbon). The reactor is a stainless steel cylinder of 105 mm inner diameter

* Corresponding author phone: (510) 486-5125; fax: (510) 486-7303; e-mail: sgchang@lbl.gov.

[†] Lawrence Berkeley National Laboratory.

[‡] Shanghai Jiao Tong University.

[§] National Energy Technology Laboratory.

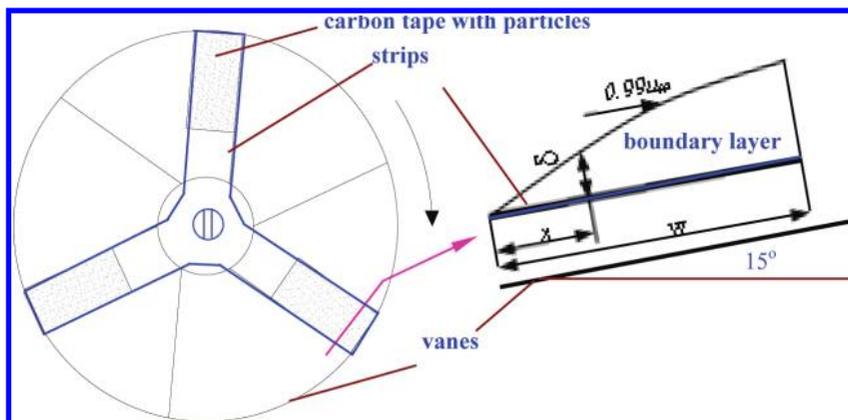


FIGURE 1. Schematic diagram of the stirrer with vanes and strips.

and a volume of 1100 mL. A rotating 6-vane stirrer, driven by a magnetic rotor, was installed inside the reactor. The diameter of the stirrer was 80 mm and its speed could be varied from 0 to 1500 rpm. Another stirrer consisting of three thin metal strips (10 mm wide and 30 mm long for each strip) was fixed to the stirrer to hold the particles which were attached with double coated carbon tape (Figure 1). To characterize the reactor's behavior, Darco-Hg-LH (denoted with AC-LH below), a commercial sorbent (brominated powdered activated carbon) which has been widely utilized in field and demonstrations for coal-fired mercury capture (1, 11), was employed as reference.

Materials and Analysis. The reactor wall was completely coated with a halocarbon wax (HC, Series-1500) to minimize adsorption and surface effects. The effects of SO₂, NO, and CO on Hg⁰ removal were investigated. Sulfur dichloride (SCl₂, 80%) and sulfur monochloride (S₂Cl₂, >98%) were from Sigma-Aldrich and Shandong Zibo Chemical plant. Both were purified by distillation before use. Elemental mercury (99.99%) and chloroform (99.99%) were from Sigma-Aldrich. Nitric oxide (>99%), carbon monoxide (9.8%), and sulfur dioxide (>99%) were from Matheson Co. and Dalian Date Standard Gas Co. Halocarbon wax was from Halocarbon Product Co., and Darco-KB/Darco-Hg-LH was from Norit American Company. A flyash (flyash-L) from burning lignite was tested. The loss of ignition (LOI) and BET surface area of the flyash-L were measured to be 1.3% and 6.56 m²/g and the BET surface area of unburned carbon in flyash-L is calculated to be 398 m²/g (9).

The Hg⁰ concentration in the reactor was measured *in situ* by CVAAS with a time resolution of 20 ms. The concentration of sulfur dichloride gases was measured with a UV/vis spectrometer at 195 nm, calibrated by FTIR at 525 cm⁻¹ (13). S₂Cl₂ was measured by UV/vis spectroscopy at its maximum absorbance at 258 nm. The uncertainties in the measured concentrations of Hg⁰ and sulfur chlorides were ±0.005 ppm and ±2 ppm, respectively. The accuracy of the data reported here was estimated to be within 20%.

Results and Discussion

Hg⁰ Removal by Gas-Phase Reaction. The oxidation efficiency of elemental mercury by sulfur dichloride and sulfur monochloride as a function of the reaction time is shown in Figure 2. Results for chlorine and elemental sulfur are shown for comparison. As can be seen, both sulfur dichloride and sulfur monochloride were more effective in oxidizing elemental mercury than chlorine gas. When the oxidant concentration was kept around 85 ppm, the oxidation efficiencies at a reaction time of 40 s were about 3%, 9%, and 50% for Cl₂, S₂Cl₂, and SCl₂, respectively.

The data shown in Figure 2 show the reactions between Hg⁰ and the oxidants to have pseudo-first-order rate kinetics.

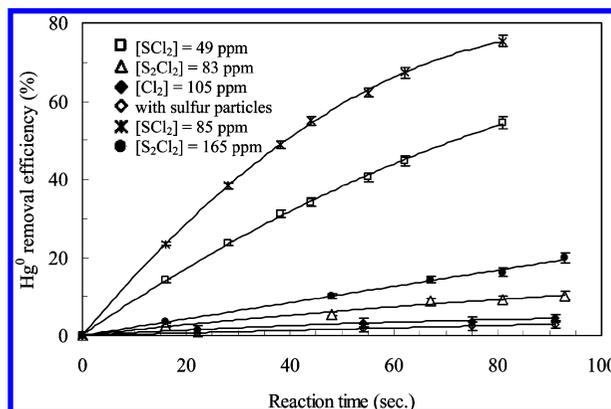


FIGURE 2. Hg⁰ removal efficiency by sulfur and/or chlorine containing compounds at 1 atm and 373 K as a function of reaction time. The initial Hg⁰ concentration was 0.08 ppmv.

The oxidation rate of Hg⁰ also appears to be directly proportional to the oxidant concentration. Therefore, it can be concluded that the gas-phase reactions of Hg⁰/SCl₂ or Hg⁰/S₂Cl₂ are second-order with respect to Hg⁰ and SCl₂ or S₂Cl₂, as expressed by eq 1 (13):

$$-dC/dt = k_2[X]C \quad (1)$$

where C is the Hg⁰ concentration in the gas phase, and $[X]$ denotes the concentration of SCl₂ or S₂Cl₂, molecules · mL⁻¹ in N₂ and k_2 is the second-order rate constant. The rate constants from our data are

$$9.1(\pm 0.5) \times 10^{-18} \text{ mL} \cdot \text{molecules}^{-1} \cdot \text{s}^{-1} \text{ for Hg/SCl}_2 \text{ and} \\ 4.2(\pm 0.5) \times 10^{-19} \text{ mL} \cdot \text{molecules}^{-1} \cdot \text{s}^{-1} \text{ for Hg/S}_2\text{Cl}_2$$

at 373 ± 2 K and 760 Torr. A second-order rate constant for Hg⁰/Cl₂ has been previously reported (8), and the reaction rate constant for Hg/SCl₂ is nearly 2 orders of magnitude larger than that for Hg/Cl₂, while the reaction rate constant for Hg/S₂Cl₂ was much less, only slightly higher than that of Hg/Cl₂. If the effects of other flue gas constituents are not considered, neither SCl₂ nor S₂Cl₂, despite having larger reaction rate constants than Cl₂, is sufficiently effective in the removal of elemental mercury based solely on gas-phase reactions.

In addition, it was found that SCl₂ showed good thermal stability up to 400 K, and increasing the temperature from 297 to 393 K reduced the oxidation efficiency from 39.3% to 24.7% at 30 s. A similar behavior was also apparent for Hg⁰/S₂Cl₂.

Hg⁰ Removal in the Presence of Fly Ash or Powdered Activated Carbon. *Mass Transfer and Hg⁰ Removal.* Since many field studies using AC-LH (Darco-Hg-LH) as a mercury

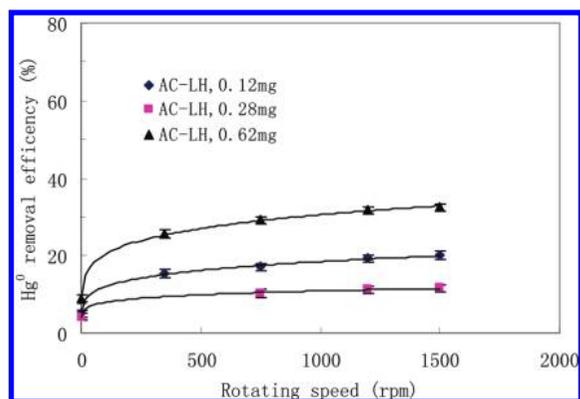


FIGURE 3. Effect of rotating speed on the Hg^0 removal efficiency. About 0.11, 0.28, and 0.62 mg of AC-LH was coated on 0.7, 1.8, and 4 cm^2 , respectively. The contacting time was 20 s at 373 K.

capture sorbent have been reported, it was used to characterize the performance of the reactor and the method. The BET surface area of AC-LH used was about $550 \text{ m}^2/\text{g}$, which was reduced to $340 \text{ m}^2/\text{g}$ when coated onto the carbon tape, a loss of about 35%. The BET surface area of flyash particles decreased by about 30% as attached on the tape.

Pieces of carbon tape with areas of 0.7, 1.8, 4, and 12 cm^2 were coated with 0.11, 0.28, 0.62, and 2 mg, respectively, of AC-LH or Darco-KB. The coated carbon tapes were mounted on metal strips over the stirring vanes. The removal efficiency at various rotation speeds is shown in Figure 3. It is apparent that turbulence from the rotating stirrer helped to increase the Hg^0 removal efficiency in the presence of activated carbon when the rotation speed is low, but higher speeds do not yield proportionate increases. The removal efficiency of Hg^0 observed at 20 s of contact time was 11.6%, 19.8%, and 33.4% with ratios of AC-LH to gas volume of $100 \text{ mg}/\text{m}^3$, $255 \text{ mg}/\text{m}^3$, and $562 \text{ mg}/\text{m}^3$, respectively. To quantitatively describe the effect of the rotation speed on the Hg^0 removal in Figure 3, the mass transfer principle was employed, and the results are listed in Table 1.

The observed depletion of Hg^0 from capture by Darco-Hg-LH conformed to a pseudo-first-order rate constant at various rotating speeds. Thus, the mercury capture rate by Darco-Hg-LH can be described by eq 2.

$$-\frac{dC}{dt} = k_1 C \quad (2)$$

where k_1 is the apparent first-order rate constant. Hg^0 depletion rate includes two components (13, 14): diffusion from the gas phase to the surface of particles with the gas-phase transfer coefficient (k_g); and chemical reaction on the surface with the reaction coefficient (k_s). Equation 3, including both mass transfer and chemical reaction processes, can be formulated.

$$-V \frac{dC}{dt} = k_g A_e (C - C_s) = m_s k_s C_s = K_g m \varepsilon_s C \quad (3)$$

where V is the gas volume, m^3 ; C_s is the local Hg^0 concentration adjacent to the surface; m is the particle mass in the gas, g; ε_s is the specific effective contacting area of the particles with the gas, m^2/g ; A_e is the gas phase diffusion area, and k_g , k_s , and K_g are the gas-phase transfer coefficient, surface reaction coefficient, and overall apparent mass transfer coefficient, m/s , respectively. Therefore, k_1 , C_s , and K_g can be further described as follows.

$$k_1 = \frac{m_s}{V} \varepsilon_s k_s \quad (4)$$

$$C_s = \left(\frac{k_g A_e}{k_g A_e + k_s m \varepsilon_s} \right) C \quad (5)$$

$$\frac{1}{K_g m \varepsilon_s} = 1 / \left(\frac{1}{k_g A_e} + \frac{1}{k_s m \varepsilon_s} \right) \quad (6)$$

Additionally, the gas phase mass transfer coefficient, k_g , can be further described with eqs 7 and 8 (14).

$$k_g = \frac{D_{\text{Hg}} Sh_x}{x} \quad (7)$$

$$Sh_x = f Re_x^a Sc^b \quad (8)$$

where x is the characteristic length parameter for various shapes of the objects. $Re_x (= (\rho x v_r) / (\mu))$, $Sc (= (\rho \mu) / (\eta))$, and Sh_x are the Reynolds number, Schmidt number, and Sherwood number, respectively. D_{Hg} is diffusion coefficient of Hg^0 in the gas phase, which is about $2 \times 10^{-5} \text{ m}^2/\text{s}$ at 373 K; ρ , μ , and v_r are the gas density, viscosity, and the relative gas flow velocity over the surface, respectively. f , a , and b are the constants that are determined by gas flow over the surface.

For tests with particles coated on the rotating strips in the reactor, the gas-phase transfer model can be regarded as a finite plate with gas stream slipping over it (shown in Figure 1, at right). According to the calculation, the flow was at the laminar mode because Re_x was far less than 10^5 even at 1500 rpm. Therefore, f , a , and b in eq 8 are 0.644, 0.5, and 0.333, respectively, based on the mass transfer principle (14). The average value of k_g can be calculated by the differential technique, and the results are shown in Table 1. Thus, $k_s \varepsilon_s$ can be evaluated with eqs 4–6.

For demonstration at the 140 MW Meramec Station (1, 13), with a feed rate of 1.5 lb/MMacf ($24 \text{ mg}/\text{m}^3$) and 3.3 lb/MMacf ($53 \text{ mg}/\text{m}^3$) of AC-LH in flue gas, the total mercury removal efficiencies were 75% and 93% using AC-LH. Considering the baseline mercury capture of about 32% (for Hg^0 and Hg^{2+}), the estimated Hg^0 removal efficiencies by just AC-LH were about 63% and 89%. Assuming the gas–solid contact time of 5 s, and the relative velocity between AC-LH particles (about $25 \mu\text{m}$ average diameter) and the gas was about 4 m/s, the gas-phase mass transfer coefficient can be calculated with eqs 5 and 6, and f , a , and b in eq 8 are 1.17, 0.585, and 0.333 for the spherical particles in flowing gas, and the estimated k_g was about $2.4 \text{ m}^{-2} \text{ s}^{-1}$ by assuming the gas solid contact time of 5 s and about 4 m/s for the relative velocity between AC-LH particles (about $25 \mu\text{m}$ average diameter) and the gas. Therefore, the estimated $k_s \varepsilon_s$ and $K_g \varepsilon_s$ were about 9.1 and $8.1 \text{ m}^3/\text{gs}$, respectively, considering the local slips of particles in the turbulent flue gas.

According to Table 1, the gas-phase transfer resistance ($1/k_g A_e$) for the AC-LH coated on the strips was almost equal to the surface reaction resistance ($1/k_s \varepsilon_s$), and the former contributed about 50% to the overall mass transfer rate. But for the case of with AC-LH dispersed in flue gas, the gas-phase transfer coefficient $1/k_g A_e$ was far smaller than $1/k_s \varepsilon_s$, and the depletion rate of Hg^0 was mainly determined by the surface reaction. The difference of $k_s \varepsilon_s$ or $\varepsilon_s K_g$ between this study and the industrial tests can be explained with the gas–solid contacting modes. AC-LH particles in this test were closely coated on the strip with one side not directly exposed to the bulk gas, which can hardly contact with the gas. Even for the surface toward the gas, there also exists a thin gas boundary layer, and it results in the gas-phase diffusion resistance on the fixed particles. Furthermore, gas concentration gradients between the mixer and the farther regions of the chamber because of local circulation around the mixer can be expected to decrease the observed overall mass transfer rate. The deterioration of gas blend between gas near the mixer due to the confined local circulation around

TABLE 1. Evaluated Hg⁰ Mass Transfer and Surface Reaction Parameters under Various Cases^a

cases	$k_g A_e$ (m ³ /s)	$k_s m \epsilon_s$ (m ³ /s)	$k_s \epsilon_s$ (m ³ /g·s)	$K_g \epsilon_s$ (m ³ /g·s)
53 mg/m ³ AC-LH in flue gas (4)	3.4 ^b	0.484	9.1	8.1
24 mg/m ³ AC-LH in flue gas (4)	1.5 ^b	0.221	9.1	8.1
0.62 mg AC-LH, on strips, 300 rpm	2.5×10^{-5}	3.75×10^{-5}	0.0614	0.024
0.62 mg AC-LH, on strips, 750 rpm	3.8×10^{-5}	3.72×10^{-5}	0.0597	0.0302
0.62 mg AC-LH, on strips, 1500 rpm	6.0×10^{-5}	3.67×10^{-5}	0.0596	0.036
0.28 mg AC-LH, on strips, 1500 rpm	3.1×10^{-5}	1.67×10^{-5}	0.0595	0.037
2 mg AC-LH, on strips, 1500 rpm	1.3×10^{-4}	1.2×10^{-4}	0.0603	0.032
10 mg, flyash on strips, 24 ppm SCl ₂ , 1500 rpm	1.2×10^{-4}	2.4×10^{-6}	0.00024	0.00023
2 mg (±0.2), AC-KB, 8.5 ppm SCl ₂ , 1500 rpm	1.3×10^{-4}	1.4×10^{-4}	0.072	0.035

^a The rotating speed was 1500 rpm at 373 K in the present tests, and the relative errors for the calculated data were about ± 10%. ^b A_e was obtained by assuming 5% of AC-LH BET surface (550 m²/g) was directly exposed to the gas phase because less than 10–20% of BET surface was from large pores and meso-pores for most activated carbon. A_e was 1.8, 4, and 12 cm² for 0.28, 0.62, and 2 mg of AC-LH or AC-KB on the strips, respectively.

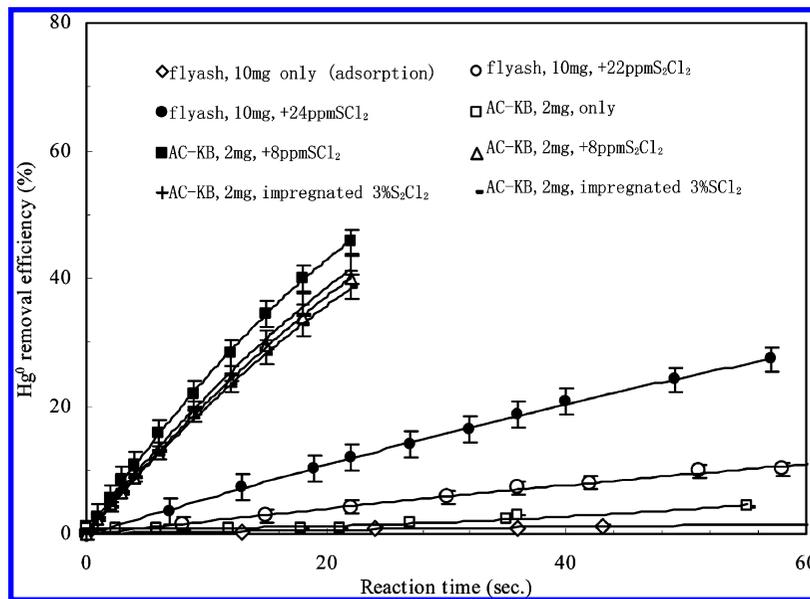


FIGURE 4. Removal efficiency of Hg⁰ by the flyash and activated carbon with sulfur chlorides. The initial Hg⁰ concentration was 0.08 ppm and the rotating speed was 1500 rpm at 373 K.

the mixer, rather than the whole volume, can also decrease the overall mass transfer rate. However, in the large scale experiments, the activated carbon particles were well dispersed in the flue gas, and most of the particles' surface, including part of micropore's surface, is exposed to the flue gas.

In addition, as can be seen from Table 1 $\epsilon_s k_g$ and $\epsilon_s K_g$ for AC-LH in the demonstration were about 150 and 220 times higher than that obtained coated on the strips at 1500 rpm. Therefore, β_{LH} , a ratio defined in eq 9, was used to extrapolate the data for AC-LH from this study to a large scale.

$$\beta_{LH} = \frac{\epsilon_s K_g |_{AC-LH, flue-gas}}{\epsilon_s K_g |_{AC-LH, on-strip}} \quad (9)$$

Hg⁰ Removal in the Presence of Flyash. Flue gas from pulverized coal boilers can contain 30 g/m³ or more of flyash depending on the mineral content in coal. Therefore, the contribution of flyash to mercury capture in the presence of the oxidant was investigated. In the tests, about 10 mg of flyash was coated on carbon tape with 12 cm² of area. Figure 4 shows the removal efficiency of Hg⁰ with flyash only and with sulfur chlorides. It can be seen that the Hg⁰ removal efficiency was significantly greater in the presence of flyash,

and it increased with the amount of flyash in the reactor. The difference between the removal efficiencies of the gas-phase reaction and the reaction with flyash can be regarded as the net contribution of flyash. To evaluate the Hg⁰ capture contribution by the flyash in presence of sulfur chlorides, AC-LH equivalence, E_{LH} , was put forward, and it was defined as the ratio of $\epsilon_s k_s$ for the flyash in the presence of sulfur chloride to that for AC-LH at the similar gas contacting condition (e.g., both coated on the strips).

$$E_{LH} = \frac{\epsilon_s k_s |_{flyash+SCl_2, on-strip}}{\epsilon_s k_s |_{AC-LH, on-strip}} \quad (10)$$

It can be calculated that the E_{LH} was about 0.0041 and 0.0036 g-LH/g-flyash for flyash-L with 24 ppm SCl₂ and 22 S₂Cl₂ in the gas, respectively. Similarly, E_{LH} was about 0.0016 g-LH/g-flyash when 5 ppm SCl₂ was used, and E_{LH} became higher as the concentration of sulfur chlorides increased. Thus, the effect of flyash on the Hg⁰ removal in the presence of sulfur chloride can be equated to the effect of AC-LH with E_{LH} , and then it can be used to evaluate the Hg⁰ removal efficiency in flue gas together with β_{LH} and eq 11.

$$\eta_t = \left[1 - \exp\left(-\frac{m_{\text{flyash}} E_{\text{LH}} \beta_{\text{LH}} \epsilon_s K_g t}{V}\right) \right] \times 100\% \quad (11)$$

Therefore, it can be predicted from eq 11 that the Hg⁰ removal efficiency is about 90% with 40 g/m³ of flyash and about 5 ppm of SCl₂ or S₂Cl₂ in flue gas.

Hg⁰ Removal in the Presence of Activated Carbon. Figure 4 also shows the removal of Hg⁰ in the reactor with Darco-KB activated carbon. Without oxidants, the removal efficiency of Hg⁰ by Darco-KB was very low. However, when about 8 ppm of SCl₂ or S₂Cl₂ was introduced, the removal efficiency increased dramatically, higher than that with the same amount of AC-LH. When the concentration of SCl₂ was decreased to 4 ppm, Hg⁰ depletion efficiency was still close to AC-LH. This indicates that the co-injection of a common powdered activated carbon and SCl₂ or S₂Cl₂ into flue gas containing elemental mercury was rather effective, and the observed efficiency was far higher than with the two used separately. It was estimated from the result of this study that 3–5 ppm of SCl₂ (or S₂Cl₂) combined with about 2–3 Lb/MMacf of untreated Darco-KB was comparable in efficiency to AC-LH.

Additionally, chemically treated Darco-KB, impregnated with SCl₂ or S₂Cl₂, was also prepared and investigated. The observed Hg⁰ removal efficiencies for Darco-KB impregnated with 3% of SCl₂ or S₂Cl₂ are also shown in Figure 4. Their performance in capturing Hg⁰ was just slightly lower than that of AC-LH, and about 90% of Hg⁰ can be removed if 3 Lb/MMacf of such pretreated carbon is added to the flue gas.

Effects of Other Typical Constituents in Flue Gas. The effects of oxygen, water vapor, SO₂, NO, and CO on the gas-phase reaction of Hg/SCL₂ were investigated. Oxygen, SO₂, CO, and water vapor had negligible effect on the gas-phase reaction rate constant; however, NO demonstrated an inhibition, exhibiting 36, 54, and 56% reduction in Hg⁰ removal efficiency with 50, 95, and 180 ppm NO, respectively. But NO appears to have little effect on the removal of Hg⁰ in the presence of flyash or activated carbon.

Analysis of Products and Proposed Reaction Mechanism. The reaction products of Hg/SCL₂ on the interior surface of the reactor were collected by washing with ethanol and soaked with powdered activated carbon. The powders were coated onto carbon tape and analyzed by XPS. It was found that all mercury on the collected sample was present as Hg²⁺.

To get enough products and to observe the variation in the UV-spectrum during the reaction, a 50 mL flask with a magnetic stirrer was employed as a reactor. A drop of elemental mercury (about 0.5 g) was introduced to the sealed flask, and the drop was dispersed by the rotating stirrer. Additional SCl₂ or S₂Cl₂ vapor was quickly introduced into the flask, to an initial concentration of about 2%. The gas constituent variation during the reaction of Hg/SCL₂ was measured with UV-spectroscopy (Figure 5). Initially the concentration of S₂Cl₂ was very low, but it increased as SCL₂ decreased in the early stages of the reaction, indicating that S₂Cl₂ was a significant product of Hg/SCL₂. S₂Cl₂ then decreased as its relatively slower reaction with Hg⁰ proceeded. Additional SCl₂ or S₂Cl₂ was added as necessary until the Hg⁰ was removed. The solid products of Hg/SCL₂ or Hg/S₂Cl₂ appeared to be black or dark gray. In addition, small yellow flecks of elemental sulfur mixed with the products were observed and identified.

The product powders produced from the above reactions were analyzed according to their solubility in various solvents. The products were initially heated at about 373 K to drive off the unreacted SCl₂ or S₂Cl₂ absorbed on the powder. This was followed by extraction of sulfur or S_xCl₂ from the products with carbon disulfide. After drying, mercuric chloride was dissolved from the products with ethanol (99.8%). Finally, a

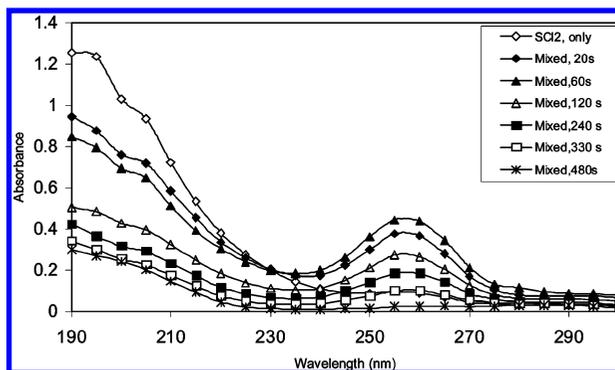
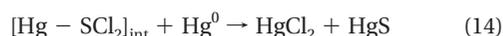
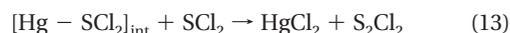
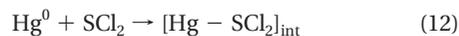


FIGURE 5. Time-dependent UV-spectra of the reaction between Hg⁰ and SCL₂. The maximum absorption peaks of SCL₂ and S₂Cl₂ were at 192 and 258 nm, respectively.

20% Na₂S solution was used to dissolve mercuric sulfide from the residual product. The weight loss in each washing step was used to calculate the content of sulfur, mercuric chloride (HgCl₂), and mercuric sulfide (HgS) in the product. The product distribution with SCL₂ as the oxidant was 74.5% HgCl₂ and 25.5% HgS at a SCL₂/Hg⁰ ratio of 2.0; and 46.0% HgCl₂ and 54.0% HgS at a SCL₂/Hg⁰ ratio of 0.3. When S₂Cl₂ was used as the oxidant, 12.6% HgCl₂ and 87.4% HgS at a S₂Cl₂/Hg⁰ ratio of 1.0; and 31.4% HgCl₂ and 68.6% HgS at a S₂Cl₂/Hg⁰ ratio of 0.2 were obtained. Apparently, HgS was the main product of Hg⁰/S₂Cl₂, and its percentage was greater at higher ratios of oxidant to elemental mercury. Though the reaction of Hg⁰/S₂Cl₂ was slower, it produced a higher percentage of HgS than did Hg⁰/SCL₂.



This work shows that SCL₂ can be effective in oxidizing Hg⁰ to form mercuric chloride and mercuric sulfide. We expect that Hg⁰ removal efficiency would be about 90% with 40 g/m³ of flyash and about 5 ppm of SCL₂ or S₂Cl₂ in flue gas. The amount of byproducts from the reaction of sulfur chlorides with flue gas components, such as SO₂ and NO_x, are expected to be insignificant based on the FTIR results. Moreover, the byproducts, such as SO₂Cl and NOCl, will undergo hydrolysis and be neutralized by alkaline slurry in the SO₂ scrubber located downstream. The formation of toxic byproducts is clearly not an issue and the conversion of mercury into a benign and stable HgS is the purpose for using sulfur chloride as oxidants.

The addition of powdered activated carbon to sulfur chloride compounds in flue gas can result in even greater Hg⁰ removal efficiency. We estimate that co-injection of 3–5 ppm of SCL₂ (or S₂Cl₂) with 2–3 Lb/MMacf of untreated Darco-KB is comparable in efficiency to the injection of 2–3 Lb/MMacf Darco-Hg-LH. Extrapolation of kinetic results also indicates that 90% of Hg⁰ can be removed if 3 Lb/MMacf of Darco-KB pretreated with 3% of SCL₂ or S₂Cl₂ is used.

Moreover, since SCL₂ and S₂Cl₂ are soluble in water, the residual amounts are easily absorbed by a wet FGD scrubber. In addition to their abilities to oxidize Hg⁰ and convert some of Hg⁰ directly to HgS, sulfide ions were produced in FGD solutions which can precipitate mercuric ion from solution as the very stable HgS, thus reducing the re-emission of mercury from the FGD liquor. The potential of SCL₂ or S₂Cl₂ to oxidize and stabilize elemental mercury in coal-fired flue gases is clearly promising for further study at a larger scale.

Acknowledgments

This work was supported by the Assistant Secretary for Fossil Energy, U.S. Department of Energy, under contract DE-AC02-05CH11231 through the National Energy Technology Laboratory, and was partially supported by the National High Technology Research and Development Program of China (2007AA06Z340) through international cooperation.

Literature Cited

- (1) Jones, A. P.; Hoffman, J. W.; Feeley, T., III; Murphy, J. T. DOE/NETL's Phase II Mercury Control Technology Field Testing Program: Preliminary Economic Analysis of Activated Carbon Injection. *Environ. Sci. Technol.* **2007**, *41*, 1365–1371.
- (2) Kellie, S.; Cao, Y.; Duan, Y.; Li, L.; Chu, P.; Mehta, A.; Carty, R.; Rile, J. T.; Pan, W. P. Factors Affecting Mercury Speciation in a 100-MW Coal-Fired Boiler with Low-NO_x Burners. *Energy Fuels* **2005**, *19*, 800–806.
- (3) Blythe, G.; Richardson, C.; Rhudy, R. Pilot Evaluation of the Catalytic Oxidation of Mercury for enhanced Removal in Wet FGD Systems. In *Proceedings of Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, September 9–12, 2002*; Energy and Environmental Research Center, University of Dakota: Grand Fork, ND, Sept. 2002.
- (4) Presto, A. A.; Granite, E. J. Survey of Catalysts for Oxidation of Mercury in Flue Gas. *Environ. Sci. Technol.* **2006**, *40*, 5602–5609.
- (5) Wu, Z. B.; Jiang, B. Q.; Liu, Y.; Wang, H. Q.; Jin, R. Drift study of manganese/titania-based catalysts for low-temperature selective catalytic reduction of NO with NH₃. *Environ. Sci. Technol.* **2007**, *41*, 5812–5817.
- (6) Hall, B. Gas phase oxidation of elemental mercury by ozone. *Water, Air Soil Pollut.* **1995**, *80*, 301–315.
- (7) Kaczur, J. Oxidation chemistry of chloric acid in NO_x/SO_x and air toxic metal removal from gas streams. *Environ. Prog.* **1996**, *15*, 245–254.
- (8) Yan, N. Q.; Liu, S. H.; Chang, S. G.; Miller, C. Method for the study of gaseous oxidants for the oxidation of mercury gas. *Ind. Eng. Chem. Res.* **2005**, *44*, 5567–5574.
- (9) Liu, S. H.; Yan, N. Q.; Liu, Z. R.; Chang, S. G.; Miller, C. Using bromine gas to enhance mercury removal from flue gas of coal-fired power plants. *Environ. Sci. Technol.* **2007**, *41*, 1405–1412.
- (10) Hall, B.; Schager, P.; Lindqvist, P. Experimental study on the rate of reaction between mercury vapour and gaseous nitrogen dioxide. *Water, Air Soil Pollut.* **1995**, *81*, 121–134.
- (11) Feeley, T. J., III; Brickett, L. A.; O'Palko, B. A.; Murphy, J. T. Field Testing of Mercury Control Technologies for Coal-Fired Power Plants, DOE/NETL Mercury R&D Program Review; Pittsburgh, PA, May 2005.
- (12) Gholiv, K.; Eslami, A. Is sulfur dichloride unstable? *Phosphorus, Sulfur Silicon* **1996**, *1*, 269–281.
- (13) Benson, S. W. *The Foundation of Chemical Kinetics*; McGraw-Hill: New York, 1960.
- (14) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*, 2nd ed.; John Wiley and Sons: New York, 2002.

ES801910W