

# Oxidation and Stabilization of Elemental Mercury from Coal-Fired Flue Gas by Sulfur Monobromide

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Sulfur monobromide ( $S_2Br_2$ ) was employed as a task-specific oxidant to capture and stabilize elemental mercury from coal-fired flue gas. Its performances on the removal of  $Hg^0$  were investigated with respect to the gas-phase reaction and particle-involved reactions. It was found that the gas-phase reaction between  $Hg^0$  and  $S_2Br_2$  was rapid, and the determined second-rate constant was about  $1.2(\pm 0.2) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  at 373 K, which was about 30 times higher than that with sulfur monochloride. The pilot tests showed that the presence of fly ash in flue gas can accelerate the removal of  $Hg^0$  significantly. It was predicted that about 90% of  $Hg^0$  removal efficiency can be obtained with 0.6 ppmv  $S_2Br_2$  and 30 g/m<sup>3</sup> fly ash in flue gas, and the unburned carbon in fly ash played an important role for  $Hg^0$  removal. The fates of  $S_2Br_2$  and mercury in the process were evaluated, and the product analysis and leaching tests indicated that mercuric sulfide was the main product of the converted  $Hg^0$  by the direct reaction and consequent series reactions, which is more stable and less toxic than other mercury species. Also, the surplus  $S_2Br_2$  in flue gas could be captured and neutralized effectively by the alkali components in fly ash or FGD liquor, and its hydrolysis products (elemental sulfur and sulfide) were also helpful to the stabilization of mercury. The result indicated that  $S_2Br_2$  is a promising oxidant for elemental mercury ( $Hg^0$ ) oxidation and stabilization for mercury emission control.

## Introduction

Coal-fired power plants are one of the major anthropogenic sources for mercury emission (1). In China, nearly 40% of the annual total emitted mercury has been from coal-fired utilities (2). Therefore, the control of mercury emission from coal-fired utilities is vital to mitigate global mercury pollution. There are three basic forms of mercury in flue gas: oxidized mercury ( $Hg^{2+}$ ), particulate-bound mercury ( $Hg^p$ , mainly  $Hg^{2+}$  adsorbed on fly ash), and elemental mercury ( $Hg^0$ ) (3). The particulate-bound mercury and oxidized mercury could be captured by existing air pollution control devices (APCDs), such as the electrostatic precipitator (ESP), fabric filters (FF), and flue gas desulfurization (FGD) (3–8). However, it is still difficult to directly remove  $Hg^0$  from flue gas with these APCDs because of its high volatility and insolubility in water (6, 9). Therefore, additional methods to convert  $Hg^0$  to its oxidized form in or ahead of APCDs are necessary for the effective capture of  $Hg^0$ .

In addition, selective catalytic reduction (SCR) catalysts for the removal of NO have been observed to be helpful to the oxidation of  $Hg^0$  in the presence of enough HCl in flue gas (7, 10). But for the utilities without SCR installation, the injection of oxidant to flue gas is also one of the most simple and effective alternatives for the control of mercury emission (11–14). According to previous studies,  $Hg^0$  conversion in the presence of added oxidant can be enhanced significantly by the entrained fly ash or other particles in flue gas. Because some mercuric compounds (e.g.,  $HgCl_2$  and  $HgBr_2$ ) on the fly ash are readily volatile to atmosphere at higher temperature or leachable by water, the potential secondary pollution of the mercury on the fly ash will become a concerned issue during the utilization of the fly ash or storage in landfills (15, 16). Therefore, it is necessary to find some additives that are capable of converting  $Hg^0$  to more stable products with lower volatilization and leachability.

We have known that sulfur could react with  $Hg^0$  and produce mercury sulfide, which is considered one of the most stable mercuric compounds (insoluble and less volatile). However, the reaction rate between sulfur and  $Hg^0$  appears too slow to meet the industrial application. Recently, we have reported the results of using sulfur chlorides (e.g.,  $SCl_2$  or  $S_2Cl_2$ ) to enhance the removal of  $Hg^0$  in a small experimental setup (14). Though the effectiveness of sulfur chloride on  $Hg^0$  removal has been proved and  $HgS$  was one of the main products, the relatively high demand dosage of sulfur chloride and its safety issue (highly irritative) would probably weaken its technical competition.

Bromine has been demonstrated to be one of the most efficient reagents to oxidize and capture elemental mercury by injecting bromine gas to flue gas or impregnated on activated carbon (5, 12). However, it was expected that most elemental mercury was converted to mercuric bromide, which was still toxic and slightly volatile and leachable from fly ash or activated carbon. Considering the characteristics of bromine and sulfur on the conversion of elemental mercury, sulfur monobromide ( $S_2Br_2$ ) might be a potential task-specific reagent used to capture and stabilize mercury from coal-fired flue gas. Meanwhile, sulfur monobromide was less irritative than  $Br_2$  and sulfur chlorides, which is more convenient for storage, transportation, and application in industry considering the safety issues.

Despite the fact that  $S_2Br_2$  has been known as one of the typical sulfur halides for a long time (17), there still lacks the necessary information on its properties because of its narrow usage in industry. Meanwhile, its performances on  $Hg^0$  capture by the gas-phase or particle-involved reaction need to be investigated, and the fates of the captured mercury and  $S_2Br_2$  in the processes are of interest. Therefore, these aspects will be focused on in this paper.

## Experimental Section

**$S_2Br_2$  Preparation and Properties.**  $S_2Br_2$  is not available commercially, but it can be readily prepared and determined in the laboratory (Supporting Information). Br-S-S-Br was believed to be the predominant product for the stoichiometric sulfur bromide compound according to theoretical calculation and instrumental analysis (17). Moreover, the saturation vapor pressures of  $S_2Br_2$  was determined to be rather low at ambient temperature, so it appeared to be much milder and less irritative compared with bromine and sulfur chlorides, but it can be readily vaporized at higher temperature for its injection to flue gas.

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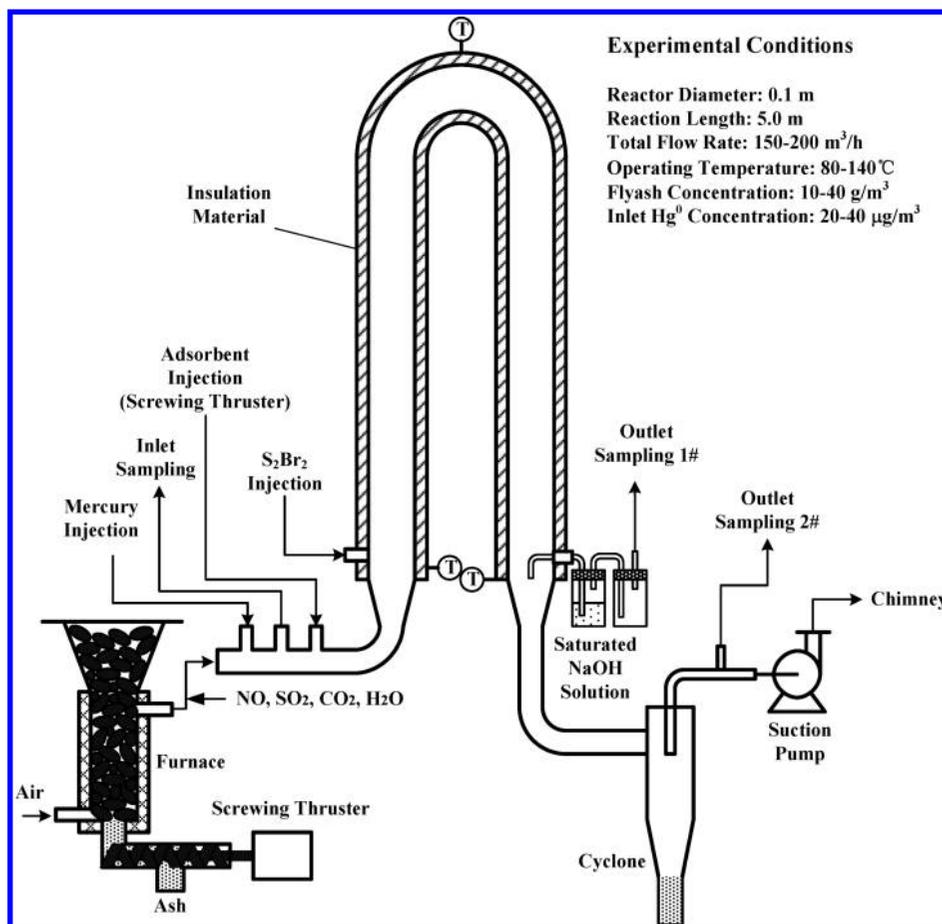


FIGURE 1. Schematic of pilot-scale setup for the removal of elemental mercury with oxidants and/or particulates injection.

**Materials and Analysis.** The fly ash employed in the study was from a 600 MW pulverized-coal boiler (Ash-A) and a 150 MW circulating fluidized boiler (Ash-B). The loss of ignition (LOI, mainly in unburnt carbon) and BET surface area were measured to be 2.1% (wt.) and 2.4 m<sup>2</sup>/g for Ash-A and 1.8% and 3.0 m<sup>2</sup>/g for Ash-B. In order to test the effect of LOI, Ash-A was calcined at 800 °C for 3 h to eliminate its LOI and then employed in the tests (marked as Ash-A\*).

Darco-KB (AC or AC-KB) and Darco-Hg-LH (AC-LH) are the all-purpose activated carbon and the task-specific carbon for mercury capture, respectively, and both are from Norit America Company. Elemental mercury (99.99%), bromine (99.5%), and sulfur (99.99%) were from Sigma-Aldrich Co. Powder graphite (Chemical Pure, ≤30 µm) was from the Sino-Pharm Chemical Reagent Co., Ltd. Nitric oxide (10.0%) and sulfur dioxide (99.9%) were from Dalian Date Standard Gas Co. Halocarbon wax was from Halocarbon Product Co. Specific detecting tubes (Gastec, Japan) for H<sub>2</sub>S and SO<sub>2</sub> measurement during hydrolysis of S<sub>2</sub>Br<sub>2</sub> were from Gastec Co.

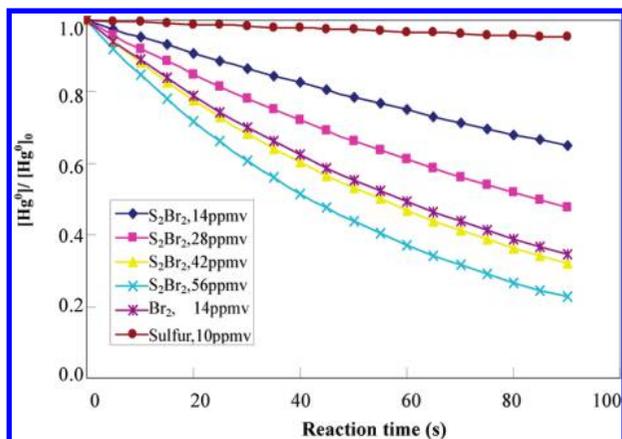
S<sub>2</sub>Br<sub>2</sub> concentration was detected with a model BRC641E UV spectrometer detector and flatbed chart recorder (B&W Tek, U.S.A.). XPS (Perkin-Elmer) was used to determine the valence of mercury on the particles. The BET technique (Brunauer, Emmett, and Teller, ASAP 2010M+C, U.S.A.) was used to test the surface area of the particles. The Hg<sup>0</sup> concentration in the reactor for gas-phase reaction tests was measured in situ by CVAAS. The pilot tests employed Lumex mercury analyzer (RA915, RU) to monitor Hg<sup>0</sup> concentration continuously.

The uncertainties in the measured concentrations of Hg<sup>0</sup> were ±2 and ±0.05 ppbv for in situ CVAAS and Lumex

analyzer, respectively. The accuracy of the data reported here was estimated to be within 10% for the tests.

**Method for Determining the Gas-Phase Reaction between Hg<sup>0</sup> and S<sub>2</sub>Br<sub>2</sub>.** The reaction kinetics for elemental mercury oxidation were tested with in situ monitoring of the concentration of Hg<sup>0</sup> in the reactor as a function of time by a mercury cold vapor atomic absorption spectrophotometer (CVAAS) described previously (11, 12, 14). The tests were performed mainly in a reactor with a volume of 1100 mL, and the experimental procedure was similar to our previous study (11).

**Pilot-Scale Tests with Particle-Involved Reaction.** To test the performance of S<sub>2</sub>Br<sub>2</sub> on mercury capture from the simulated flue gas, a pilot-scale setup was built (Figure 1). It can provide 150–200 m<sup>3</sup>/h of the “semi-actual” flue gas with temperatures from 80 to 140 °C. The initial concentration of Hg<sup>0</sup> was kept at about 20 µg/m<sup>3</sup> in the pilot tests, if it was not stated clearly. In order to investigate the effect of actual flue gas components on mercury removal, SO<sub>2</sub>, NO, CO<sub>2</sub>, and water vapor in the simulated gas were supplied by injecting extra pure gases from the gas cylinders. The reactor was a stainless steel cylinder with the inner diameter of 100 mm and 5.0 m for its valid length. The gas residence time in the reactor was about 0.9 s. The Hg<sup>0</sup> concentration of flue gas was continuously monitored by a Lumex mercury analyzer together with a self-assembled sampling unit and method, which can successfully minimize the interference of SO<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, and fly ash on the continued monitoring of Hg<sup>0</sup> (detail information about pilot-scale tests is in the Supporting Information). In addition, the mass balances of mercury in the inlet and outlet gases were evaluated by Ontario Hydro method (OHM) (13).



**FIGURE 2.** Depletion curves of  $\text{Hg}^0$  by gas-phase reaction with various oxidants at 373 K. The concentration of  $\text{Hg}^0$  was 0.16 ppmv (about  $1400 \mu\text{g}/\text{m}^3$ ), and the performance was at 760 Torrs. Elemental sulfur was attached on the reactor wall, if it was employed.

**Products Determination and Leaching Tests.** The products distribution of  $\text{Hg}/\text{S}_2\text{Br}_2$  was tentatively determined with the multistage dissolution and weighing methods, in which  $\text{CS}_2$ , alcohol, and  $\text{Na}_2\text{S}$  solutions (1M) were used as solvents to separate the residue of  $\text{S}_2\text{Br}_2$ , sulfur,  $\text{HgBr}_2$ , and  $\text{HgS}$  by steps (14). The products were defined as two kinds: primary products and secondary products. The former are the products of  $\text{Hg}/\text{S}_2\text{Br}_2$  without moisture or water involved in the reaction, and the secondary products are from the primary products and the surplus  $\text{S}_2\text{Br}_2$ , which undergoes hydrolysis in water or moisture. The preparation of the primary and secondary products has been described in the Supporting Information. In addition, the hydrolysis products of  $\text{S}_2\text{Br}_2$  in water and aqueous alkali solutions were also determined with various methods, including ionic chromatography for  $\text{Br}^-$  and  $\text{SO}_4^{2-}$  and specific detecting tubes for  $\text{H}_2\text{S}$  and  $\text{SO}_2$ .

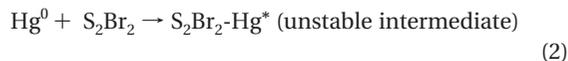
The stabilization of mercury on fly ash or activated carbon was evaluated by a leaching test, which was subjected to the Extraction Procedure Toxicity Test Method and Structural Integrity Test (18, 19). Three samples, activated carbon impregnated with 2.5%  $\text{S}_2\text{Br}_2$  (AC- $\text{S}_2\text{Br}_2$ ), Ash-A with 0.2%  $\text{S}_2\text{Br}_2$  (Ash- $\text{S}_2\text{Br}_2$ ), and Ash-A with 0.2%  $\text{Br}_2$  (Ash- $\text{Br}_2$ ) were tested in leaching tests after adsorbed about  $80 \mu\text{g}/\text{g}$  (AC samples) and  $10 \mu\text{g}/\text{g}$  (Ash-A sample) of  $\text{Hg}^0$ . The mercury soaked solids and extracted liquid were all analyzed (Supporting Information).

## Results and Discussion

**Gas-Phase Reaction between  $\text{Hg}^0$  and  $\text{S}_2\text{Br}_2$ .** The oxidation efficiencies of elemental mercury by  $\text{S}_2\text{Br}_2$  as a function of reaction time are shown in Figure 2, and results of bromine and elemental sulfur are shown as the comparison. As is shown,  $\text{S}_2\text{Br}_2$  was more effective at oxidizing  $\text{Hg}^0$  than sulfur, but it was slightly less effective than bromine with the same concentration. In Figure 2, the depletion of  $\text{Hg}^0$  for all curves under various  $\text{S}_2\text{Br}_2$  concentrations appeared to be exponential to the reaction time, which indicated the reaction conformed to the pseudo first-order with respect to  $\text{Hg}^0$  ( $k_1$ ). Meanwhile, the obtained  $k_1$  values for the curves were nearly linear to the concentration of  $\text{S}_2\text{Br}_2$  ( $k_1 = k_2[\text{S}_2\text{Br}_2]$ ), so the overall reaction can be considered as second-order with respect to  $\text{Hg}^0$  and  $\text{S}_2\text{Br}_2$  as a whole (12).

$$-d[\text{Hg}^0]/dt = k_1[\text{Hg}^0] = k_2[\text{S}_2\text{Br}_2][\text{Hg}^0] \quad (1)$$

where,  $[\text{S}_2\text{Br}_2]$  denotes the concentration of  $\text{S}_2\text{Br}_2$ , molecules in  $\text{mL}^{-1}$ , and  $k_2$  is the second-order rate constant.



Similar to our previous observation and speculation (12, 14),  $\text{Hg}^0$  may react with  $\text{S}_2\text{Br}_2$  first to form an unstable intermediate,  $\text{Hg-S}_2\text{Br}_2^*$  ( $\text{Hg}^0:\text{S}_2\text{Br}_2 = 1:1$ , eq 2) before it forms a stable oxidized state. The formation of intermediate was considered to be the rate-determining reaction step, so the apparent reaction between  $\text{Hg}^0/\text{S}_2\text{Br}_2$  appeared to be second-order. In addition, the rate constant from our data was  $1.2(\pm 0.2) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  for  $\text{Hg}/\text{S}_2\text{Br}_2$  at  $373 \pm 2 \text{ K}$ , which was about one-third of that for  $\text{Hg}/\text{Br}_2$  but almost 30 times higher than that for  $\text{Hg}/\text{S}_2\text{Cl}_2$  (12, 14). This indicated that the bromine atom became less reactive to  $\text{Hg}^0$  after the combination with sulfur, but it was still more active than chlorine.

### Role of Fly Ash on $\text{Hg}^0$ Removal in the Presence of $\text{S}_2\text{Br}_2$ .

Most of flue gas from pulverized-coal boilers or cycling fluidized boiler (CFB) often entrain tens of grams of fly ash per cubic meters (e.g.,  $10\text{--}40 \text{ g}/\text{m}^3$  for the usual) ahead of the particulate collection devices, and the surface-induced reaction by fly ash might play an important role to  $\text{Hg}^0$  removal.

As shown in Figure 3,  $\text{Hg}^0$  removal efficiency was rather low only with  $\text{S}_2\text{Br}_2$  or fly ash alone in flue gas. One ppmv of  $\text{S}_2\text{Br}_2$  in the gas without fly ash can only result in about 5% of  $\text{Hg}^0$  removal. Meanwhile,  $\text{Hg}^0$  removal efficiency was only about 4% and 6% with  $20 \text{ g}/\text{m}^3$  Ash-A and Ash-B, respectively, which indicated that both the ashes showed very weak adsorption to  $\text{Hg}^0$ . However, the coexistence of fly ash and  $\text{S}_2\text{Br}_2$  in the simulated flue gas can remove  $\text{Hg}^0$  effectively.  $\text{Hg}^0$  removal efficiency was about 46% with  $20 \text{ g}/\text{m}^3$  Ash-A and 1 ppmv  $\text{S}_2\text{Br}_2$  in the gas, which was by far higher than the sum of these from gas-phase reaction and adsorption by original fly ash. The results indicated that fly ash showed significant synergetic with  $\text{S}_2\text{Br}_2$  for the removal of  $\text{Hg}^0$ , and it was even better than that with AC-LH (about 34% with  $32 \text{ mg}/\text{m}^3$  or 2 Lb/MMacf of AC-LH in the gas).

In addition, the LOI and its BET surface in fly ash also played an important role on  $\text{Hg}^0$  removal in the presence of  $\text{S}_2\text{Br}_2$ .  $\text{Hg}^0$  removal efficiency decreased to about 13% if the LOI of Ash-A was burnt out (Ash-A\* in Figure 3). Therefore, it was believed that the adsorption of  $\text{S}_2\text{Br}_2$  on the fly ash was the first step, and then the fly ash with adsorbed  $\text{S}_2\text{Br}_2$  can capture  $\text{Hg}^0$  efficiently by chemical adsorption, which performed like AC-LH. The presence of LOI on fly ash and its high BET were helpful to  $\text{S}_2\text{Br}_2$  adsorption on fly ash and resulted in higher  $\text{Hg}^0$  removal efficiency.

Figure 4 illustrates the comparison of  $\text{S}_2\text{Br}_2$  and the other oxidants for  $\text{Hg}^0$  removal in the presence of Ash-A.  $\text{Hg}^0$  removal efficiency with 1 ppmv  $\text{S}_2\text{Br}_2$  was slightly lower than that with 1 ppmv  $\text{Br}_2$  in the gas with the difference of about 5%, and  $\text{S}_2\text{Br}_2$  appeared to be reactive in the particle-involved reaction. In addition, the  $\text{Hg}^0$  removal efficiency with 1 ppmv of  $\text{S}_2\text{Br}_2$  was apparently higher than that with 2 ppmv  $\text{HBr}$  even in the same stoichiometric value of bromine atom, which indicated the bromine atom in  $\text{S}_2\text{Br}_2$  was more reactive to  $\text{Hg}^0$  than in  $\text{HBr}$ . Meanwhile,  $\text{S}_2\text{Br}_2$  appeared to be more effective than  $\text{S}_2\text{Cl}_2$  for  $\text{Hg}^0$  removal, and the efficiency was only about 21% with 1 ppmv  $\text{S}_2\text{Cl}_2$  in the gas at 393 K. This indicated much less dosage of  $\text{S}_2\text{Br}_2$  was demanded than that with  $\text{S}_2\text{Cl}_2$  as the oxidant for the same  $\text{Hg}^0$  removal efficiency. This result can be tentatively explained with the bond energy comparison among  $\text{H-Br}$  (363 kJ/mol),  $\text{S-Cl}$  (213 kJ/mol), and  $\text{Br-S}$  (176 kJ/mol) in the these molecules (20, 21); the weakly bonded  $\text{Br}$  or  $\text{Cl}$  atom in the molecule may show stronger affinity to chemically adsorb  $\text{Hg}^0$  on fly ash and obtain a higher  $\text{Hg}^0$  removal efficiency. Meanwhile,

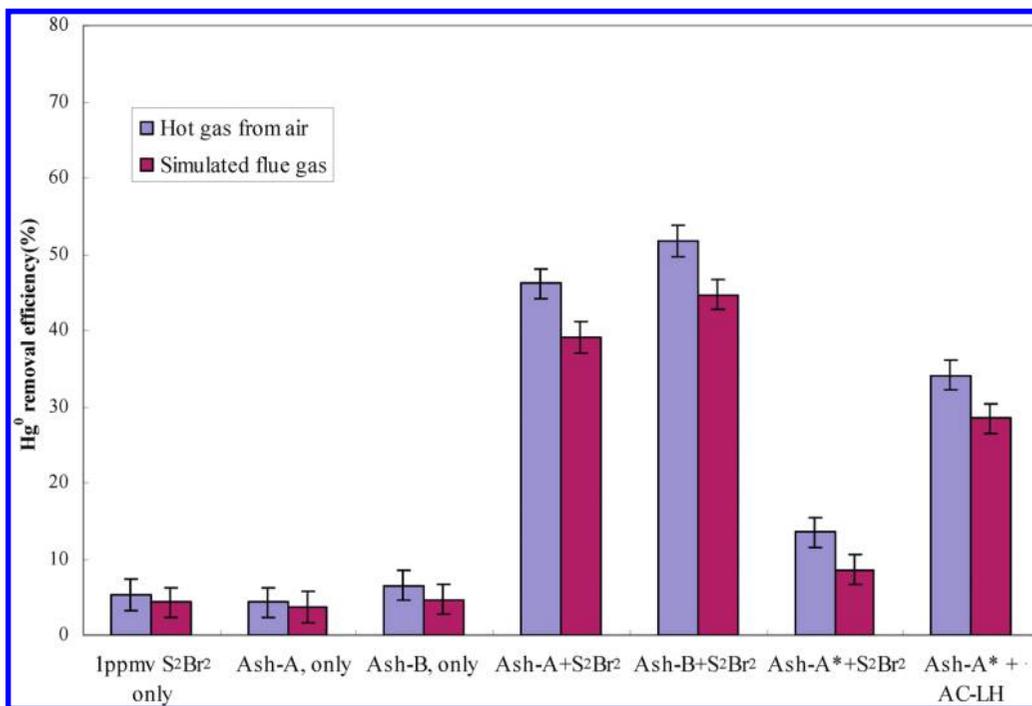


FIGURE 3. Hg<sup>0</sup> removal efficiencies in the presence of fly ash and/or S<sub>2</sub>Br<sub>2</sub> at 393 K. Ash-A\* is the Ash-A that was calcined at 800 °C for 3 h to remove the LOI. The concentration of S<sub>2</sub>Br<sub>2</sub> was 1 ppmv. Fly ash content in the simulated flue gas was 20 g/m<sup>3</sup>, and the dosage of Darco-LH was 32 mg/m<sup>3</sup>, if it was employed. Hot gas from air meant the gas free of SO<sub>2</sub>, CO<sub>2</sub>, and NO, and the simulated gas was composed of SO<sub>2</sub> (1000 ppmv), NO (200 ppmv), CO<sub>2</sub> (2–4%), water vapor (5%), and air as the makeup. Initial Hg<sup>0</sup> concentration in the gas was about 20 μg/m<sup>3</sup>, and the gas resident time was about 0.9 s.

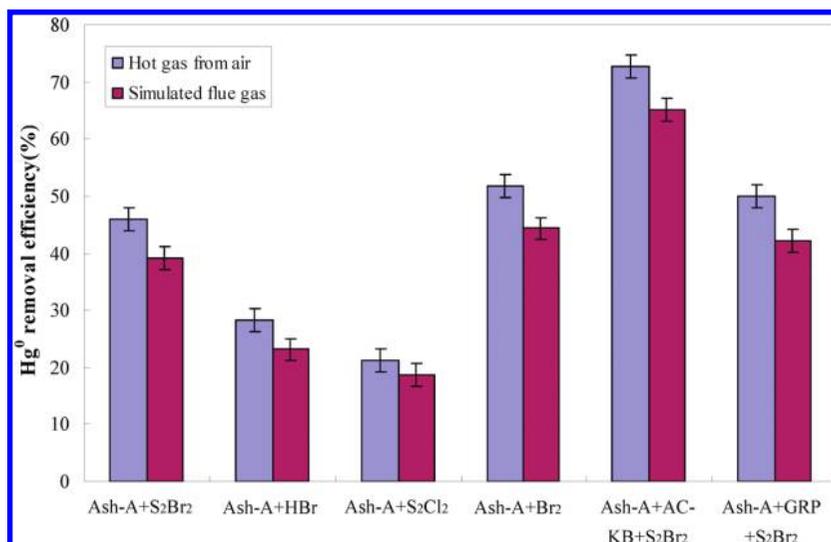


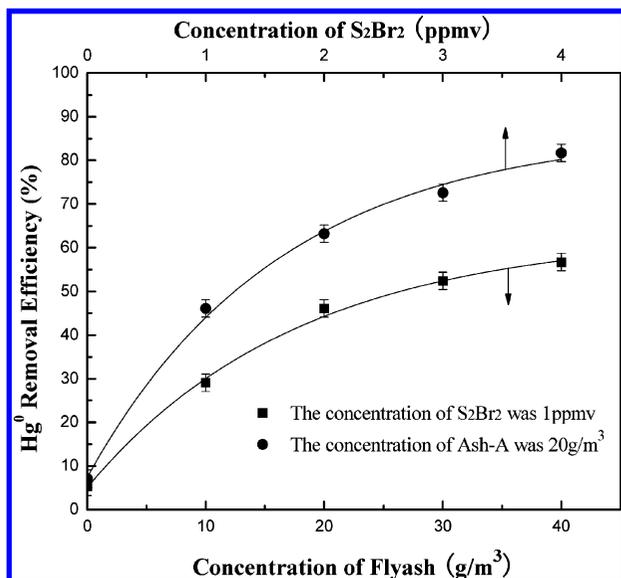
FIGURE 4. Comparison of Hg<sup>0</sup> removal efficiencies in the presence of various oxidants and fly ash or other particles at 393 K. The concentration of HBr, S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, and Br<sub>2</sub> was 2 ppmv, 1 ppmv, 1 ppmv, and 1 ppmv, respectively. AC-KB and GRP represented 32 mg/m<sup>3</sup> of AC-KB and powder graphite added into the gases, respectively. The initial Hg<sup>0</sup> concentration in the gas was about 20 μg/m<sup>3</sup>, and the gas resident time was about 0.9 s.

bromine has been proved to be more effective at capturing Hg<sup>0</sup> than chlorine (11, 12). Accordingly, S<sub>2</sub>Br<sub>2</sub> showed better performance at mercury capture than S<sub>2</sub>Cl<sub>2</sub> and HBr.

In addition, adding extra activated carbon to the gas with S<sub>2</sub>Br<sub>2</sub> (defined as the coinjection) can also enhance the removal of Hg<sup>0</sup> significantly. Though the Hg<sup>0</sup> removal efficiency was only about 5% with 32 mg/m<sup>3</sup> AC-KB alone, it dramatically increased to about 73% with the presence of 1 ppmv S<sub>2</sub>Br<sub>2</sub> and 20 g/m<sup>3</sup> Ash-A, and the added carbon corresponded to only a 0.16% LOI increase in fly ash. In addition, about 32 mg/m<sup>3</sup> of powder graphite (≤30 μm, BET < 5 m<sup>2</sup>/g) was also used to increase LOI or carbon content in fly ash, and it was found that the Hg<sup>0</sup> removal efficiency increased about 5% under the same condition. The results

indicated that only activated carbon with higher BET surface was more effective at Hg<sup>0</sup> removal in the presence of S<sub>2</sub>Br<sub>2</sub>.

Meanwhile, it is observed from Figures 3 and 4 that Hg<sup>0</sup> removal efficiency in the simulated flue gas (with SO<sub>2</sub>, 1000 ppmv; NO, 200 ppmv; CO<sub>2</sub>, 2–4%; water vapor, 5%; and air as the makeup) was lower than that in the “clean” hot gas. In order to identify the main components influencing Hg<sup>0</sup> removal, the effect of NO, SO<sub>2</sub>, water vapor, and CO<sub>2</sub> were investigated. Despite the fact that NO showed remarkable inhibition to Hg<sup>0</sup> oxidation through the gas-phase reaction with S<sub>2</sub>Br<sub>2</sub>, its effect was almost neglectable when fly ash was present in the gas. On the contrary, SO<sub>2</sub> displayed an obviously negative impact on Hg<sup>0</sup> removal, though it showed insignificant effect in the gas-phase reaction. When 1000 ppmv



**FIGURE 5.** The relationship of Hg<sup>0</sup> removal efficiency and S<sub>2</sub>Br<sub>2</sub> or fly ash concentrations in flue gas at 393 K. The initial Hg<sup>0</sup> concentration in the gas was about 20 μg/m<sup>3</sup>, and the gas resident time was about 0.9 s.

SO<sub>2</sub> was injected into the reactor, Hg<sup>0</sup> removal efficiency decreased from 46% to 39% in the presence of 1 ppmv S<sub>2</sub>Br<sub>2</sub> and 20 g/m<sup>3</sup> Ash-A. The effects of water vapor and CO<sub>2</sub> were insignificant on Hg<sup>0</sup> removal at 393 K or higher. Therefore, SO<sub>2</sub> was considered as the main component to decrease the Hg<sup>0</sup> removal efficiency, and it can be also adsorbed on fly ash competitively with S<sub>2</sub>Br<sub>2</sub> or Hg<sup>0</sup> for the activated sites and cause a decrease in Hg<sup>0</sup> capture.

The influences of the concentration of fly ash and S<sub>2</sub>Br<sub>2</sub> are shown in Figure 5. With an increase in concentration of Ash-A from 10 to 40 g/m<sup>3</sup>, the mercury removal efficiency increased from 29% to 57%. Increasing fly ash content in flue gas can provide more gas–solid surface for S<sub>2</sub>Br<sub>2</sub> adsorption and Hg<sup>0</sup> capture on fly ash, but it became flat when fly ash content was over 20 g/m<sup>3</sup>. Likewise, the mercury removal efficiency increased from 46% to 82% when S<sub>2</sub>Br<sub>2</sub> concentration increased from 1 ppmv to 4 ppmv. Fly ash can adsorb more S<sub>2</sub>Br<sub>2</sub> at higher concentration, and it was helpful for the capture of Hg<sup>0</sup>.

Meanwhile, the balance of mercury in the inlet and outlet gases was well consistent (within ±10% fluctuation) by OHM tests, and most of the converted Hg<sup>0</sup> (over 90%) was in the form of particulate bounded in the presence of fly ash.

#### Modeling for the Prediction of Hg<sup>0</sup> Removal Efficiency.

As is observed from Figure 5, the Hg<sup>0</sup> removal efficiency increased with the rise of S<sub>2</sub>Br<sub>2</sub> concentration and fly ash content in the simulated flue gas. According to the preliminary assessment of the above results for the surface-involved reaction, the reaction rate can be tentatively described with a simplified model (eq 4), mainly considering the effect of fly ash and S<sub>2</sub>Br<sub>2</sub> concentration and fly ash specific surface area. Hg<sup>0</sup> removal efficiency can be calculated with eq 5.

$$\frac{d[\text{Hg}^0]}{dt} = k_s \varepsilon (M)^\alpha [\text{S}_2\text{Br}_2]^\beta [\text{Hg}^0] \quad (4)$$

$$\eta = [1 - \exp(-k_s \varepsilon M^\alpha [\text{S}_2\text{Br}_2]^\beta t)] \times 100\% \quad (5)$$

in which,  $k_s$  is the apparent first-order surface-induced reaction rate constant, s<sup>-1</sup> m<sup>-2</sup>;  $\varepsilon$  is the valid specific surface area of fly ash or other particles, m<sup>2</sup>/g;  $M$  denotes the fly ash (or other particles) content, g/m<sup>3</sup>; and S<sub>2</sub>Br<sub>2</sub> concentration is in ppmv.  $\alpha$  and  $\beta$  are the power index for the two concentrations, respectively.

**TABLE 1.** Kinetics Parameters for Hg<sup>0</sup> Removal for Various Cases at 373 K<sup>a</sup>

cases	$k_s \varepsilon$ (s <sup>-1</sup> g <sup>-1</sup> )	$\alpha$ (dimensionless)	$\beta$ (dimensionless)
AC-LH <sup>b</sup>	9.1	1	—
AC-LH	9.3	0.94	—
Ash-A + S <sub>2</sub> Br <sub>2</sub>	0.14	0.48	0.86
AC-KB + S <sub>2</sub> Br <sub>2</sub>	6.8	0.88	0.84

<sup>a</sup> The relative errors for  $k_s \varepsilon$ ,  $\alpha$ , and  $\beta$  were within 15%.

<sup>b</sup> The original data were from the literature (5).

**TABLE 2.** Products Distribution from the Reaction of Hg<sup>0</sup>/S<sub>2</sub>Br<sub>2</sub>

different cases	primary products <sup>a</sup>		secondary products <sup>b</sup>	
	Hg in HgBr <sub>2</sub>	Hg in HgS	Hg in HgBr <sub>2</sub>	Hg in HgS
S <sub>2</sub> Br <sub>2</sub> :Hg <sup>0</sup> = 1.0	62%	38%	—	—
S <sub>2</sub> Br <sub>2</sub> :Hg <sup>0</sup> = 5.5	76%	24%	27%	73%

<sup>a</sup> Products from the reaction without moisture. <sup>b</sup> Primary products were mixed with water (1:5).

Therefore,  $k_s \varepsilon$ ,  $\alpha$ , and  $\beta$  for various cases can be calculated with the data obtained above, and the results are listed in Table 1. It can be seen that  $k_s \varepsilon$  for activated carbon was by far larger than that for fly ash. The larger BET surface area and its functional groups on activated carbon might make bromine species more reactive to Hg<sup>0</sup> capture. Nevertheless, the high fly ash (with LOI) concentration in flue gas would play a substantial role on Hg<sup>0</sup> removal in the presence of S<sub>2</sub>Br<sub>2</sub>. It should be noted that there may exist other important factors that affect the model (e.g., LOI content, its property, and gas-particle contacting condition), so it can be regarded as the semiempirical equation for the prediction to the practice.

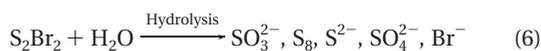
On the basis of the data in Table 1, it was predicted that Hg<sup>0</sup> removal efficiency was about 92% with 52 mg/m<sup>3</sup> (3.3 Lb/MMacf) of AC-LH in flue gas and about 5 s resident time, which was very close to the demonstration results in the field tests (5, 14). Similarly, it was calculated that Hg<sup>0</sup> removal efficiency was up to 90% when 30 g/m<sup>3</sup> Ash-A and 0.6 ppmv S<sub>2</sub>Br<sub>2</sub> were present in the flue gas (393 K) for 5 s. In addition, the coinjection of activated carbon and S<sub>2</sub>Br<sub>2</sub> was also very effective at capturing Hg<sup>0</sup>, and only about 20 mg/m<sup>3</sup> of AC and 0.3 ppmv S<sub>2</sub>Br<sub>2</sub> were needed to obtain about 95% of Hg<sup>0</sup> removal efficiency at 393 K.

Meanwhile, for the semidry FGD system with rather high recycling fly ash and sorbents (as high as 500–1000 g/m<sup>3</sup>), only about 0.06 ppmv of S<sub>2</sub>Br<sub>2</sub> was demanded to obtain 90% of Hg<sup>0</sup> removal efficiency. Therefore, S<sub>2</sub>Br<sub>2</sub> appeared to be more promising in semidry FGD systems for mercury capture and stabilization.

#### Fates of S<sub>2</sub>Br<sub>2</sub> and Hg<sup>0</sup> and Their Environmental Impacts.

The products distribution of Hg/S<sub>2</sub>Br<sub>2</sub> was determined with the multistage dissolution and weighing method described above. The primary products of Hg/S<sub>2</sub>Br<sub>2</sub> were obtained under a dry environment to avoid the interference of moisture to the products distribution. It was found that about 38% and 24% of the oxidized mercury in the primary products were in the form of HgS when the mole ratios of S<sub>2</sub>Br<sub>2</sub> to Hg<sup>0</sup> were at 1.0 and 5.5, respectively (Table 2). The secondary products from the primary products of Hg<sup>0</sup>/S<sub>2</sub>Br<sub>2</sub> and then accompanied with surplus S<sub>2</sub>Br<sub>2</sub> hydrolysis were also investigated, and the results are also shown in Table 2. The ratio of HgS was found to increase remarkably in the secondary products, which implicated that part of HgBr<sub>2</sub> in the primary products of Hg<sup>0</sup>/S<sub>2</sub>Br<sub>2</sub> can be further converted to HgS by means of sulfide from the hydrolysis of S<sub>2</sub>Br<sub>2</sub>.

The fate of the residual  $S_2Br_2$  in flue gas or adsorbed on fly ash should also be considered.  $S_2Br_2$  in flue gas was found to be readily absorbed by water or FGD liquor if a FGD system was installed downstream.  $S_2Br_2$  can be gradually hydrolyzed in moisture gas or water, especially in the aqueous alkali solutions with rather high dissolution and hydrolysis rate. The hydrolysis products of  $S_2Br_2$  in water solutions were quantitatively determined. It was found that sulfur atoms in  $S_2Br_2$  can either lose or gain electrons during the hydrolysis process. About 5–8% of the total sulfur in  $S_2Br_2$  was converted to sulfide (released in the form of  $H_2S$  after acidization) in water or weak alkali solutions, and about 50–60% of the total sulfur was converted to elemental sulfur as well. Meanwhile, sulfite and sulfate were the other sulfur species. The presence of sulfide in the products was helpful to convert the dissolved  $Hg^{2+}$  in aqueous solution to  $HgS$  (e.g., in FGD liquors) and the potential secondary pollution of  $Hg^{2+}$  in FGD liquors could be minimized accordingly.



Additionally, some of  $S_2Br_2$  adsorbed on fly ash can also be gradually neutralized by the alkali components in fly ash (such as  $CaO$  and  $MgO$ ) to form the bromide salts and sulfur species, which were helpful for the further stabilization of mercury on fly ash. Therefore, the adsorbed  $S_2Br_2$  on fly ash would not bring any new undesirable problems.

In the leaching tests, three samples, AC- $S_2Br_2$ , Ash- $S_2Br_2$ , and Ash- $Br_2$  were employed in leaching tests after adsorbed  $Hg^0$ , and XPS analysis indicated that all the mercury on the samples were in the oxidized form (Supporting Information). According to the tests on the soaked sorbents and leaching liquids, it was found that about 20(±5)% of adsorbed mercury was leached out from Ash- $Br_2$ . However, mercury was hardly leached out from the other two samples with  $S_2Br_2$ , and mercury in the leaching liquid was not detectable. The results implicated that mercury can be fixedly captured in the presence of  $S_2Br_2$ , and the secondary pollution from mercury leaching could be minimized efficiently.

In summary, we have demonstrated that  $S_2Br_2$  in flue gas with fly ash can accelerate the removal of  $Hg^0$  significantly, and it was predicted that about 90% of  $Hg^0$  removal efficiency can be obtained with 0.6 ppmv  $S_2Br_2$  and 30 g/m<sup>3</sup> fly ash in flue gas at 393 K. Meanwhile, for the semidry FGD system with rather high recycling fly ash and sorbents, only about 0.06 ppmv of  $S_2Br_2$  was demanded to obtain 90% of  $Hg^0$  removal efficiency.

Meanwhile, most of  $Hg^0$  can be converted to a more stable formation ( $HgS$ ) by the direct reaction and secondary process accompanied with  $S_2Br_2$  hydrolysis. The residual  $S_2Br_2$  on fly ash or in flue gas can be readily removed and converted to a more benign species, and some of them were helpful for the further conversion of  $Hg^{2+}$  to  $HgS$ . Furthermore,  $S_2Br_2$  is less irritative than  $Br_2$  and sulfur chlorides, which is more convenient for preparation, storage, transportation, and application in industry considering the safety issues. Therefore,  $S_2Br_2$  appears to be a very promising and task-specific oxidant for the removal and stabilization of elemental mercury from coal-fired flue gas.

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## Supporting Information Available

Description of the preparation of  $S_2Br_2$ , pilot setup, leaching tests of mercury, and results sections. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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