Enhanced Elemental Mercury Removal from Coal-fired Flue Gas by Sulfur-chlorine Compounds

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Abstract

Oxidation of Hg^0 with any oxidant or converting it to a particle-bound form can facilitate its removal. Two sulfur-chlorine compounds, sulfur dichloride (SCl_2) and sulfur monochloride (S_2Cl_2), were investigated as oxidants for Hg^0 by gas phase reaction and by surface-involved reactions in the presence of flyash or activated carbon. The gas phase reaction rate constants between Hg^0 and the sulfur/chlorine compounds were determined, and the effects of temperature and the main components in flue gases were studied. The gas phase reaction between Hg^0 and SCl_2 is shown to be more rapid than the gas phase reaction with chlorine, and the second order rate constant was $9.1(\pm0.5) \times 10^{-18}$ mL-molecules$^{-1} \cdot$s^{-1} at 373ºK. Nitric oxide (NO) inhibited the gas phase reaction of Hg^0 with sulfur-chlorine compounds. The presence of flyash or powdered activated carbon in flue gas can substantially accelerate the reaction. The predicted Hg^0 removal is about 90% with 5 ppm SCl_2 or S_2Cl_2 and 40 g/m^3 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 SCl_2 (or S_2Cl_2) 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

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also indicates that 90% of Hg^0 can be removed if 3 Lb/MMacf of Darco-KB pretreated with 3% of SCl_2 or S_2Cl_2 is used. Unlike gas phase reactions, NO exhibited little effect on Hg^0 reactions with SCl_2 or S_2Cl_2 on flyash or activated carbon. Mercuric sulfide was identified as one of the principal products of the Hg^0/SCl_2 or Hg^0/S_2Cl_2 reactions. Additionally, about 8% of SCl_2 or S_2Cl_2 in aqueous solutions is converted to sulfide ions, which would precipitate mercuric ion from FGD solution.

Introduction

Coal-fired power generating plants contribute approximately one third of the mercury released into the environment in the United States. USEPA's Clean Air Mercury Rule (CAMR) of 2005 mandated a transition to capped mercury emissions to be phased in over the next decade. It is possible that more stringent regulations may replace CAMR, which was vacated by the District of Columbia Court of Appeals in 2008. China is similarly interested in reducing mercury emissions from its rapidly increasing number of coal-fired generating plants (1-3).

The mercury is emitted in either oxidized form or as elemental mercury, Hg^0, and either in the particulate or vapor phase (3), with the most difficult to control being vapor-phase Hg^0, 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 (3-8). 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 (4), 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 Hg^0, 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 Hg^0 to an oxidized or particle-bound form during its short residence time in the ducts before it encounters the APCDs. The Hg^0 oxidation methods used for this include heterogeneous catalysis and homogeneous gas phase oxidation (7-14). 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 (7). The lower chlorine content of lower rank coals greatly reduces the efficiency of mercury oxidation by SCR catalysts (5,8). 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 Hg^0 is relatively simple to implement. The challenge is the selection of the proper oxidants to be utilized (9-14). Given the short residence time of flue gas in the ducts and/or APCDs (typically less than 10 seconds), the reaction between Hg^0 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 H_2S, while readily available, were unable to efficiently oxidize Hg^0 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 di-chloride are widely used as sulfurating reagents in the rubber industry (15).

Based on the above considerations, we performed a series of experiments to determine the gas phase reaction rate constants for the oxidation of Hg^0 by sulfur chlorides, the effect on the reaction rate of the main components of flue gas (including flyash), and the main reaction products.

Experimental

Gas phase reaction of Hg^0

The reaction kinetics and removal efficiency for elemental mercury oxidation were studied with in-situ monitoring of the concentration of Hg^0 in the reactor as a function of time by a mercury cold vapor atomic absorption spectrophotometer (CVAAS) described previously (11,12). 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 (12), but this introduces a diffusion-limitation factor in processing. In order 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 105mm inner diameter and a volume of 1100ml. A rotating 6-vane stirrer, driven by a magnetic rotor, was installed inside the reactor. The diameter of the stirrer was 80mm and its speed could be varied from 0 to 1500rpm. A thin metal strip (3−10mm in width and 80mm in length) was fixed to the stirrer to hold the particles which were attached to double coated carbon tape (Ted Pella, Inc.).

To characterize the reactor's behavior, Darco-Hg-LH, a commercial sorbent (brominated powdered activated carbon) which has been widely utilized in field and demonstrations for coal-

fired mercury capture (4,14), was employed as reference. The amount of activated carbon (Darco-KB or Darco-Hg-LH) or flyash on the carbon tape was approximately 0.12mg per square centimeter.

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 SO_2, NO, and CO on Hg^0 removal were investigated. Sulfur dichloride (SCl_2, 80%) and sulfur monochloride (S_2Cl_2, >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%) from Matheson Co. and Dalian Date Standard Gas Co., Halocarbon wax from Halocarbon Product Co., and Darco-KB / Darco-Hg-LH 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 m^2/g, and the BET surface area of unburned carbon in flyash-L is calculated to be 398 m^2/g.

The Hg^0 concentration in the reactor was measured in situ by CVAAS with a time resolution of 20 milliseconds. The concentration of sulfur dichloride gases was measured with a UV/Vis Spectrometer (Lambda-02, Perkin Elmer) at 195nm, calibrated by FTIR (MAGNA-760, Nicolet) at a wave-number of 525 cm^{-1} (13). S_2Cl_2 was measured by UV/Vis spectroscopy at its maximum absorbance at 258nm. The uncertainties in the measured concentrations of Hg^0 and sulfur chlorides were ±0.005 ppm and ±2ppm, 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 1. 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 oxidization efficiencies at a reaction time of 40 seconds were about 3%, 9% and 50% for Cl_2, S_2Cl_2 and SCl_2, respectively.

The data shown in Fig.1 show the reactions between Hg^0 and the oxidants to have pseudo first-order rate kinetics. The oxidation rate of Hg^0 also appears to be directly proportional to the oxidant concentration. Therefore, it can be concluded that the gas phase reactions of Hg^0/SCl_2 or Hg^0/S_2Cl_2 are second-order with respect to Hg^0 and SCl_2 or S_2Cl_2, as expressed by eq 1 (16):

$$-d[Hg^0]/dt=k_2[X][Hg^0] \qquad (1)$$

where, $[X]$ denotes the concentration of SCl_2 or S_2Cl_2, molecules·mL^{-1} in N_2 and k_2 is the second-order rate constant. The rate constants from our data are:

$9.1(\pm0.5)\times10^{-18}$ mL·molecules^{-1}·s^{-1} for Hg/SCl$_2$ and

$4.2(\pm0.5)\times10^{-19}$ mL·molecules^{-1}·s^{-1} for Hg/S$_2$Cl$_2$

at 373 ± 2 °K and 760 torr. A second-order rate constant for Hg^0/Cl_2 of $1.1(\pm0.5)\times10^{-19}$ mL·molecule^{-1}·s^{-1} at 373 ± 2 °K has been reported (11). The reaction rate constant for Hg/SCl$_2$ is nearly two orders of magnitude larger than Hg/Cl$_2$, while the reaction rate constant for Hg/S$_2$Cl$_2$ was much less, only about 4 times higher than that of Hg/Cl$_2$. If the effects of other flue gas constituents are not considered, neither SCl_2 nor S_2Cl_2, despite having larger reaction rate constants than Cl_2, is sufficiently effective in the removal of elemental mercury based solely on gas phase reactions.

Effect of the reaction temperature

The thermal stability of SCl_2 and the effect of temperature on the rate constant of the Hg^0/SCl_2 oxidation were studied. It was found that SCl_2 showed good thermal stability up to $400^\circ K$, with a loss through thermal decomposition of less than 5% when it was heated for 300 seconds at $400^\circ K$. Therefore, the loss of SCl_2 resulting from thermal decomposition was negligible in our tests since the duration of most were 200 seconds or less.

The temperature dependence of the oxidation efficiency of the reaction of Hg^0/SCl_2 is shown in Figure 2. The Hg^0 oxidation efficiency decreased with increasing temperature for the gas phase reaction in the range of $297-393^oK$. Increasing the temperature from $297\ ^oK$ to $393\ ^oK$, reduced the oxidation efficiency from 39.3% to 24.7% at 30 seconds. A similar behavior was also apparent for Hg^0/S_2Cl_2.

Hg^0 removal in the presence of fly ash or powdered activated carbon

Mass transfer and Hg^0 removal

Since many field studies using Darco-Hg-LH as a mercury capture sorbent have been reported, it was used to characterize the performance of the reactor and the method. The BET surface area of Darco-Hg-LH used was about $520m^2/g$, and which was reduced to $340\ m^2/g$ when coated onto the carbon tape, a loss of about 35%.

Pieces of carbon tape with areas of 0.7, 1.8 and $4cm^2$ were coated with 0.11mg, 0.28mg and 0.62 mg of Darco-Hg-LH, respectively. The coated carbon tapes were mounted on metal strips above and attached to 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 15 seconds of contact time was 11.6%, 19.8% and 33.4% with ratios of Darco-Hg-LH to gas volume of 100 mg/m^3, 255 mg/m^3 and 562 mg/m^3, respectively.

The observed depletion of Hg^0 from capture by Darco-Hg-LH conformed to a pseudo 1st order rate constant at various rotating speeds. Thus, the mercury capture rate by Darco-Hg-LH can be described by eq2.

$$-V\frac{d[Hg^0]}{dt} = M\varepsilon K_g [Hg^0] \qquad (2)$$

where, V is the gas volume, m^3; M is the particles mass in the gas, g; ε is the effective area of the particles, m^2/g; and K_g is the overall apparent mass transfer coefficient, m/s. Thus, the removal efficiency with respect to contact time can be described by eq 3.

$$\eta_t = [1-exp(-M\varepsilon K_g/Vt)] \times 100\% \qquad (3)$$

From the data in Figure 3, εK_g at 1500rpm was approximately 0.032-0.035m^3/gs.

A demonstration at the 140 MW Meramec Station (4,14), with a feed rate of 3.2 lb/MMacf (52mg/m^3) of Darco-Hg-LH in flue gas, the total mercury removal efficiency was 93% using Darco-Hg-LH. Given a gas-solid contact time of 5 sec, the estimated εK_g reported in this industrial demonstration was about 6-7 m^3/g-s for Darco-Hg-LH, about 200 times greater than that obtained in this study.

The difference of εKg between this study and the industrial tests can be explained with the gas-solid contacting modes. Darco-Hg-LH particles in this test were closely coated on the strip with one side not directly exposed to the bulk gas, which would reduce the chance of the lower surface contacting the gas because there is inevitably a thin boundary layer over the fixed particles. The

effective gas-solid contact surface was approximately the tape area coated with Darco-Hg-LH. In the large scale experiments, the activated carbon particles were well dispersed in the flue gas, and almost all the surface, including the internal pore surface, of the particles is exposed to the flue gas. This suggests that a correction coefficient of 200 for εKg can be used to extrapolate the data for activated carbon from this study to a large scale. As a conservative estimate, the correction coefficient of εKg for flyash was set at 100.

Hg^0 removal in the presence of flyash

Flue gas from pulverized coal boilers can contain 30 g/m^3 or more of flyash depending on mineral content in coal. Therefore, the contribution of flyash to mercury capture in the presence of the oxidant should be investigated. Ten and twenty square centimeter pieces of carbon tape were coated with flyash at approximately 1.2mg/cm^2. Figure 4 shows the removal efficiency of Hg^0 with flyash only and with different amounts of SCl_2. It can be seen that the Hg^0 removal efficiency was significantly greater in the presence of flyash, and it increased with the amount of flyash in the reactor. The difference of the depletion efficiencies between the gas phase reaction and the reaction with flyash can be regarded as the net contribution of flyash. It can be calculated that the εKg was 0.00015 m^3/gs and 0.00013 m^3/gs when SCl_2 and S_2Cl_2 were at 24 and 22ppm, respectively. Given that εKg of flyash in the Meramec flue gas was still about as 100 times that observed in this study, eq. 3 predicts that the Hg^0 removal efficiency is about 90% with 40g/m^3 of flyash and about 5ppm of SCl_2 or S_2Cl_2 in flue gas, most of which was converted to particle-bound mercury.

Hg^0 removal in the presence of activated carbon

Figure 5 shows the removal of Hg^0 in the reactor with Darco-KB activated carbon. Without oxidants, the removal efficiency of Hg^0 by Darco-KB was very slow. However, when about 8ppm of SCl_2 or S_2Cl_2 was introduced, the removal efficiency increased dramatically, higher than that with the same amount of Darco-Hg-LH. When the concentration of SCl_2 was decreased to 4ppm, Hg^0 depletion efficiency was still close to Darco-Hg-LH. This indicates that the co-injection of a common powdered activated carbon and SCl_2 or S_2Cl_2 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, 3-5ppm of SCl_2 (or S_2Cl_2) combined with about 2-3Lb/MMacf of untreated Darco-KB was comparable in efficiency to Darco-Hg-LH.

Additionally, chemically treated Darco-KB, impregnated with SCl_2 or S_2Cl_2, was also prepared and investigated. The observed Hg^0 removal efficiencies for Darco-KB impregnated with 3% of SCl_2 or S_2Cl_2 are also shown in Figure 5. Their performance in capturing Hg^0 was just slightly lower than that of Darco-Hg-LH, and about 90% of Hg^0 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, SO_2, NO and CO on the gas phase reaction of Hg/SCl_2 were investigated. Oxygen, SO_2, CO and water vapor had negligible effect on the gas phase reaction rate constant of Hg/SCl_2, however NO reduced the Hg^0 removal efficiency .

Figure 6 illustrates that NO significantly inhibited the gas phase reaction of Hg/SCl_2. NO appears to have little effect on the reduction of Hg^0 in the presence of flyash or activated carbon alone. The slight decrease of Hg^0 removal efficiency by NO in the presence of flyash may be

attributable to the decrease of the gas phase reaction contribution to the overall removal efficiency.
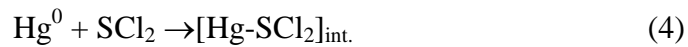
Analysis of Products and Proposed Reaction Mechanism

The reaction products of Hg/SCl_2 on the interior surface of the reactor were collected by washing with ethanol and transfered to 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 Hg^{2+}.

In order to get enough products and to observe the variation in the UV-spectrum during the reaction, a 50ml flask with a magnetic stirrer was employed as a reactor. A drop of elemental mercury (about 0.5g) was introduced to the sealed flask, and the drop was dispersed by the rotating stirrer. Additional SCl_2 or S_2Cl_2 vapor was quickly introduced into the flask, to an initial concentration of about 2%. The gas constituent variation during the reaction of Hg/SCl_2 was measured with UV-spectroscopy, and it is shown in Figure 7. Initially the concentration of S_2Cl_2 was very low, but it increased as SCl_2 decreased in the early stages of the reaction, indicating that S_2Cl_2 was a significant product of Hg/SCl_2. S_2Cl_2 then decreased as its relatively slower reaction with Hg^0 proceeded. Additional SCl_2 or S_2Cl_2 was added as necessary until the Hg^0 was removed. The solid products of Hg/SCl_2 or Hg/S_2Cl_2 appeared to be black or dark gray. In addition, small yellow spots 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 $100^{o}C$ to drive off the unreacted SCl_2 or S_2Cl_2 absorbed on the powder. This was followed by extraction of sulfur or S_xCl_2 from the products with carbon disulfide. After drying, mercuric chloride was dissolved

from the products with ethanol (99.8%). Finally, a 20% Na_2S 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 and mercuric sulfide in the product. The analysis results for various test conditions are shown in Table 1. It can be seen that HgS was the main product of Hg^0/S_2Cl_2, and its percentage was greater at higher ratios of oxidant to elemental mercury. Though the reaction of Hg^0/S_2Cl_2 was slower, it produced a higher percentage of HgS than did Hg^0/SCl_2.

$$Hg^0 + SCl_2 \rightarrow [Hg\text{-}SCl_2]_{int.} \qquad\qquad (4)$$

$$[Hg\text{-}SCl_2]_{int} + SCl_2 \rightarrow HgCl_2 + S_2Cl_2 \qquad\qquad (5)$$

$$[Hg\text{-}SCl_2]_{int} + Hg^0 \rightarrow HgCl_2 + HgS \qquad\qquad (6)$$

This work shows that SCl_2 can be effective in oxidizing Hg^0 to form mercuric chloride and mercuric sulfide. Although NO in flue gas can decrease the gas phase reaction rate of Hg/SCl_2, the presence of flyash upstream of the particulate matter control devices can accelerate the oxidation reaction significantly. We expect that Hg^0 removal efficiency would be about 90% with $40g/m^3$ of flyash and about 5ppm of SCl_2 or S_2Cl_2 in flue gas.

The addition of powdered activated carbon to sulfur chlorides compounds in flue gas can result in even greater Hg^0 removal efficiency. We estimate that co-injection of 3-5 ppm of SCl_2 (or S_2Cl_2) 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 Hg^0 can be removed if 3 Lb/MMacf of Darco-KB pretreated with 3% of SCl_2 or S_2Cl_2 is used.

Moreover, since SCl_2 and S_2Cl_2 are soluble in water, the residual amounts are easily absorbed by a wet FGD scrubber. In addition to their abilities to oxidize Hg^0 and convert some of Hg^0 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 SCl_2 or S_2Cl_2 to oxidize and stabilize elemental mercury in coal-fired flue gases is clearly promising for further study at a larger scale.

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Figure Captions

Figure 1. The Hg^0 removal efficiency by sulfur and/or chlorine containing compounds at 1 atm and 373°K as a function of reaction time. The initial Hg^0 concentration was 0.08 ppmv.

Figure 2. The Hg^0 removal efficiency by SCl_2 or S_2Cl_2 at 373°K after 30 sec as a function of temperature. The initial Hg^0 concentration was 0.08 ppmv.

Figure 3. The effect of rotating speed on the Hg^0 removal efficiency by 0.11 mg, 0.28 mg, and 0.62 mg of Darco-Hg-LH after 15 sec at 373°K. The initial Hg^0 concentration was 0.08 ppmv.

Figure 4. The removal efficiency of Hg^0 by flyash combined with SCl_2 or S_2Cl_2 as a function of reaction time at 373°K. The initial Hg^0 concentration was 0.08 ppm and the rotating speed was 1500 rpm.

Figure 5. Comparison of the removal efficiency of Hg^0 by conventional untreated PAC (Darco-KB) combined with sulfur chlorides to that by brominated PAC (Darco-Hg-LH) at 373°K as a function of reaction time. The Darco-KB and Darco-Hg-LH were 0.62 g, the initial Hg^0 concentration was 0.08 ppmv, and the rotating speed was 1500 rpm.

Figure 6. The effect of NO on the removal efficiency of Hg^0 by: 1. SCl_2, 2. SCl_2 combined with flyash, and 2. SCl_2 with PAC (Darco-KB) after 30 sec and at 373°K. The initial Hg^0 concentration was 0.08 ppmv, and the rotating speed was 1500 rpm.

Figure 7. Time dependent UV-spectra of the reaction between 0.5 g Hg^0 and 2% SCl_2 in a 50 ml flask at 298°K. The maximum absorption peaks of SCl_2 and S_2Cl_2 were at 192 nm and 258 nm, respectively.
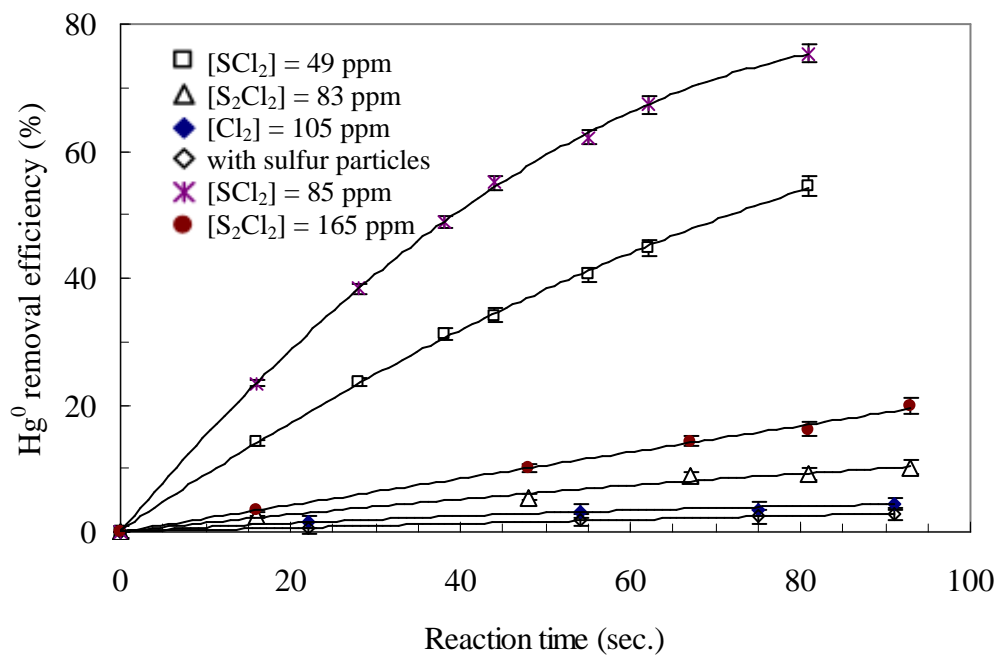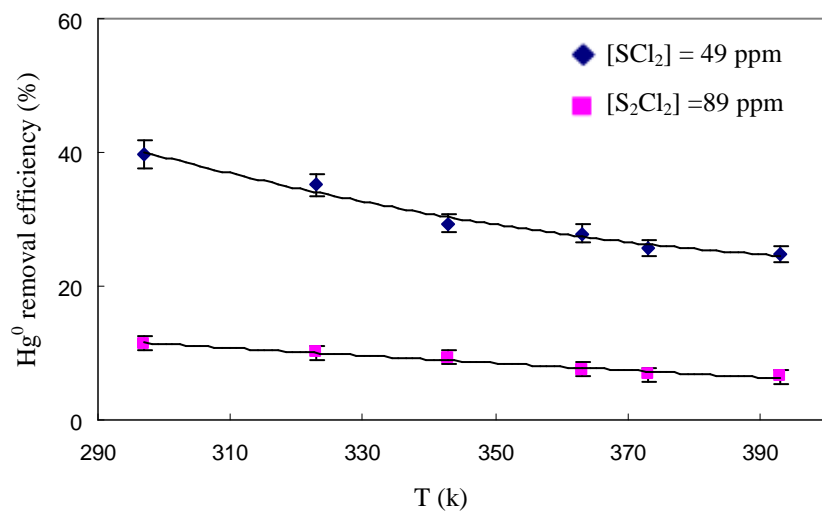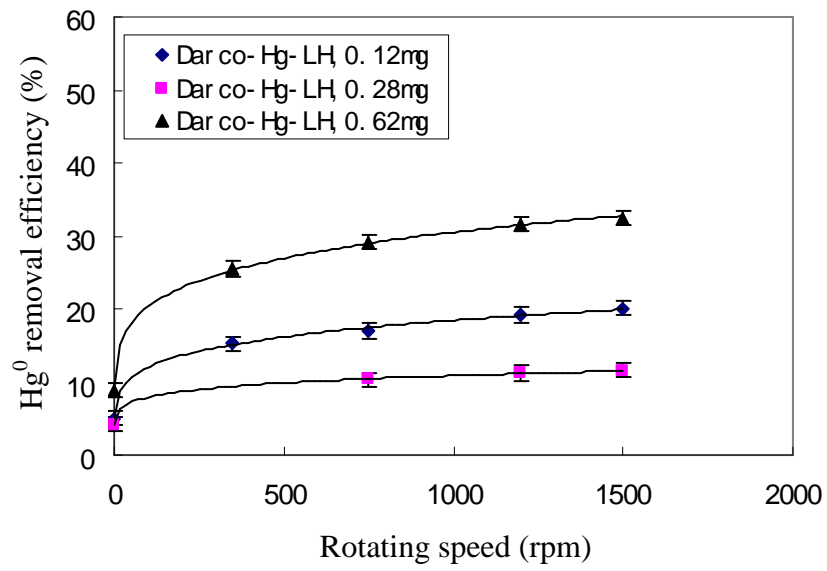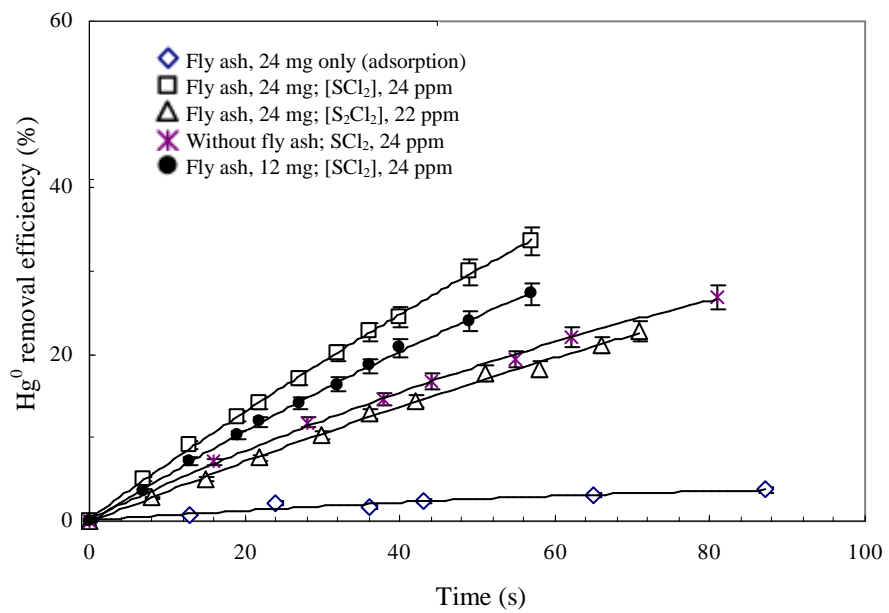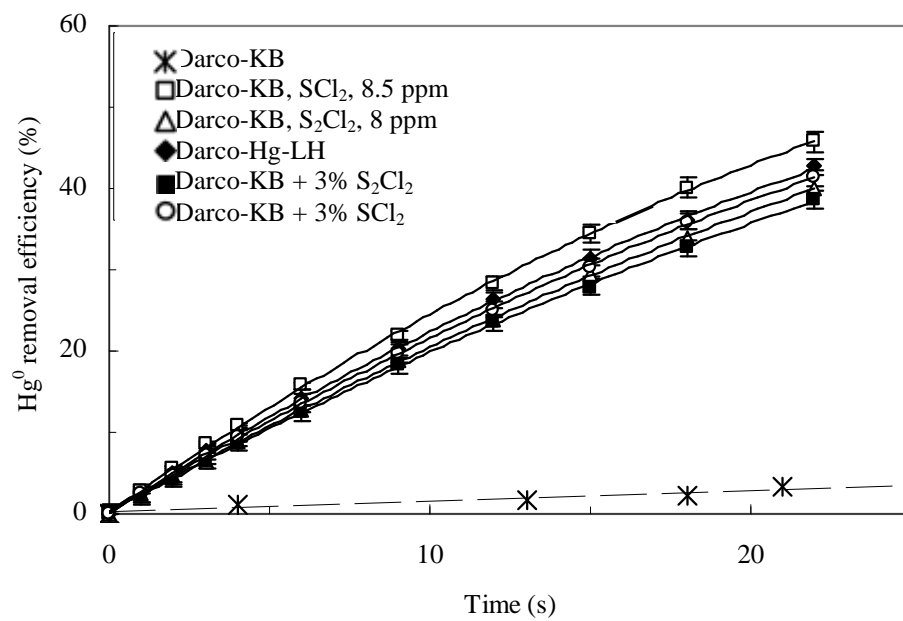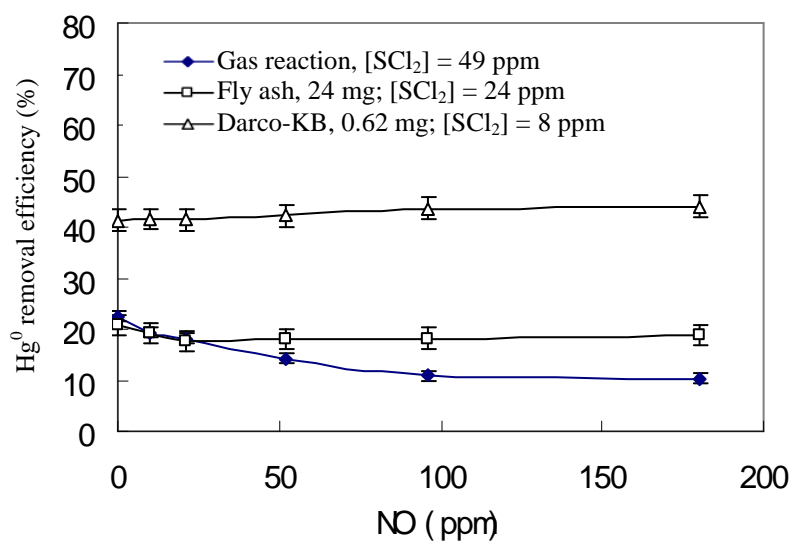
Figure 1.

Figure 2.

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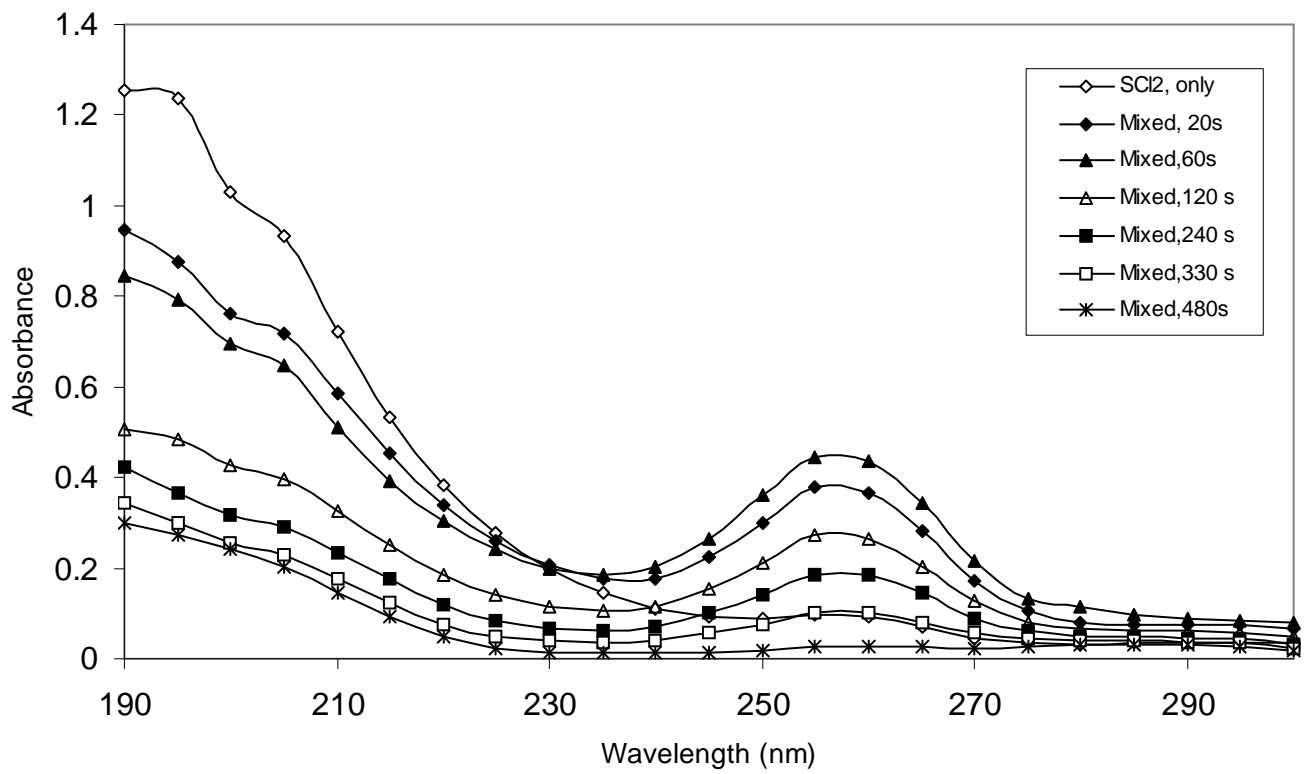
Figure 7.

Table 1 The distribution of the oxidized mercury at various molar ratios of SCl_2/Hg^0 and S_2Cl_2/Hg^0.

Reaction condition[*]	HgCl$_2$ (%)	HgS (%)
SCl_2: Hg^0=2.0	74.5	25.5
SCl_2: Hg^0=0.3	46.0	54.0
S_2Cl_2: Hg^0=1.0	12.6	87.4
S_2Cl_2: Hg^0=0.2	31.4	68.6
* Molar ratio of the oxidant to elemental mercury		