



The performance of iodine on the removal of elemental mercury from the simulated coal-fired flue gas

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ABSTRACT

In order to facilitate the removal of elemental mercury (Hg^0) in flue gas, iodine was used as the oxidant to convert Hg^0 to the oxidized or particulate-bound form. The removal of Hg^0 by the homogenous gas phase reaction and the heterogeneous particle-involved reactions was investigated under various conditions, and a method to test the particle-involved reaction kinetics was developed. Iodine was found to be efficient in Hg^0 oxidation, with a 2nd-order rate constant of about $7.4(\pm 0.2) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 393 K. Nitric oxide showed significant inhibition in the homogenous gas reaction of Hg^0 oxidation. The oxidation of Hg^0 with iodine can be greatly accelerated in the presence of fly-ash or powder activated carbon. SO_2 slightly reduced Hg^0 removal efficiency in the particle-involved reaction. It was estimated that Hg^0 removal efficiency was as high as 70% by adding 0.3 ppmv iodine into the flue gas with 20 g/m^3 of fly-ash. In addition, the predicted removal efficiency of Hg^0 was as high as 90% if 10 mg/m^3 of activated carbon and 0.3 ppmv iodine were injected into the flue gas with fly-ash. The results suggest that the combination of iodine with fly-ash and/or activated carbon can efficiently enhance the removal of Hg^0 in coal-fired flue gas.

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1. Introduction

Mercury often exists in coal in trace amounts, and the emission of mercury from coal-fired utilities has become the main anthropogenic air pollution source for countries utilizing coal as their principal energy input [1,2]. It has been estimated that mercury emissions from coal combustion in China increased from 202 ton in 1995 to 257 ton in 2003 an average annual increase of 3.0% [3,4].

Mercury in coal-fired flue gas often presents as elemental mercury (Hg^0), oxidized mercury vapor (Hg^{2+}) and particulate-bound mercury (Hg^p). The distribution of various forms is dependent on coal rank (mainly on chlorine concentration in coal) and the unburned carbon on fly-ash. Hg^0 is highly volatile and insoluble in water; once it has entered the atmosphere, it can remain aloft for nearly several months and as a result is likely to cause global mercury pollution through atmospheric transportation [1,5]. It has been reported that mercury content in most Chinese coals is higher, but the chlorine content is lower [6]. Therefore, it can be estimated that Hg^0 in flue gases will be relatively higher in China.

It has been demonstrated that existing air pollution control devices (APCDs) can capture mercury to some degree in addition to removal other pollutants, as is called co-benefit [7–10]. How-

ever, the removal efficiency for various forms of mercury varied markedly. Electrostatic precipitator (ESP) or fabric filter (FF) can remove Hg^p efficiently and flue gas desulfurization demonstrates a good absorption performance on Hg^{2+} . But all these devices were ineffective in capturing Hg^0 . In order to obtain higher mercury capture efficiency, powdered activated carbon injection (ACI) technology has been put into application in power plants in the U.S. [9]. But in addition to its higher operation expenses and deterioration to fly-ash, ACI employed with common activated carbon (untreated) has been proven to still be inefficient in capturing Hg^0 .

Since the wet flue gas desulfurization (WFGD) system has been widely used in Chinese utilities, using WFGD to capture mercury will be one of the best choices as a co-benefit. Since WFGD cannot scrub Hg^0 efficiently, it is reasonable to find a cost-effective method to convert the Hg^0 to an oxidized or even a particle-bound form before entering WFGD systems.

The Hg^0 oxidation methods used for this purpose include heterogeneous catalysis and homogeneous gas phase oxidation. But the installation of such a system for the sole purpose of removing Hg^0 would be expensive. By comparison, the direct oxidation method of injecting a type of oxidant into flue gas to oxidize Hg^0 appeared to be a simpler method. The challenge is the selection of the proper oxidants to be utilized. Given the short residence time of flue gas in the ducts and/or APCDs (typically several seconds), the reaction between Hg^0 and the oxidant needs to be quite rapid [11–14].

Due to the fact that bromine is more reactive than chlorine [12,13], it is expected that iodine (I_2) would be more effective than

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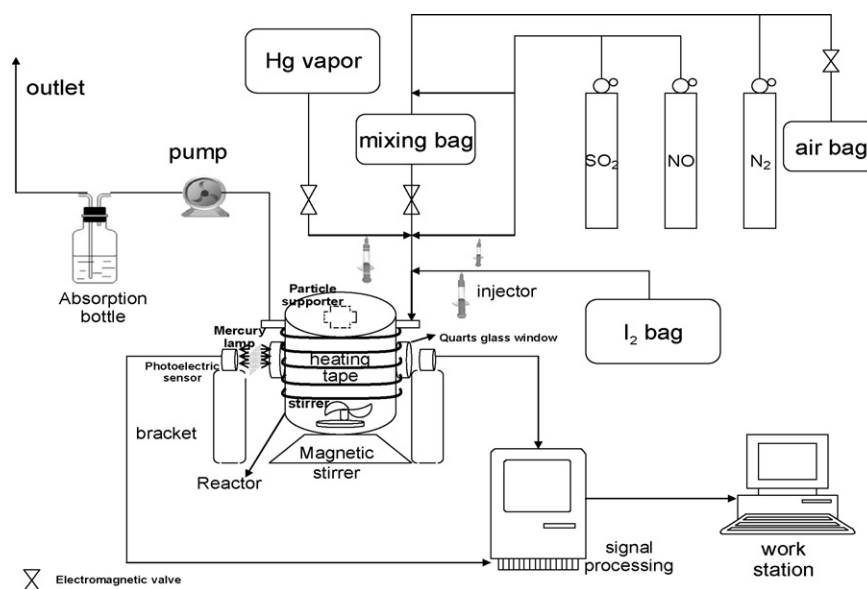


Fig. 1. The schematic flow diagram of the setup.

bromine in Hg^0 oxidation. In addition, iodine is a solid with low vapor pressure at room temperature and due to safety issues it is more convenient to handle, transport and store than bromine and chlorine. However, there still lacks of necessary information on how iodine or its compound acts on Hg^0 in terms of the homogeneous gas reaction and the heterogeneous reactions with fly-ash or other particulates in flue gas. Therefore, a series of experiments conducted to determine the gas phase reaction rate constant, the effect on the reaction rate of the main components of flue gas (including fly-ash), and the estimated potential application of using iodine to enhance mercury removal from coal-fired power plants.

2. Experimental methods and materials

2.1. Experimental methods

2.1.1. The method for determining the homogenous gas reaction

Based on the principle of cold vapor atom absorption spectroscopy (CVAAS), a setup capable of in-situ monitoring of Hg^0 concentration in the reactor was designed and installed. The schematic of the setup is shown in Fig. 1. The reactor was made of a stainless steel cylinder with a volume of 1100 ml. The entire inner wall of the reactor was evenly coated with Halocarbon wax in order to minimize the acceleration effect of the wall in the homogenous gas reaction of Hg^0 with I_2 .

The light source of the optical system was a low-pressure mercury lamp (GP³Hg-1, Haining Youliang) with a main spectrum of 253.7 nm. Two opposite windows with quartz slices were installed on the reactor, which allowed the monitor beam to pass efficiently. After the optical assembly, the light was divided into two beams, one as the reference and the other as the monitor. With respect to Hg^0 concentration, the signal was collected with a data transition and acquisition device (N2000, Zhejiang Zhida) and stored in a computer. The time resolution of the acquisition device was 20 ms.

2.1.2. The method for the determination of particle-involved reaction

Generally, there are about 10–40 g/m³ of fly-ash in the flue gas from pulverized-coal boilers. Therefore, the contribution of fly-ash to Hg^0 capture is not negligible in the presence of any oxi-

dants. Meanwhile, ACI is used for mercury control in power plants [8]. Since the common activated carbon has been shown to be ineffective in capturing Hg^0 in flue gas, the co-injection of activated carbon and iodine may be an alternative to enhance Hg^0 capture. Meanwhile, activated carbon impregnated with iodine or an iodine compound is also supposed to improve Hg^0 capture.

However, for investigating the Hg^0 capture behavior with a laboratory scale system, it is difficult to evenly disperse the fine particles in the gas. The dynamic behavior of particles in the fixed bed was far different from that in the dispersed state. As an attempt, a new method was developed to test the reaction in the presence of particles (fly-ash or powdered activated carbon). As shown in Fig. 1, a rotating 6-vane stirrer driven by a magnetic rotor was installed inside the reactor to blend the gas well. The diameter of the stirrer was 80 mm; its speed could be adjusted from 0 to 1500 rpm. Fly-ash or activated carbon particles were evenly fixed on the vanes with double-sided carbon tape (Ted Pella, Inc.), and the rotating stirrer enabled the gas to contact fully with the particles' surface, thus minimizing the gas diffusion-limitation from the gas to the particles.

To characterize the behavior of the particles in the reactor, Darco-Hg-LH, which has been widely utilized in field tests and demonstrations for coal-fired mercury capture [7], was employed as the comparison.

2.2. Materials

The gas sources, including the saturated mercury gas and the saturated iodine gas, were prepared with elemental mercury and iodine (Sigma–Aldrich) in Teflon bags. The gases – NO (1.53%), SO₂ (99.9%) and N₂ (99.9%) – stored in the cylinders were from Dalian Date Gas Co. Ltd. The iodine concentration was measured with a UV–vis spectrophotometer (B&W Tek).

The fly-ash used in the tests was from a type of lignite coal fired in pulverized-coal boilers. The loss of the ignition and BET surface area of the fly-ash were measured at 1.1% and 6.56 m²/g, respectively. The general-purpose activated carbon (Darco-KB) and the brominated activated carbon (Darco-Hg-LH) were both produced by Norit America Inc. The activated carbon impregnated with I₂ was prepared with Darco-KB.

3. Result and discussion

3.1. The oxidation of Hg^0 by iodine through the gas-phase reaction

3.1.1. The comparison of Hg^0 oxidation by iodine, bromine and chlorine

Fig. 2 illustrates the concentration depletion curves of Hg^0 as a function of the reaction time in the presence of iodine or bromine at 297 K. The depletion of Hg^0 by iodine or bromine appeared to be semi-logarithmic with the reaction time, indicating a pseudo 1st order rate reaction. Hence, the reaction rate can be described as follows [15].

$$\frac{d[\text{Hg}^0]}{dt} = -k_1[\text{Hg}^0] \quad (1)$$

in which $[\text{Hg}^0]$ is the concentration of gas-phase Hg^0 in ppbv, t is the reaction time in seconds (s), and k_1 is the pseudo 1st order rate constant in s^{-1} .

In addition, the oxidation rate of Hg^0 was observed to increase linearly with the iodine concentration, following the 2nd order rate reaction with respect to the two reactants. Therefore, the reaction between Hg^0 and elemental halogens can be described as follows:

$$\frac{d[\text{Hg}^0]}{dt} = -k_2[X][\text{Hg}^0] \quad (2)$$

$$k_2 = \frac{k_1}{[X]} \quad (3)$$

where, k_2 is the 2nd order rate constant with units of $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$, and $[X]$ is the concentration of elemental halogens in the reactor, with units of molecule number per milliliter (molecules cm^{-3}). From the data in Fig. 2, the 2nd order rate constant for the reaction between Hg^0 and bromine was about $6.5(\pm 0.3) \times 10^{-17} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ at 297 K. This result was very close to the previous results [13], indicating that the setup installed in this study was reliable.

Similarly, the 2nd order rate constant for the reaction between Hg^0 and iodine was $1.8(\pm 0.05) \times 10^{-16} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ at 297 K, nearly three times larger than that for the reaction between Hg^0 and bromine.

Generally, the chemical reactivity of halogens becomes weaker as the atomic number increases, but this cannot explain the oxidation of Hg^0 by comparing the rate constants. The trend can be tentatively explained by comparing the London dispersion forces between the reactants [16]. Hg^0 is a large atom with 80 electrons moving around its nucleus. As a result, it is highly polarizable and

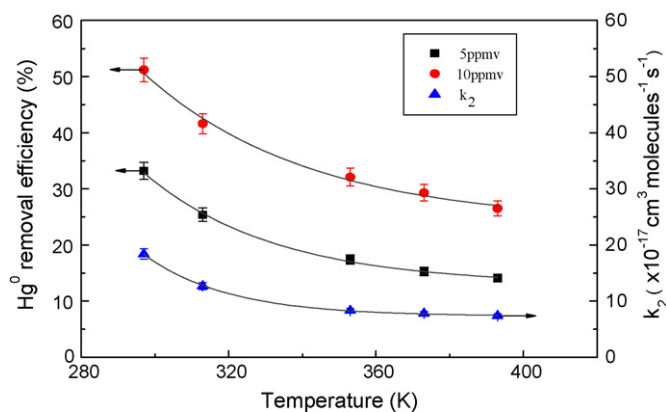


Fig. 3. The temperature dependence of Hg^0 oxidation efficiencies and the 2nd rate constants with iodine. The initial concentration of Hg^0 , $[\text{Hg}^0]_0$, was about 80 ppbv, and the reaction time was 20 s at 760 Torr with nitrogen balance.

the London dispersion forces play an important role in their interaction with surrounding atoms and molecules. It was assumed that the larger the London dispersion forces between the halogen and Hg^0 molecules, the higher the physical attachment reaction rate is between them to form the transient species (such as $\text{Hg}^0 \cdot \cdot \text{I}_2^*$). This is assumed to be the initial step for further reactions. Then, as $\text{Hg}^0 \cdot \cdot \text{I}_2^*$ collide with another gas molecule M (M can be any gaseous molecules in the reaction system or any solid surface), it forms a stable product HgI_2 after shifting the extra energy to M . The London dispersion forces increase greatly as the size of the atom increases. I_2 has 106 electrons around its nucleus compared to 34 and 70 electrons on the chlorine and bromine molecules, respectively. Thus the combination of Hg^0 and iodine to form the transient species $\text{Hg}^0 \cdot \cdot \text{I}_2^*$, is expected to be easier and more rapid than for the other two halogens.



3.1.2. The temperature dependence of Hg^0 oxidation by iodine

The effect of temperature on the Hg^0/I_2 reaction was determined experimentally within the temperature range of 297–393 K. The results are illustrated in Fig. 3. It was observed that the oxidation efficiency decreased as the temperature rose; it dropped from 51% to 26% as the temperature increased from 297 to 397 K with 10 ppm of iodine concentration. Obviously, increasing temperature slows down the Hg^0 oxidation rate.

Similarly, the 2nd order rate constant between Hg^0 and iodine at various temperatures was estimated to be around $7.4(\pm 0.3) \times 10^{-17} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ at 393 K. This was only about 40% of that at 297 K. This result deviated from most of the ordinary chemical reactions, in which the reaction rates are accelerated with rising temperature. This trend can be attributed to the momentum of Hg^0 and iodine molecules in the gas which increases as the temperature rises, and is therefore unfavorable to the formation rate of the transient species because of the London dispersion force. In addition, the effect of temperature on Hg^0 oxidation by iodine was similar to that of chlorine and bromine (about $4.1 \times 10^{-17} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ at 393 K), but iodine was still more effective than the other two elements at the higher temperature.

3.2. The removal of Hg^0 by iodine through particle-involved reaction

As previously stated, fly-ash was the main component in flue gas, and its contribution to the oxidation of mercury in the presence of oxidants needs to be considered. Meanwhile, the performance of

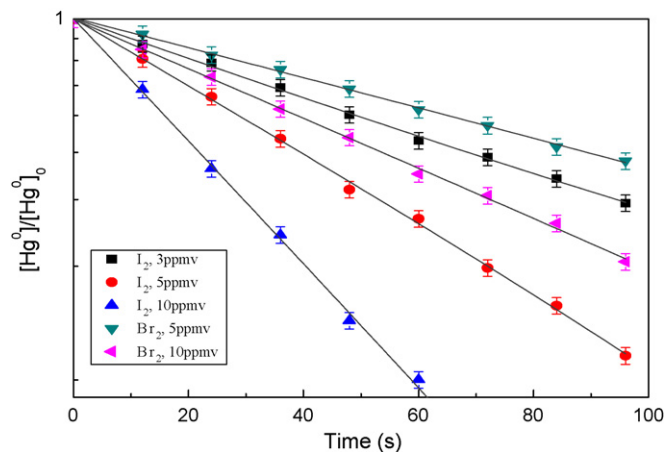


Fig. 2. The concentration depletion curves of Hg^0 by the oxidation of iodine and bromine. The initial concentration of Hg^0 , $[\text{Hg}^0]_0$, was about 80 ppbv, and the tests were conducted at 297 K and 760 Torr with nitrogen balance.

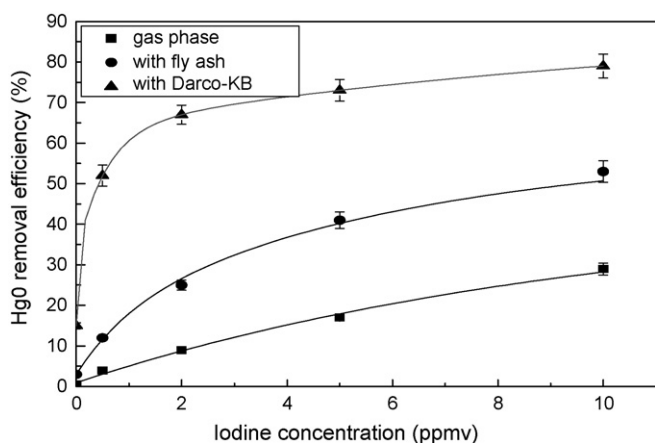


Fig. 4. Iodine concentration dependence of Hg^0 removal efficiency in the presence of fly-ash and activated carbon (Darco-KB). About 15 mg fly-ash or 1.86 mg Darco-KB activated carbon was stuck on 12 cm^2 of carbon tape. The rotating speed was at 1500 rpm, and the contacting time was 20 s at 373 K. The initial of Hg^0 concentration was about 80 ppbv.

powdered activated carbon in the removal of Hg^0 in flue gas also deserved observation in the presence of iodine or iodide compound.

3.2.1. Hg^0 removal by iodine in the presence of fly-ash or powdered activated carbon

Since many field tests or demonstrations using Darco-Hg-LH as a mercury capturing sorbent have been reported, it was used as a reference to evaluate the behaviors of the reactor with particles and the method for the Hg^0 removal. The particles were fixed on one side of the double-sided carbon tape by daubing, and the unstuck particles were eliminated by blowing them with compressed air. The fixed particles resided one by one on the tape with an average density of 0.15 mg/cm^2 . The BET surface area of the Darco-Hg-LH was about $520 \text{ m}^2/\text{g}$; it decreased to $340 \text{ m}^2/\text{g}$ when coated with the carbon tape, a loss of about 35%.

In order to investigate the effect of particles on the Hg^0 removal with iodine gas, the fly-ash or powdered activated carbon (Darco-KB) particles were attached to the carbon tape via the above-mentioned method. About 14.6 mg fly-ash or 1.86 mg Darco-KB activated carbon was attached to 12 cm^2 of carbon tape. The rotating speed of the stirrer was still set at 1500 rpm.

As shown in Fig. 4, the presence of the fly-ash or powdered activated carbon in the reactor can significantly increase Hg^0 conversion efficiency. Compared to the gas phase reaction, Hg^0 oxidation efficiency at 20 s was about 25% and 67%, respectively, when the fly-ash and powdered activated carbon were used with 2 ppmv of iodine concentration. The removal efficiency of Hg^0 was significantly higher than the sum of their respective contributions of the homogenous gas reactions and the adsorption of particles (without iodine) in the separate tests. The results indicated that the surface-induced reaction was more rapid than the gas-phase reaction, especially for the powdered activated carbon. Comparing this with the result of Darco-Hg-LH, about 1 ppmv of iodine combined with the common activated carbon (Darco-KB) obtains the same Hg^0 conversion efficiency. The promotion of fly-ash on Hg^0 removal with iodine was relatively weaker than that with activated carbon, but due to the high concentration of fly-ash in flue gas (up to 40 g/m^3), would make a significant contribution to Hg^0 removal.

3.2.2. Hg^0 removal by fly-ash and activated carbon impregnated with iodine

Instead of injecting gaseous iodine into flue gas, it is possible to use iodine or iodine compounds as oxidants for impregnation on solid particles. This would be similar to the Darco-Hg-LH product,

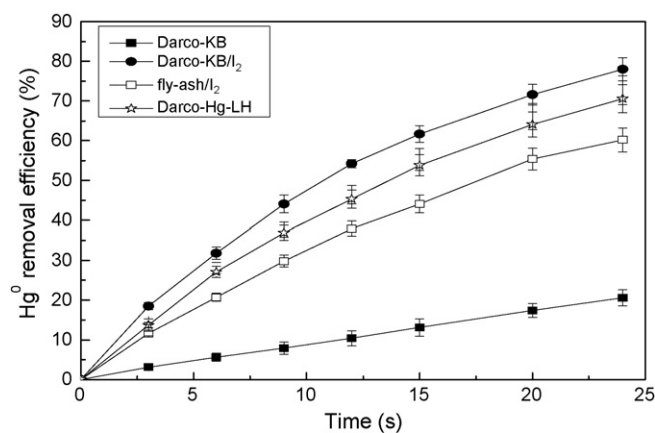


Fig. 5. The Hg^0 removal efficiency for various particles vs. the contacting time. About 15 mg fly-ash or 1.86 mg activated carbon was stuck on 12 cm^2 of carbon tape. About 2% of iodine as impregnated on the fly-ash or Darco-KB. The rotating speed was at 1500 rpm at 373 K. The initial of Hg^0 concentration was about 80 ppbv.

an activated carbon chemically treated with bromine. The removal of Hg^0 by these particles is shown in Fig. 5, in which the tests were performed at 373 K with a rotating stirring speed of 1500 rpm.

Among the investigated particles, it was obvious that the activated carbon impregnated with iodine showed the most effective Hg^0 capture. The removal efficiency was as high as 71% with 20 s of contact time, about 7% higher than that for Darco-Hg-LH at the same conditions. However, the fly-ash impregnated with the 2.5% of iodine was less effective than that with activated carbon or Darco-Hg-LH. The results indicate that iodine impregnated on activated carbon were more efficient than that on fly-ash. This is due to the porous structure of activated carbon and its good electron conductivity, which is considered to be favorable in activating iodine or iodide ions in Hg^0 capture.

3.3. The effects of the gaseous components of flue gas on the gas-phase Hg^0 oxidation

3.3.1. Effects on the gas-phase reaction of Hg^0 by iodine

The effects of the main components in flue gas on Hg^0 removal were investigated separately. For oxygen, carbon dioxide, and water vapor, no perceptible effects were observed on the oxidation of Hg^0 by iodine. However, nitric oxide (NO) displayed obvious inhibition on the oxidation of Hg^0 , as shown in Fig. 6. The oxidation efficiency

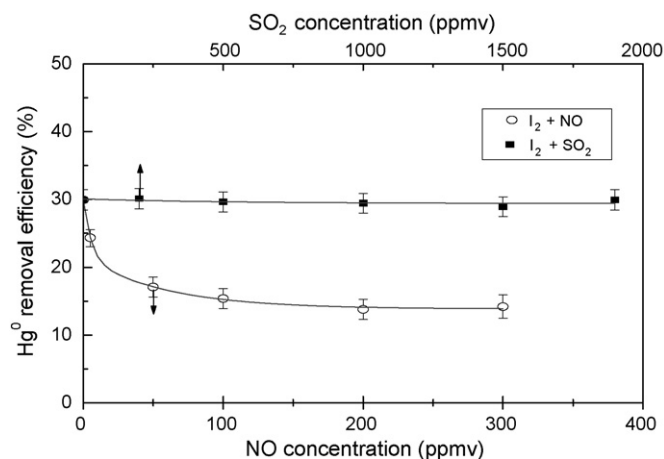


Fig. 6. The effect of NO and SO_2 on the Hg^0 removal efficiency. The iodine concentration was 10 ppmv at 373 K. The rotating speed of the stirrer was at 1500 rpm, and the contacting time was 20 s. The initial of Hg^0 concentration was about 80 ppbv.

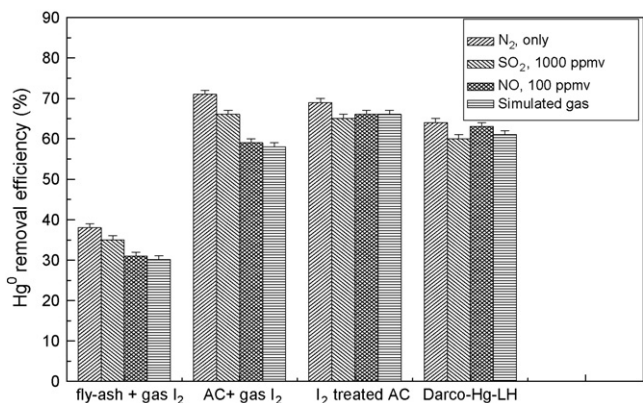
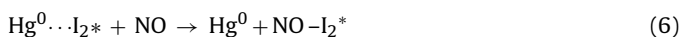


Fig. 7. The effects of gas constitutes on Hg⁰ removal efficiency by particle-involved reactions. The iodine concentration was 2 ppmv if the gas iodine was employed, and the treated AC meant iodine (2.0%) was impregnated on Darco-KB. The amount activated carbon and fly-ash was 1.86 and 15 mg on the carbon tape, respectively. The rotating speed of the stirrer was at 1500 rpm with the contacting time of 20 s. The initial of Hg⁰ concentration was about 80 ppbv at 373 K. The simulated flue gas consists of 100 ppm of NO, 1000 ppm of SO₂, 5% of O₂, 5% of water vapor, 10% of CO₂, and the rest of N₂.

of Hg⁰ by 10 ppm of iodine decreased from 29% (without NO) to 23% when 5 ppm of NO was added to the gas, and it dropped to 17% as NO increased to 50 ppm. The declining trend then became nearly flat with the further increase of NO concentration, from 50 to 300 ppm. The effect of SO₂ on the removal efficiency of Hg⁰ by iodine is also shown in Fig. 6. SO₂ demonstrated a very insignificant effect on the gas-phase reaction between Hg⁰ and I₂ with SO₂ concentration ranging from 200–2000 ppm.

The mechanism by which NO inhibits the oxidation of Hg⁰ with iodine is not yet well understood. The possibility that iodine is competitively consumed by NO to produce NOI, thus would reduce the Hg⁰ oxidation efficiency, has been excluded by calculating the reaction rates [17]. Therefore, another conjecture was tentatively proposed as an explanation. As stated above, Hg⁰··I₂^{*} were the transient species during Hg⁰ oxidation. However, Hg⁰··I₂^{*} could be disassociated back to Hg⁰ and I₂ by the reversible reaction. There was an unpaired electron in the NO molecule, so it was easy for NO to enhance the disassociation of Hg⁰··I₂^{*} by electrostatic force.



In addition, the simulated flue gases – consisting of 100 ppm of NO, 1000 ppm of SO₂, 5% of O₂, 5% of water vapor, 10% CO₂ with the remainder of N₂ – were used to study the oxidation of Hg⁰ in the simulated flue gas. The concentration of iodine in this experiment was 10 ppmv. Comparing this with the Hg⁰/I₂ reaction only with nitrogen balance, the Hg⁰ removal efficiency decreased from about 30% to 18%. NO was still the main component depressing Hg⁰ oxidation.

3.3.2. The effects of gas constitutes on Hg⁰ removal by particle-involved reaction

The effects of the main components on the particle-involved reaction of Hg⁰ were investigated, and the results are shown in Fig. 7. Iodine was used either by gas injection or by particle impregnation. It was observed that the presence of NO did not decrease Hg⁰ removal efficiency by the activated carbon impregnated with iodine.

This indicates that NO did not depress such particle-involved reactions for Hg⁰ capture. For the tests containing both gas-phase and particle-involved reactions, the decrease of Hg⁰ removal efficiency by NO was simply due to the inhibition of NO in the gas

phase reaction. In addition, SO₂ displayed a slight inhibition on the particle-involved reaction for Hg⁰ removal (Fig. 7). For the activated carbon impregnated with iodine, Hg⁰ removal efficiency decreased by about 4% with 1000 ppmv of SO₂ in the gas. The same trend was true for the case with both particles and iodine gas. The competitive adsorption of SO₂ on the active sites that can chemically bond with Hg⁰ was considered to be a main factor in reducing Hg⁰ removal efficiency. Fortunately, this competition caused only a slight reduction to Hg⁰ removal.

The removal of Hg⁰ by a particle-involved reaction in the simulated flue gas is also shown in Fig. 7. The removal efficiency of Hg⁰ by various particles was very close to that of using only 1000 ppmv SO₂ in the gas (nitrogen balance), indicating that SO₂ was the main constituent in slowing down the Hg⁰ removal rate.

3.4. Industrial implication

Based on the above experimental results, the potential industrial application was evaluated. Compared to the previously investigated oxidants, iodine appeared to be the most effective in Hg⁰ conversion. From the gas phase reaction perspective, injecting 5 ppmv of iodine into flue gas at 373 K oxidizes about 10% of Hg⁰ in flue gas with a gas contact time of 5 s. This meant the contribution of the gas-phase reaction to Hg⁰ oxidation was relatively small, and in order to make use of fly-ash, the injection of iodine into flue gas should be upstream of the particulate collectors.

To evaluate the importance of the fly-ash or activated carbon (injected) in actual flue gas with iodine, Darco-Hg-LH was employed as the reference. According to an industrial demonstration at Meramec Station [9], approximately an additional 85% of Hg⁰ was removed by the injection of about 52 mg/m³ Darco-Hg-LH for several seconds as compared to employing another activated carbon that was ineffective in capturing Hg⁰ in flue gas. Given that the particle-involved reaction for Hg⁰ in the demonstration obeyed the pseudo 1st order kinetics, Eq. (8) can be tentatively used to describe the removal rate of Hg⁰ [14].

$$\frac{d[\text{Hg}^0]}{dt} = -\frac{m}{V} \varepsilon_e K_g [\text{Hg}^0] \quad (8)$$

where, m/V is the employed amount of the particles per unit volume gas in mg/m³, ε_e notes the effective area of particle that can be well-contacted with the gas, K_g is the overall mass transfer coefficient in the process, and t is the gas-particle contacting time. Consequently, the removal efficiency of Hg⁰ with respect to the contacting time can be described with Eq. (8).

$$\eta_t = \left[1 - \exp\left(-\frac{m}{V} \varepsilon_e K_g t\right) \right] \times 100\% \quad (9)$$

Therefore, in this study, $\varepsilon_e K_g$ for Darco-Hg-LH was estimated to be about 0.031(±0.002) m³/gs at fan rotating speeds of 1500 rpm according to our tests. Similarly, $\varepsilon_e K_g$ for the Darco-Hg-LH in the reported industrial demonstration was calculated to be at least 6.6 m³/gs (with 5 s of the contacting time); this is more than 200 times higher than that obtained in this study for Darco-Hg-LH.

The difference of $\varepsilon_e K_g$ between this study and the industrial tests can be explained by the gas–solid contacting condition. Darco-Hg-LH particles in this test were attached to vanes of the stirrer with one side opposite to the bulk gas; therefore the gas–solid contact was very limited. However, in the demonstration test, powdered Darco-Hg-LH particles were well dispersed into flue gas, thus creating excellent contact with Hg⁰ in flue gas. According to the comparison, a calibration coefficient of 200 for $\varepsilon_e K_g$ involving activated carbon can be used to extrapolate the results in this test to industrial cases at the stirrer's rotating speed of 1500 rpm. A conservative estimate for the calibration coefficient of $\varepsilon_e K_g$ involving fly-ash was tentatively set at 100.

Meanwhile, $\varepsilon_e K_g$ for fly-ash in the presence of 0.5 ppmv and 2 ppmv in the simulated flue gas was calculated to be $1.8 \times 10^{-4} \text{ m}^3/\text{gs}$ and $5.1 \times 10^{-4} \text{ m}^3/\text{gs}$, respectively. On the grounds of the above calibration and Eq. (9), the predicted Hg^0 removal efficiency for the particle-involved reaction alone was as high as 85% if 0.5 ppmv of iodine were added into the flue gas with $20 \text{ g}/\text{m}^3$ of fly-ash and 1000 ppmv of SO_2 at 373 K (with 5 s of the contacting time). Further, it predicted an Hg^0 removal efficiency of approximately 70% with 0.3 ppmv of iodine and $20 \text{ g}/\text{m}^3$ of fly-ash in flue gas, successfully meeting the Phase-II cap of CAMR stated by U.S.E.P.A.

In addition, the prediction from Eq. (9) increased the removal efficiency of Hg^0 up to 90% if $10 \text{ mg}/\text{m}^3$ (corresponding to a dosage of 0.6 Lb/MMacf) of Darco-KB and 0.3 ppmv iodine were injected into the flue gas with $20 \text{ g}/\text{m}^3$ of fly-ash; this could save 80% of activated carbon compared to the demonstration. Even for the flue gas without fly-ash, the co-injection of 0.5 ppm of iodine and $50 \text{ mg}/\text{m}^3$ of Darco-KB can remove 60% of Hg^0 .

4. Conclusion

In order to facilitate the removal of Hg^0 , iodine and zinc iodide were employed as oxidants to forcibly convert Hg^0 to its oxidized or particulate-bound form. The removal of Hg^0 by the homogenous gas phase reaction and the particle-involved heterogeneous reactions were investigated under various conditions and a methodology was developed to test the particle-involved reaction kinetics. Iodine was found to be the most efficient oxidant for Hg^0 oxidation, having a 2nd order reaction rate constant of about $7.4(\pm 0.2) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 393 K. Nitric oxide showed significant inhibition to the homogenous gas reaction of Hg^0 oxidation. The oxidation of Hg^0 with iodine can be significantly accelerated in the presence of fly-ash or the powdered activated carbon. SO_2 slightly reduced Hg^0 removal efficiency for the particle-involved reaction. It was estimated that Hg^0 removal efficiency was up to 70% if 0.3 ppmv of iodine were added into the flue gas with $20 \text{ g}/\text{m}^3$ of fly-ash. In addition, the predicted Hg^0 removal efficiency increased to 90% if $10 \text{ mg}/\text{m}^3$ of activated carbon and 0.3 ppmv iodine were added into the flue gas with fly-ash. The results suggested that the combination of iodine with fly-ash and/or activated carbon can enhance the removal of Hg^0 efficiently, and the potential of iodine to oxidize elemental mercury in coal-fired flue gases is clearly promising for further study on a larger scale.

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