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Bromine Chloride as an Oxidant to Improve Elemental Mercury Removal from Coal-Fired Flue Gas

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The equilibria and kinetics of the reaction between bromine (Br_2) and chlorine (Cl_2) to form bromine chloride (BrCl) at various temperatures were determined. BrCl was employed to oxidize elemental mercury (Hg^0) under simulated flue gas conditions. The removal of Hg^0 from the gas phase by a homogeneous gas-phase oxidation reaction and the heterogeneous reactions involving flyash were investigated. The second-order gas phase rate constant was determined to be $2.3(\pm0.2) \times 10^{-17}$ $cm^3 \cdot molecules^{-1} \cdot s^{-1}$ at 373K. The reaction of Hg^0/BrCl was significantly accelerated in the presence of flyash, and the estimated Hg^0 removal efficiency in the presence of 0.6 ppmv BrCl and 20 g/m^3 flyash was up to 90%. Unexpectedly, the major product was found to be $HgCl_2$, rather than $HgBr_2$, indicating that bromine in part acted as the accelerant in Hg^0 oxidation in $BrCl/Br_2/Cl_2$ system by facilitating the formation of intermediates. As a result, bromine consumption is much less than if only bromine gas is utilized alone. These results were helpful not only for understanding the mechanism of Hg^0 removal in coal-fired flue gas but also in any atmosphere in which bromine and chlorine species coexist.

Introduction

The United Nations Environment Programme (UNEP) approved at the UNEP 25th GC Session in February 2009 an agreement in UNEP Mercury Treaty Negotiations (*1*). Coal-fired electric power plants are recognized as one of the primary sources of mercury emission, particularly in countries in which such plants are the major source of electric power (*2*). Because of the intense dependence on coal for the production of electricity, China is regarded as one of the largest emitters of mercury. To reduce the emission from coal-fired plants, China, as well as the U.S., has recognized capturing mercury from flue gas is vitally important.

Mercury in flue gas is present in three forms: elemental mercury (Hg^0), particulate-bound mercury (Hg^p), and oxidized mercury (Hg^{2+}) (*3, 4*). Generally, mercury in the flue gas from low-rank coal or low chlorine in coal is primarily in the form of elemental mercury. Existing air pollution control devices (APCDs) can capture mercury to some degree as a cobenefit in addition to removing other pollutants (*4*−*7*). Electrostatic precipitators (ESP) or fabric filters (FF) can remove Hg^p efficiently, and flue gas desulfurization systems are effective in removing Hg^{2+}. However, elemental mercury in flue gas is not removed efficiently by APCDs because of its high volatility and its insolubility in water (*8*).

Because wet flue gas desulfurization (WFGD) systems are widely used by Chinese utilities for sulfur dioxide control (*9*), using WFGD to capture mercury seems an obvious choice. However, WFGD can not directly scrub Hg^0 efficiently, so it is necessary to find a cost-effective method to convert the Hg^0 to an oxidized or even a particle-bound form before entering the WFGD system.

Conversion of Hg^0 to Hg^{2+} or particulate-bound mercury can be accomplished by heterogeneous catalysis or homogeneous gas phase oxidation. Injection of an oxidant into the flue gas (upstream of WFGD) to oxidize Hg^0 appears to be the simplest method to implement. The challenge is the selection of the proper oxidants for such a purpose. Due to 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 rapid. Though many chemical kinetic models and laboratory studies have indicated that chlorine increases the percentage of oxidized mercury in hot flue gas (>500 °C), the reaction between Cl_2 and Hg^0 has been proven to be too slow to meet the industrial application at lower temperature (<300 °C) (*10*). According to prior studies, bromine or bromide salt has been proved to be more effective than chlorine in enhancing mercury removal from flue gas (*10*−*15*). Adding bromide salts (e.g., $CaBr_2$ or NaBr) to low-chlorine coal or injecting solutions of the salts into furnaces has been demonstrated to be effective in oxidizing elemental mercury if there are SCR catalysts (selective catalytic reduction of nitric oxide) installed downstream of the furnaces (*13, 14*). But for plants without SCR catalysts, the required dosage of bromide salts was very high (more than 100 ppmv bromine to the dry coal) because the gas-phase reaction of HBr (produced by bromide salts at high temperature in furnaces) with Hg^0 was slow. Furthermore, there is still concern of whether adding too much bromide directly to furnaces will cause corrosion to furnace or heat-exchange surfaces, or possibly result in unexpected brominated compounds under unfavorable combustion conditions.

It has been found that bromine molecule (Br_2) showed far higher reactivity to oxidize elemental mercury than HBr at lower temperature, and injecting Br_2 to flue gas downstream of the furnace can convert Hg^0 to oxidized mercury efficiently (*11*). However, Br_2 is more expensive than bromide salts, and it is highly volatile and irritating, which would complicate its safe transportation and storage in the power plant.

Bromine, unlike chlorine, is not a usual component in coals or flue gas, and introducing too much of it into the flue gas system brings a risk of secondary pollution problems. Therefore, reduction of bromine consumption, and the use of cheaper and safer bromide salts as raw materials to replace Br_2 are compelling reasons for industry to consider this change.

Br_2 can be produced from bromide salt solutions by gas chlorine stripping in industrial processes, and the primary Br_2 gas often contains surplus Cl_2. Meanwhile, chlorine can react with bromine to form the interhalogen, bromine chloride, BrCl (*16, 17*), so the primary bromine gas can be readily converted to BrCl without any pretreatment. Employing BrCl to oxidize Hg^0 would be a promising choice to obtain higher conversion efficiency and to reduce the use of bromine. Figure 1 is an illustration on how to generate BrCl in situ with the safer raw materials, in which chlorine can be readily prepared in situ by electrolyzing a chloride salt solution to produce Cl_2 (eq 1), and then Cl_2 gas is used

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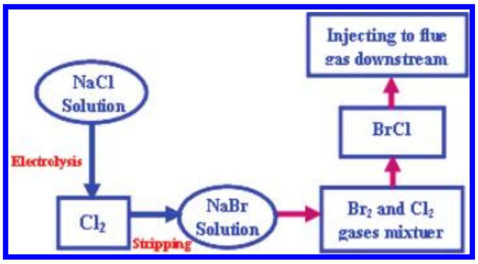

FIGURE 1. Proposed approach for generating BrCl from chloride and bromide solutions.

to strip bromide salt solutions (eq 2) and to produce BrCl (eq 3).

$$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + H_2\uparrow + Cl_2\uparrow \qquad (1)$$

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2\uparrow \qquad (2)$$

$$Br_2 + Cl_2 \underset{k_-}{\overset{k_+}{\rightleftharpoons}} 2BrCl \qquad (3)$$

in which k_+ and k_- are the rate constants for the forward and reverse reactions, respectively.

Because the needed amount of BrCl for Hg^0 oxidation is relatively small, the energy consumption by the compact electrolysis cell would not be a problem for power plants. In addition, it has been observed that BrCl is much less likely to condense or deposit on solid surfaces than Br_2, which can minimize the corrosion of transport tubes and ducts.

Equations 1 and 2 are well understood, but the necessary information on the reaction kinetics for the BrCl production from Br_2 and Cl_2 (eq 3) and its oxidation of elemental mercury has not been reported previously. In addition to its potential for mercury oxidation in flue gas, BrCl can also be present in atmosphere environment (*21*), and it is supposed to have effects on atmospheric mercury circulation.

Therefore, we performed a series of experiments to test the kinetic parameters of eq 3 and to investigate on the performance of BrCl in the removal of elemental mercury. The effects on Hg^0 removal by the main components of flue gas (including flyash) and the operating parameters were also determined.

Experimental Section

BrCl was prepared by directly mixing chlorine gas with bromine gas in Teflon bags (Dalian Date) at various temperatures, and their concentrations were determined with a UV/vis spectrometer (BWTEK BRC641E, USA). The reaction equilibrium constant and the reaction rate constants between chlorine and bromine were determined using a photocell located in the oven with two opposing quartz windows. The cell with a volume of 250 mL was also fitted with quartz windows. First, the cell was vacuumized. Then, Cl_2 and Br_2 gas were injected into the cell, respectively. Meanwhile, air was injected into the cell to keep up the pressure at 760 Torr. The reaction between chlorine and bromine in the cell was monitored in situ by a UV/vis spectrometer equipped with an optical fiber for UV-beam transmission and a detector in the range of 200−800 nm. The maximum UV absorbances for bromine, chlorine, and BrCl are at approximately 415, 330, and 375 nm, respectively (*16*−*20*).

The reaction kinetics between Hg^0 and BrCl 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) as in our previous studies (*10, 11*). A reference beam was added to minimize the noise in the monitoring signal, improving the sensitivity of the system. The reactor was a stainless steel cylinder with a volume of 1100 mL. The signal was collected with a data transition and acquisition device (N2000, Zhejiang Zhida). The Hg^0 concentrations employed were about 0.16 ppmv. To minimize the adsorption of Hg^0 by the surface, the reactor's wall was coated with halocarbon wax (HW).

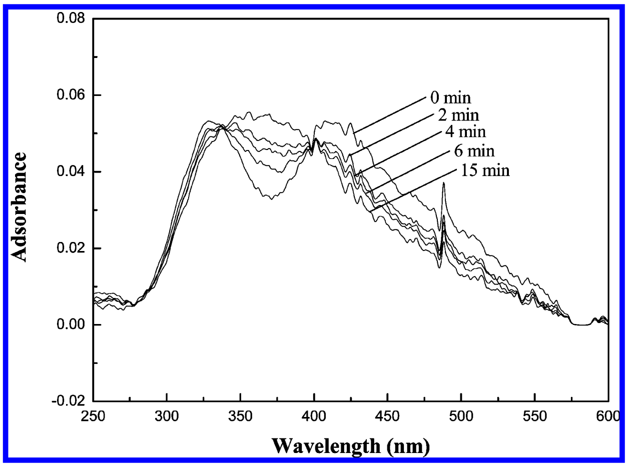

FIGURE 2. Spectra of bromine chloride, Br_2, and Cl_2 during the combination reaction; $[Br_2] = 300$ ppmv and $[Cl_2] = 800$ ppmv at 373 K. After the cell was vacuumized, Cl_2 and Br_2 gas were injected into the reactor, respectively. Meanwhile, dry air was used to balance the pressure to 760 Torrs.

To evaluate the effect of flyash or activated carbon, a rotating 6-vane stirrer driven by a magnetic rotor was installed inside the reactor to mix the gas. Approximately 10.0 mg of bituminous flyash or 2.0 mg of activated carbon (AC) was attached on the leading edge of the vanes with double-sided carbon tape (Ted Pella, Inc.). The continuous stirring enabled good contact between the particles and Hg^0 in the simulated flue gas, and minimized the gas diffusion-limitation from the gas to the particle surfaces. The accuracy of the data reported here was estimated to be within 10%.

The chemicals employed were mercury (99.99%), chlorine (99.9%), bromine (99.9%) from Sigma-Aldrich Co.; halocarbon wax (HW, Series-1500) from Halocarbon Product Co.; Darco-KB (AC-KB) and Darco-Hg-LH (AC-LH) activated carbons (AC) from Norit American Company. The flyash was provided by Shanghai Wujing Power Plant with a BET surface area of 2.0(±0.2) m^2/g. Loss of ignition (LOI) of the flyash was test by sintering at 800 °C for 4 h, and it was about 1.6(±0.2)%. The flyash was analyzed with inductively coupled plasma (ICP) spectrometer (Iris Advantage 1000, Thermo), and it consisted of about 22(±2)% for Al_2O_3, 12(±2)% for CaO; 8(±1)% for Fe_2O_3, and 1.2(±0.5)% for Na_2O. Ionic chromatography (MIC, Metrohm) was employed to analyze the product from the reaction between Hg^0 and BrCl.

Results and Discussion

The time-dependent evolution of the complex UV absorption curves of bromine, chlorine, and BrCl are shown in Figure 2. At first, there are separate peaks for Cl_2 and Br_2 in the curve. As the reaction proceeded, the absorption peak of BrCl gradually increased while the peaks of Cl_2 and Br_2 decreased. The concentrations of Br_2, Cl_2, and bromine chloride can be calculated by their specific absorbance at the various wavelengths.

Equations 4−6 were employed to separate the contributions of each substance to the overall absorption intensity in the curve, allowing the concentrations of the bromine, chlorine, and bromine chloride to be evaluated (*16*−*20*).

$$I_{330} = \varepsilon_{Cl_2,330} L C_{Cl_2} + \varepsilon_{BrCl,330} L C_{BrCl} + \varepsilon_{Br_2,330} L C_{Br_2} \qquad (4)$$

$$I_{375} = \varepsilon_{Cl_2,375}LC_{Cl_2} + \varepsilon_{BrCl,375}LC_{BrCl} + \varepsilon_{Br_2,375}LC_{Br_2} \quad (5)$$

$$I_{415} = \varepsilon_{Cl_2,415}LC_{Cl_2} + \varepsilon_{BrCl,415}LC_{BrCl} + \varepsilon_{Br_2,415}LC_{Br_2} \quad (6)$$

where I_{330} is the intensity of the absorption peak at 330 nm; $\varepsilon_{Cl_2,330}$, $\varepsilon_{BrCl,330}$, $\varepsilon_{Br_2,330}$ are the absorption coefficients of Cl_2, Br_2, and BrCl at 330 nm, $cm^2 \cdot molecules^{-1}$, respectively. L is the optical path length in the cell, cm; and C_{Cl_2}, C_{BrCl}, C_{Br_2} are the concentrations of the Cl_2, BrCl, and Br_2, $molecules \cdot cm^{-3}$.

The reaction rate constant of BrCl can be expressed by eq 7 according to the reversible reaction 3 and the mass balance.

$$\frac{d([BrCl])}{dt} = 2k_+[Br_2]\cdot[Cl_2] - k_-([BrCl])^2 \quad (7)$$

where $[Br_2]$, $[Cl_2]$, and [BrCl] denote the concentrations of Br_2, Cl_2, and BrCl at reaction time t, respectively. In addition, the reaction equilibrium constant, K_a, can be described by eq 8 as

$$K_a = \frac{([BrCl])^2}{[Br_2][Cl_2]} = \frac{2k_+}{k_-} \quad (8)$$

The reaction equilibrium constant and rate constant at different temperatures are shown in Table 1. It was found that K_a at about 298 K was very close to the data proposed previously in the literature (*16–20*). Apparently both the forward and the reverse rate constants increase with the rise of the temperature. The reaction was observed to reach 90% of the equilibrium concentration within 20 and 15 min at 313 and 373 K, respectively, with the equilibrium coefficient being lower at higher temperature. Approximately 61% of the bromine and chlorine was converted to BrCl at 293 K when bromine and chlorine was mixed with stoichiometric amount, with approximately 57% converted to BrCl at 373 K. Using a mole ratio of Cl_2 to Br_2 of 2:1 and 3:1, approximately 75% and 83% of bromine was converted at 373 K, respectively.

Gas Phase Oxidation of Hg^0 by BrCl. Since there exists an equilibrium among BrCl, chlorine, and bromine, pure BrCl cannot be obtained. To get a more exact rate constant for the reaction between Hg^0 and $BrCl/Br_2/Cl_2$, the contributions of bromine and chlorine to the oxidation of Hg^0 should be deducted.

$$\frac{d[Hg^0]}{dt} = -\{k_{BrCl}[BrCl] + k_{Br_2}[Br_2] + k_{Cl_2}[Cl_2]\}[Hg^0] \quad (9)$$

where k_{BrCl}, k_{Br_2}, and k_{Cl_2} are the reaction rate constants of $Hg^0/BrCl$, Hg^0/Br_2, and Hg^0/Cl_2, respectively. The oxidation of Hg^0 by chlorine or bromine has been previously investigated (*10, 11*), and rate constants of $3.2(\pm0.2) \times 10^{-17}$ $cm^3 \cdot molecules^{-1} \cdot s^{-1}$ and $2.5(\pm0.5) \times 10^{-19}$ $cm^3 \cdot molecules^{-1} \cdot s^{-1}$ were determined at 373 K for Hg/Br_2 and Hg/Cl_2 here, respectively.

TABLE 1. Rate Constant for the Formation of Bromine Chloride and the Equilibrium Constants in $BrCl/Br_2/Cl_2$ System under Various Temperatures

temperature	293 K	333 K	373 K
k_+ ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$)	1.31×10^{-19}	1.71×10^{-19}	1.86×10^{-19}
k_- ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$)	2.71×10^{-20}	3.90×10^{-20}	5.29×10^{-20}
K_a (equilibrium constant)	9.7	8.8	7.0

The relative errors range about ±10% for k_+ and k_-, and it is about ±5% for K_a.

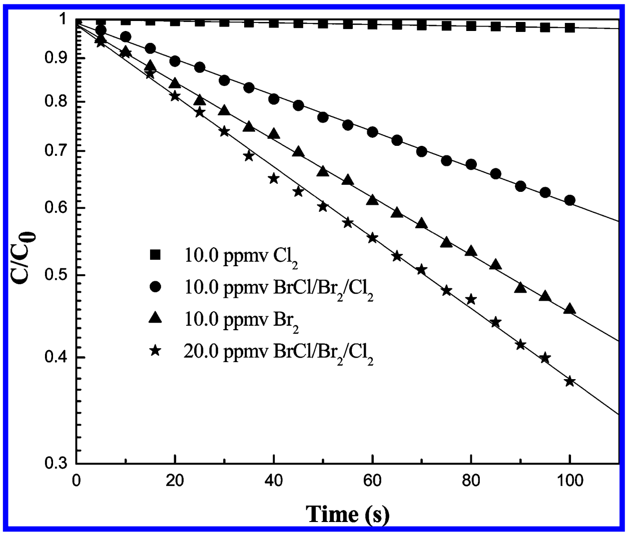

FIGURE 3. Depletion of Hg^0 by reacting with Cl_2, Br_2, and $BrCl/Br_2/Cl_2$, respectively. 10 ppmv of $BrCl/Br_2/Cl_2$: about 5.8 ppmv BrCl equilibrium with about 2.1 ppmv of Br_2 and Cl_2, respectively; 20 ppmv of $BrCl/Br_2/Cl_2$: about 11.6 ppmv BrCl equilibrium with about 4.2 ppmv of Br_2 and Cl_2, respectively. The initial concentration of Hg^0 was about 0.16 ppmv, and the tests were conducted at 373 K and 760 Torrs with nitrogen balance.

The overall depletion of Hg^0 in the presence of BrCl, chlorine, and bromine at various concentrations is shown in Figure 3. The mixture in the reactor was allowed to reach equilibrium before the introduction of Hg^0. The concentration of BrCl in the gas was about 11.4 ppmv when the reaction of Br_2 and Cl_2 reached equilibrium, much higher than the Hg^0 concentration in the gas. As shown in Figure 3, the depletion rate of Hg^0 was higher with the mixture of bromine chloride, chlorine, and bromine than the sum of the separate contributions of chlorine and bromine to the Hg^0 oxidation. The second rate constant of $Hg^0/BrCl$, k_{BrCl}, was calculated using eq 9 and the data in Table 1 to be $2.3(\pm0.2) \times 10^{-17}$ $cm^3 \cdot molecules^{-1} \cdot s^{-1}$ at 373 K. Br_2 exhibited the fastest Hg^0 oxidation, followed by BrCl, and Cl_2, the slowest among the three oxidants. However, the apparent first-order rate constant for Hg^0 oxidation increased by about 30% with BrCl comparing to the sum of that with bromine and chlorine separately. This indicates that bromine chloride shows a significant synergistic effect in oxidizing Hg^0. Furthermore, about 30% less bromine is consumed for the same Hg^0 oxidation efficiency if Br_2 is converted to BrCl.

The influence of temperature on the $Hg^0/BrCl$ reaction was also investigated. It was found that the second rate constant of $Hg^0/BrCl$ decreased from $3.9(\pm0.2) \times 10^{-17}$ to $2.1(\pm0.2) \times 10^{-17}$ $cm^3 \cdot molecules^{-1} \cdot s^{-1}$ as the temperature rose from 273 to 393 K. The rate of change was less for temperatures beyond 373 K.

Surface-Involved Conversion of Hg^0 by Flyash and $BrCl/Br_2/Cl_2$ System. Generally, flue gas from pulverized coal boilers can contain about 10–40 g/m^3 of flyash depending on the mineral content in coal. Therefore, the contribution of flyash to mercury removal in the presence of the oxidant should be considered. About 10.0 mg of flyash was attached on the vanes of the stirrer with 12 cm^2 of carbon tape, with the rotating speed set at 1500 rpm.

As shown in Figure 4, the presence of the flyash 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 40.5% when the flyash was used together with 10 ppmv of $BrCl/Br_2/Cl_2$ (about 5.8 ppmv BrCl equilibrium with about 2.1 ppmv each for Br_2 and Cl_2). The removal efficiency of Hg^0 was also significantly higher than the sum of the respective contributions of homogeneous gas reactions with chlorine or bromine in separate tests.

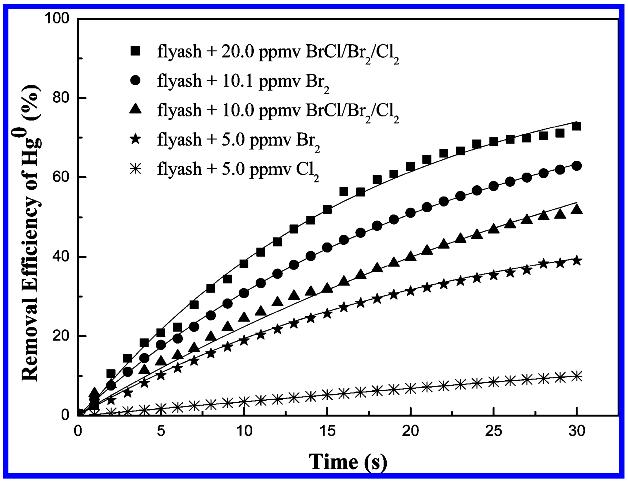

FIGURE 4. Hg^0 removal efficiency by $BrCl/Br_2/Cl_2$ in the presence of the flyash. About 10.0 mg of flyash was stuck on 12 cm^2 of carbon tape. The rotating speed was at 1500 rpm at 373 K. The initial Hg^0 concentration was about 0.16 ppmv.

Effects of the Gaseous Components of Flue Gas on the Mercury Capture. The effect of the main flue gas components on Hg^0 removal efficiency was investigated. No obvious effect was observed except for SO_2 and NO. It was found that SO_2 in the reactor had no significant effect on the Hg^0 removal efficiency by gas-phase reaction. However, it appeared to cause a slight decrease when the particulate-induced reaction with flyash was involved (a reduction of 2−5% in Hg^0 oxidation efficiency with 1500 ppmv of SO_2 in the gas). As for NO, the Hg^0 removal by the gas-phase reaction was notably inhibited, but its effect became negligible when flyash was employed. The inhibiting mechanism of NO on Hg^0 oxidation in the gas phase reaction has been discussed previously (*11*).

Products Analysis and Hg^0 Oxidation Mechanism in $BrCl/Br_2/Cl_2$. Figure 5 is the spectra of Br_2, Cl_2, and BrCl as they reacted with Hg^0. The concentration of Cl_2, BrCl, and Br_2 could also be calculated according to eqs 4−6 with their respective spectra (*16*−*20*). The concentration of Cl_2 and BrCl in the gas phase decreased significantly as the Hg^0 oxidation proceeded, but Br_2 concentration increased unexpectedly. The balance of total chlorine and bromine in the gas phase indicated that chlorine was the main element consumed by oxidized mercury (about 80%), and the total bromine consumption from BrCl and Br_2 by gas phase Hg^0 oxidation reaction was significantly less than chlorine. The results also implicated that Hg^0 was more ready to extract chlorine atom from BrCl, and the reaction rate for BrCl consumption was more rapid than the formation of BrCl.

In addition, the mercury products oxidized by BrCl (mixed with the equilibrium Br_2 and Cl_2) were analyzed by ion chromatography by dissolving and diluting the products into ultrapure water, and the result is shown in Figure 6. Since BrCl and Br_2 were found to be more reactive than Cl_2 in oxidizing Hg^0 by 2 orders of magnitude, bromide ion (Br^-) was expected to be the main anion in the products. However, unexpected observation that chloride ion (Cl^-) was the dominant anion in the product, with the bromide ion accounting for less than 20% of total anions, was consistent with the UV analysis on the gas phase.

From the above results, the reaction mechanism for Hg^0 oxidation by BrCl (with the equilibrium Br_2 and Cl_2) was postulated. Although Cl_2 was expected to be more active than Br_2 as an oxidant by comparing their redox potential values, it was found that Br_2 or BrCl were both more effective than chlorine in oxidizing Hg^0 by the gas-phase reaction. This phenomenon is tentatively explained with London forces (*11*), which result in the formation of van der Waals intermediate molecules, such as $Hg-Br_2^*$ and $Hg-Cl_2^*$. For the reaction in the presence of BrCl, $Hg-BrCl^*$ can be also regarded as one of the intermediates, which is also the rate-determining step for Hg^0 oxidation (eq 10).

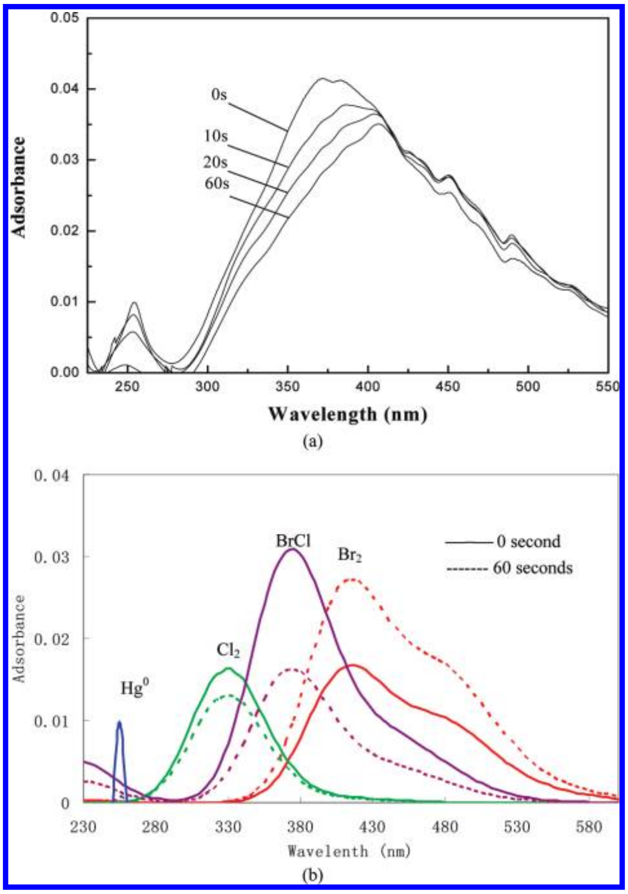

FIGURE 5. Spectrum evolution with the reaction time for Hg^0 in $BrCl/Br_2/Cl_2$ system at 373 K (a): the accumulative spectrum of BrCl, Br_2, Hg^0, and Cl_2; (b) the deconvoluted spectra of BrCl, Br_2, Cl_2, and Hg^0 at 0 and 60 s. The initial gas concentrations (0 s): BrCl, 370 ppmv; Br_2, 45 ppmv; Cl_2, 330 ppmv; and Hg^0, 230 ppmv.

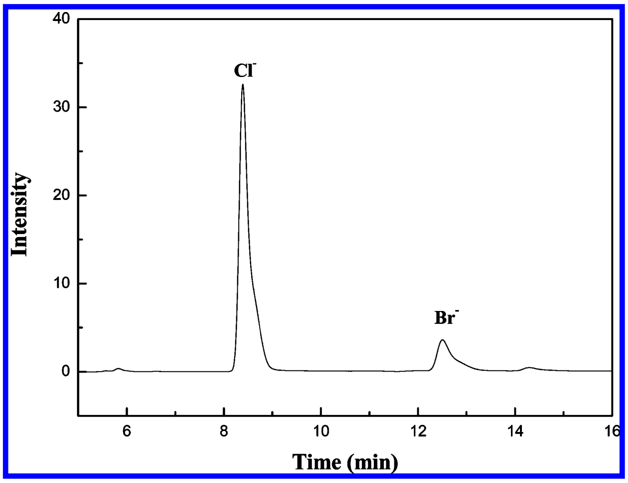

FIGURE 6. Ionic chromatography analysis for the product from the reaction between Hg^0 and BrCl.

The fact that the product analysis results were inconsistent with expectations indicates that chlorine will play a more important role in converting the intermediate to the end products by a series of reactions, and the higher redox potential value of chlorine makes it more competitive than bromine to bond with the oxidized mercury. Therefore, most bromine atoms in the $Hg-BrCl^*$ and $Hg-Br_2^*$ intermediates could be replaced by chlorine. Equations 11−15 are some of

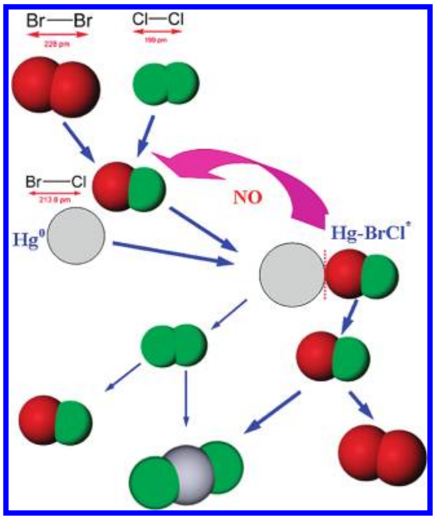

FIGURE 7. Speculated approach for Hg^0 oxidation by BrCl in the gaseous $BrCl/Br_2/Cl_2$ system.

the possible reactions during Hg^0 conversion, and Figure 7 is the proposed schematic for Hg^0 oxidation by BrCl. Of these reactions, eq 11 is regarded as the most important because the increase of Br_2 was significant (Figure 5).

$$Hg^0 + BrCl \leftrightarrow Hg{-}BrCl^* \text{ (intermediate complex)} \tag{10}$$

$$Hg{-}BrCl^* + BrCl \rightarrow HgCl_2 + Br_2 \tag{11}$$

$$Hg{-}BrCl^* + Cl_2 \rightarrow HgCl_2 + BrCl \tag{12}$$

$$Hg{-}BrCl^* + M \rightarrow HgClBr + M \tag{13}$$

$$HgBrCl + BrCl \rightarrow HgCl_2 + Br_2 \tag{14}$$

$$HgClBr + Cl_2 \rightarrow HgCl_2 + BrCl \tag{15}$$

in which M is the third molecule in the gas to collide with the intermediate. Therefore, it can be concluded that bromine in gaseous $BrCl/Br_2/Cl_2$ system mainly acted as an accelerant for Hg^0 oxidation by facilitating formation of the intermediates, which was the rate-determining step among the series of reactions. Then, chlorine can further convert the intermediate to the $HgCl_2$. Bromine appears to be recycling in the series of reactions, which can reduce the consumption of bromine in such systems. In addition to the utilization for the enhancement of Hg^0 conversion by bromine in flue has, this phenomenon could also be important in the oxidation of atmospheric mercury in the presence of various halide species in the natural environment.

Evaluation of BrCl in Industrial Application. Using the above results, the feasibility of industrial application of BrCl on mercury capture was evaluated. From the gas-phase reaction data, injecting 10.0 ppmv BrCl into flue gas at 373 K can oxidize only about 7% of Hg^0 in flue gas with a gas contact time of 5 s. This means that the contribution of the gas-phase reaction to Hg^0 oxidation was relatively small.

Darco-Hg-LH (AC-LH), which has been widely used in many field tests and demonstrations for Hg^0 capture (*6*), was employed as the reference to evaluate the importance of flyash or activated carbon (injected) into actual flue gas with BrCl. The role of Br_2 in enhancing Hg^0 removal from flue gas has been estimated previously (*11*). Therefore, such data can be used to estimate the effect BrCl in the actual flue gas with flyash.

Based on a demonstration at the 140 MW Meramec Station with Darco-Hg-LH (*6*), it has also been tentatively estimated from the laboratory and field test results to be able to achieve about 60% Hg^0 oxidation efficiency with 0.4 ppmv Br_2 in flue gas with 5.6 g/m^3 of flyash (*11*). According to the data in Figure 4, it was predicted that only about 0.6 ppmv BrCl (produced from 0.3 ppmv of Br_2) would be needed to get the same Hg^0 oxidation efficiency. Hg^0 oxidation efficiency should increase with further increase in flyash concentration in flue gas, and the Hg^0 removal efficiency in the presence of 0.6 ppmv BrCl and 20 g/m^3 flyash was about 90% at about 120 °C. Though the exact performance with BrCl gas injection to the actual flue gas cannot be accurately estimated before a scale-up demonstration is finished, the results imply that BrCl could be a potential oxidant for Hg^0 conversion from flue gas, especially for flue gas with high flyash concentration.

In summary, bromine chloride (BrCl) can be readily produced from safer raw materials onsite, and it appears to be effective for Hg^0 oxidation with a second-order rate constant about $2.3(\pm 0.2) \times 10^{-17}\ cm^3 \cdot molecules^{-1} \cdot s^{-1}$ at 373 K. Using BrCl, instead of bromine or chlorine alone, to oxidize elemental mercury by gas-phase reaction can reduce bromine consumption by about 30% for the same Hg^0 oxidation efficiency. Bromine in the BrCl mainly performed like an accelerant for Hg^0 oxidation by facilitating formation of intermediates. Bromine appears to be recycling in the postulated series reactions, potentially reducing the consumption of bromine in this application. In addition to Hg^0 oxidation in flue gas, our findings on the role of bromine in Hg^0 oxidation in the presence of chlorine may also have important implications to understanding the fate of Hg^0 in the atmosphere with various halide species.

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