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TECHNICAL PAPER

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Effects of Sulfur Dioxide and Nitric Oxide on Mercury Oxidation and Reduction under Homogeneous Conditions

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ABSTRACT

This paper is particularly related to elemental mercury (Hg^0) oxidation and divalent mercury (Hg^{2+}) reduction under simulated flue gas conditions in the presence of nitric oxide (NO) and sulfur dioxide (SO_2). As a powerful oxidant and chlorinating reagent, Cl_2 has the potential for Hg oxidation. However, the detailed mechanism for the interactions, especially among chlorine (Cl)-containing species, SO_2, NO, as well as H_2O, remains ambiguous. Research described in this paper therefore focused on the impacts of SO_2 and NO on Hg^0 oxidation and Hg^{2+} reduction with the intent of unraveling unrecognized interactions among Cl species, SO_2, and NO most importantly in the presence of H_2O. The experimental results demonstrated that SO_2 and NO had pronounced inhibitory effects on Hg^0 oxidation at high temperatures when H_2O was also present in the gas blend. Such a demonstration was further confirmed by the reduction of Hg^{2+} back into its elemental form. Data revealed that SO_2 and NO were capable of promoting homogeneous reduction of Hg^{2+} to Hg^0 with H_2O being present. However, the above inhibition or promotion disappeared under homogeneous conditions when H_2O was removed from the gas blend.

INTRODUCTION

Of the hazardous and toxic pollutants identified under Title III of the 1990 Clean Air Act Amendments, mercury (Hg) is a leading concern because of its environmental and health impacts. According to the Mercury Study Report to Congress, coal-fired utility boilers are concluded as the primary source of anthropogenic emissions in the United States, contributing ~48 t or ~30% of all U.S. Hg emissions. In March 2005, U.S. Environmental Protection Agency (EPA) promulgated the first-ever Clean Air Mercury Rule, through which EPA plans to reduce Hg emissions in two phases. In the first phase, due by 2010, emissions of Hg will be reduced by taking advantage of "cobenefit" reduction while reducing SO_2 and nitrogen oxides (NO_x) under Clean Air Interstate Rule. The second phase will reduce Hg emissions to 15 t by 2018, an overall reduction of nearly 70%.

Development of Hg control technologies has been ongoing over the past years. However, although progress has been made, based on the data to date, there is currently no single best control technology that can be broadly applied. Capture of Hg in wet scrubbers, the same devices that capture sulfur dioxide $(SO)_2$, shows promise. However, none of the wet scrubbers can effectively capture and remove elemental mercury (Hg^0).[1–5] Therefore, if the Hg control target is to be met by taking advantage of cobenefit reduction with scrubbers currently used for SO_2 removal, effective methods to transform Hg^0 to water-soluble divalent mercury (Hg^{2+}) must be developed.

In recent years, research efforts have been and continue to shed light on various aspects of Hg oxidation, especially with chlorine-containing species, under conditions relevant to those encountered in coal-fired utility boilers.[6–21] Through these efforts, the Hg^0 oxidation chemistry with chlorine (Cl)-containing species was progressively elucidated. Hg leaves the high-temperature combustion zone as elemental Hg, part of which transforms into oxidized form during the postcombustion zone as flue gas cools.[5,12] One-step global reaction mechanisms have been proposed to model this observed depletion of Hg^0 in the presence of chlorine (Cl_2) and hydrogen chloride (HCl).[16] Although such mechanisms can give plausible qualitative results, the global mechanisms, nevertheless, provide little insight into the details of the conversion process and, hence, are not instrumental for the examination of other flue gas effects, such as SO_2 and NO_x.

Efforts to describe Hg transformation through a sequence of elemental reactions have been initiated by Sliger et al.[7] The basic finding of this effort was that the

IMPLICATIONS

Coal-fired utility boilers are the primary stationary sources of anthropogenic Hg emissions, accounting for ~48 t or 30% of total U.S. emissions annually. In developing Hg emission control technology, if Hg control is to be met by taking advantage of "cobenefit" multipollutant control technologies, such as wet scrubbers, effective methods to transform Hg^0 to water-soluble Hg^{2+} must be developed. One of the proposed ways is to add Cl-containing reagents. However, the fundamental data as to how the flue gas constituents, such as SO_2 and NO, affect Hg^0 oxidations are yet not adequate. This research, therefore, was intended to develop a mechanism to elucidate and interpret the interactions among SO_2, NO, and Cl-containing species.

dominant oxidizing species was Cl at relatively high temperatures, which first oxidized Hg^0 into HgCl. The formed intermediate HgCl, in turn, reacted with Cl, HCl, and Cl_2 to produce thermodynamically stable $HgCl_2$, as presented in eq 1–4:

$$Hg^0 + Cl + M \rightarrow HgCl + M \quad (1)$$

$$HgCl + Cl \rightarrow HgCl_2 \quad (2)$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl \quad (3)$$

$$HgCl + HCl \rightarrow HgCl_2 + H \quad (4)$$

The pivotal parameters that were identified to affect the Hg^0 conversion through this mechanism were Cl and Cl_2 concentrations in flue gas, the flue gas quench rate, and the rate at which Cl recombines into Cl_2.

From a more theoretical perspective, Widmer et al.[9], expanded this mechanism in eq 1–8 by including the important roles for other chlorinating species, such as HCl, Cl_2, and HOCl. With regard to the role of HOCl, Li et al.[18] later on confirmed that Hg^0 might react with HOCl to form a stable intermediate without activation energy. This intermediate subsequently broke down into HgCl and free-radical OH:

$$Hg^0 + Cl_2 \rightarrow HgCl + Cl \quad (5)$$

$$Hg^0 + HCl \rightarrow HgCl + H \quad (6)$$

$$Hg^0 + HOCl \rightarrow HgCl + OH \quad (7)$$

$$HgCl + HOCl \rightarrow HgCl_2 + OH \quad (8)$$

After Sliger et al.[7] and Widmer et al.,[9] Niksa et al.[6] expanded these initial efforts. They further found that the essential sequence for Hg^0 oxidation was a Cl atom recycle process. Once a pool of Cl-atoms was established, Hg^0 was first oxidized via Cl into HgCl, which, in turn, oxidized by Cl_2 into $HgCl_2$ with an associated regeneration of Cl atoms. In their mechanism, the only channel that initiated Hg^0 oxidation at an appreciable rate was $Hg^0 + Cl + M \rightarrow HgCl + M$. The dissociation of HgCl via attack by OH to form Hg^0 and HOCl was a significant competitor. Although HOCl can subsequently oxidize HgCl into HgCl, the primary production channel for $HgCl_2$ was $HgCl + Cl_2 \rightarrow HgCl_2 + Cl$. When simulating the test conditions of Sliger et al.,[7] Niksa et al.,[6] furthermore, found that the impact of NO on homogeneous Hg^0 oxidation was surprisingly strong, capable of inhibiting Hg^0 from being oxidized through the elimination of OH radicals via eq 9:

$$NO + OH + M \rightarrow HONO + M \quad (9)$$

This finding was one of the evidence for NO in inhibiting Hg^0 oxidation.

Following Widmer et al.[9] and Niksa et al.,[19] Qiu et al.[20] incorporated the SO_2 chemistry to describe the inhibitory role of SO_2 in Hg oxidation. Their sensitivity analysis of $HgCl_2$ formation to Cl species reactions showed that the produced Cl atoms through Cl_2 decomposition at the initial stage reacted with H and OH radicals to generate HCl and HOCl. When oxidation began, the Cl_2 concentration declined rapidly, whereas the Cl radical concentration correspondingly increased rapidly. During this reaction process, HCl remained the most abundant Cl species, followed by Cl, HOCl, Cl_2, and ClO. The elementary reactions $OH + Cl \rightarrow HOCl$ and $Cl_2 + OH \rightarrow Cl + HOCl$ generated HOCl, which, in turn, played an important role in HgCl oxidation into $HgCl_2$. In sharp contrast to the conclusion by Niksa et al.,[19] the reaction $HgCl + Cl_2 \rightarrow HgCl_2 + Cl$ did not appear to be a key in Hg oxidation. The elimination of OH radicals by SO_2 via eq 10 and 11

$$SO_2 + OH + M \rightarrow HOSO_2 + M \quad (10)$$

$$SO_2 + OH + M \rightarrow SO_3 + H + M \quad (11)$$

resulted in a decline of Hg^0 oxidation as a result of salient decline of HOCl.

It is apparent that both Niksa et al.[19] and Qiu et al.[20] supported such an idea, because Hg^0 oxidation was inhibited by the elimination of OH radicals. However, with respect to the specific inhibitory pathways, in particular, how the role of OH was involved, the indication by Niksa et al.[19] was somewhat vague. Although the explanation by Qiu et al.[20] was capable of characterizing the inhibitory role of SO_2 through arguing for the importance of HOCl, they cannot interpret the simulations of Niksa et al.,[19] where Cl_2 was thought to be the dominant species in oxidizing HgCl into $HgCl_2$. In addition, because HOCl was formed through Cl reacting with OH, Qiu et al.[20] cannot account for such an instance as the elimination of OH by SO_2, which will, instead, result in more Cl radicals or Cl_2 to directly react with HgCl. Thus, in this paper, the specific objective is to advance these initial efforts such that the inhibitory roles of NO and SO_2 can be theoretically elucidated by depicting the inhibitory roles of NO and SO_2 under homogeneous reactions when Cl_2 is the primary Cl-containing species.

EXPERIMENTAL WORK

A bench-scale system (Figure 1) was constructed to investigate the inhibitory effects of NO and SO_2 in this research. This system mainly consisted of a quartz reactor, a temperature-controlled furnace, a chemical conversion unit, and an Hg^0 online analytical instrument. The quartz reactor, horizontally sitting in a temperature-controlled furnace, consisted of two sections with one responsible for preheating gas and the other functioning as the reaction chamber where Hg^0 oxidation subsequently occurred. When $HgCl_2$ reduction was investigated, both sections functioned as reaction chambers. The preheating section was 120 cm in length to ensure that reactant gases

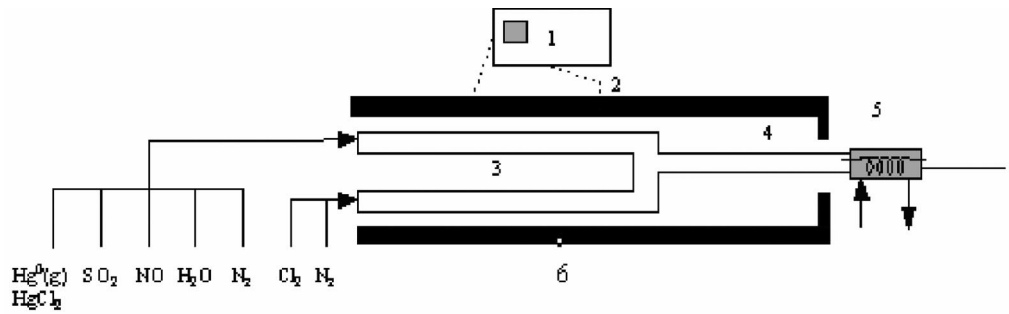

Figure 1. The schematic drawing of experimental equipment (1. Temperature controller; 2. Thermocouple (showing setting temperature); 3. Preheat section; 4. Reaction section; 5. Double cooling condenser. 6. Furnace).

are sufficiently preheated before being sent to the reaction chamber. Testing demonstrated that the inlet of the reaction chamber could be heated to 750 °C (the setting temperature for the furnace is indicated by the thermocouple in Figure 1). The 65-cm–long reaction section (2.2 cm in diameter) provided the reaction zone where a series of oxidation tests were performed. The temperature profile in the reaction chamber was measured by sliding a thermocouple into various locations and was found not to be uniformly distributed, but followed a declining pattern as shown in Figure 2. Reactant gases, such as Cl_2, NO, and SO_2, from cylinders were added into the simulated gas blend to obtain the desired testing conditions. Gas-phase Hg^0 and Hg^{2+} were obtained by passing a portion of dry N_2 through permeation devices that contain either Hg^0 permeation tubes or $HgCl_2$ crystals at elevated temperatures. Moisture vapor was generated by pumping a measured flow of deionized water into a diffusion chamber where water was heated to 200 °C. For these tests, the rate was controlled to establish 8% H_2O in the simulated gas stream. To rapidly quench the reaction when gas leaves from the reaction tube, a 10-cm–long double-cooling condenser was added at the exit of the reactor, which was able to lower the gas temperature quickly down to 280 °C.

Continuous online measurement of Hg was performed with a Sir Galahad (an amalgamation atomic fluorescence spectrometer) or a Semtech Hg Analyzer (a cold vapor atomic adsorption spectrometer). Ontario Hydro speciation was performed for the inlet Hg comparison, and results were consistent with the instrument analysis. Relative to the Sir Galahad analyzer, the response of the Semtech is less precise, but faster. The detection limit for the Semtech Hg Analyzer was 1 $\mu g/m^3$ compared with 1 ng/m^3 for the Sir Galahad. Therefore, to lower the bias, relatively high Hg concentration was used when the Semtech Hg Analyzer was used. The experimental system bias (with Sir Galahad) according to the statistical analysis of inlet Hg^0 was about ±3.5% based on 90% confidence intervals. Mass balance closure was also performed, showing an average ±10% error for Hg^{total}, again with 90% confidence. Hg^0 oxidation or Hg^{2+} reduction ratios were simply calculated by eq 12 and 13. It should be noted that the $HgCl_2$ concentration in eq 13 was measured as the molar equivalent Hg^0 concentration:

$$\text{Hg}^{\text{o}}\ \text{oxidation, \%} = \frac{\text{Hg}^0_{\text{initial}} - \text{Hg}^0_{\text{Final}}}{\text{Hg}^0_{\text{Initial}}} \times 100 \quad (12)$$

$$\text{HgCl}_2\ \text{reduction, \%} = \frac{\text{Hg}^0_{\text{Generated}}}{\text{HgCl}_{2\text{Initial}}} \times 100 \quad (13)$$

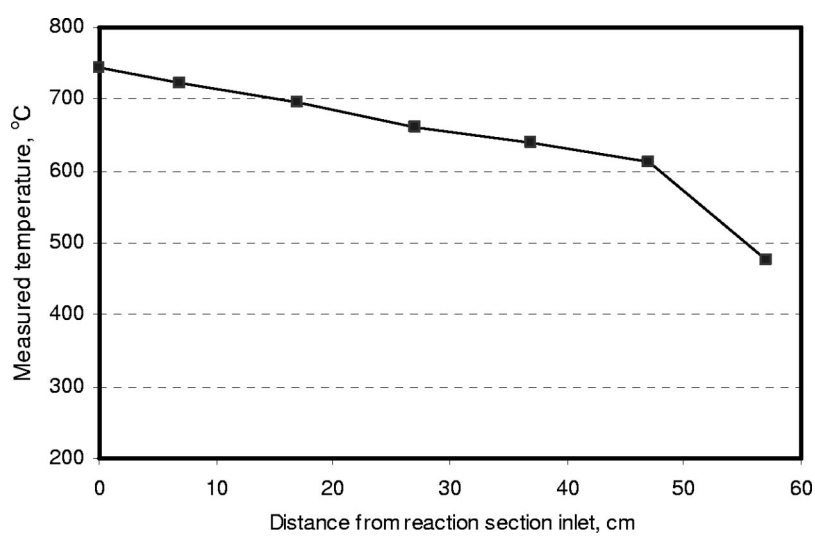

Figure 2. The measured temperature profile for a setting furnace temperature of 750 °C.

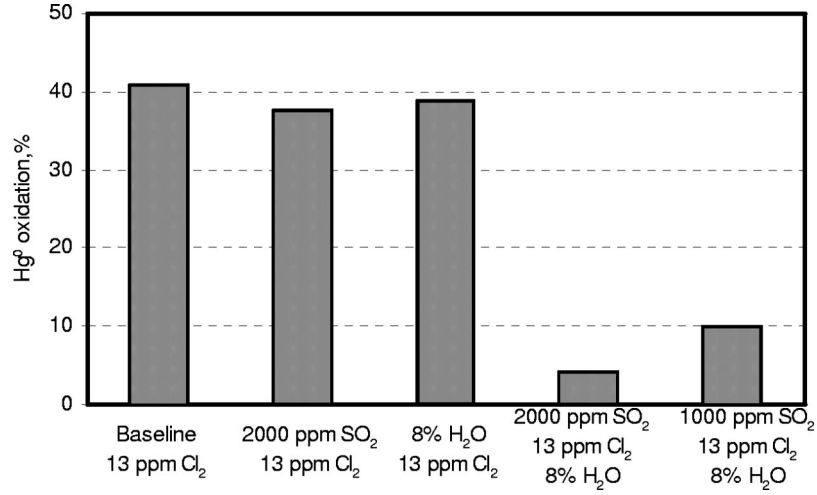

Figure 3. The effect of SO_2 on Hg^0 oxidation.

RESULTS AND DISCUSSION

Effects of SO_2 and NO on Mercury Oxidation

The first set of data was obtained to evaluate the effect of SO_2 on Hg^0 oxidation at an elevated temperature. The first four tests were in effect a 2^2 factorial design to identify the interaction effects of SO_2 and H_2O. During testing, the temperature at the reaction chamber inlet was maintained at 750 °C, which is indicated by the thermocouple in Figure 1, with the temperature profile along the reaction chamber presented in Figure 2. At the initial stage, ~12 μg/m^3 Hg^0 and 13 ppmv Cl_2 were simultaneously added into the gas blend at a total flow rate of 14 L/min. Under this simulated condition, ~7 μg/m^3 gas-phase Hg^0 was detected at the outlet of the reactor. The residence time in this reactor chamber was ~0.31 sec. The calculated Reynolds numbers at 600 and 700 °C were 414 and 378, respectively. Subsequently, SO_2 (2000 ppmv) was added to the gas blend. As displayed in Figure 3, there was little change to the Hg^0 concentration within 60 min, indicating that dry SO_2, in essence, had no significant effect on Hg^0 oxidation with Cl_2 as the primary Cl-containing species. Then, SO_2 was removed from the gas blend, and 8% H_2O was instead added. In comparison with the baseline data, the result also revealed that Hg^0 oxidation was unaffected by the presence of moisture. This was consistent with the findings of Widmer et al.[4] and Hall et al.,[9] where nearly identical extents of Hg^0 oxidation were identified with and without moisture for temperatures >800 °C when 300 ppmv HCl was present. However, when 2000 ppmv SO_2 was readded into the gas blend along with the 8% H_2O, strong inhibition on Hg^0 oxidation was observed according to the striking increase of gas-phase Hg^0 concentration at the outlet of reactor. The calculated Hg^0 oxidation lowered to ~5%. A subsequent decrease of SO_2 from 2000 to 1000 ppmv in the gas blend was capable of increasing the extent of Hg^0 oxidation to slightly more than 10%, still suggesting that SO_2, in conjunction with H_2O, had a salient effect on Hg^0 oxidation when the primary Cl-containing reagent was Cl_2.

The NO chemistry on Hg^0 oxidation was also examined in this effort by following the same procedure as mentioned above with the replacement of SO_2 by NO. As illustrated in Figure 4, when 600 ppmv NO and 13 ppmv Cl_2, without H_2O, was added in to the gas blend, it showed insignificant decline of Hg^0 oxidation as compared with the baseline result. The subsequent replacement of NO by 8% H_2O in gas blend basically confirmed

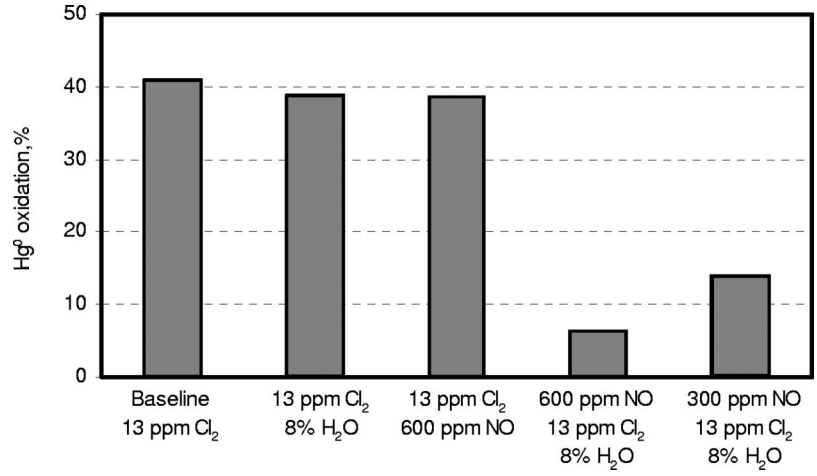

Figure 4. The effect of NO on Hg^0 oxidation.

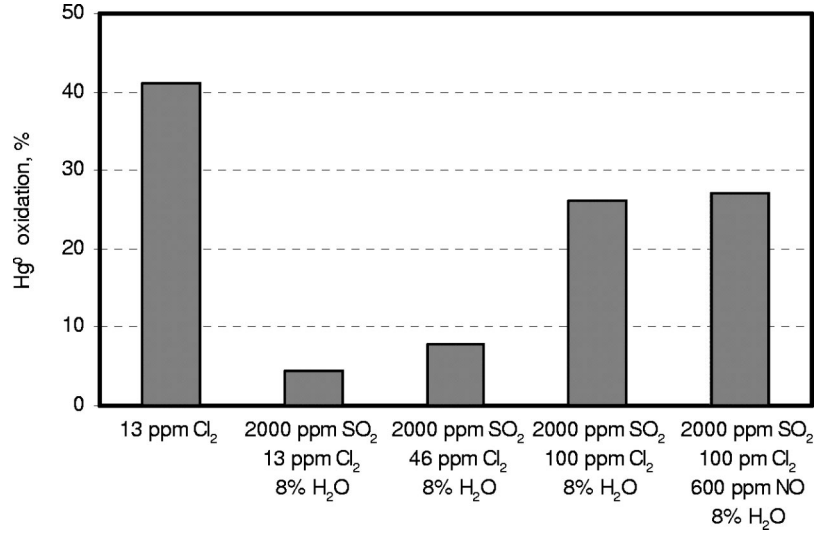

Figure 5. The effect of increasing Cl_2 concentration Hg^0 oxidation.

that H_2O had a minor effect on Hg^0 oxidation, as expected. Of interest was the combined roles of 600 ppmv NO and 8% H_2O, which exhibited a similar effect as the combination of SO_2 and H_2O to inhibit Hg^0 from oxidization. In comparison with the baseline case (~40% oxidation), 7% of Hg^0 was oxidized for this testing. When the concentration of NO in the gas blend was reduced from 600 to 300 ppmv (in the presence of 8% H_2O), >10% of Hg^0 oxidation was observed, but still significantly less than the 40% Hg^0 oxidation corresponding to the baseline testing case.

These two sets of tests basically identified the adverse effects of SO_2 and NO on Hg^0 oxidation in the presence of 8% of H_2O. However, as the Cl_2 concentration was increased, as seen in Figure 5, more Hg^0 was effectively transformed into its oxidized form. Cl_2 of 100 ppmv in the gas with 8% H_2O and 2000 ppmv SO_2 had oxidation rates of >25%. These results first suggested that the adverse effects of SO_2 and NO on Hg^0 oxidation can be alleviated by enhancing Cl-containing species concentration. It also implies that the inhibitory roles of SO_2 and NO in Hg^0 oxidation are to reduce the effective concentration of Cl-containing species, Cl and Cl_2.

Effects of SO_2 and NO on Mercury Reduction

Examination of the impacts of SO_2 and NO on Hg^{2+} reduction was subsequently carried out with Hg^0 being replaced by Hg^{2+}. The specific goal was to determine how SO_2 and NO affect the backward reaction of $Hg^0 + Cl_2 \leftrightarrow HgCl_2$. The reaction temperatures in the 160-cm–long preheating section were assumed to be as low as 200 °C at the inlet and as high as 750 °C (as indicated by the thermocouple in Figure 1) at the outlet of preheating section. The temperature profile in the 60-cm–long reaction section was presented in Figure 2. A 14-L/min gas blend containing ~12 $\mu g/m^3$ $HgCl_2$ (balanced with N_2) was first sent through the reaction system. At steady state, ~6.5 $\mu g/m^3$ Hg^0 at the outlet of the quartz reactor was constantly detected, which accounted for ~44% of Hg^{2+} thermal decomposition. Subsequently, the individual effects of SO_2 and NO on Hg^{2+} reduction were evaluated in sequence. In the SO_2 case (Figure 6), the Hg^{2+} reduction, similar to the Hg^0 oxidation, was minimally affected by the addition SO_2 in the absence of H_2O. NO exhibited some inhibitory effects on Hg^{2+} reduction without H_2O (Figure 7). The measurement indicated slightly less than 35% of Hg^{2+} being decomposed (or reduced) when 600

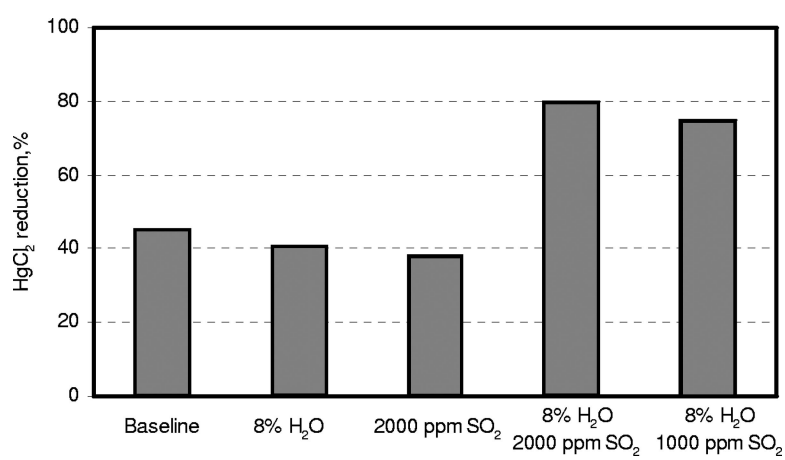

Figure 6. The effect of SO_2 on $HgCl_2$ reduction.

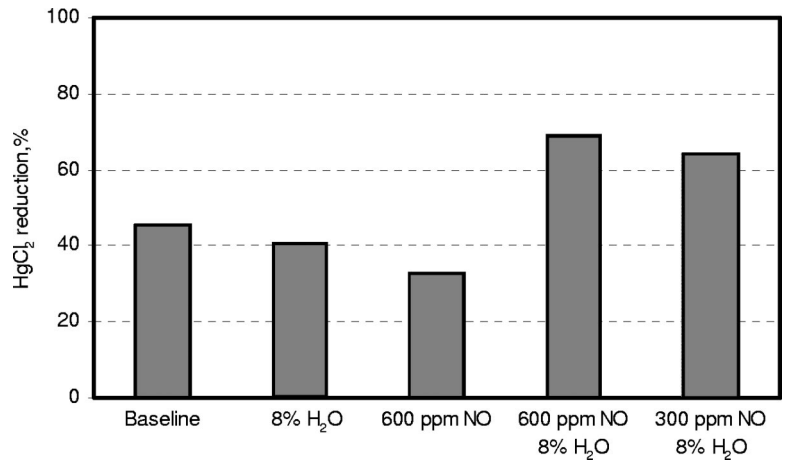

Figure 7. The effect of NO on $HgCl_2$ reduction.

ppmv NO was introduced into the gas blend. Duplicated tests under various conditions, such as slower flow rate and lower NO concentration, confirmed this result as reproducible.

Before proceeding to verify the effects of SO_2 and NO on Hg^{2+} reduction, particularly in the presence of H_2O, a second baseline of Hg^{2+} reduction was established by adding only 8% H_2O into the gas blend, which showed that H_2O basically had no effect on Hg^{2+} reduction, much resembling the occurrence during Hg^0 oxidation testing. The subsequent addition of either SO_2 or NO individually showed that Hg^{2+} reduction was greatly enhanced from ~41% of baseline to 80% and 70%, respectively. Consequently, the participation of H_2O is of importance for SO_2 and NO to result in Hg^{2+} reduction.

These aforementioned tests were performed at relatively high temperatures and measured with the Sir Galahad. The Cl and Cl_2 generated through the thermal decomposition of $HgCl_2$ were essentially high. Tests performed at relatively low temperature settings (400–600 °C) were also used to further determine the effects of SO_2 and NO, in combination with H_2O, on Hg^{2+} reduction. Less Cl and Cl_2 were generated from the thermal decomposition of Hg^{2+} at these lower temperatures. In this array of tests, gas blend totaling 3.5 L/min was sent through the reactor. The concentration of Hg^{2+}, determined by the Semtech 2000, was ~50 $\mu g/m^3$, and the temperature along the reactor, although not uniformly distributed, was assumed to be as high as the setting temperature of the furnace and as low as 200 °C at the inlet of reactor. For each temperature test, Hg^{2+} alone was first introduced into the reactor to identify its own thermal decomposition. Subsequently, 8% H_2O was added into the gas blend to establish a second baseline data to compare the effects of SO_2 and NO. After that, individual SO_2 (2000 ppmv) and NO (600 ppmv) were, in turn, brought into the gas blend. Interesting observations are apparent based on the data presented in Figure 8. First, the reduction of Hg^{2+} across the reactor, in the presence of SO_2, NO, and H_2O, was shown as a function of temperature. Second, consistent with foregoing results, SO_2 and NO showed significant effects on Hg^{2+} reduction in comparison with the baseline data, but the effects declined with decreasing temperature. Because less Cl and Cl_2 were generated at the lower temperatures, it was, therefore, conjectured that the promotional roles of SO_2 and NO on Hg^{2+} reduction, in effect, depended on

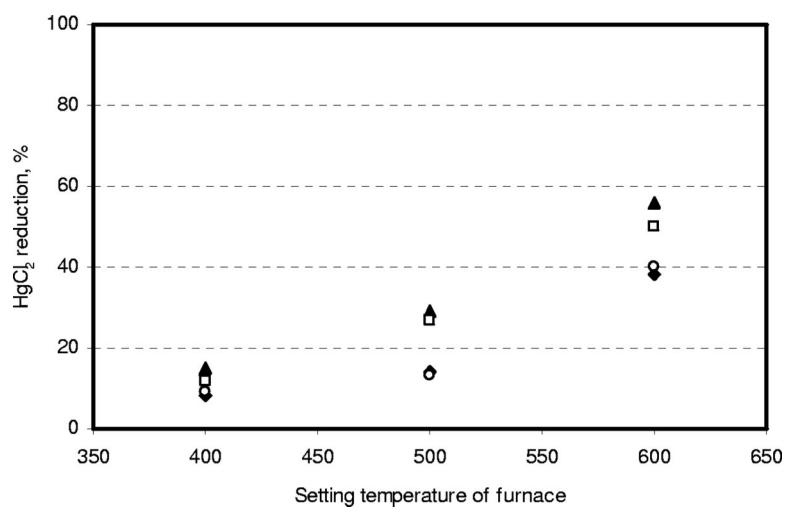

Figure 8. The effects of SO_2 and NO on $HgCl_2$ reduction at various setting temperatures (indicated by the thermocouple) of furnace. (▲) $HgCl_2$ + 8% H_2O + 2000 ppm SO_2; (♦) $HgCl_2$; (□) $HgCl_2$ + 8% H_2O + 600 ppm NO; (○) $HgCl_2$ + 8% H_2O.

reaction temperature and the yield rate of Cl and Cl_2 in the gas.

Mechanism Discussion

As with the conclusion by Niksa et al.[19] reached at temperatures of 400–900 °C, the essential reaction sequence for Hg^0 oxidation is a Cl atom recycle process. Once a pool of Cl atoms is established, Hg^0 is first oxidized via Cl into HgCl, which, in turn, is oxidized by Cl_2 into $HgCl_2$ with an associated regeneration of Cl atoms. The proposed mechanism in this paper, to a large extent, supports the key roles of Cl and Cl_2. Whereas SO_2 itself does not react with Hg^0,[16] it was nevertheless expected to affect the oxidation potential of chlorine species through the extensively recognized eq 14 and 15:

$$Cl_2 + SO_2 \rightarrow SO_2Cl_2 \quad (14)$$

$$Cl + SO_2 \rightarrow SO_2Cl \quad (15)$$

However, in Figures 3 and 6, the data apparently indicated that Hg oxidation and reduction were little changed by SO_2 without the participation of H_2O. It is, therefore, speculated that the formed SO_2Cl and SO_2Cl_2 are capable of decomposing back to Cl and Cl_2 or have nearly an equal oxidizing property as Cl and Cl_2, respectively. Although individual H_2O and SO_2 had negligible effects on Hg oxidation and reduction, the conjunction of H_2O and SO_2 revealed pronounced impacts, which was highly consistent with that of reported.[20]

Because SO_2Cl and SO_2Cl_2 have the property of readily reacting with H_2O, a reaction mechanism to characterize the affecting role of SO_2 in Hg oxidation and reduction is proposed in eq 16 and 17[15,21,22]:

$$Cl_2 + SO_2 + H_2O \rightarrow 2HCl + SO_3 \quad (16)$$

$$Cl + SO_2 + H_2O \rightarrow HCl + HOSO_2 \quad (17)$$

in which the hydrolysis of chlorinating species moves reactions toward the right, ultimately to render less Cl and Cl_2 present in the gas. Once the chlorinating species, Cl, Cl_2, SO_2Cl, and SO_2Cl_2, are largely consumed, the Hg^0 oxidation via Cl into HgCl, which, in turn, is oxidized by Cl or Cl_2 into $HgCl_2$, will be frozen. This, in essence, coincides with the conclusion of Niksa et al.[19] that the Hg^0 oxidation rate diminished when Cl atoms were eliminated, becoming negligible when the Cl concentration vanished. On the other hand, the consumption of Cl and Cl_2 in Hg^{2+} decomposition by the hydrolysis tends to accelerate such a decomposition that eventually has more Hg^{2+} to be reduced, on the surface, by SO_2. The generated HCl from eq 16 and 17 was thought capable of transforming Hg^0 into Hg^{2+} again in the presence of O_2. However, testing of 75 ppmv HCl in the presence of 6% O_2 showed approximately a 5% oxidation ratio for the setting temperature of 750 °C.

Having the similar property as SO_2, NO has been well known to react with Cl and Cl_2 to yield NOCl and $NOCl_2$. Furthermore, resembling SO_2Cl and SO_2Cl_2, the corresponding NOCl and $NOCl_2$ are also capable of readily reacting with H_2O through eq 18 and 19[19,22]:

$$Cl_2 + NO + H_2O \rightarrow NO_2 + 2HCl \quad (18)$$

$$Cl + NO + H_2O \rightarrow HONO + HCl \quad (19)$$

to form HCl, NO_2, and HONO with the result of less Cl and Cl_2 in the gas blend, which is favorable for Hg^{2+} reduction and adverse for Hg^0 oxidation, although not clearly indicated in the equations. Of interest was the slightly inhibitory effect of dry NO (no H_2O present in the gas blend) on Hg^{2+} reduction. It has been identified capable of enhancing Hg^0 oxidation elsewhere,[19] yet the specific process and products were not clear.

It was noticed that both Niksa et al.[19] and Qiu et al.[20] addressed the concept that the OH radicals were eliminated when either SO_2 or NO was added into the gas blend. One might wonder why the elimination of OH radicals has such a pronounced effect on Hg^0 oxidation and Hg^{2+} reduction. As reflected in eqs 17 and 19, the formation of $HOSO_2$ and HONO implicitly confirms the consumption of OH radicals and implies that in effect the OH radicals resulted from H_2O in this study. Thus, when detailed elementary reactions for eqs 16–19 are specified, eqs 16–19 are still able to include the roles of NO and SO_2 in consuming OH radicals. In sharp contrast to the arguments by Qiu et al.[20] where the key role of HOCl in Hg^0 oxidation was emphasized, eqs 16–19 otherwise support the key roles of Cl and Cl_2 in oxidizing Hg^0, which agreed well with the conclusion of Niksa et al.[19] In particular, our results showed that SO_2 and NO, in the absence of H_2O, had a negligible inhibitory impact on Hg^0 oxidation, which apparently did not support the key role of HOCl in this study, although HOCl is capable of oxidizing Hg^0 as well. Therefore, the emphasis of OH consumption might lead researchers to focus more on the role of HOCl instead of Cl and Cl_2. Instead, eqs 16–19 allow us to concentrate on the concentrations and generation rate of atomic and molecular chlorine that are vital to Hg^0 oxidation and Hg^{2+} reduction by hiding the consumption of OH. It should be specially noted that the formed HCl in eqs 16–19 had little oxidizing capability without the assistance of oxidizing reagents, such as O_2/O.[15] In comparison with Cl_2, Laudal et al.[23] found that the addition of Cl_2 (10 ppmv) decreased the amount of flue gas Hg^0 by 31%, whereas the addition of HCl (50 ppm) only resulted in a decrease of 1%. In the verification test by the authors for the oxidation capability of HCl, the addition of 75 ppmv HCl in the presence of 6% O_2 only caused an Hg^0 decrease ~5%.

CONCLUSIONS

The primary objective of this study was to identify the inhibitory effects of SO_2 and NO in the simulated flue gas under homogeneous conditions. Although it was well recognized that the Cl atom recycle process plays a prominent role in Hg^0 oxidation, data and mechanisms currently available do not yet elaborate the inhibition process of SO_2 and NO on Hg^0 oxidation. The testing

conducted here showed that neither SO_2 nor NO individually can substantially inhibit Hg^0 oxidation and promote $HgCl_2$ reduction. However, in the presence of H_2O, SO_2 and NO exhibited pronounced differences. This difference can be characterized by the mechanism in which SO_2 and NO can largely scavenge atomic and molecular chlorine with the assistance of H_2O. The scavenging of available atomic and molecular chlorine led less Hg^0 to be oxidized and, accordingly, more Hg^{2+} to be reduced. At low temperatures, the effects of SO_2 and NO on Hg^{2+} reduction were greatly reduced, indicating that such effects are temperature dependent and can be alleviated by lowing temperature.

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DISCLAIMER

This paper has not been subjected to EPA's required peer and policy review and, therefore, does not necessarily reflect the views of EPA, and no official endorsement should be inferred.

REFERENCES

1. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A.. Status Review of Mercury Control Options for Coal-Fired Power Plants; *Fuel Process. Technol.* **2003**, *82,* 89-165.
2. Chang, J.C.S.; Ghorishi, S.B. Simulation and Evaluation of Elemental Mercury Concentration Increase in Flue Gas across a Wet Scrubber; *Environ. Sci. Technol.* **2003**, *37*, 5763-5766.
3. Niksa, S.; Fujiwara, N. The Impact of Wet Flue Gas Desulfurization Scrubbing on Hg Emissions from Coal-Fired Power Stations. Presented at the Combined Power Plant Air Pollutant Control Mega Symposium; Washington, DC, 2004.
4. Amrhein, G.T.; Kudlac, G.A.; Yurchison, D.M. Full Scale Testing of Mercury Control for Wet FGD Systems. Presented at the 27th International Technical Conference on Coal Utilization and Fuel Systems; Clearwater, FL, 2002.
5. Nolan, P.S.; Redinger, K.E.; Amrheim, G.T.; Kudlac, G.A. Demonstration of Additive Use for Enhanced Mercury Emissions Control in Wet FGD Systems; *Fuel Process. Technol.* **2004**, *85,* 587-600.
6. Niksa, S.; Helble, J.J.; Fujiwara, N. Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H_2O in Predicting Oxidation in Coal-Derived Systems; *Environ. Sci. Technol.* **2001**, *35*, 3701-3706.
7. Sliger, R.N.; Kramlich, J.C.; Marinov, N.M. Towards the Development of Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species; *Fuel Process. Technol.* **2000**, *65-66*, 423-438.
8. Sliger, R.N. *Development of a Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species: A Tool for Mercury Emissions Control*. University of Washington: Seattle, WA, 2001.
9. Widmer, N.C.; West, J.; Cole, J.A. Thermochemical Study of Mercury Oxidation in Utility Boiler Flue Gases. In *Proceedings of A&WMA Annual Conference*; Salt Lake City, UT, 2000.
10. Gasper, J.A., Widmer, M.C.; Cole, J.A., Seeker, W.R. Study of Mercury Speciation in a Simulated Municipal Waster Incinerator Flue Gas. Presented at the International Conference on Incineration and Thermal Treatment Technologies Proceedings; Oakland, CA, 1997.
11. Procaccini, C.; Bozzelli, J.W.; Longwell, J.P.; Sarofim, A.F.; Smith, K.A. Presence of Chlorine Radicals and Formation of Molecular Chlorine in the Post-Flame Region of Chlorocarbon Combustion; *Environ. Sci Technol.* **2000**, *34*, 4565-4570.
12. Senior, C.L.; Sarofim, A.F.; Zeng, T.; Helble, J.J.; Mamani-Paco, R. Gas-Phase Transformations of Mercury in Coal-Fired Power Plants; *Fuel Process. Technol.* **2000**, *63,* 197-213.
13. Senior, C.L. Behavior of Mercury in Air Pollution Control Devices on Coal-Fired Utility Boilers. Presented at the Power Production in the 21st Century: Impacts of Fuel Quality and Operations, Engineering Foundation Conference; Snowbird, UT, 2001.
14. Chen, Z.; Senior, C.L.; Sarofim, A.F. Modeling of Mercury States in Coal-Fired Boilers. Presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems; Clearwater, Fl, 2002.
15. Galbreath, K.C.; Zygarlicke, C.J. Mercury Transformations in Coal Combustion Flue Gas. *Fuel Process. Technol.* **2000**, *65-66*, 289-310.
16. Hall, B.; Schager, P.; Lindqvist, O. Chemical Reactions of Mercury in Combustion Flue Gases; *Water Air Soil Pollut.* **1991**, *56,* 3-14.
17. Hall, B.; Schager, P.; Ljungstrom, E. An Experimental Study on the Rate of Reaction between Mercury Vapour and Gaseous Nitrogen Dioxide; *Water Air Soil Pollut.* **1995**, *81*, 121-134.
18. Li, L.-C., Deng, P.; Tian, A.-M.; Xu, M.-H.; Zheng, C.-G.; Wong, N.-B. A Study on the Reaction Mechanism and Kinetics of Mercury Oxidation by Chlorine Species; *J. Mol. Struct. (Theochem).* **2003**, *625*, 277-281.
19. Niksa, S.; Fujiwara, N.; Fujita, Y. A Mechanism for Mercury Oxidation in Coal-Derived Exhausts; *J. Air & Waste Manage. Assoc.* **2002**, *52*, 894-901.
20. Qiu, J.; Sterling, R.O.; Helble, J.J. Development of an Improved Model for Determining the Effects of SO_2 on Homogeneous Mercury Oxidation. Presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems; Clearwater, FL, 2003.
21. Xie, Y.; Liu, K.; Pan, W.-P.; Riley, J.T. The Effect of Sulfur Dioxide on the Formation of Molecular Chlorine during Co-Combustion of Fuels; *Energy Fuels,* **2000**, *14*, 597-602.
22. Mueller, M.A.; Yetter, R.A.; Dryer, F.L. Kinetic Modeling of the CO/H_2O/O_2/NO/SO_2 System: Implications for High-Pressure Fall-Off in the SO_2 + O (+ M) = SO_3 (+ M) Reactions; *Int J. Chem. Kinet.* **2000**, *32*, 317-339.
23. Laudal, D.L.; Brown, T.D.; Nott, B.R. Effects of Flue Gas Constituents on Mercury Speciation. *Fuel Process. Technol.* **2000**, *65-66*, 157-165.

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