

Impacts of Halogen Additions on Mercury Oxidation, in A Slipstream Selective Catalyst Reduction (SCR), Reactor When Burning Sub-Bituminous Coal

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This paper presents a comparison of impacts of halogen species on the elemental mercury (Hg(0)) oxidation in a real coal-derived flue gas atmosphere. It is reported there is a higher percentage of Hg(0) in the flue gas when burning sub-bituminous coal (herein Powder River Basin (PRB) coal) and lignite, even with the use of selective catalytic reduction (SCR). The higher Hg(0) concentration in the flue gas makes it difficult to use the wet-FGD process for the mercury emission control in coal-fired utility boilers. Investigation of enhanced Hg(0) oxidation by addition of hydrogen halogens (HF, HCl, HBr, and HI) was conducted in a slipstream reactor with and without SCR catalysts when burning PRB coal. Two commercial SCR catalysts were evaluated. SCR catalyst no. 1 showed higher efficiencies of both NO reduction and Hg(0) oxidation than those of SCR catalyst no. 2. NH₃ addition seemed to inhibit the Hg(0) oxidation, which indicated competitive processes between NH₃ reduction and Hg(0) oxidation on the surface of SCR catalysts. The hydrogen halogens, in the order of impact on Hg(0) oxidation, were HBr, HI, and HCl or HF. Addition of HBr at approximately 3 ppm could achieve 80% Hg(0) oxidation. Addition of HI at approximately 5 ppm could achieve 40% Hg(0) oxidation. In comparison to the empty reactor, 40% Hg(0) oxidation could be achieved when HCl addition was up to 300 ppm. The enhanced Hg(0) oxidation by addition of HBr and HI seemed not to be correlated to the catalytic effects by both evaluated SCR catalysts. The effectiveness of conversion of hydrogen halogens to halogen molecules or interhalogens seemed to be attributed to their impacts on Hg(0) oxidation.

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1. Introduction

Studies of the occurrence of speciated mercury (Hg) in flue gas are critical for reasons associated with both their environmental impacts and effective control by conventional air pollution control devices (APCDs) in coal-fired utility boilers (1–3). Mercury can be oxidized by the chlorine species in coal-fired flue gas. This oxidation process is likely to be enhanced by selective catalytic reduction (SCR) catalysts (4–9). The oxidized mercury could be easily captured by the wet flue gas desulfurization process (W-FGD) (10–14). Therefore, the combined utilization of SCR and W-FGD in coal-fired utilities has been regarded to be an economic means for multiple controls of SO_x, NO_x and mercury (Hg). However, this works well for utilities when burning bituminous coals, but does not work well for utilities when burning Powder River Basin (PRB) coal. Thus, mercury control at utilities burning PRB coal has faced more challenges (1). PRB coal or lignite, with lower sulfur and chlorine content, is cheap and plentiful in the South Central (Texas) and North Central (Wyoming, Montana, and South Dakota) areas of the U.S. (15). They are widely used by American coal-fired utilities. However, lower chlorine content in PRB and lignite is reported to be associated with their lower Hg(0) oxidation even with the enhancement effect of SCR. Methods to effectively convert Hg(0) to Hg(2+) (the oxidized mercury) seem very critical for utility boilers where PRB coal or lignite is burned.

Generally, chlorine is the major halogen species in coals (16). According to the United States Geological Survey (USGS), there are some halogens other than chlorine, such as fluorine, bromine and iodine in coals (17–19). Chlorine and fluorine content in PRB coal is generally comparable, but always 100–1000 times higher than the bromine and iodine contents, which is too low to be detected by ASTM methods (20). This was why very few reports were made on halogens other than chlorine. Most previous studies indicated the correlation between chlorine and Hg(0) oxidation was largely scattered (1, 3), which inspired us to investigate the possible impact of halogens on Hg(0) oxidation and their mechanisms. This work attempts first to investigate performance of the SCR catalyst in PRB coal flue gas, including the impact of flue gas composition of PRB coal on NO_x reduction and Hg(0) oxidation under SCR conditions. Second, to explore impacts of hydrogen halogens on Hg(0) oxidation and their mechanisms. Answering these questions could allow utilities to use some additives with or without SCRs as part of mercury compliance planning. This work was accomplished using a slipstream facility. The greatest benefits of slipstream tests can be flexible control and isolation of specific factors.

2. Experimental Section

Test Utility, Slipstream Facility, and SCR Catalysts. The detailed information on test utility, the schematic of the experimental setup and quality assurance and quality control (QA/QC) of mercury measurement can be found in previous studies (8, 21). The average temperature of the SCR facility in this study varied between 620 and 690 °F, which was dependent on boiler loads when tests were conducted. The residence time of flue gas inside the slipstream reactor was controlled to be about 1 s. When the SCR catalyst was loaded, the space velocity (the ratio of volumetric gas flow to catalyst volume) was set at 3600 h⁻¹. Two tested honeycomb SCR catalysts were provided by two commercial vendors, CORMETECH, Inc. and BASF/CERAM, Inc. The pitch sizes and cell numbers are 8.4 mm and 18 × 18 for catalyst no. 1

(CORMETECH, Inc.), and 10 mm and 15 × 16 for catalyst no. 2 (BASF/CERAM, Inc.). The main components of both these two SCR catalysts are V₂O₅–WO₃–TiO₂.

Characterizations of Coal, Ash, and Flue Gas of PRB Coal. Coal was sampled as it was transferred into the coal bunkers. The sampled coal represents coal fueled to the test unit. Ash is a composite of all fly ash removed from the electrostatic precipitator (ESP) hoppers from the test unit. The coal and ash analysis results are shown in Table S1 in the Supporting Information (SI). Analysis methods and QA/QC procedures can be found in ref 21. There were three testing phases in this study. During phase 1, tests without SCR catalysts in the slipstream reactor were conducted. The average sulfur, chlorine, and mercury contents in the PRB coal burned were about 0.37%, 72 ppm, and 0.08 ppm. The bromine and iodine contents in tested coals were under the detection limit (less than 5 ppm). During phase 2 and phase 3, tests with SCR catalyst no. 1 and no. 2 in the SCR slipstream reactor were conducted, respectively. The average sulfur, chlorine, and mercury contents in the burned PRB coal were approximately 0.44%, 127 ppm, and 0.07 ppm in the second phase and 0.39%, 88 ppm, and 0.09 ppm in the third phase.

Additive Injections. NH₃, HCl, and HBr gases were injected in the slipstream reactor by the control of a mass flow controller (MFC). HI and HF were injected using HI and HF solutions. Static mixers in the slipstream reactor ensured good mixing of additives and the flue gas. All additives were injected through several ports, which were located after the mercury sampling port at the SCR inlet, thus keeping the inlet sampling port unaffected by additives. In this study, the additional concentration of the individual additives or spike gases in the flue gas were controlled at ranges of 0–300 ppm for HCl, 0–9 ppm for HBr, 0–20 ppm for HF, and 0–15 ppm for HI.

SCR Slipstream Facility and Mercury Measurement. In this study, the SCR slipstream reactor was used as the testing facility. The detailed description of this facility, along with mercury measurement methods, are shown in ref 9.

3. Results and Discussion

3.1. Performances of NO (Nitric Oxide) Reduction by SCR Catalysts. The reduction performance of the two SCR catalysts were evaluated by monitoring the NO concentration at the inlet and outlet locations of the SCR slipstream reactor. IMR combustion-gas analyzer System 5000 with integrated gas-conditioning system, which is based on electro-chemical principle (from IMR Environmental Equipment, Inc.) was used as NO monitor (with detection limit of 1 ppm). Because of the low-NO burner installed in the test unit, NO concentration, which was introduced into the slipstream reactor, was found to be low: about 90 ppm (with 3% O₂ correction) at the SCR inlet location. Under NH₃ addition, both SCR catalysts worked properly in the SCR slipstream reactor. Lower NO at the slipstream outlet location could be achieved by SCR catalyst no. 1 than by SCR catalyst no. 2. A 92.5% NO reduction was observed by SCR catalyst no. 1 and 86.5% of NO reduction by SCR catalyst no. 2 when NH₃:NO was close to 1, as indicated in SI Figure S1. The corresponding NO concentrations at the slipstream outlet were 6 and 12 ppm (3% O₂ correction), respectively.

3.2. Effects of Halogen Additions on Mercury Oxidation. Hg(0) oxidation in the SCR may occur through two processes (8, 22–24), (1) homogeneous oxidation, which occurs in the gas phase, and (2) heterogeneous oxidation, which occurs on the interface of solids (SCR catalyst or fly ash). To determine the contribution of SCR on Hg(0) oxidation, two kinds of tests were conducted. Tests with the empty bed of the slipstream reactor were conducted to investigate the possible Hg(0) oxidation mechanism including both Hg(0) homogeneous oxidation and Hg(0) heterogeneous oxidation

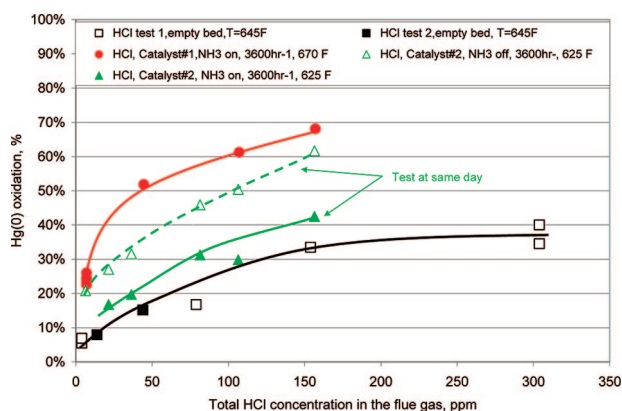


FIGURE 1. Effect of HCl addition on Hg(0) oxidation.

by interaction with “in-flight” fly ash. Tests with SCR catalyst in the SCR slipstream reactor were conducted to investigate the additional Hg(0) oxidation compared to the tests in the empty bed. The comparison of Hg(0) oxidation rates between two kinds of tests should be solely due to the catalytic effect of the SCR catalyst. Results were presented as the incremental percentage variation between the Hg(0) concentration at the SCR reactor inlet, $(\text{Hg}(0)_{\text{in}})$, and the Hg(0) concentration at the SCR reactor outlet, $(\text{Hg}(0)_{\text{out}})$, as indicated in eq (1).

$$\% \text{ Hg}(0) \text{ oxidation} = 100 * \{ [\text{Hg}(0)]_{\text{in}} - \text{Hg}(0)_{\text{out}} \} / [\text{Hg}(0)]_{\text{in}} \quad (1)$$

3.2.1. Addition of Hydrogen Chloride (HCl). In the coal-derived flue gases, chlorine is believed to be mainly HCl. It is a most important species affecting mercury oxidation since the major oxidized mercury species in coal-fired flue gas is Hg(Cl)₂. The effects of the spike gas HCl on the Hg(0) oxidation during tests in the empty slipstream reactor or those in the SCR slipstream reactor with two catalysts are shown in Figure 1. Whether the SCR catalysts were available or not, HCl showed a positive impact to increase Hg(2+) in the flue gas when burning PRB coal in this study. Tests in the empty slipstream reactor indicated that the percentage of Hg(0) oxidation increased to 7.9, 15.2, 16.7, 33.5, and 37.5% with incremented concentrations of HCl at 10, 40, 75, 150, and 300 ppm (total chlorine concentration in the flue gas at approximately 16.9, 44, 79, 154, and 304 ppm in the flue gas), respectively. When the HCl addition concentration was increased to above 150 ppm, the Hg(0) oxidation curve became flat.

During tests with SCR catalyst no. 1 in the SCR slipstream reactor at a NH₃ addition ratio at 1 (NH₃/NO~1), the percentage of Hg(0) oxidation was largely increased by approximately 30% in comparison to those under tests in the empty slipstream reactor at similar HCl addition concentrations. With the HCl additions at 100 and 150 ppm, the Hg(0) oxidation increased to about 62 and 68%, respectively. During tests with SCR catalyst no. 2 at a similar NH₃ addition ratio (NH₃/NO~1), the additional oxidations of Hg(0) were approximately 30 and 45%, respectively at HCl additions at 100 and 150 ppm. The additional Hg(0) oxidation with SCR catalyst no. 2 over those in the empty slipstream reactor was approximately only 10% at similar HCl addition concentrations. It was apparently lower than those tests with SCR catalyst no. 1. Thus, both SCR catalysts were shown to have catalytic effects, but to a different extent, on Hg(0) oxidation. For SCR catalyst no. 2, stopping injection of NH₃ apparently could improve Hg(0) oxidation by approximately 15%. That implies NH₃ had a negative impact on the Hg(0) oxidation process, at least for SCR catalyst no. 2. This study confirms that NO reduction by NH₃ and Hg(0) oxidation by chlorine

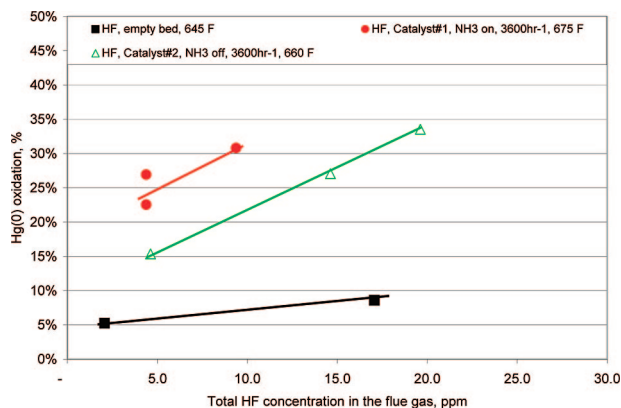


FIGURE 2. Effect of HF addition on Hg(0) oxidation.

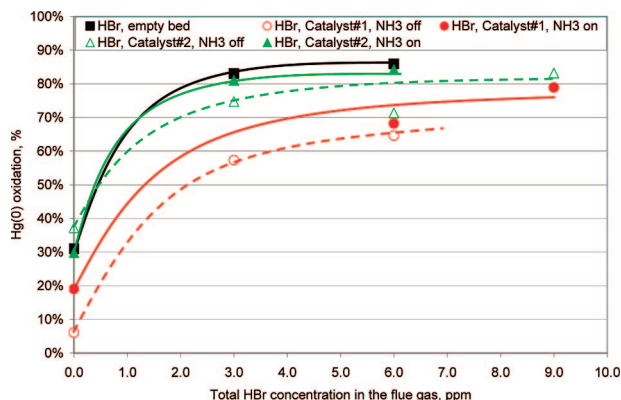


FIGURE 3. Effect of HBr addition on Hg(0) oxidation.

species simultaneously, but competitively occur on the surface of the SCR catalysts.

3.2.2. Addition of Hydrogen Fluoride (HF). Fluorine is another common halogen element in PRB coal, whose content varied between 20 and 50 ppm and was comparable to that of chlorine (100 ppm on average) in PRB coal, as indicated in SI Table S1. The effects of spike HF gases on Hg(0) oxidation during tests in the empty slipstream reactor and SCR slipstream reactor are shown in Figure 2. In both cases, HF additions showed a positive impact to increase the Hg(2+) in the flue gas of PRB coal. However, the capability of HF addition on the Hg(0) oxidation seemed limited as that of HCl. In the empty slipstream reactor, the percentage of Hg(0) oxidation was only 8.5% with HF addition, concentration up to 15 ppm (the total fluorine concentration in the flue gas was approximately 17.5 ppm). In the SCR slipstream reactor with catalyst no. 1 under the condition of NH₃ addition, the Hg(0) oxidations were about 25 and 30% with the addition of HF at about 3–8 ppm (the total fluorine concentrations in the flue gas at about 5 and 10 ppm). In the SCR slipstream reactor with catalyst no. 2, however without NH₃ addition, the Hg(0) oxidations were approximately 15, 26, and 34 with HF addition at 3, 13, and 18 ppm (the total fluorine concentrations in the flue gas at about 5, 15, and 20 ppm). Thus, both SCR catalysts in this study promoted Hg(0) oxidation in comparison to the case of the empty slipstream reactor. Considering the negative effect of NH₃ addition on the Hg(0) oxidation, SCR catalyst no. 1 should have higher oxidation activity than catalyst no. 2 during the addition of HF.

3.2.3. Addition of Hydrogen Bromide (HBr). The effects of HBr additions on Hg(0) oxidation in the empty slipstream reactor and in the SCR slipstream reactor are shown in Figure 3. Whether the SCR catalysts were available or not, HBr showed a very strong impact in increasing Hg(0) oxidation in the PRB coal-derived flue gas atmosphere. Tests in the

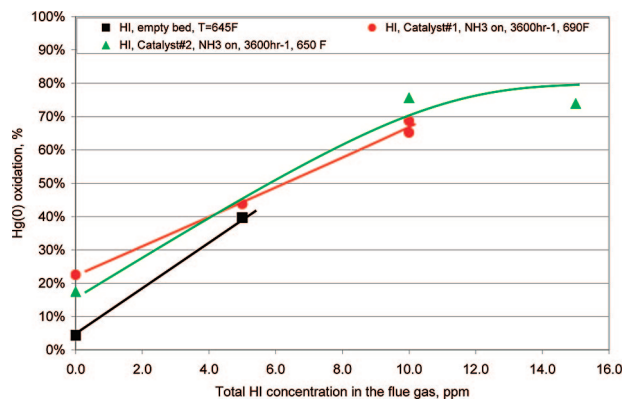


FIGURE 4. Effect of HI addition on Hg(0) oxidation.

empty slipstream reactor indicated the percentage of Hg(0) oxidation increased to 83 and 85.9% with additional concentrations of HBr at only 3 and 6 ppm, respectively. With the increase of HBr addition concentration from 3 to 6 ppm, the Hg(0) oxidation curve became flat. This may indicate that no apparent additional Hg(0) oxidation could be achieved by continuous addition of the HBr. During tests with SCR catalyst no. 1 at a preferred NH₃ addition ratio (NH₃/NO~1), the percentages of Hg(0) oxidation were approximately 68.2 and 78.9% at HBr addition concentrations of 6 and 9 ppm, respectively. If addition of NH₃ was turned off, the percentages of Hg(0) oxidation were approximately 57.3 and 64.4% at HBr addition concentrations of 3 and 6 ppm, respectively. During tests with SCR catalyst no. 2, at a similar NH₃ addition ratio (NH₃/NO~1), the percentages of Hg(0) oxidation were approximately 74.7 and 83.2% at HBr addition concentrations of 3 and 9 ppm, respectively. If addition of NH₃ was turned off, the percentages of Hg(0) oxidation were approximately 81 and 84.2% at HBr addition concentrations of 3 and 6 ppm, respectively.

There was good match between results from tests in the empty slipstream reactor and SCR slipstream reactor with both catalyst no. 1 and catalyst no. 2. This indicated the SCR catalyst did not have apparent promotion of Hg(0) oxidation and thus consequently was independent of impacts of NH₃ additions. This finding may indicate the promising function of HBr on Hg(0) oxidation and simultaneously Hg(0) oxidation was less dependent on the availability of SCR catalysts. This was different from those by additions of HCl or HF. In this study, The Hg(0) oxidation efficiencies were slightly lower at approximately 6.1 and 19% at baseline level (without addition of HBr) during tests with SCR catalyst no. 1 when NH₃ addition was on and off. During tests with SCR catalyst no. 2, its baseline values increased to 37.2 and 29.8% when NH₃ addition was on and off. During test with the empty slipstream reactor, this baseline value was also higher at approximately 29.5%. Thus, tests with SCR catalyst no. 1 showed a little lower Hg(0) oxidation efficiency by HBr addition, compared to cases in the empty slipstream reactor and SCR slipstream reactor with catalyst no. 2.

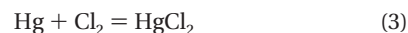
3.2.4. Addition of Hydrogen Iodine (HI). The effects of additions of HI on Hg(0) oxidation during tests in the empty slipstream reactor and SCR slipstream reactor are shown in Figure 4. In both cases, HI additions showed a stronger impact to increase the Hg(2+) in the flue gas of PRB coal. In the empty slipstream reactor, the addition of HI at 5 ppm could achieve approximately 40% of Hg(0) oxidation. With the same addition concentration of HI at 5 ppm in the SCR slipstream reactor with catalyst no. 1, similarly 40% Hg(0) oxidation efficiency could be achieved. When HI addition concentrations increased to 10 ppm, nearly the same Hg(0) oxidation efficiencies (approximately 70%) could be achieved for both SCR catalysts. These may indicate that Hg(0) oxidation by HI

addition was also independent of the availability of a SCR catalyst. A further increase of HI addition concentration to 15 ppm did not continuously increase Hg(0) oxidation efficiency for SCR catalyst no. 2, which is possibly limited by its reaction kinetics. Hg(0) oxidation was independent of the availability of SCR catalysts when HI was added in the flue gas. This was also observed when HBr was added, but was not observed when HCl and HF were added. It is believed that Hg(0) oxidation by HI and HBr may be through a similar mechanism.

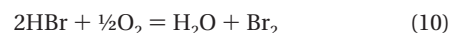
3.3. Comparison of Impacts on Hg(0) Oxidation by Different Halogen Additives. Figure S2 in the Supporting Information presents a comparison of impacts of different halogens (HCl, HF, HBr, and HI) on Hg(0) oxidation under a PRB coal-derived flue gas atmosphere, which was made using results from the empty slipstream reactor. The maximum Hg(0) oxidation efficiency at approximately 40% could be achieved by total HCl concentration at 300 ppm in the flue gas. The increase of Hg(0) oxidation efficiency by HF addition seemed to follow the same trend, and was also comparable to the HCl addition at the same addition concentration. As indicated in Figures 1 and 2, both SCR catalysts seemed to promote Hg(0) oxidation by HCl and HF at the same addition concentrations. The tests by additions of HCl and HF in this study were consistent with the lower Hg(0) oxidation efficiencies in the full scale utility boilers by burning PRB coal since its chlorine and fluorine contents are lower. As expected, addition of HCl could further increase Hg(0) oxidation, which can be catalyzed by both of the evaluated SCR catalysts. For comparison, by achieving the same Hg(0) oxidation efficiency at approximately 40% in the empty slipstream reactor (the baseline Hg(0) oxidation at about 5%), the addition of HI concentration in the flue gas only needed to be 5 ppm. Moreover, HBr addition concentration at only 3 ppm could achieve the Hg(0) oxidation efficiency as high as above 80% in the empty slipstream reactor (the baseline Hg(0) oxidation at about 30%). Both HBr and HI showed much stronger impacts on the Hg(0) oxidation than those by HCl and HF at the same addition concentrations. As indicated in Figures 3 and 4, the catalytic effects by SCR catalysts seemed not to be correlated with Hg(0) oxidation during additions of HBr and HI in the flue gas of PRB coal, at least for both evaluated SCR catalysts in this study.

The sequence, according to their impact strength on Hg(0) oxidation, were HBr, HI, and HCl or HF. It seemed to follow their inversed atom sequence in the Periodic Table of the Elements, except for the order between HBr and HI. The larger the halogen atom is, the greater its impact on Hg(0) oxidation. Two categories could be sorted by considering their interaction with the SCR catalyst and also interaction with NH₃ on the surface of SCR catalysts. SCR catalysts seemed to promote the Hg(0) oxidation through HCl and HF in Category 1, but not through HBr and HI in Category 2. NH₃ seemed to impact the Hg(0) oxidation only by HCl and HF through both SCR catalysts in Category 1.

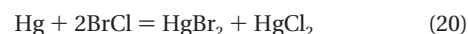
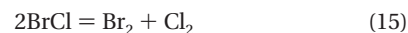
There were some clues to explicate the findings in this study. First, reaction paths for Hg(0) oxidation through halogen molecules (Br₂, I₂, Cl₂ and F₂), as indicated in eqs 2–5 were generally favored in kinetics than those through hydrogen halogens, as indicated in eqs 6–9. This was at least clarified by previous investigation of Hg(0) oxidation mechanisms, which the chlorine or bromine species were involved in (25). That means kinetics of Hg(0) oxidation should be faster through halogen molecules than those through hydrogen halogens if previous studies on Hg(0) oxidation mechanisms by HCl and HBr could be further extended to those by HF and HI.



Second, additions of HBr and HI into the elevated temperature conditions would generate almost total conversion of HBr to Br₂, and HI to I₂. The generation of Br₂ could be through the Deacon reaction of bromine, as indicated in eq 10 (25). By a different reaction routine, I₂ could be generated through decomposition of HI (26, 27), as indicated in eq 11. However, this was not the case for HCl since the depletion of Cl₂ would occur by the enriched SO₂ in the coal-derived flue gases (8, 25), as indicated in eq 12.



Third, a more complicated mechanism was proposed to occur by additions of HBr and HI in the flue gas, in which interhalogen species (such as BrCl or ICl) were likely to be involved in the elemental mercury oxidation processes. The interhalogen of BrCl may be generated through reaction, as indicated in eqs 13 or 14, and depleted through reaction, as indicated in eq 15. And the interhalogen of ICl may be generated through reactions, as indicated in eqs 16 or 17, and depleted through reaction, as indicated in eq 18. Generally the interhalogens are unstable and extremely reactive chemically (28). The elemental mercury oxidation may occur through reactions by BrCl and ICl (29, 30), as indicated in eqs 19 and 20, respectively. Thus, outcomes of elemental oxidation may include mutual species of either HgCl₂ and HgBr₂, or HgCl₂ and HgI₂, respectively. Interhalogen species such as ClF also could be possibly generated, but did not seem important due to comparable impact of Cl and F on Hg(0) oxidation kinetics by tests in this study.



Under a temperature of around 300 °C, thermodynamics studies indicated there was a limitation on HgBr₂ or HI₂ occurrence in the coal-fired flue gas, but not for HgCl₂ (9). HgCl₂ can proceed to the extent of approximately 100% conversion under the temperature range in this study if kinetics of mercury oxidation by chlorine is quick enough in the slipstream reactor. The enhanced Hg(0) oxidation rate by bromine additions in this study, and likely iodine additions, exceeded the limitation of thermodynamics prediction (9). It may indicate that the formation of HgBr₂ or likely HgI₂ were not the only new products by the addition of bromine or iodine. It was possible for the simultaneous formation of HgBr₂ and HgCl₂ by bromine addition, or HgI₂ and HgCl₂ by

iodine addition. Bromine or iodine seems to have the capability to attack chlorine species in the flue gas to promote the generation of activated chlorine, which was involved in improving the kinetics of mercury oxidation (28). This may explain why the total mercury oxidation rate exceeded the thermodynamics limitation on maximum occurrence of HgBr_2 and HgI_2 . Vosteen, et al. proposed the possible mechanisms on enhanced mercury oxidation by the addition of Bromine species based on their extensive studies (25). Larger generation of free bromine molecule (Br_2), other than free chlorine molecule (Cl_2) by HBr and HCl additions in the flue gas, was his point to distinguish the different impacts of bromine and chlorine on the elemental mercury oxidation kinetics. The bromine Deacon reaction will be favored to produce comparatively much more free Br_2 , as shown in eq 10, whereas the reversed chlorine Deacon reaction will be favored by the depletion effect of SO_2 in the flue gas. However, it was noticed that the bromine addition in the flue gas was conducted by cofiring of bromine species and coal in Vosteen's tests (higher temperature circumstance than in the current study) and the oxidized mercury included both HgBr_2 and HgCl_2 in their tests. This evidence may have revealed that, first bromine species had enough residence time (in several seconds) to produce Br_2 ; and second, Br_2 could not make a conversion of all mercury to HgBr_2 and left some of the $\text{Hg}(0)$ to be reacted with active Cl species to produce HgCl_2 , even in this longer residence time than the current study. Chlorine species seemed to be involved in its competition to bromine species on the $\text{Hg}(0)$ oxidation process. This evidence could support our findings by thermodynamics prediction that there exists a limitation of mercury oxidation by bromine species. Considering test conditions in this study that residence time of flue gas in an empty slipstream reactor was just one second, which may be too short for total conversion of HBr to Br_2 , there must be other mechanisms regarding mercury oxidation with both bromine and chlorine species in the flue gas. To figure out the conflict and thermodynamics prediction and test results, the occurrence of the intermediate species of BrCl and ICl , was proposed in this study, which brought in the competition of chlorine on mercury oxidation under enhanced kinetics.

Thus, by a combination of findings in this study and previous studies, one may reasonably find that different impacts of halogens on $\text{Hg}(0)$ oxidation should result from different kinetics between the $\text{Hg}(0)$ and halogens in the kinetics-controlled $\text{Hg}(0)$ oxidation process. Comparably, HCl was not effective to oxidize $\text{Hg}(0)$ due to its ineffective conversion to their molecule (Cl_2) under coal-fired flue gas atmospheres. Thus, eq 7 may be the main reaction routine for $\text{Hg}(0)$ oxidation through HCl. HF addition most likely follows the same mechanisms, as indicated in eq 6, if the presumption of ineffective conversion of HF to F_2 in the flue gas could be valid. With HBr or HI additions in the flue gas, $\text{Hg}(0)$ oxidation will occur through two different routines, which are dependent on temperature ranges. Under higher temperature (generally higher than 650°C (27)), HBr and HI will be converted to Br_2 and I_2 . Br_2 and I_2 will make $\text{Hg}(0)$ oxidation proceed very fast through reactions eqs 8 and 9), respectively. Thus, HgBr_2 and HgI_2 will be the main oxidized mercury in the flue gas, respectively. Under a lower temperature range (around 300°C such as in this study), HBr and HI will interact with HCl, which is available in the coal-fired flue gas, to generate interhalogens such as BrCl and ICl (30). BrCl and ICl also will make $\text{Hg}(0)$ oxidation proceed fast through reactions eqs 19 and 20. Thus, both HgBr_2 and HgCl_2 , or HgI_2 and HgCl_2 , are occurrences of oxidized mercury in the flue gas. All reactions listed in this study were presented as global reactions. Detailed mechanism studies should be addressed in further studies.

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Supporting Information Available

Two figures and one table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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