STUDY OF MERCURY OXIDATION BY SCR CATALYST IN AN ENTRAINED-FLOW REACTOR UNDER SIMULATED PRB CONDITIONS

Sung J. Lee[+], Chun W. Lee*, and Shannon D. Serre
U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC 27711. [+]Korea Science and Engineering Foundation (KOSEF) Visiting Scientist. [*]Corresponding author.

Yongxin Zhao and Jarek Karwowski
ARCADIS G&M, Inc., Research Triangle Park, NC 27709

Thomas W. Hastings
Cormetech, Inc., Durham, NC 27712

ABSTRACT

A bench-scale entrained-flow reactor system was constructed for studying elemental mercury (Hg^0) oxidation under selective catalytic reduction (SCR) reaction conditions. The system consists of a natural gas burner for producing combustion flue gas, and an electrically heated cylindrical quartz reactor (4 cm I.D., 310.5 cm in length) with SCR catalyst placed in the middle of the reactor. Simulated flue gas was doped with fly ash collected from a subbituminous Powder River Basin (PRB) coal-fired boiler along with other coal combustion flue gas components such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), hydrogen chloride (HCl), reductant ammonia (NH_3) for the NOx reduction reaction over SCR catalyst, and trace Hg^0. Concentrations of Hg^0 and Hg^{2+} upstream and downstream of the SCR catalyst were measured using a continuous emission monitor (CEM). The effects of HCl concentration, SCR operating temperature, and feed rate of PRB coal fly ash on Hg^0 oxidation were studied.

It was concluded that HCl plays an important role of providing a source of Cl for Hg^0 oxidation under conditions simulating SCR systems for PRB coal-fired boilers. Good Hg mass balance closure was observed for tests at 20 ppm HCl. Poor Hg mass balance closure at 0-10 ppm HCl indicated that transient Hg capture on the SCR catalyst occurred at the short test exposure periods and that the outlet speciation observed may not be representative of steady-state operation at longer exposure times. The effect of temperature on Hg speciation and capture by the catalyst was a secondary effect. Introduction of PRB coal fly ash resulted in slightly decreased outlet Hg^{2+} as a percentage of total inlet Hg and correspondingly resulted in a slight incremental increase in Hg capture. Significant transient effects of NO_x, SO_2, and temperature on Hg speciation and capture were observed in the absence of NH_3 and fly ash. Our observations suggest that Hg^0 oxidation may occur near the exit region of the SCR reactors in the field. Passage of flue gas through SCR systems without NH_3 injection, such as during the non-ozone season, may also impact Hg speciation and capture in the flue gas.

INTRODUCTION

Coal combustion is the largest anthropogenic source of mercury (Hg) emissions in the U.S., which causes environmental and health concerns.[1] EPA recently issued the Clean Air Mercury Rule (CAMR) for reducing mercury emissions from coal-fired power plants.[2] It is well known that the split (speciation) amongst chemical forms of Hg species, has a strong influence on the control and environmental fate of Hg emissions from coal combustion.[3] The high-temperature coal combustion process releases Hg in elemental form (Hg^0). However, a significant fraction of the Hg^0 can be subsequently oxidized in the coal-fired boiler's low-temperature, post-combustion environment. Relative to Hg^0, oxidized Hg (Hg^{2+}) is more effectively removed by air pollution control systems (APCDs). For example, water-soluble Hg^{2+} is much more easily captured than insoluble Hg^0 in flue gas desulfurization (FGD) units.[3-6]

Coal combustion is also a significant anthropogenic source of nitrogen oxide (NO_x) emissions that are associated with several environmental concerns including acid rain, fine particulate matter ($PM_{2.5}$), and tropospheric ozone formation.[7] Selective catalytic reduction (SCR) technology, which achieves high levels of NO_x emission reduction (> 90%) for power plants, will be more widely used for meeting more stringent regulations for ozone, $PM_{2.5}$, and regional haze. The application of SCR technology also affects the speciation of mercury in the coal combustion flue gases. Recent full-scale field tests conducted in the U.S. showed increases in Hg oxidation across the SCR catalysts for plants firing bituminous coals with sulfur (S) content ranging from 1.0 to 3.9%.[8] Two plants firing subbituminous Powder River Basin (PRB) coals which contains significantly lower chlorine (Cl) and S content and higher calcium (Ca) content than those of the bituminous coals, showed very little change in mercury speciation across the SCR reactors.[8] Our recent pilot-scale study also found high Hg oxidation across SCR catalyst in tests firing Illinois coals with different S (1.1 - 3.5%) and Cl (0.13 – 0.29%) content, and no significant increase in oxidation across the catalyst in tests firing a PRB coal with low S (0.3%) and Cl (< 0.01%) content.[9] The observed coal-type dependence effect on Hg oxidation occurring in SCR systems requires further investigation.

Our previous studies have suggested that hydrogen chloride (HCl) in the flue gas provides a source of chlorine required for mercury oxidation occurring under SCR reaction conditions.[10] A recent study suggested that in addition to HCl, sulfur trioxide (SO_3) is another important oxidant for Hg oxidation catalyzed by an SCR catalyst.[11] These two bench-scale studies were conducted in the absence of coal combustion fly ash and using gas mixtures provided by gas cylinders for simulating coal combustion flue gases. However, the effect of fly ash on mercury oxidation is not known. The field data showed that SCR is not effective for producing Hg^{2+} in the flue gas for boilers firing PRB coals. The high alkaline content of PRB coal combustion fly ash may play a role in low extent of oxidation of Hg^0 in SCR systems.

This paper reports a study to investigate the effect of SCR catalyst on Hg speciation in simulated PRB coal combustion flue gases in the presence and absence of PRB fly ash. In this project, an entrained-flow reactor was modified for evaluating the mercury oxidation ability of an SCR catalyst in the presence of PRB coal combustion fly ash entrained in the simulated coal combustion flue gas. Several parameters such as the presence of the entrained PRB fly ash, the concentration of HCl, and SCR operating temperature were evaluated to determine their effects on the oxidation of Hg^0 under simulated PRB conditions. The

objectives of this project were to evaluate mercury oxidation and speciation under simulated PRB coal firing SCR system conditions and to gather insights into effects of individual gaseous species on the reaction mechanisms involved in mercury oxidation promoted by metal oxides in $V_2O_5 \cdot WO_3/TiO_2$ (vanadium pentoxide and tungsten trioxide supported on titania) type SCR catalyst. The change of mercury speciation in the flue gas is very important for selecting the appropriate mercury control technology and predicting its mercury removal efficiency for PRB coal-fired boilers.

EXPERIMENTAL

Entrained-Flow SCR Reactor System

An entrained-flow reactor that had been used for studying the in-flight capture of Hg in simulated coal combustion flue gas by sorbent injection in a previous study[12] was modified for studying mercury oxidation by SCR catalyst under simulated PRB conditions in this project. Details of the reactor are available elsewhere.[12] The reactor was modified for supporting SCR catalyst in the reactor and for injecting ammonia (NH_3) to provide SCR NO_x reduction conditions. Fig. 1 shows a schematic drawing of the bench-scale entrained-flow
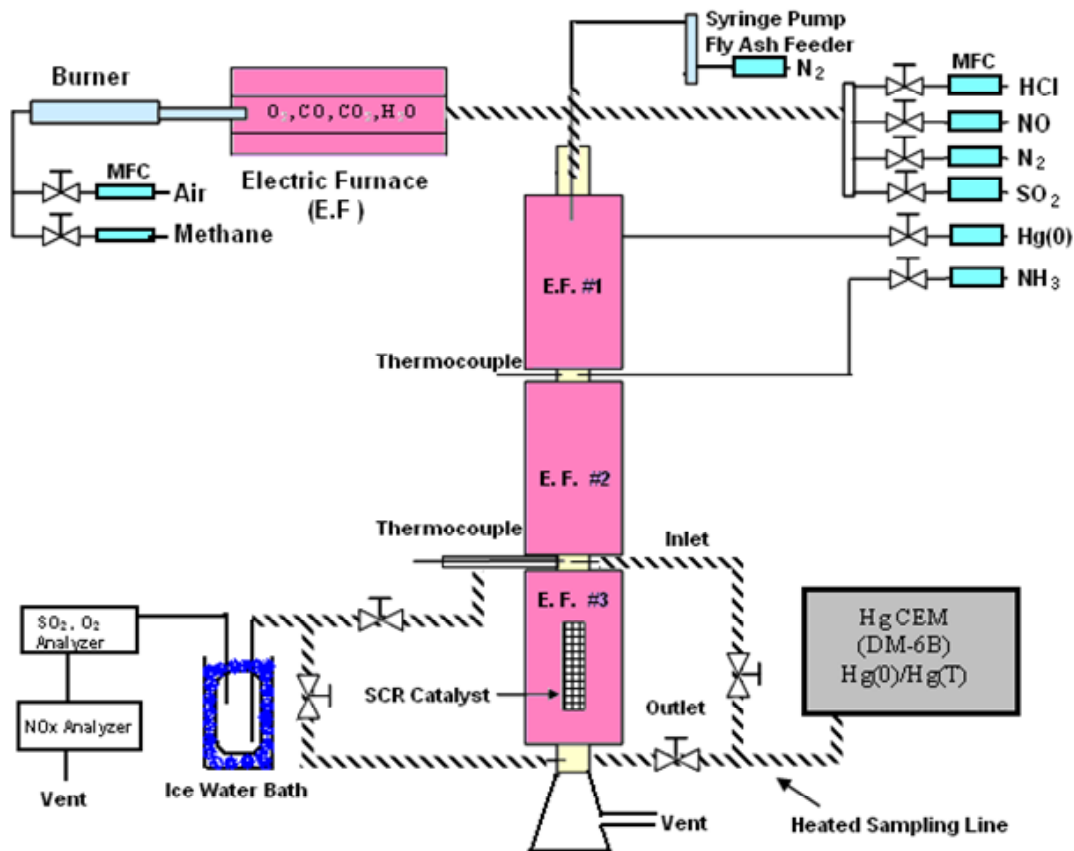

Fig. 1. Schematic diagram of the entrained-flow SCR reactor system.

reactor system with the SCR catalyst placed inside the reactor. The entrained-flow reactor was 310.5 cm in length with 4 cm inner diameter, and the reactor was heated by three temperature-controlled electric furnaces to maintain SCR reaction temperature at about 350

°C. A methane gas burner provided combustion flue gases including carbon monoxide (CO), carbon dioxide (CO_2), water vapor (H_2O), and oxygen (O_2). Other coal combustion flue gas components including sulfur dioxide (SO_2), NO_x, and HCl were supplied by gas cylinders and introduced into the top of the reactor at constant flows by using mass flow controllers (MFCs) for making a simulated PRB coal combustion flue gas. A constant quantity of Hg^0 vapor generated by a permeation system (VICI Metronic Dynacalibrator model 190) was carried by a constant flow of nitrogen gas (N_2) and introduced near the top of the reactor by using a MFC. NH_3 gas supplied by a gas cylinder was injected into the reactor in a port located between the first and the second heating furnaces of the reactor. The injection rate was controlled by a MFC.

A fly ash sample collected in baghouse of a PRB coal-fired boiler was tested in this study. The composition of the fly ash sample from analysis by X-ray fluorescence (XRF), is presented in Table 1. The alkaline PRB coal fly ash contains calcium oxide (CaO), alumina,

Table1. Composition of the PRB coal fly ash sample.

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	$CaSO_4$	Na_2O	TiO_2
Wt %	31.5	25.2	19.7	7.3	6.3	3.4	2.0	1.7

and silica as its major components. Minor components include oxides of transition metals (Fe_2O_3, MgO, TiO_2), sodium (Na_2O), and calcium sulfate ($CaSO_4$). It is assumed all the metals are presented as oxides in the fly ash, as the metals are most likely to be oxidized during the high temperature combustion process. It also assumed all the sulfur is presented as $CaSO_4$. The fly ash was injected into the reactor at a controlled feed rate by using a syringe-type particle feeder and mixed with the flue gas at the top of the reactor. A feed rate of 4.8 g/hr was used in the tests, or 5.7 g/Nm^3 of fly ash in the flue gas. Such flue gas fly ash loading is similar to those measured for the PRB-fired boilers in the field.

A fresh $V_2O_5 \cdot WO_3/TiO_2$ SCR catalyst sample was tested in this study. The honeycomb catalyst was 622 mm in length with a square cross-section containing 9 channels (3x3 cell arrangement) with a pitch of 8.25 mm. The catalyst sample was located at the center of the third furnace zone of the reactor. The total gas flow rate through the reactor was fixed at 14 L/min. The space velocity through the catalyst was calculated to be 2100 hr^{-1}, which is within the normal operating range of commercial SCR systems. The experimental conditions used for studying Hg oxidation under simulated PRB conditions are summarized in Table 2. The SO_2, NO_x and HCl concentrations used in this project are those typical levels for a PRB coal flue gas. An online ultraviolet (UV) SO_2 and O_2 analyzer (Bovar Engineering, Inc. model 721AT2) was used for measuring SO_2 and O_2 near the inlet and outlet of the SCR catalyst zone. An online chemiluminescent NO_x analyzer (Advanced Pollution Instrumentation, model 200AH) downstream of the SO_2 and O_2 analyzer was used for measuring NO_x. No online analyzers were available for measuring NH_3 and HCl in the flue gas.

Table 2. Simulated PRB conditions used for studying Hg oxidation.

Parameters	Condition	Remark
Simulated Flue Gas		
HCl	0, 10, 20 ppm	Provided by gas cylinders.
SO_2	500 ppm	
NO_x	200 ppm	
NH_3	180 ppm	
CO_2	3.5 %	Provided by methane burner.
CO	5 ppm	
O_2	7.1 %	
H_2O	6.8 %	
Total Flow Rate	14 L/min	
NH_3/NO_x ratio	0.9	
Mercury Source	20–25 $\mu g/Nm^3$	Provided by Hg^0 permeation tube.
Fly Ash Feeding	0, 4.8 g/hr	
Space Velocity	2100 hr^{-1}	
Flue Gas Temperature	350, 400 ℃	

Mercury Measurements

An Hg continuous emission monitor (CEM) was used for measuring Hg speciation in the simulated coal combustion flue gas near the inlet and outlet of the SCR catalyst zone. The Hg CEM (Nippon Instrument Corporation, model DM-6B) is designed to measure Hg speciation in combustion flue gases emitted from coal-fired power plants and waste incinerators without the using wet chemistry. This Hg CEM uses a dry reduction catalyst to reduce Hg^{2+} to Hg^0. The sample gas (1 L/min flow rate) passes through a dust filter and then is separated into two sections, total mercury [Hg(T)] section and Hg^0 section. In the Hg(T) section, all of the oxidized Hg (Hg^{2+}) is reduced in a reduction catalyst column to Hg^0. The reduced total Hg is then separated into gas and solution in a gas-liquid separation tube, and any interfering substances remaining in the gas stream are removed by an interfering substance removal column. Prior to entering into the cold vapor atomic absorption (CVAA) total Hg analyzer for Hg measurement, the sample gas is dehumidified by a dehumidification tube where the sample gas is cooled to low temperature.

In the Hg^0 section, the sample gas goes into a chiller directly, bypassing the reduction catalyst column. Interfering substances and moisture in the cooled sample gas are removed by an interfering substance removal column and another dehumidification tube respectively, before the gas is introduced into another CVAA Hg^0 analyzer. The measurement data are received and stored in the computer every 1 sec. The Hg^{2+} concentration is calculated by the difference between total Hg and Hg^0 using the following simple formula:

$$Hg(T) - Hg^0 = Hg^{2+}$$

Where, Hg(T) is total Hg concentration in the flue gas (ug/m^3), Hg^0 is elemental Hg concentration in the flue gas (μg/m^3).

$$Hg^{2+} \ percentage \ in \ flue \ gas \ (\%)_{inlet/outlet} = \frac{Hg(T)_{inlet/outlet} - Hg^0_{inlet/outlet}}{Hg(T)_{inlet/outlet}} \times 100$$

Where, Hg (T)$_{inlet/outlet}$ is total Hg concentration at the inlet or the outlet of the SCR zone, respectively. Hg$^0_{inlet/outlet}$ is elemental Hg concentration at the inlet or the outlet of the SCR zone, respectively. The CEM has a measurement range of 0 – 50 μg/m^3 with an accuracy of $\pm$ 0.5 μg/m^3. In addition, this Hg CEM has a self-calibration function.

Test Procedures

The SCR catalyst was heated overnight at 350 °C under air flow prior to the Hg speciation experiment. This cleanup procedure was followed before each test for removing the adsorbed species such as Hg to minimize any residue effect caused by the previous test. The methane burner was first turned on the next morning, and air and N$_2$ flows were then adjusted to a total reactor outlet flow of 14 L/min. Subsequently, the three temperature-controlled electric furnaces were adjusted accordingly to bring the SCR catalyst zone to the desired operating temperature (350 or 400 °C). Then, the flows of all other gas flue gas components such as gaseous HCl, NO, NH$_3$, SO$_2$, and Hg^0 were simultaneously sent to the reactor. By adjusting dilution N$_2$, the total flow was still maintained at 14 L/min. The concentrations of all flue gas components were well controlled by the mass flow controllers (MFCs) to the predetermined values as shown in Table 2. Unless otherwise indicated, for Hg speciation tests without fly ash injection, the inlet Hg concentrations, including total and elemental mercury [Hg(T) and Hg^0], were first measured with the Hg CEM. Then valves were diverted to the outlet sampling location in order to continuously monitor the changes of outlet mercury concentrations. The time required for reaching the steady state outlet Hg concentrations varied from two to three hours. Then, fly ash was injected using a syringe–type feeder. The Hg speciation test was started after the steady state outlet Hg concentrations were observed, which was generally within 30 min after the fly ash was injected. Fly ash injection was continued for another 2 hours, and the concentrations of Hg (T) and Hg^0 at the outlet of the SCR catalyst zone were measured and recorded continuously. The NO$_x$ concentration was measured at the inlet at the beginning of the Hg speciation test, and the outlet concentration were measured continuously during the test.

RESULTS AND DISCUSSION

Effects of HCl Concentration, Temperature, and PRB Fly Ash on Hg Speciation

A summary of the Hg speciation tests conducted under simulated PRB conditions is presented in Table 3. Results of Hg speciation for the tests are summarized in Table 4.

Table 3. Summary of Hg speciation tests under simulated PRB conditions.

Run No.	HCl Conc. pm	Fly Ash Feed Rate g/hr	Temperature °C
1	0	0	350
2	20	0	350
3	20	0	400
4	0	0	400
5	10	0	350
6	10	0	400
7	20	0	350
8	20	4.9	350
9	20	0	400
10	20	5.0	400
11	20	0	400
12	20	4.9	400
13	20	0	350
14	20	4.9	350
15	0	0	350
16	0	4.7	350
17	20	0	350
18	20	4.8	350
19	10	0	350
20	10	4.8	350
21	0	0	400
22	0	4.8	400

Table 4. Summary of Hg speciation test Results.

	Inlet Hg^o Conc. $\mu g/Nm^3$	Inlet Hg(T) Conc. $\mu g/Nm^3$	Outlet Hg^o Conc. $\mu g/Nm^3$	Outlet Hg(T) Conc. $\mu g/Nm^3$	Calculated Outlet Hg^{2+} Conc. $\mu g/Nm^3$
1	21.8	22.2	11.3	11	0
2	22.3	23.4	2.1	22.9	20.8
3	25.8	26.1	3.9	25.9	22
4	26.2	26.3	14.4	15	0.6
5	24.3	25	5.5	22.1	16.6
6	25.3	24.4	9	18.9	9.9

7	23.3	23.9	2.7	23	20.3
8	23.3	23.9	2.8	18.9	16.1
9	21.6	21.4	5.9	19.9	14
10	21.6	21.4	6.3	19.4	13.1
11	20.3	19.7	5.7	19.2	13.5
12	20.3	19.7	6	18.2	12.2
13	20.9	21.3	2.5	18.2	15.7
14	20.9	21.3	2.7	17.8	15.1
15	22.6	23.3	9.4	9.5	0.1
16	22.6	23.3	9.3	8.9	0
17	19.9	20.1	2.7	17.4	14.7
18	19.9	20.1	2.5	17.2	14.7
19	20.1	20.2	3.9	15.8	11.9
20	20.1	20.2	4.2	16.4	12.2
21	20.2	20	11.8	12.3	0.5
22	20.2	20	11.8	12.5	0.7

The tests were conducted under two different SCR operating temperatures (350 and 400 °C), three different HCl concentrations (0, 10, and 30 ppm), and two different fly ash feeding rates (0 and 4.8 g/hr). Other experimental parameters including concentrations of NO_x (200 ppm), NH_3 (180 ppm), SO_2 (500 ppm), H_2O (6.8%), CO (5 ppm), CO_2 (3.5%), and O_2 (7.1%), and space velocity (2100 hr^{-1}) were maintained constant at the levels shown in Table 2. A nominal NO_x reduction level of 90% was observed for all 22 tests at a nominal NH_3 to NO_x ratio of 0.9, indicating that the entrained-flow reactor system and the operating conditions used in this study reasonably simulated the SCR NO_x reduction conditions encountered in commercial SCR systems, although incomplete mass balance closure for Hg for some experiments (below) indicates that transient Hg capture effects rather than steady-state effects occurred during those experimental conditions. Note that inlet Hg(T) was somewhat variable (20 to 26 $\mu g/m^3$) and mostly all Hg^0.

The first seven tests (Run 1 to 7) were conducted without fly ash injection to evaluate Hg speciation behavior of the SCR catalyst in the absence of the PRB fly ash. It can be observed from Fig. 2 that HCl has a significant effect on oxidation of Hg^0 in the absence of PRB fly ash and under the normal SCR NO_x reduction conditions. Fig. 2 shows that Hg^{2+} measured at the outlet of the SCR catalyst (as a percentage of total inlet Hg) increases from near 0 to 86-91% when the HCl concentration is increased from 0 to 20 ppm. The strong effect of HCl on promoting Hg^{2+} formation under simulated SCR NO_x reduction conditions was also observed in our previous study.[10] It appears that HCl plays an important role for providing the source of Cl as an oxidant for the oxidation of Hg^0 to Hg^{2+} species such as $HgCl_2$.
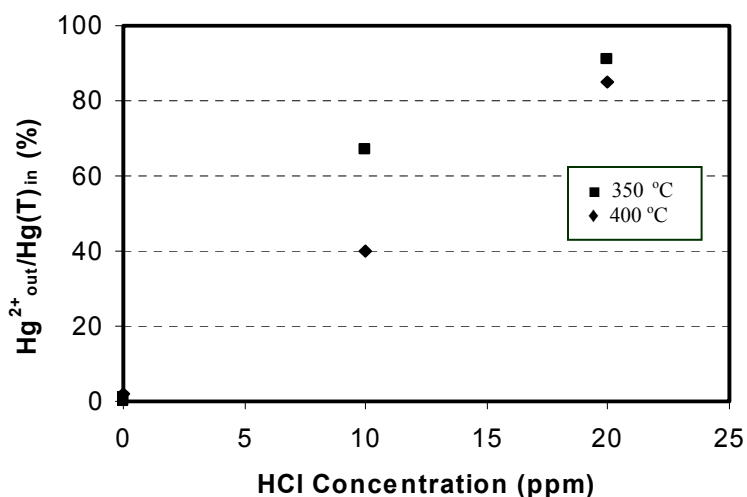
Fig. 2. Effect of HCl Concentration and SCR Operating Temperature on Hg^0 Oxidation under Simulated PRB Conditions without Fly Ash injection.

The generally lower Hg(T) concentrations measured at the outlet of the SCR catalyst zone compared to those measured at the inlet are likely to be caused by partial capture of Hg by the catalyst. Fig. 3 shows that significant Hg capture (45–50%) occurs at 0 ppm of HCl. The
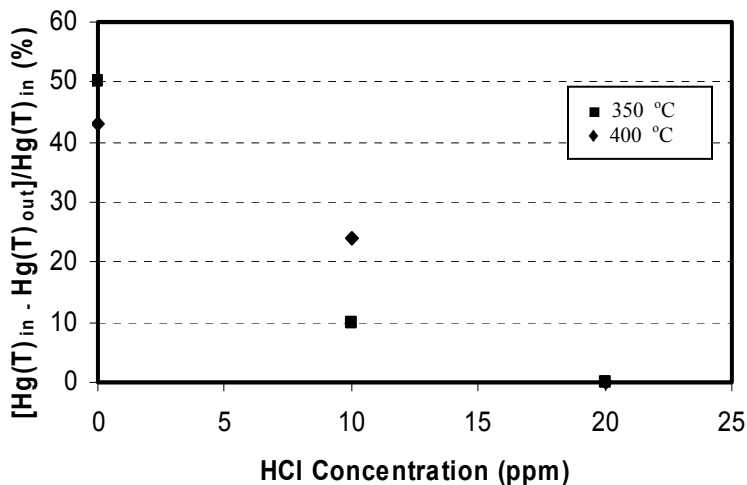

Fig. 3. Effect of HCl Concentration and SCR Operating Temperature on Hg Capture under Simulated PRB Conditions without Fly Ash injection.

capture reduces to zero as HCl concentration increases to 20 ppm. The significant loss of Hg(T) at the outlet of an SCR catalyst in the absence of HCl for simulated PRB conditions was also observed in our previous study.[10] The opposite trends of increased outlet Hg^{2+} level and decreased degree of Hg capture with respect to increased HCl concentration provide further evidence that HCl plays an important role in the Hg chemistry under SCR NO_x reduction conditions. It appears that Hg^0 oxidation does not proceed without HCl. Furthermore, the absence of HCl may also make more active sites existing on the SCR catalyst surface available for capturing Hg^0. A strong acid, HCl is more polar than Hg, and

the active catalyst sites have a stronger affinity for capturing the HCl than Hg^0. It is also likely that HCl and NH_3 compete for the active sites.

Figs 2 and 3 show a minor temperature effect on Hg oxidation and capture between 350 and 400 °C. The effect appears to be relatively strong at the 10 ppm HCl condition, and the effect tends to diminish at the zero and 20 ppm HCl test conditions. The outlet Hg^{2+} is at or near zero in the absence of HCl, and the oxidation of Hg^0 to Hg^{2+} proceeds to near completion at 20 ppm HCl. It appears that the temperature effect is secondary to the dominant effect of HCl within the ranges of temperature (350 to 400 °C) and HCl concentration (0 to 20 ppm) of this study.

More tests (Run 8 to 22) were conducted to further investigate the effects of PRB coal fly ash on Hg speciation under simulated SCR NOx reduction conditions. Fig. 4 presents the Hg
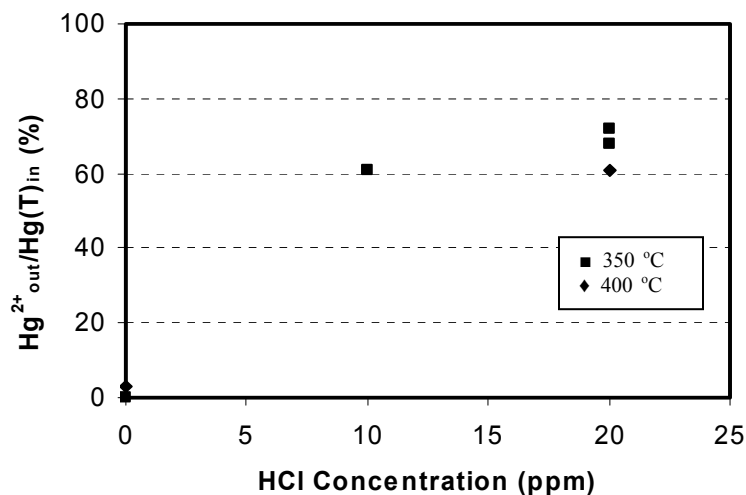

Fig. 4. Effect of HCl Concentration and SCR Operating Temperature on Hg^0 Oxidation under Simulated PRB Conditions with Fly Ash injection.

oxidation results with fly ash injection. Fly ash had no effect on oxidizing Hg^0 when no HCl was present, and minimal effect at 10 ppm HCl. At 20 ppm HCl, the presence of PRB fly ash resulted in decrease of outlet Hg^{2+} (as a percentage of total inlet Hg) from 86–91% (Fig. 2) to 61–74% (Fig. 4). No significant impact on SCR operating temperature on Hg oxidation is observed (Fig. 4), consistent with those data without fly ash injection (Fig. 2).

After fly ash was first being injected into the reactor system in Run 8, later repeated tests for duplicating the previous tests without fly ash injection (Run 1 to 7) produced lower SCR outlet Hg^{2+} values than those of the tests prior to Run 8. For example, Runs 9 and 11 (at 400 °C and 20 ppm HCl) produced lower outlet Hg^{2+} values as a percentage of total inlet Hg (65 and 68%, respectively) than that (86%) for the similar test (Run 3) conducted prior to the first fly ash injection test. Similarly, Runs 13 and 17 (at 350 °C and 20 ppm HCl) generated lower outlet Hg^{2+} as a percent of total inlet Hg (74%) than those (91 and 86%, respectively) for the similar tests (Runs 2 and 7). It should be noted that repeating physical cleaning of the SCR

catalyst after Run 9 by passing compressed air into the catalyst did not restore the Hg oxidation activity of the catalyst back to its original higher values prior to the first fly ash injection test. Apparently some of the fine fly ash particles were retained within the catalyst pores. Such an effect may have reduced diffusion rates of bulky Hg species entering and leaving the porous catalyst for subsequent test runs after the first test with fly ash injection. The speculated retention of fly ash within the catalyst may explain the consistent decrease in outlet Hg^{2+} as a percentage of total inlet Hg that was observed in subsequent Hg speciation test runs. It should be noted that NO_x reduction remained at a nominal level of about 90% for for subsequent test runs after the first test with fly ash injection. It appears that the retention of some fine fly ash particles within catalyst pores has no effect on NO_x reduction reactions.

An incremental increase of about 10 percentage points in Hg capture was observed when comparing the Hg capture results with fly ash injection (Fig. 5) vs. those without fly
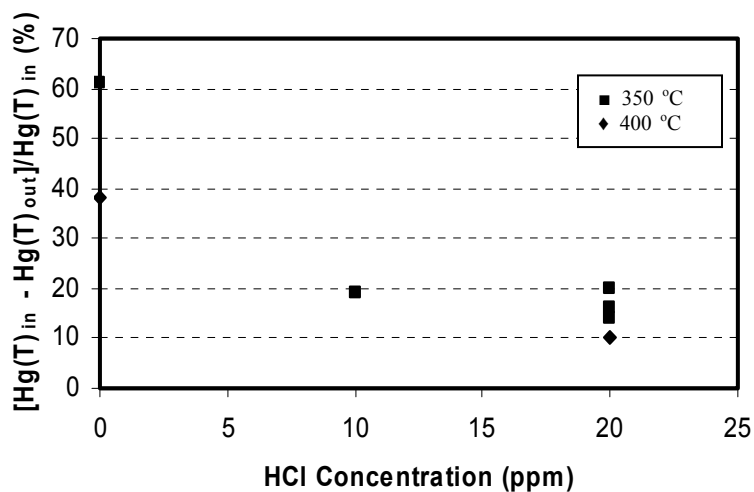

Fig. 5. Effect of HCl Concentration and SCR Operating Temperature on Hg Capture under Simulated PRB Conditions with Fly Ash Injection.

injection (Fig. 3). In the absence of fly ash, the capture of Hg seems to depend strongly on HCl concentration. The incremental increase in Hg capture in the cases of fly ash injection is somewhat independent of HCl concentration (see Figs. 3 and 5). It appears that the incremental increase in Hg capture at 20 ppm of HCl (from 0 to 10–20%) also matches the decrease of outlet Hg^{2+} as a percentage of total inlet Hg (from 86–91% to 61–74%). A noticeable loss of Hg was also observed across a pilot-scale SCR reactor firing bituminous and PRB coals in our previous studies.[9] The capture of Hg may have resulted from the complex heterogeneous Hg reactions occurring in a SCR system, but this requires further study.

Transient Effects of NO_x, SO_2, and Temperature on Hg Speciation in the Absence of NH_3 and Fly Ash

A series of tests were conducted in the absence of NH_3 to investigate the transient effects of NO_x, SO_2, and temperature on Hg speciation in an SCR catalyst. Some of the field SCR units, especially those without a bypass duct around the SCR reactor, may operate

periodically without injection of NH_3. Reactions involving other flue gas components such as NO_x and SO_2 may occur in the SCR reactor in the absence of NH_3 to impact Hg speciation in the flue gas.

The Hg speciation results measured during the tests are shown in Fig. 6. The inlet Hg
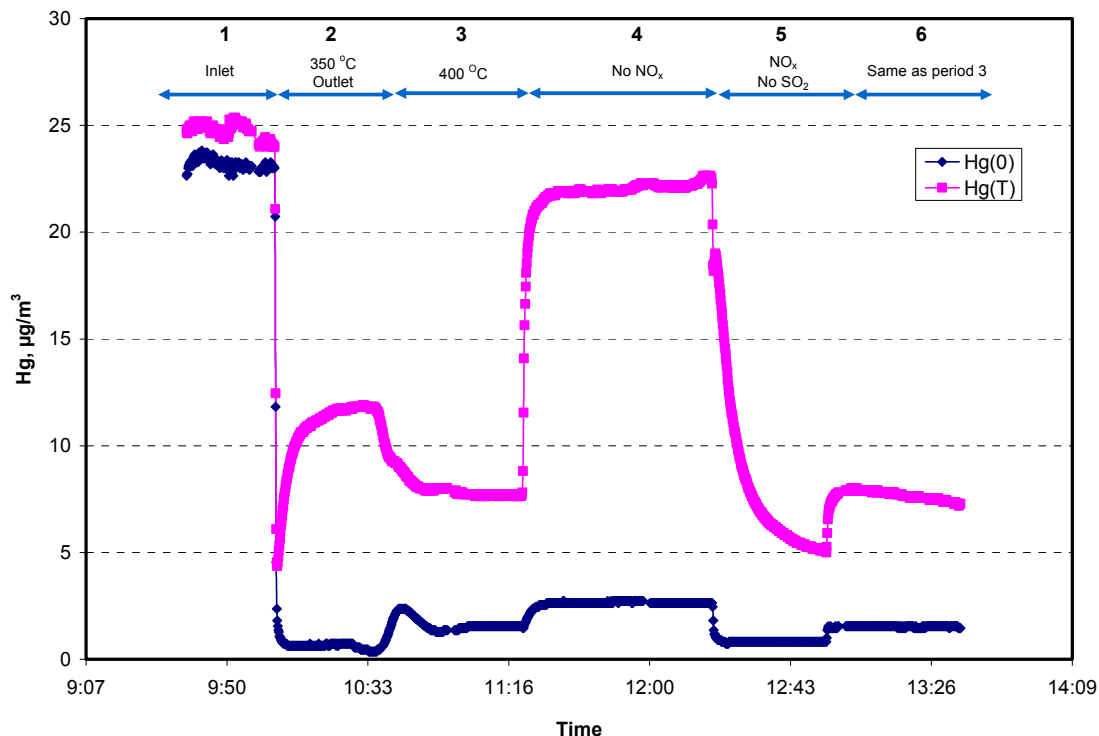

Fig. 6. Transient Effects of NO_x, SO_2, and Temperature on Hg Speciation using SCR Catalyst without NH_3 Injection.

concentrations were measured at the initial period of the test (period one shown in Fig. 6). The first outlet speciation test was conducted during period two at the inlet conditions established during period 1 with no NH_3, 20 ppm of HCl, 25 $\mu g/Nm^3$ of Hg in the flue gas, and a temperature of 350 °C. All other experimental parameters are specified in Table 1. After switching the Hg CEM to the outlet of the SCR catalyst zone at the end of period one, the transient response of the Hg CEM during period two reached constant values in 25 min. of about 0.9 $\mu g/m^3$ of Hg^0 and 12 of Hg(T) at the outlet. The temperature was increased from 350 to 400 °C at the start of period three. Constant Hg^0 and Hg(T) measurements (1.6 and 7.5 $\mu g/m^3$, respectively) were measured 10 min after the temperature was raised to 400 °C. The flow of NO_x to the reactor was turned off at the beginning of subsequent period four. The constant Hg^0 and Hg(T) measured at the end of this period were 2.6 and 22.5 $\mu g/m^3$, respectively. The flow of NO_x was turned on again and the flow of SO_2 was turned off at the beginning of period five. The constant Hg^0 and Hg(T) measured were 1 and 5.2$\mu g/m^3$, respectively. The flow of SO_2 was turned on again at the beginning of period six. The Hg^0 and Hg(T) were restored back to those of period three.

Significant capture of Hg (50%, calculated based on total Hg measured at the outlet), very little Hg^0 (5%) with predominantly Hg^{2+} (45%), both as a percentage of total inlet Hg, were

observed at the SCR catalyst zone outlet in period two in the absence of NH_3. The increase in temperature from 350 to 400 °C in period 3 resulted in more Hg capture, which is surprising. The Hg capture results (50–70%) in the absence of NH_3 were significantly different from those (0–2%) in the presence of NH_3. It is well known that the active sites of SCR catalyst adsorb NH_3 during the NO_x reduction process. The absence of NH_3 is likely to make more active sites available for adsorbing Hg or catalyzing the formation of captured Hg species, potentially explaining the observed increase in Hg capture. The increased Hg capture at increased temperature in the absence of NH_3 is consistent with a catalytic mechanism for Hg capture rather than an adsorptive mechanism, and the exact sites involved in such a mechanism would require further study. In the absence of both NH_3 and NO_x (period four), the low Hg capture (12%) and high Hg^{2+} as a percentage of total inlet Hg (78%) were very similar to those (0 and 85%) observed for the test (Run 3) with NH_3 and NO_x present at 180 and 200 ppm, respectively. Test results in the absence of NH_3 and NO_x are similar to those near the exit region of the SCR units in the field where NO_x reduction proceeds close to completion. It is likely that the completion of NO_x reduction promotes more Hg oxidation in that region in the presence of adequate Cl in the flue gas.

The reader is cautioned that the transient effects observed in this study were not studied at long enough exposure time to determine the steady state Hg level on the catalyst that would be achieved at much longer exposure times to a given test condition that would eventually correspond to a steady-state condition, nor the resultant steady-state Hg oxidation. The apparent steady-state observations during the transient test periods did not achieve complete Hg mass balance closure (except in the absence of NO and NH_3 in period four), indicating that the Hg capture process had not proceeded to completion (except possibly for period four). The test runs in the presence of NH_3 where zero Hg capture was observed should correspond to steady-state conditions.

CONCLUSIONS

A bench-scale, entrained-flow reactor has been modified for simulating the SCR NO_x reduction conditions in the field. The system was tested using flue gases produced in a methane burner and doped with gas mixtures and injected coal combustion fly ash simulating the combustion of a low-S and low-Cl PRB subbituminous coal. A nominal NO_x reduction level (90%) similar to those achieved in field units was also observed for the system under all the PRB coal firing conditions tested in this study. Confirming previous studies, it was observed that HCl concentration has the strongest effect on influencing the speciation and capture of Hg under the simulated PRB conditions used in this study. The observed strong HCl effect suggests that HCl provides the source of Cl, an important oxidant for Hg^0 oxidation under SCR emission reduction conditions. The effect of temperature on Hg speciation and capture appears to be a secondary effect. The presence of PRB coal fly ash in the flue gas reduced Hg^0 oxidation somewhat with a corresponding incremental increase in Hg capture. Significant transient effects of NO_x, SO_2, and temperature on Hg speciation and capture were observed in the absence of NH_3 and fly ash. The observed high Hg^0 oxidation in the absence of both NH_3 and NO_x suggests that Hg^0 oxidation is likely to occur near the exit region of the SCR reactor. Operation of SCR systems without NH_3 injection is expected to cause changes in Hg speciation and capture in the flue gas such as those observed during short-term exposure conditions in this study, although steady-state outlet Hg speciation and Hg capture levels would require tests with longer exposure time.

REFERENCES

1. Keating, M.H.; Mahaffey, K.R.; Schoeny, R.; Rice, G.E.; Bullock, O.R.; Ambrose, R.B., Jr.; Swartout, J.; Nichols, J.W. *Mercury Study Report to Congress*, EPA-452/R-97-003 through 010; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards and Office of Research and Development; Research Triangle Park, NC, 1997; Volumes I-VIII.

2. U.S. Environmental Protection Agency; Clean Air Mercury Rules, March 2005; http://www.epa.gov/mercuryrule/index.htm.

3. Brown, T.D.; Smith, D.N.; Hargis, R.A., Jr.; O'Dowd, W.J. Mercury measurement and its control: what we know, have learned, and need to further investigate. *J. Air &Waste Manage. Assoc.* **1999**, 49, 628-640.

4. Carey, T.R.; Hargrove, O.W.; Seeger, D.M.; Richardson, C.F.; Rhudy, R.G.; Meserole, F.B. Effect of Mercury Speciation on Removal Across Wet Process. Presented at the AIChE Spring National Meeting, Session 47, New Orleans, LA, February 1996; Paper No. A-05.

5. Blythe, G.M.; Carey, T.R.; Richardson, C.F.; Meserole, F.B; Rhudy, R.G.; Brown, T.D. Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems. In *Proceedings of the A&WMA's 92nd Annual Meeting & Exhibition*, *St. Louise, MO, June 20-24, 1999*; A&WMA: Pittsburgh, PA, 1999; Paper 99-174.

6. Ghorishi, S.B.; Gullett, B.K. Sorption of mercury species by activated carbons and calcium-based sorbents: effects of temperature, mercury concentration and acid gases. *Waste Manage Res*. **1998**, 16 (6), 582-593.

7. Price, D.; Birnbaum, R.; Batiuk, R.; McCullough, M.; Smith, R. *Nitrogen Oxides: Impacts on Public Health and the Environment*; EPA-452/R-97-002 (NTIS PB 98-104631); U.S. Environmental Protection Agency, Office of Air and Radiation: Washington, DC, 1997.

8. Laudal, D.L.; Thompson, J.S.; Wocken, C.A. *Selective Catalytic Reduction Mercury Field Sampling Project*; EPA-600/R-04-147; U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, 2004.

9. Lee, C.W.; Srivastava, R.K.; Ghorishi, S.B.; Karwowski, J.; Hastings, T.W.; Hirschi, J. Pilot-scale study of the effect of selective catalytic reduction catalyst on mercury speciation in Illinois and Powder River Basin coal combustion flue gases," *J. Air and Waste Manage. Assoc.*, in press.

10. Lee, C.W.; Srivastava, R.K.; Ghorishi, S.B; Hastings, T.W.; Stevens, F.M. Investigation of selective catalytic reduction impact on mercury speciation under simulated NO_x emission control conditions. *J. Air & Waste Manage. Assoc.* **2004**, 54, 1560-1566.

11. Eswaran, S; Stenger, H.G. Catalytic Oxidation of Elemental Gas-Phase Mercury. In

Proceedings of the A&WMA's 82th Annual Meeting & Exhibition, Minneapolis*, MN, June 21-24, 2005*; A&WMA: Pittsburgh, PA, 2005; Paper 05-1088.

12. Serre, S.D.; Gullett, B.K.; Ghorishi, S.B. Entrained-flow adsorption of mercury using activated carbon; *J. Air and Waste Manage. Assoc*. **2001**, 51, 733-741.