Pilot-Scale Evaluation of Mercury Oxidation across SCR Catalysts

1010157

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Technical Update, December 2005

EPRI Project Manager

P. Chu

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1395 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

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CITATIONS

This document was prepared by

Reaction Engineering
77 west 200 South, Suite 210
Salt Lake City, UT 84101

Principal Investigator
C. Senior

Western Kentucky University
1 Big Red Way
Bowling Green, KY 42101

Principal Investigator
W.P. Pan

This document describes research sponsored by the Electric Power Research Institute (EPRI).

This publication is a corporate document that should be cited in the literature in the following manner:

Pilot-Scale Evaluation of Mercury Oxidation across SCR Catalysts. EPRI, Palo Alto, CA: 2005 1010157.

ABSTRACT

Measurements were conducted to evaluate the mercury chemical reactions using a pilot-scale SCR operating on flue gas slipstream from an eastern bituminous (~1.75% sulfur, ~750 ppm Cl) coal-fired power plant. Tests were conducted by the Western Kentucky University (WKU) to evaluate the impact of flue gas constituents (HCl, Cl2, SO2, SO3, NH3:NOx) as well as two commercially-available SCR catalysts. The results and data were reviewed by Reaction Engineering International, who prepared this technical update. The results indicate that HCl and to a lesser extent SO3 are the key flue gas constituents that affect elemental mercury oxidation. Temperature and catalyst design (space velocity, formulation) likely impact mercury oxidation, although definitive conclusions could not be developed since these parameters were not rigorously evaluated.

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Background

In March 2005 US EPA announced two final rules for air pollution that affect coal-fired electric utility boilers: the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR). EPA directed states in affected regions to cap emissions and revise their State Implementation Plants (SIPs) for NO_x and SO_2 emissions. The CAMR established a cap-and-trade program for national emissions of mercury. EPA previously estimated that US power plants emit 48 tons per year of mercury. The CAMR set caps for mercury emissions in two phases: 38 tons per year starting in 2010; 15 tons per year starting in 2018. EPA set the Phase I cap for mercury with the anticipation that this would be met by compliance with the CAIR, for example, by the increase in the number of plants that have both SCR and a scrubber. The annual cap on NO_x emissions might mean that utilities will choose to run their SCRs year-round, instead of only May to September. The mandate for reduced SO_2 emissions might mean that certain utilities will install new wet flue gas desulfurization (FGD) or spray dryer absorber (SDA) units.

Mercury can be removed by the existing air pollution control devices used at utility power plants, particularly FGD systems. Removal of oxidized mercury (Hg^{2+}) is generally high, greater than 90% in most of the wet scrubbers tested to date. Elemental mercury (Hg^0) is not very water-soluble and therefore wet scrubbers do not remove much elemental mercury. Selective catalytic reduction (SCR) systems have been observed to convert Hg^0 to Hg^{2+} in coal-fired power plants. If the amount of Hg^{2+} in the flue gas can be maximized upstream of a wet FGD, combining an SCR with a wet FGD system offers a low-cost option for control of mercury from coal-fired power plants.

Objectives

Previously, EPRI has funded small-scale experiments using simulated flue gas and flue gas taken from full-scale power plants. Simulated flue gas does not always produce mercury oxidation behavior that is consistent with that observed in flue gas from full-scale power plants. However, flue gas from full-scale power plants does not allow control of the gas composition, which is necessary for understanding the impact of different fuels and additives. The work described here used flue gas from a full-scale power plant (in a slipstream configuration), but the concentrations of certain key acid gas species could be increased by spiking these gases at the inlet to the slipstream reactor.

The objectives of this study were to identify the specific flue constituents that promote (or inhibit) mercury oxidation and to determine if there was an effect of catalyst geometry and composition on mercury oxidation.

Answering these questions could allow utilities to use SCRs as part of mercury compliance planning. In particular, utilities must be able to predict reliably and with reasonable accuracy the impact of the following on mercury oxidation:

- Fuel composition
- Flue gas additives
- Catalyst selection

Methods

The slipstream reactor, described below, was installed across the air preheater at a utility boiler in Kentucky, which burns a low-sulfur bituminous coal. The 200 MW_e boiler was a front-wall fired B&W boiler with low-NO_x burners and a cold-side ESP. The boiler did not have post-combustion NO_x or SO_2 control devices. NO_x concentrations measured at the economizer outlet were on the order of 300 ppmv.

Figure 1 shows a sketch of the reactor. Western Kentucky University (WKU) and one of the catalyst vendors designed the pilot SCR reactor to simulate full-scale operation as closely as possible. The slipstream reactor had two layers of catalyst with sampling ports at the inlet, middle and outlet. The inlet temperature of the reactor was on the order of 600°F; the temperature drop across the slipstream reactor was about 30°F. The reactor was designed by produce space velocities on the order of 2,000 hr^{-1}.

The slipstream reactor had soot blowers to prevent ash build-up on the catalysts. Spike gases and/or ammonia were added upstream of the first layer. Static mixers were installed downstream of ammonia or spike-gas injection in order to distribute these well in the flue gas.

Flue gas mercury speciation measurements were made at the inlet and outlet of the catalysts using PS Analytical (PSA) semi-continuous emission monitors (SCEMs) with PSA pre-treatment systems. A modified Apogee inertial sampling probe was used for the SCEMs.) modified the inertial sampling probe for operation at high temperature (700°F) to minimize mercury conversion in the probe. Ontario Hydro measurements (OHM) were made at three locations: inlet, outlet and in between the two catalyst layers. OHM was used to verify the SCEM results.

Commercial monolith (honeycomb) SCR catalysts were provided by two vendors. Catalyst #1 had an 8.4 mm pitch; the square cross section had an array of 18 x 18 channels. Catalyst #2 had a ~7.5 mm pitch; the square cross section had an array of 20 x 20 channels. Each catalyst section was one meter in length; the total length of catalyst was therefore two meters.

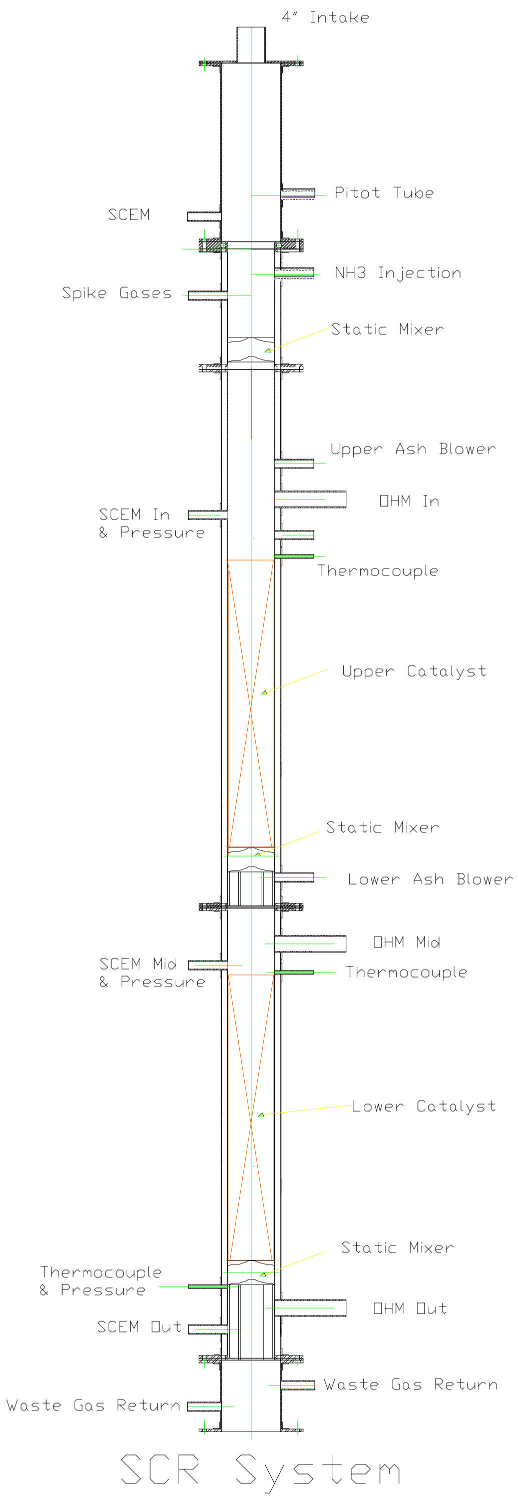


Figure 1:
Diagram of SCR slipstream system (flow from top to bottom)

Results

Coal properties during the testing are summarized in Table 1. The chlorine concentration of the coal varied considerably, ranging from 354 µg/g (ppmw) to 1378 µg/g, corresponding to approximately 30 to 100 ppmv of HCl in the flue gas (dry, at 3% O_2). Sulfur concentration varied from 1.2 wt% to 2.2 wt%, corresponding to approximately 1,000 to 1,800 ppmv of SO_2 in the flue gas (dry, at 3% O_2). Loss on ignition (LOI) of the fly ash was on the order of 2.5 wt% during the March 2005 test period. During the late-April to early-May test period, the LOI was on the order of 7 wt%. NO_x removal across both catalysts was approximately 93% with a ratio of NH_3/NO of 1.1. Blank experiments (with no catalyst in the reactor) showed little mercury oxidation across the slipstream reactor without catalyst at the baseline HCl concentration of approximately 100 ppmv.

Table 1. Key Coal Properties.

Test Date	Catalyst Type	Cl (ppmw) dry	Hg (ppmw) dry	S (wt %) dry	Ash (wt %) dry
3/5/2005	#1	550	0.08	1.5	6.2
3/9/2005	Empty	1270	0.10	1.56	11.39
3/18/2005	#1	710	0.15	1.42	9.7
3/20/2005	#1	1186	0.13	1.39	9.9
3/21/2005	#1	963	0.13	1.34	10.8
3/22/2005	#1	685	0.12	1.48	11.8
3/25/2005	#2	571	0.12	1.89	10.3
3/26/2005	#2	354	0.16	1.95	9.0
3/28/2005	#2	423	0.14	1.89	13.1
3/29/2005	#2	842	0.15	1.76	7.7
3/29/2005	#2	842	0.15	1.76	7.7
3/30/2005	#2	396	0.15	2.17	9.9
4/30/2005	#1	1282	0.13	1.23	11.4
5/6/2005	#2	1378	0.09	1.67	9.9

Table 2 summarizes the experimental conditions. For the experiments in March 2005, the catalyst temperature was in the range of 560°F to 590°F, which is lower than typical operating temperatures for full-scale SCRs at coal-fired power plants. For the experiments in April-May 2005, the catalyst temperature was 615°F to 645°F. The space velocity in the catalyst was on the order of 1,900 hr^{-1} for the experiments in March 2005, while the space velocity was on the order of 4,500 hr^{-1} for the experiments in April-May 2005. The latter space velocity is higher than typical for full-scale coal-fired SCR reactors.

Addition of HCl to the blank reactor configuration caused measurable oxidation of mercury: addition of 200, 400 and 500 ppmw of HCl caused mercury oxidation of 6.5%, 20% and 35%, respectively, across the reactor. Addition of Cl_2, SO_2 or NO did not result in significant changes in oxidized mercury across the empty reactor. Addition of 4 ppmw of HBr, however, resulted in a 30-50% reduction of total vapor-phase mercury across the empty reactor. Vapor-phase mercury concentrations slowly recovered when the HBr was turned off. This suggested that deposits (on the reactor or in the sampling system) might be responsible for the loss of vapor-phase mercury. Additional studies are necessary to further evaluate the effects of HBr.Heading, Level 2

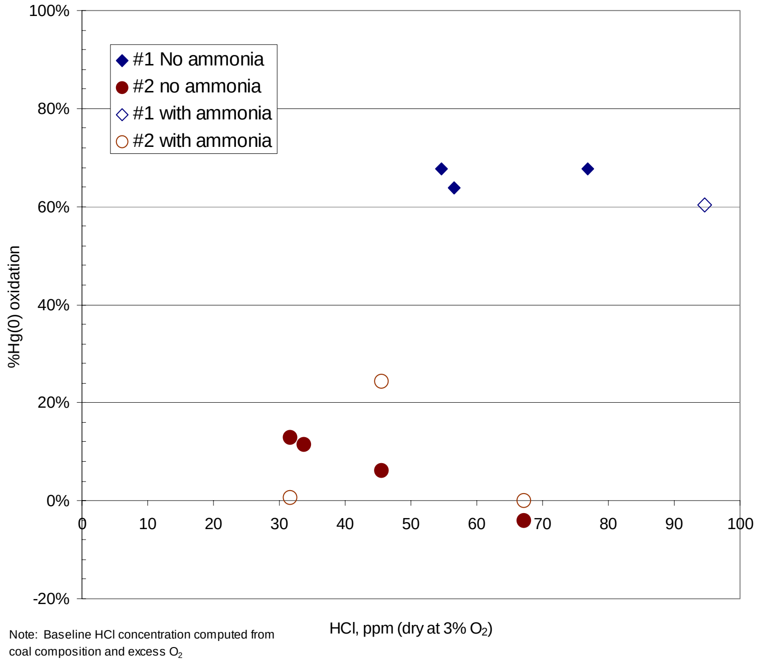
Table 2. Conditions for Slipstream Reactor Testing.

	Catalyst Information			**Added Flue Gas Concentrations [dry basis]**					
Test Date	**Catalyst Type**	**Space Velocity (hr^{-1})**	**Catalyst Temp. (^{o}F)**	**NH_3:NO_x ratio**	**HCl (ppm)**	**Cl_2 (ppm)**	**SO_2 (ppm)**	**SO_3 (ppm)**	**HBr (ppm)**
3/5/2005	#1	1800	700	1	100				
3/9/2005	None	NA	NA	0	200-500				
3/18/2005	#1	1870	596	0				0-50	
3/20/2005	#1	1935	560	0	0-500				
3/20/2005	#1	1870	596	1.02	0-500				
3/21/2005	#1	1885	577	0		0-20			
3/22/2005	#1	1875	576	0			0-2,000		
3/25/2005	#2	1920	565	1.03	0-500				
3/25/2005	#2	1935	565	0		0-25			
3/26/2005	#2	1850	576	1.02			0-2,000		
3/28/2005	#2	1883	580	0				0-50	
3/29/2005	#2	1880	582	0	0-500				
3/29/2005	#2	1865	590	1.07	0-500				
3/30/2005	#2	1865	590	0			0-2,000		
3/30/2005	#2	1865	590	1.04			0-2,000		
3/30/2005	#2	1875	590	1.01				0-50	
4/30/2005	#1	4500	615	0					0-3
4/30/2005	#1	4500	615	1.03					0-3
5/6/2005	#2	4357	645	1.05					0-6.3

Figure 2 shows the amount of mercury oxidation calculated from the inlet and outlet concentrations of Hg^0 for the baseline catalyst results taken for multiple days in March 2005 for Catalysts #1 and #2, with ammonia (NH_3/NO~1) and without ammonia. The HCl concentration in the flue gas was calculated from the coal composition, assuming no HCl adsorption onto the fly ash and 3% O_2 dry condition. Observed mercury oxidation was higher for Catalyst #1 than for Catalyst #2 over similar ranges of HCl concentrations. Differences in catalyst pitch and catalyst formulation might have been responsible for the differences between the two catalysts. In the baseline experiments, there was no clear effect of ammonia on mercury oxidation.

Figures 3 through 6 summarize the effects of adding acid gas components to the flue gas upstream of the slipstream reactor. The baseline concentrations of acid gases were estimated from the coal composition. Baseline Cl_2 was assumed to be 5% of the total chlorine in the coal. Baseline SO_3 was assumed to be 1% of the total sulfur in the coal. The x-axes represent an estimate of the *total* concentration of the gas species in the flue gas, that is, the sum of the added gases and estimated baseline gas concentration.

Figure 3 shows the effect of HCl addition for both catalysts and for the empty reactor. Gas-phase mercury oxidation did not appear to be significant at the concentrations of HCl less than approximately 100 ppmv (dry, at 3% O_2). However, the empty-reactor data show that as the HCl concentration increased to 500 ppm, the gas-phase mercury oxidation increased to 35%. Catalyst #1 showed a high degree of mercury oxidation at the baseline HCl concentration and there was little effect of additional HCl on mercury oxidation. Catalyst #1 also appeared to be insensitive to temperature (over this temperature range), since the data in the two curves for Catalyst #1 in Figure 3 were taken at different temperatures, 560°F and 596°F. Neither catalyst showed a clear effect of ammonia on mercury oxidation.

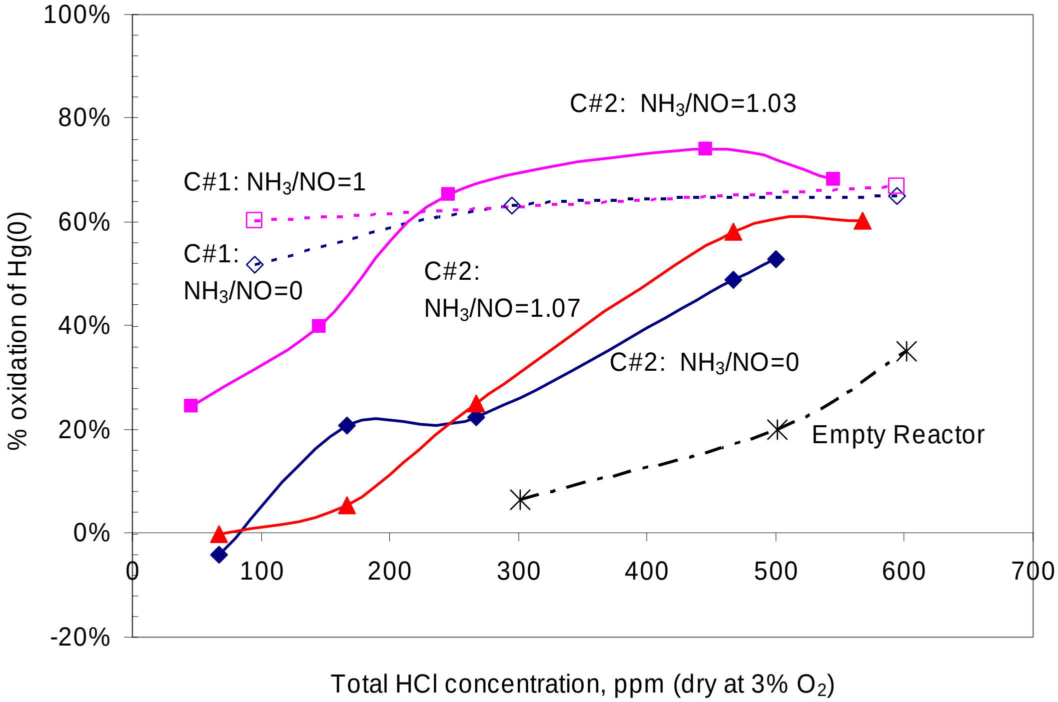


Note: Baseline HCl concentration computed from coal composition and excess O_2

Figure 2. Oxidation of elemental mercury across catalysts with no spike gas additions, with (NH_3/NO~1) and without ammonia.

Catalyst #2 showed little or no mercury oxidation at the baseline HCl concentration and an increase in mercury oxidation with additional HCl. In Figure 3, there are two sets of experiments for Catalyst #2 with NH_3/NO~1. One difference between the two “with ammonia” runs for Catalyst #2 is temperature. The shapes of these curves are similar, but the magnitude of the mercury oxidation was considerably different between the two curves. The higher curve (NH_3/NO=1.03) corresponds to a temperature of 565°F while the lower curve (NH_3/NO=1.07) corresponds to a temperature of 590°F. Models of mercury oxidation across SCR catalysts and other sets of slipstream data have shown higher Hg oxidation at lower temperatures. The difference between these two curves could be due to the differences in operating temperature.

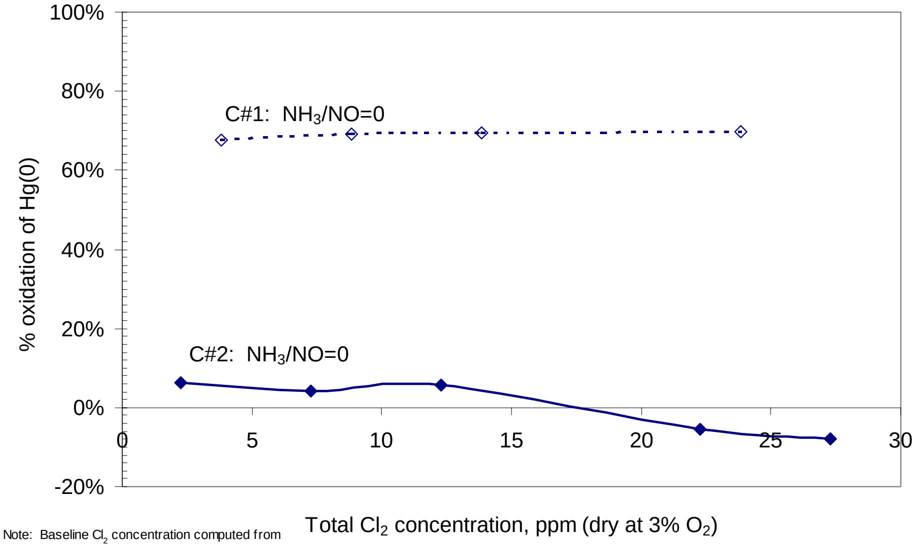
Mercury oxidation by HCl across Catalyst #2 appeared to be affected by both temperature and HCl concentration, but mercury oxidation across Catalyst #1 did not show sensitivity to temperature or HCl concentration (over the range tested). It is possible that Catalyst #1 had achieved the near maximum oxidation at ~100 ppm HCl concentration, thus further increases in HCl concentrations were of limited benefit.. Recently models for mercury oxidation across SCR catalysts have been developed that include the effects of mass transfer and surface chemistry. Certain catalyst designs are more sensitive to temperature or gas species concentrations than others, because of the relative influence of mass transfer and chemical reaction.



Note: Baseline HCl concentration computed from coal composition and excess O_2

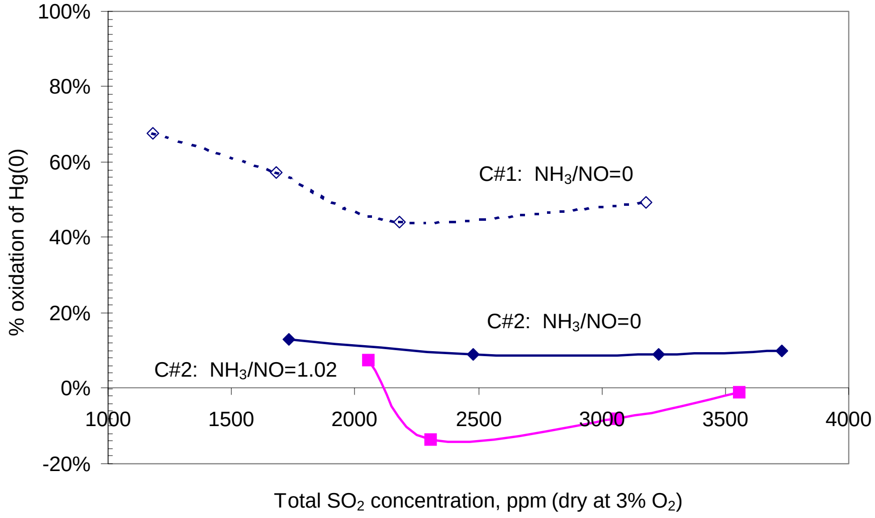
Figure 3. Oxidation of elemental mercury across catalysts with no spike gas additions, with (NH_3/NO~1) and without ammonia

Addition of Cl_2 without ammonia present (Figure 4) had little effect on mercury oxidation, which suggests that Cl_2 is not the active chlorine species for catalytic oxidation across the SCR. Addition of SO_2 (Figure 5) resulted in a decrease in mercury oxidation for Catalyst #1 (without NH_3 injection), while there was no apparent effect on mercury oxidation for Catalyst #2. There might have been a more significant effect of SO_2 addition in suppressing mercury oxidation for Catalyst #2 in the presence of ammonia, although the amount of mercury oxidation was small for Catalyst #2 across the entire range of SO_2 concentration. Addition of SO_3 (Figure 6) increased mercury oxidation for both catalysts without ammonia. For Catalyst #2 with NH_3/NO~1, there was little effect of SO_3 addition on mercury oxidation.



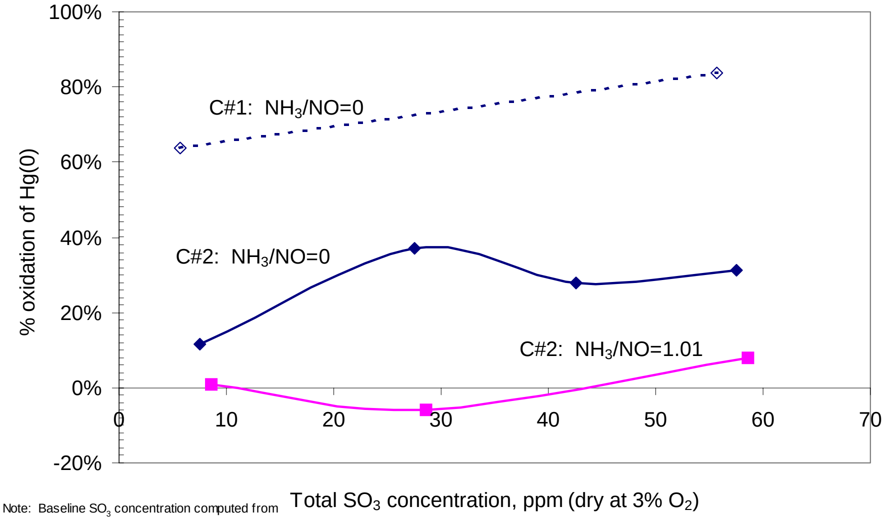
Note: Baseline Cl_2 concentration computed from coal composition and excess O_2, assuming 5% of chlorine present as Cl_2 at SCR inlet

Figure 4. Effect of Cl_2 addition on oxidation of elemental mercury across two catalysts in slipstream reactor.



Note: Baseline SO_2 concentration computed from coal composition and excess O_2

Figure 5. Effect of SO_2 addition on oxidation of elemental mercury across two catalysts in slipstream reactor.



Note: Baseline SO_3 concentration computed from coal composition and excess O_2, assuming 1% of sulfur present as SO_3 at SCR inlet

Figure 6. Effect of SO_3 addition on oxidation of elemental mercury across two catalysts in slipstream reactor.

Addition of HBr caused a reduction in the measured total mercury at the outlet to the SCR reactor, which was not consistent from one trial to another. There may have been an interaction between bromine compounds and fly ash in the inertial separation probe. Cleaning the probe of ash deposits resulted in less observed loss of total mercury at the outlet location relative to the inlet location. HBr did not have a significant effect on the amount of elemental mercury at the outlet of the SCR.

Conclusions

This study evaluated the effects of addition of various acid gas species on the oxidation of elemental mercury across two commercial SCR catalysts in a pilot SCR reactor operating on a slipstream from a low-sulfur bituminous coal-fired power plant.

Previous work on mercury oxidation across SCRs has suggested that chlorine compounds are involved in mercury oxidation by these catalysts. This study demonstrated that HCl, not Cl_2, is the chlorine compound that affects mercury oxidation by SCR catalysts. Previous work on mercury oxidation across SCRs has also suggested sulfur compounds are also involved in mercury oxidation. This study demonstrated that SO_2 has little effect on mercury oxidation, but SO_3 did have an effect, under certain conditions.

Addition of HBr to the flue gas caused a reduction of total vapor-phase mercury with or without the presence of the catalyst in the slipstream reactor. The reduction of total mercury might have occurred in the mercury SCEM sampling system, associated with ash deposits in the inertial probe. Further work is needed to understand the impact of HBr addition.

Two different monolith catalysts were evaluated; each had different mercury oxidation behavior. One catalyst measured a high amount of baseline mercury oxidation, and additional mercury oxidation was not observed by the addition of acid gases (including HCl). In addition, mercury oxidation was not affected by the presence of ammonia. The other catalyst measured little or no baseline mercury oxidation, however increasing HCl flue gas concentrations yielded an increase in both gas-phase and catalytic oxidation. Neither catalyst showed an effect of ammonia on mercury oxidation.

Recently models for mercury oxidation across SCR catalysts have been developed that include the effects of mass transfer and surface chemistry. Differences among commercial catalysts relative to mercury oxidation are expected to arise from differences in catalyst geometry (which affects the mass transfer of mercury within the catalyst) and catalyst formulation (which affects the catalytic oxidation reaction). The results of this study demonstrate the variability of mercury oxidation behavior that could be found among commercial catalysts.

The data appear to indicate that catalyst temperature affects mercury oxidation, but a definitive conclusion can not be drawn since the temperature was not varied in a systematic way.

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