

# Effect of SCR Catalyst on Mercury Speciation

Paper # 7

**Chun W. Lee and Ravi K. Srivastava**

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division (MD-E305-01), Research Triangle Park, NC 27711

**S. Behrooz Ghorishi\* and Jarek Karwowski**

ARCADIS Geraghty & Miller, Inc., P.O. Box 13109, Research Triangle Park, NC 27709

**Thomas W. Hastings**

Cormetech, Inc., 5000 International Drive, Durham, NC 27712

**Joseph Hirschi**

Illinois Clean Coal Institute, 5776 Coal Drive, Carterville, IL62819

## ABSTRACT

A pilot-scale research study was conducted to investigate the effect of selective catalytic reduction (SCR) catalyst on mercury (Hg) speciation in bituminous and subbituminous coal combustion flue gases. Three different Illinois bituminous coals (from high to low sulfur and chlorine) and one Powder River Basin (PRB) coal with very low sulfur (S) and very low chlorine (Cl) were tested in a pilot-scale combustor equipped with a SCR reactor for controlling nitrogen oxides (NO<sub>x</sub>) emissions. The SCR catalyst induced high oxidation of Hg<sup>0</sup>, decreasing the percentage of Hg<sup>0</sup> at the outlet of the SCR to values below 12% for the three Illinois coal tests. The PRB coal test indicated a low oxidation of Hg<sup>0</sup> by the SCR catalyst, with the percentage of Hg<sup>0</sup> decreasing from about 96% at the inlet of the reactor to about 80% at the outlet. The test results indicate a strong coal-type dependent effect of SCR on promoting Hg oxidation. The results also suggest the viability of reducing Hg emissions using SCR systems in Illinois bituminous coal-fired boilers that are equipped with FGD systems or other effective equipment for capture of oxidized Hg species is a viable option for reducing Hg emissions. SCR applications on PRB coal-fired boilers equipped with wet FGD systems may not achieve increased mercury removal resulting from such applications. The coal type dependence of mercury speciation observed in this study is consistent with the available field data.

---

\* Currently at Babcock & Wilcox Research Center, 1562 Beeson Street, Alliance, OH 44601

The mercury oxidation performance of SCR catalyst with respect to catalyst aging is an important consideration for SCR to be a viable multi-pollutant technology for reducing  $\text{NO}_x$  and Hg emissions. Bench-scale tests of the oxidation of  $\text{Hg}^0$  with simulated coal combustion flue gases were conducted on fresh and field-aged SCR catalyst samples. The effect of space velocity of the catalyst on  $\text{Hg}^0$  oxidation was also studied. Data reflect that the SCR catalyst used for bituminous coal firing showed no apparent aging effect on reducing  $\text{Hg}^0$  oxidation. Space velocity seems to have a significant effect on  $\text{Hg}^0$  oxidation, suggesting a heterogeneous mechanism is involved in the oxidation.

## INTRODUCTION

Coal combustion is a major source of mercury (Hg) emissions that have caused environmental health concerns.<sup>1</sup> Mercury speciation, the split amongst chemical forms of Hg species, has a great influence on the control and environmental fate of Hg emissions from coal combustion.<sup>2</sup> Elemental mercury ( $\text{Hg}^0$ ) is released from coal during the high-temperature combustion process. However, depending on the coal type, a significant fraction of the Hg can be oxidized in the low-temperature, post-combustion environment of a coal-fired boiler. Relative to  $\text{Hg}^0$ , oxidized Hg ( $\text{Hg}^{2+}$ ) is more effectively captured in conventional pollution control systems such as flue gas desulfurization (FGD) systems. It is known that controlling the emissions of  $\text{Hg}^{2+}$ , the water-soluble mercuric chloride ( $\text{HgCl}_2$ ) in particular, is much easier than controlling the insoluble  $\text{Hg}^0$ .<sup>3-5</sup>

Coal-fired power plants are also a significant anthropogenic source of nitrogen oxide ( $\text{NO}_x$ ) emissions that are associated with several environmental concerns such as acid rain, fine particulate ( $\text{PM}_{2.5}$ ), and ozone formation.<sup>6</sup> Selective catalytic reduction (SCR) technology, which has commercially reduced  $\text{NO}_x$  emissions by  $> 90\%$  at utility power plants, will be increasingly used to meet future stricter regulations for ozone,  $\text{PM}_{2.5}$ , and regional haze. Approximately 100 gigawatts of coal-fired capacity in the U.S. will employ SCR for  $\text{NO}_x$  control by 2005.<sup>7</sup> The operation of SCR units affects the speciation of mercury in the coal combustion flue gases. Limited field data obtained from European coal-fired boilers equipped with SCR systems suggest that SCR catalysts promote the formation of  $\text{Hg}^{2+}$  species.<sup>8</sup> Results of pilot-scale screening tests on the impact of SCR on mercury speciation also indicate that SCR systems could promote the formation of  $\text{Hg}^{2+}$  species.<sup>9</sup> The screening test results reflected that the impact of SCR on mercury speciation appears to be dependant on coal type. For the three bituminous coals and one subbituminous Power River Basin (PRB) coal tested, only the high-sulfur bituminous coal showed a significant increase in  $\text{Hg}^{2+}$  in the outlet of the SCR. The PRB coal with low-sulfur and also low chlorine (Cl) content showed very little impact of SCR on mercury speciation. The results for the other two bituminous coals were between the two extreme cases. Results of the recent full-scale field tests conducted in the United States at

utility plants showed there was an increase in Hg oxidation across the SCR catalysts for plants firing bituminous coals with sulfur (S) contents ranging from 1.1 to 4.2%.<sup>10</sup> A subbituminous PRB coal, which contains significantly lower Cl and S content and higher calcium (Ca) content compared to those of the bituminous coals, showed very little change in mercury speciation across a SCR reactor.<sup>10</sup>

The increase in oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup> across the SCR reactor could result from the changes in flue gas chemistry caused by the SCR catalysts. The SCR catalysts, which contain oxides of vanadium, titanium, and tungsten or molybdenum, have the potential to catalyze the formation of sulfur trioxide (SO<sub>3</sub>) from sulfur dioxide (SO<sub>2</sub>) and gas-phase chlorine (Cl<sub>2</sub>) from hydrogen chloride (HCl) in coal combustion flue gases. Both SO<sub>3</sub><sup>11</sup> and Cl<sub>2</sub><sup>12</sup> have been suggested to react with Hg<sup>0</sup> to cause its oxidation. However, not much is known about either the detailed mechanism or the effect of the flue gas species and chemical reactions on the extent of Hg<sup>0</sup> oxidation across SCR reactors.

This paper reports a study conducted by the EPA, Cormetech, Inc., and Illinois Clean Coal Institute (ICCI) to investigate the effect of SCR catalyst on Hg speciation in coal combustion. The study consists of both pilot- and bench-scale experiments to evaluate the viability of SCR technology for mercury speciation modification in Illinois and PRB coal combustion flue gases. Since SCR and FGD are increasingly being used at power plants to control NO<sub>x</sub> and SO<sub>2</sub> emissions, respectively, an understanding of Hg<sup>0</sup> reaction behavior over SCR catalysts has the potential to optimize the mercury control levels achievable with such a combination of pollution control devices.

Initial bench-scale experiments were conducted in EPA's laboratories to investigate Hg<sup>0</sup> oxidation in the presence of simulated coal combustion flue gases and under SCR reaction conditions, and results were reported in the previous Mega Symposium.<sup>13</sup> Flue gas mixtures with different concentrations of HCl and SO<sub>2</sub> for simulating the combustion of Illinois and PRB coals with different Cl and S contents were tested in these experiments. It was observed that HCl is the critical flue gas component that causes conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> under SCR reaction conditions, and SO<sub>2</sub> seems to have very little impact on Hg<sup>0</sup> oxidation. A subsequent pilot-scale research study to further evaluate the effect of the SCR catalyst on Hg speciation in combustion of coals with different Cl and S contents is reported in this paper. A pilot-scale SCR system, designed and manufactured by Cormetech, Inc., was installed in a pilot-scale combustor located at EPA's Research Triangle Park facility to evaluate Hg<sup>0</sup> oxidation capabilities during combustion of three different Illinois coals (from high to low sulfur/chlorine) and one PRB coal (very low sulfur and chlorine). The objective of the research was to get a better understanding of the effect of coal type on Hg<sup>0</sup> oxidation kinetics over SCR catalysts and the resultant impact on mercury speciation.

The effect of SCR catalyst age on  $\text{Hg}^0$  oxidation is an important technical issue that needs to be addressed in order to assess the viability of SCR technology for Hg speciation modification in a coal combustion process. Consistent  $\text{Hg}^0$  oxidation performance of the SCR catalyst with aging of the catalyst would provide the ability for the SCR technology to facilitate Hg speciation modification. The limited field data available for two test sites showed a decrease in Hg oxidation across the catalyst with time.<sup>10</sup> The decrease was minimal which could be caused by changes in plant operations. Bench-scale research to evaluate the effects of SCR catalyst aging and residence time (space velocity) on  $\text{Hg}^0$  oxidation under simulated SCR  $\text{NO}_x$  control conditions is reported in this paper. A catalyst sample collected from an SCR field unit after it was operated for two ozone seasons (ca. 8,000 hr.) and a fresh catalyst sample with composition identical to that of the field sample were tested for  $\text{Hg}^0$  oxidation in a bench-scale SCR system. The objective of the research was to get a better understanding of the effects of catalyst age and residence time on  $\text{Hg}^0$  oxidation under SCR reaction conditions.

## **EXPERIMENTAL**

### **Pilot-scale Tests**

In the first part of this study, tests were performed in a pilot-scale 34.9 kW (150,000 Btu/h), refractory lined, down-fired cylindrical furnace fired with coal. Natural gas was fired during the startup and shutdown of the unit. The furnace, which is shown in Figure 1 and referred to in this paper as the innovative furnace reactor (IFR), has an inner diameter of 15.2 cm and overall length of about 4 m. The IFR is used to simulate and generate a coal combustion environment and flue gas quenching conditions similar to those upstream of SCR units in coal-fired utility boilers. Viewing ports and injection/probe ports are provided along the length of the furnace for testing flexibility.

The IFR system was retrofitted with a downward-flow pilot-scale SCR reactor containing two full-length catalyst elements. Figure 1 illustrates the dimensions of this two-stage SCR system. The first stage of the SCR catalyst is equipped with a flow straightener, a soot blower, and a honeycomb catalyst. The second stage has a soot blower and a honeycomb catalyst. The two honeycomb catalysts are a commercial SCR catalyst manufactured by Cormetech with a vanadia/titania/tungsten oxide formulation having a length of 1250 mm each consisting of 64 flow channels in an array of 8 x 8 cells. The calculated space velocity of the two stage SCR reactor was  $2943 \text{ hr}^{-1}$ , which is comparable to that used in the previous bench-scale tests ( $2609 \text{ hr}^{-1}$ )<sup>13</sup> and is also comparable to those SCR space velocities observed in the field. Sampling ports along the horizontal ducts at the inlet and the outlet of the vertical SCR reactor allow gas and particle monitoring.

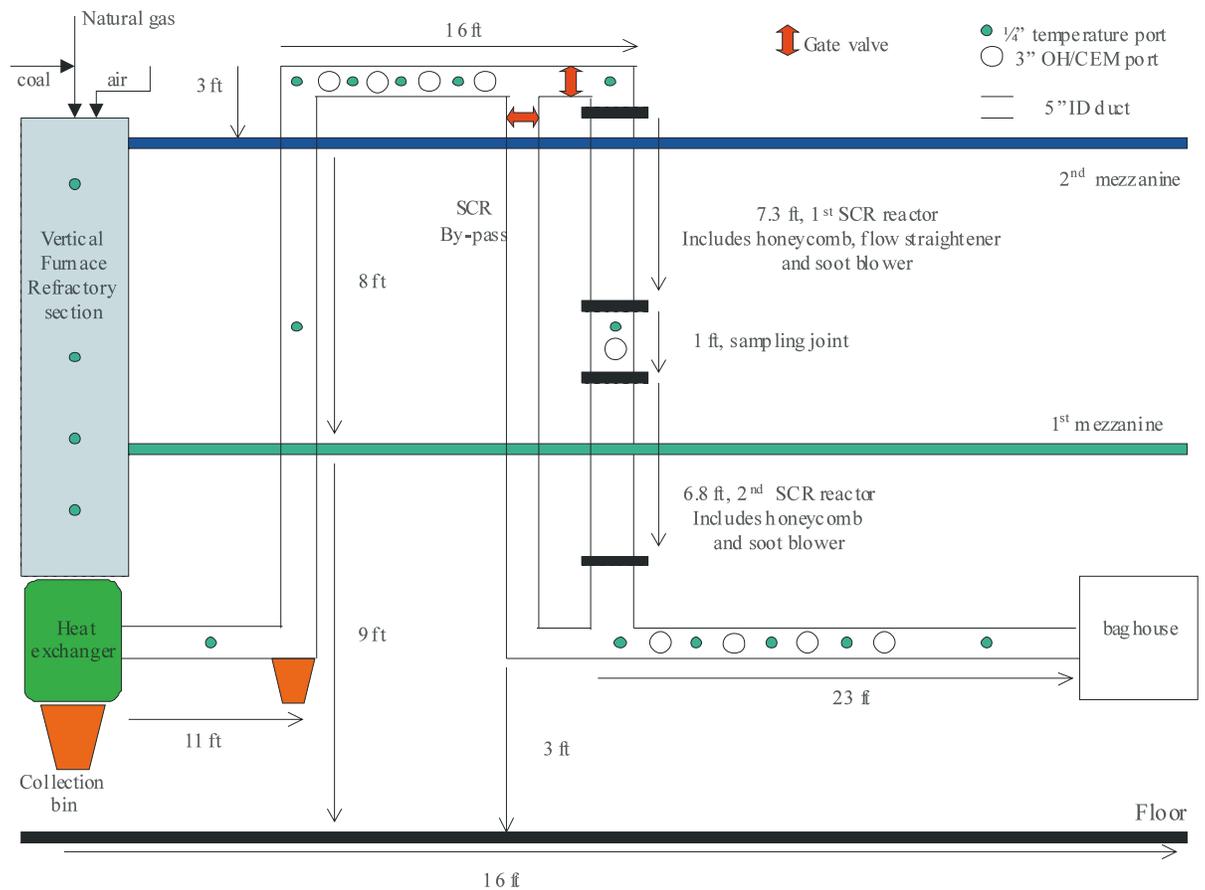


Figure 1. Schematic of the IFR equipped with the SCR used for mercury oxidation tests

The IFR is equipped with a continuous emission monitoring system for O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub>, and SO<sub>2</sub> which allows measuring flue gas composition at the inlet and outlet of the SCR reactor. The IFR is also equipped with 12 thermocouples for determining the time-temperature history of the combustor. A fabric filter and a scrubber are installed downstream of the SCR reactor for treating the flue gas before it is released into the atmosphere. The mercury speciation method<sup>14</sup> developed by Ontario Hydro (OH) was used for measuring Hg<sup>0</sup>, Hg<sup>2+</sup>, and particulate-bound Hg (Hg<sub>p</sub>) in the pilot-scale tests. Isokinetic OH trains were used for making mercury speciation measurements at the inlet and the outlet of the SCR reactor simultaneously during the tests.

## Bench-scale Tests

A bench-scale reactor system was designed and constructed to simulate the SCR reaction conditions for studying  $\text{Hg}^0$  oxidation. A schematic of the reactor system is shown in Figure 2. A detailed description of the system is provided in the initial study reported previously.<sup>13</sup> The system consists of the preheating and premixing sections, the mercury generation unit, the SCR reactor, and the on-line reactor effluent measurement unit. Most of the flue gas components were mixed and preheated to SCR reaction temperature (365 °C) and then mixed with another preheated stream of nitrogen oxide (NO) and HCl in nitrogen at the main heating section. Water was metered into the hot section for simulating the moisture content in flue gas, and mixed therein with the other flue gas components. Ammonia ( $\text{NH}_3$ ) was preheated and flowed into the static mixing section to get better mixing with all other flue gas components. The gas mixture then flowed into the Pyrex reactor (4 cm in inner diameter and 35 cm in length). The simulated flue gas mixture was preheated at 365 °C to prevent the alkaline  $\text{NH}_3$  from reacting with the acid gas components in the gas mixture to form ammonium salts at temperatures lower than the SCR reaction temperatures. The fine-particle ammonium salts formed from the neutralization of  $\text{NH}_3$  are sticky and would otherwise tend to deposit on the reactor walls and adsorb Hg species in the flue gas mixture, making the measurement of trace Hg species in the reactor very difficult. Proper preheating and mixing of the gas mixture are very important for simulating the SCR reaction conditions and for measuring Hg speciation.

A mercury generation unit consisting of a mercury permeation tube placed in a temperature control system (DYNACALIBRATOR, VICI Metronics, Inc.) was used to generate  $\text{Hg}^0$  vapor for the oxidation experiments. The  $\text{Hg}^0$  vapor in  $\text{N}_2$  carrier gas was mixed with the flue gas mixture near the top of the reactor. The flue gas mixture containing  $\text{Hg}^0$  passed through a honeycomb flow straightener to produce a good velocity distribution before passing through the honeycomb SCR catalyst. A thermocouple was positioned near the inlet of the catalyst for controlling and monitoring the SCR catalyst temperature.

An on-line  $\text{Hg}^0$  analyzer (Hg Monitor 3000, Seefelder Messtechnik) was used for  $\text{Hg}^0$  measurement for the bench-scale experiments. The analyzer is equipped with an internal pump to draw a 1600  $\text{cm}^3/\text{min}$  flow for  $\text{Hg}^0$  measurement, and it has a detection limit of 0.5  $\mu\text{g}/\text{m}^3$ . The total outlet flow of the SCR reactor was 400  $\text{cm}^3/\text{min}$ . An additional 1600  $\text{cm}^3/\text{min}$  of  $\text{N}_2$  (controlled by a mass flow controller) was added to the outlet flow. A knockout impinger cooled by an ice water bath and a Nafion Dryer (Perma Pure, Inc.) were located downstream of the dilution point to remove salt particles and water vapor. Salt particle formation and deposition could otherwise occur as a result of the reaction of slip  $\text{NH}_3$  and HCl in the cooler regions downstream of the SCR reactor. The  $\text{Hg}^0$  analyzer

thus draws 1600 cm<sup>3</sup>/min of moisture-free and particle-free flue gas for Hg<sup>0</sup> measurement. The remaining flow (400 cm<sup>3</sup>/min) passes through an online ultraviolet (UV) SO<sub>2</sub> analyzer (Bovar Engineering, Inc., model 721-M; accuracy of about ±5%) for measuring SO<sub>2</sub>. An on-line chemiluminescent NO<sub>x</sub> analyzer (Advanced Pollution Instrumentation, Inc., model 200AH; accuracy of about ±5%) was located downstream of the SO<sub>2</sub> analyzer for measuring NO<sub>x</sub>. The presence of SO<sub>2</sub> in the flue gas creates a positive and linear interference in the UV Hg<sup>0</sup> analyzer. A previously developed subtraction technique<sup>5</sup> was used to correct for this interference.

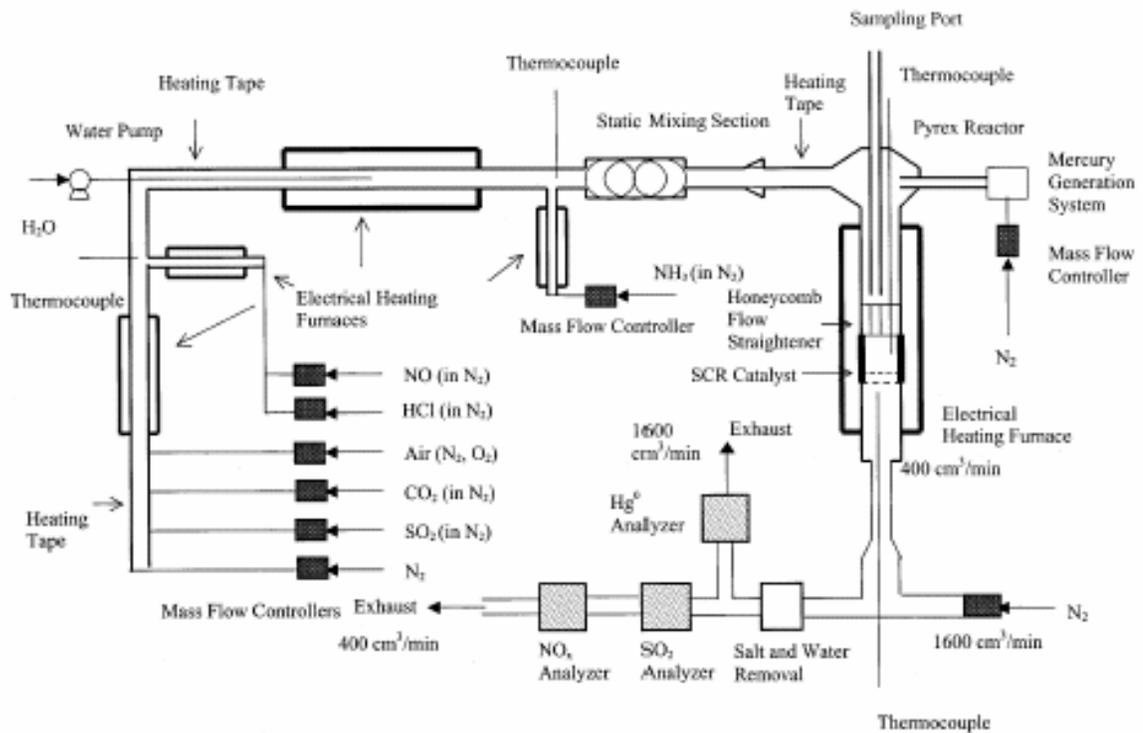


Figure 2. Schematic of the SCR Reactor System

### Bench-Scale Test Procedures

A catalyst sample collected from a bituminous coal-fired SCR system after it was operated for two ozone seasons (approximately 8000 hr.) was used for testing the aging effect of the catalyst on Hg<sup>0</sup> oxidation in this study. The sample was manufactured by Cormetech, Inc. with a vanadia/titania formulation and a honeycomb configuration. A fresh sample of the same catalyst by Cormetech was also tested. A small piece (1.7 cm by 3.7 cm in length) of the catalyst sample was placed into the catalyst compartment of the SCR reactor. The reactor system was heated overnight at 425 °C under an N<sub>2</sub> atmosphere. This cleanup procedure was employed prior to each test for removing any

adsorbed species in the catalyst and minimizing the residue effect caused by the previous test. The temperature of the reactor was then lowered to below 365 °C, and SO<sub>2</sub> and HCl gases were added to the reactor at 2250 and 40 ppm, respectively, at the same levels for the next day's experiment. The temperature of the reactor was raised to 365 °C and maintained overnight. This catalyst preconditioning procedure was applied prior to each test. The next morning, the remaining components of the simulated flue gas mixture were added into the reactor, consisting of CO<sub>2</sub> (4.2%), NO (590 ppm), H<sub>2</sub>O (7.1%), and NH<sub>3</sub> (531 ppm) plus Hg<sup>0</sup> (20 ppb). The flows of the flue gas components were maintained at the levels designed for the test by using the mass flow controllers. The variability of the gas concentrations is about ±2.5%. A constant total flow rate of 400 cm<sup>3</sup>/min [at a standard temperature of 25 °C and pressure of 101.4 kPa (STP)] was used for all tests. The conditions employed in the aging tests were chosen to accurately simulate the commercial design operating conditions for the SCR field unit where the aged catalyst sample was obtained.

At the beginning of each test, the concentration of Hg<sup>0</sup> vapor generated by the permeation tube (hereafter, inlet concentration, Hg<sub>in</sub>) was registered by the Hg<sup>0</sup> analyzer, while the simulated flue gas passed through the SCR reactor. It is important to note that the analyzer does not respond to oxidized Hg species. During each test with the reactor on-line, the post-reaction or outlet Hg<sup>0</sup> concentration (Hg<sub>out</sub>) was measured continuously using the Hg<sup>0</sup> analyzer. Considering the fact that Hg in the flue gas exists in either the elemental or oxidized form, the difference between the inlet and outlet Hg<sup>0</sup> concentrations was used to quantify the extent of Hg<sup>0</sup> oxidation in the reactor. Percent oxidation is expressed as:

$$\% \text{ Oxidation} = 100 \times (\text{Hg}_{\text{in}} - \text{Hg}_{\text{out}}) / \text{Hg}_{\text{in}}$$

Since water vapor causes interference in the UV Hg<sup>0</sup> analyzer, it was removed from the outlet gas stream of the reactor by using a Nafion dryer located downstream of the knockout impinger. The UV Hg<sup>0</sup> analyzer used for the tests also responds to SO<sub>2</sub>, so the signal collected by the SO<sub>2</sub> analyzer was used to correct the Hg<sup>0</sup> analyzer response and eliminate the SO<sub>2</sub> interference. During each test, the concentrations of Hg<sup>0</sup>, SO<sub>2</sub>, and NO<sub>x</sub> at the outlet of the reactor were monitored continuously for four hours by using the Hg<sup>0</sup>, SO<sub>2</sub> and NO<sub>x</sub> analyzers, respectively. The NO<sub>x</sub> measurement was conducted to ensure that the NO<sub>x</sub> reduction reached a steady state during the test. At the end of the test (about four hours after the test started), the concentration of Hg<sup>0</sup> vapor generated by the permeation tube (Hg<sub>in</sub>) was measured again by using the Hg<sup>0</sup> analyzer to ensure that the Hg<sup>0</sup> concentration was at a steady state during the test.

## RESULTS AND DISCUSSION

### Pilot-scale Tests

Three different Illinois coals designated as Turriss, Crown II, Galatia Mines and one PRB designated as Black Thunder were tested in the pilot-scale combustor. Table 1 summarizes the characteristics of the coals tested. Turriss coal contains medium levels of sulfur (3.11%) and chlorine (0.17%). Crown II is a high sulfur (3.48%) and low chlorine (0.13%) content coal. Galatia contains high chlorine (0.29%) and low sulfur (1.13%) content. Black Thunder is a PRB coal with very low sulfur (0.29%) and chlorine (about 0.01%) content. The Hg content of the Illinois coals are within the 0.07-0.09 ppm range.

The Illinois and PRB coals were tested under combustion conditions listed in Table 2. The IFR was operated at firing rates of about 140,000 Btu/hr for the Illinois coal tests. The PRB coal was tested at a slightly higher firing rate (156,00 Btu/hr) than those for the Illinois coal tests. Comparison between measured and calculated values of CO<sub>2</sub> and O<sub>2</sub> indicated an insignificant in-leakage of air into the combustor (about 2-4%) during the tests. There was no in-leakage between the inlet and the outlet of the SCR. Very good combustion conditions were achieved for all the tests as indicated by the low CO emissions (30-40 ppm) measured in the tests. The axial temperature gradient across the SCR catalyst was around 50 °C. Uncontrolled levels of NO<sub>x</sub> emissions were varied from relatively high levels for the Turriss test (850 ppm) to relatively low levels for the PRB test (525 ppm). NH<sub>3</sub> was injected at a nominal NH<sub>3</sub>/NO<sub>x</sub> ratio of 0.9. Consistently high NO<sub>x</sub> reductions (86-90%) across the SCR were observed for all the tests. The emissions of SO<sub>2</sub> from the Illinois coals varied significantly from the high-sulfur Turriss coal (2921 ppm) to the low-sulfur Galatia coal (929 ppm), and emissions from the very low sulfur PRB coal were much lower (222 ppm). The calculated SO<sub>2</sub> emissions are all in very good agreement with the measured values.

**Table 1.** Proximate and ultimate analysis of coals in pilot study (three Illinois Basin coals and one PRB coal).

Content	PRB Black Thunder	Turriss (Illinois) (Medium S/Cl)	Crown II (Illinois) (High S/low Cl)	Galatia (Illinois) (Low S/high Cl)
% Moisture	14.00	16.99	16.07	11.33
% Ash	5.92	9.26	7.34	6.29
% Volatile	37.33	33.89	37.05	34.16
% Fixed C	42.76	39.85	39.55	48.22
HV (Btu/lb)	9903	10531	10877	12179
%C	59.71	59.00	60.48	68.31
%H	3.83	4.32	4.70	4.50
%N	0.82	1.19	1.07	1.50
%S	0.29	3.11	3.48	1.13

%O	15.44	5.96	5.73	6.94
%Cl	NA	0.17	0.13	0.29
Hg, ppmw	NA	0.07	0.07	0.09

NA: Not Available

**Table 2.** Combustion conditions for the Illinois Coals (Turriss, Galatia, and Crown II) and the PRB coal (Black Thunder)

Parameter	Turriss	Galatia	Crown II	PRB
Coal feed rate (lb/hr)	14.0	11.5	13.4	15.7
IFR firing rate, Btu/hr	147540	140424	145208	155873
Total air flow (scfm)	28.6	28.2	28.4	28.9
Excess air, %	11	18	11	5
Top SCR temperature (°C)	373±8	354±1	363±4	380±2
Middle SCR temperature (°C)	365±5	342±1	352±3	364±1
Bottom SCR temperature (°C)	323±4	304±2	315±2	325±1
Measured CO, ppm (dry)	38±6	30±7	40±4	0±1
Uncontrolled NOx, ppm (dry)	960	850	650	525
NOx reduction across SCR, %	90	86	90	90
Measured SO <sub>2</sub> , ppm (dry)	2921 ± 49	929 ± 63	2739 ± 26	222 ± 2
Calculated SO <sub>2</sub> , ppm (dry)	3064	915	3006	274
O <sub>2</sub> , measured (%), dry	2.7	4.0	4.4	4.1
O <sub>2</sub> , calculated (%), dry	1.8	3.0	1.9	0.1
In-leakage based on O <sub>2</sub> , %	5	5	13	19
CO <sub>2</sub> , measured (%), dry	15.6	14.8	14.3	15.6
CO <sub>2</sub> , calculated (%), dry	16.0	15.4	15.7	18.0
In-leakage based on CO <sub>2</sub> , %	3	3	9	13
Calculated flow based on O <sub>2</sub> in-leakage, scm/min	0.879	0.896	0.944	1.008
Calculated flow based on CO <sub>2</sub> in-leakage, scm/min	0.858	0.853	0.911	0.956
Measured HCl, ppm (wet)	NM	246±23	NM	NM
Calculated HCl, ppm (wet)	141	208	96	7.9
PM conc., mg/dscm, SCR inlet*	5863	3070±555	3946	2418±504
PM conc., mg/dscm, SCR outlet*	3506	1735±194	2560	1606±160

NM: Not Measured

\* Measured using the filter weight of the isokinetic OH method at the inlet and outlet of the SCR

The Hg speciation measurement results obtained from the OH method are presented in Table 3. In general, the results showed Hg<sup>0</sup> was the predominant Hg species present at the inlet of the SCR. The outlet Hg species was dominated by Hg<sup>2+</sup> for the three Illinois coal tests. The results indicate significant Hg<sup>0</sup> oxidation was occurring across the SCR

catalyst for the Illinois coal tests. For example,  $\text{Hg}^0$  was decreased from 84 to 12% and  $\text{Hg}^{2+}$  was increased from 15 to 85% across the SCR catalyst for the Crown II test. Such high levels of  $\text{Hg}^0$  oxidation are consistent with the almost complete oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  observed in the previous bench-scale tests for simulating the combustion of three different bituminous coals with Cl and S contents similar to those of the Illinois coals tested in the current pilot-scale tests.<sup>13</sup> The pilot results are also consistent with the high levels of  $\text{Hg}^0$  oxidation to  $\text{Hg}^{2+}$  observed over commercial SCR systems firing bituminous coals.<sup>10</sup>

**Table 3.** Summary of mercury speciation measurement results

Mercury Speciation	SCR Sampling Location	Test				
		Turriss	Galatia	Crown II	PRB	PRB*
$\text{Hg}^0$ Concentration ( $\mu\text{g}/\text{dscm}$ )	Inlet	4.7	7.2	4.6	7.0	4.9
	Outlet	0.3	0.3	0.5	4.5	3.5
$\text{Hg}^{2+}$ Concentration ( $\mu\text{g}/\text{dscm}$ )	Inlet	0.6	2.1	0.8	0.2	0.2
	Outlet	2.6	5.1	3.5	0.5	1.0
$\text{Hg}_p$ Concentration ( $\mu\text{g}/\text{dscm}$ )	Inlet	1.5	0.6	0.1	0.0	0.0
	Outlet	0.4	1.8	0.1	0.1	0.1
Total Mercury Concentration ( $\mu\text{g}/\text{dscm}$ )	Inlet	6.9	9.9	5.5	7.2	5.1
	Outlet	3.3	7.2	4.1	5.1	4.6
$\text{Hg}^0$ (%)	Inlet	68	73	84	97	96
	Outlet	9	4	12	88	76
$\text{Hg}^{2+}$ (%)	Inlet	9	21	15	3	4
	Outlet	79	71	85	10	22
$\text{Hg}_p$ (%)	Inlet	23	6	1	0	0
	Outlet	12	25	3	2	2

\*PRB Repeat Test

The  $\text{Hg}^{2+}$  concentration ( $2.1\mu\text{g}/\text{dscm}$ , 21%) measured at the inlet of the SCR for the Galatia test was higher than those of the other two tests ( $0.6$  and  $0.8\mu\text{g}/\text{dscm}$  or 9 and 15% for Turriss and Crown II, respectively), suggesting that a low level of  $\text{Hg}^0$  oxidation

may be occurring prior to the SCR reactor for this bituminous coal which has relatively high Cl content (0.29%) compared to tests with the other two bituminous coals (0.17 and 0.13%). Coal Cl content has been shown to correlate positively with  $\text{Hg}^0$  oxidation in coal combustion flue gas.<sup>15</sup> The Turriss coal test showed relatively high  $\text{Hg}_p$  in the inlet of the SCR (1.5  $\mu\text{g}/\text{dscm}$ , 23%). The isokinetic OH filter weights were used to determine the fly ash concentration in the flue gas, and results are shown in Table 2. High fly ash concentration (5,863  $\text{mg}/\text{dscm}$ ) was measured at the inlet of the SCR during the Turriss test, which is consistent with the high ash content (9.3%) of the Turriss coal. The high fly ash concentration in flue gas of this test may create the bias of higher  $\text{Hg}_p$  measured by the OH method. More fly ash captured by the OH sampling train filter may adsorb additional mercury from the gas stream drawn through the sampling train, and may partly explain higher  $\text{Hg}_p$  measured by the OH method. It is also noted that the mercury recovery was unusually low for the Turriss test (only about half of the total inlet mercury was measured at the outlet for this test). The mercury recovery obtained in the other pilot-scale SCR tests has occurred in field studies,<sup>10</sup> and might possibly be due to the adsorption of mercury by the catalyst. Significant reduction in fly ash concentration across the SCR was also found for the Turriss test (see Table 2). The significant retention of fly ash by the SCR reactor in this pilot-scale test may also have contributed to the low recovery of mercury at the outlet of the reactor for this test.

The Black Thunder PRB coal was tested in a duplicate run. The combustion conditions were identical for both tests and are listed in Table 2 under the PRB column. Table 3 summarizes the results of the OH sampling for the first and second PRB coal combustion tests. A reasonable mercury recovery was obtained across the SCR catalyst during the second PRB test (5.1  $\mu\text{g}/\text{dscm}$  at the inlet vs. 4.6  $\mu\text{g}/\text{dscm}$  at the outlet), which was better than those obtained during the first test (7.2  $\mu\text{g}/\text{dscm}$  at the inlet vs. 5.1  $\mu\text{g}/\text{dscm}$  at the outlet). It appears that, at the inlet, almost all Hg was  $\text{Hg}^0$  with no appreciable  $\text{Hg}^{2+}$  or  $\text{Hg}_p$ . The comparison of data measured between inlet and outlet of the catalyst shows only a small drop in  $\text{Hg}^0$ , from 97% to 88% for the first test and from 96% to 76% for the second test. This is equivalent to only 20-percent oxidation of  $\text{Hg}^0$  (9-percent oxidation of  $\text{Hg}^0$  for the first test). Limited field data available to date indicates similarly low  $\text{Hg}^0$  oxidation for the only reported result on a PRB coal fired SCR system.<sup>10</sup> PRB coals in general have significantly lower chlorine and higher alkaline contents than those of the bituminous coals. It is likely that the alkalinity may tie up Cl resulting in very low levels of available Cl in the PRB coal combustion flue gas. The low oxidation of  $\text{Hg}^0$  across the SCR catalyst observed for the PRB coal test supports the hypothesis that HCl, which serves as the chlorine source, is critical in  $\text{Hg}^0$  oxidation across the SCR catalyst. The importance of HCl in  $\text{Hg}^0$  oxidation across the SCR catalyst had been demonstrated in our bench-scale SCR mercury oxidation simulation study reported previously.<sup>13</sup> It has been shown that  $\text{V}_2\text{O}_5$  is a reactive catalyst for the absorption of HCl to produce a stable vanadium oxychloride complex.<sup>16</sup> Further reaction of the complex with  $\text{Hg}^0$  might

oxidize the  $\text{Hg}^0$  to produce  $\text{Hg}^{2+}$  species such as  $\text{HgCl}_2$ .

### **Bench-scale Tests on the Effect of Catalyst Aging on $\text{Hg}^0$ Oxidation**

A catalyst sample collected from a bituminous coal firing SCR unit in the field after it was operated for two ozone seasons (ca. 8000 hr) was tested for its  $\text{Hg}^0$  oxidation reactivity. A fresh catalyst sample with composition identical to that of the field sample was also tested for  $\text{Hg}^0$  oxidation to compare the  $\text{Hg}^0$  oxidation reactivity of the field-aged and fresh samples. All the tests were conducted under the conditions designed for this particular catalyst in the field: temperature of 365 °C, space velocity of 2263  $\text{hr}^{-1}$ , 2250 ppm  $\text{SO}_2$ , 590 ppm  $\text{NO}_x$ , 531 ppm  $\text{NH}_3$  ( $\text{NH}_3/\text{NO}_x$  ratio of 0.9), 40 ppm HCl, 4.2%  $\text{O}_2$ , 13.2%  $\text{CO}_2$ , and 7.1%  $\text{H}_2\text{O}$ . A small piece (1.7 cm by 3.7 cm in length) of the fresh and field aged catalyst sample was used in the tests. Shorter pieces of the fresh and aged SCR catalyst samples (2.7 cm in length) with correspondingly higher space velocity (3031  $\text{hr}^{-1}$ ) were also tested for evaluating the effect of catalyst residence time on  $\text{Hg}^0$  oxidation. All the tests were performed in triplicate to assess the reproducibility of the results.

The  $\text{NO}_x$  reduction and mercury speciation results measured in the bench-scale study are summarized in Table 4. It is shown in Table 4 that the average  $\text{NO}_x$  reductions for the four different tests are very similar, in the 85 – 91% range. Such high levels of reduction are also typical to those achieved by SCR units in the field during normal operation. The average root-mean-square standard deviations (RSDs) are in the 1 – 3% range, indicating good reproducibility of the  $\text{NO}_x$  reduction tests. These results suggest that after operating for two ozone seasons, the aged catalysts still maintained high  $\text{NO}_x$  reduction efficiencies similar to those of the fresh samples. A significant increase in space velocity from the value (2263  $\text{hr}^{-1}$ ) designed for this particular catalyst to a higher one (3031  $\text{hr}^{-1}$ ) does not seem to reduce  $\text{NO}_x$  reduction efficiencies for both the fresh and aged samples tested under the commercial design operating conditions for the full-scale SCR system. It appears that this catalyst is reactive enough to maintain its  $\text{NO}_x$  reduction reactivity after a significant operating period (8000 hr) and also with a significant reduction in catalyst residence time.

The  $\text{Hg}^0$  oxidation results are also shown in Table 4. The RSDs for the oxidation test results are in the range of 1 – 3%, indicating good reproducibility of the tests similar to that for the  $\text{NO}_x$  reduction tests. The high  $\text{Hg}^0$  oxidation levels achieved by both the aged (85%) and fresh (88%) catalyst samples tested at the catalyst's design space velocity (2263  $\text{hr}^{-1}$ ) showing that the catalyst still maintained a high  $\text{Hg}^0$  oxidation reactivity after operating for about 8,000 hr. In prior field studies on coal-fired SCR units<sup>10</sup>, catalyst aging effects on the extent of change in  $\text{Hg}^0$  oxidation was also observed to be small. An increase in space velocity from the design value seems to reduce  $\text{Hg}^0$  oxidation, and the reduction for the aged catalyst test seems to be more significant than that for the fresh

catalyst but it may be the same considering the overall experimental error. For example, Hg<sup>0</sup> oxidation of the fresh catalyst was decreased from 88 to 76% when the space velocity was increased from 2263 to 3031 hr<sup>-1</sup> (25% increase), whereas the corresponding Hg<sup>0</sup> oxidation for the aged catalyst decreased from 85 to 69%. The significant reduction in Hg<sup>0</sup> oxidation as a result of increase in space velocity indicates that residence time is an important parameter in the Hg<sup>0</sup> oxidation. The importance of residence time in the Hg<sup>0</sup> oxidation process occurring in an SCR system suggests that a heterogeneous mechanism is involved.

**Table 4.** Summary of NO<sub>x</sub> reduction and mercury speciation results

	Catalyst			
	Fresh	Aged	Fresh	Aged
Space Velocity (hr <sup>-1</sup> )	2263	2263	3031	3031
NO <sub>x</sub> Reduction (%)	84	90	92	90
	87	86	91	92
	87	85	91	92
Average Reduction (%)	85 ± 2	87 ± 3	91 ± 1	91 ± 1
RSD (%)	2	3	1	1
Hg <sup>0</sup> Oxidation (%)	87	84	74	70
	88	86	78	68
	89	85	77	68
Average Oxidation (%)	88 ± 1	85 ± 1	76 ± 2	69 ± 1
RSD (%)	1	1	3	2

## SUMMARY

A pilot-scale combustion system has been constructed in the present study to closely simulate the SCR emission control conditions in the field. The system was used for the combustion of three Illinois coals and a PRB coal with different S and Cl levels to test their Hg speciation and oxidation behavior under SCR reaction conditions. High NO<sub>x</sub> reduction levels (86-90%) similar to those observed in the field were achieved for all the coals tested in this study. It was found that the SCR catalyst has a strong ability to

promote  $\text{Hg}^0$  oxidation, decreasing  $\text{Hg}^0$  to an insignificant level at the outlet of the SCR for the three Illinois bituminous coals tested. The SCR catalyst showed a very low amount of  $\text{Hg}^0$  oxidation for the PRB coal tested. The effect of SCR on promoting  $\text{Hg}^0$  oxidation appears to be coal-type dependent. Such effect was not found for the PRB coal which has Cl content at least an order of magnitude lower than those of the Illinois coals. These observations suggest that a chlorine-containing species such as HCl is an important source of Cl for  $\text{Hg}^0$  oxidation under SCR emission control conditions. The use of SCR systems in Illinois coal-fired boilers that are equipped with SCR systems seems to be a viable option for increasing the oxidized mercury content in flue gases, implying viability for reducing Hg emissions when used in conjunction with effective downstream equipment for capture of oxidized mercury, such as FGD systems. However, the low  $\text{Hg}^0$  oxidation observed for PRB coal combustion flue gases over SCR catalyst needs to be improved in order to achieve lower stack emissions of mercury when coupled with effective downstream  $\text{Hg}^{+2}$  capture equipment.

A bench-scale reactor system has been modified to test the  $\text{Hg}^0$  oxidation behavior of fresh and field-aged SCR catalyst samples with simulated coal combustion flue gases. A catalyst sample taken from the SCR system of a full-scale commercial facility firing bituminous coal after 8,000 hr of operation showed no apparent aging effect on decreasing the extent of  $\text{Hg}^0$  oxidation within the experimental error of the tests. Such an aging effect became apparent when the space velocity used in the test was increased significantly from the commercial design value for this catalyst. The more significant decrease in  $\text{Hg}^0$  oxidation for the aged catalyst as a result of reduction in SCR residence time observed in this study suggests that heterogeneous reactions are occurring in the  $\text{Hg}^0$  oxidation chemistry occurring in SCR systems.

## **ACKNOWLEDGEMENTS**

This project was supported, in part, by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein necessarily state or reflect those of the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, or the Illinois Clean Coal Institute.

## **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*, volumes I-VIII; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards and Office of Research and Development, Research Triangle Park, NC, December 1997;

EPA-452/R-97-003 through 010.

2. Brown, T.D., Smith, D.N.; Hargis, R.A., Jr.; O'Dowd, W.J. *J. Air & Waste Manage. Assoc.* **1999**, 49, 628-640.
3. Hargrove, O.W. Jr.; Peterson, IR; Seeger, D.M.; Skarupa, RC.; Moser, RE. "Update of EPRI Wet FGD Pilot-Scale Mercury Emissions Control Research," presented at EPRI-DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, ON, Canada, Aug 1995.
4. Holmes, M.J.; Redinger, K.E.; Evans, A.P.; Nolan, P.S. "Control of Mercury in Conventional Flue Gas Emissions Control Systems," presented at the Managing Hazardous Air Pollutants 4th International Conference, Washington, DC, Nov, 1997.
5. Ghorishi, S.B.; Gullett, B.K.; Jozewicz, W. *Waste Management Research.* **1998**, 16:6, 582-593.
6. Price, D.; Birnbaum, R.; Batiuk, R.; McCullough, M.; Smith, R. *Nitrogen Oxides: Impacts on Public Health and the Environment*; U.S. Environmental Protection Agency, Office of Air and Radiation, Washington, DC, August 1997; EPA-452/R-97-002 (NTIS PB 98-104631).
7. Cichanowicz, J.E.; Muzio, L.J. "Factors Affecting Selection of a Catalyst Management Strategy," presented at the Combined Power Plant Air Pollutant Control Mega Symposium; Washington, DC, May 2003.
8. Gutberlet, H.; Schluten, A; Lienta, A. "SCR Impacts on Mercury Emissions on Coal-fired Boilers," presented at EPRI's SCR Workshop, Memphis, TN, April, 2000.
9. Laudal, D.L.; Pavlish, J.H.; Galbreath, K.C.; Thompson, J.S.; Weber, G.F.; Sondreal, E.A. Pilot-Scale Screening Evaluation of the Impact of Selective Catalytic Reduction for NOx on Mercury Speciation. Electric Power Research Institute Report No. 1000755. Palo Alto, CA, 2000.
10. Brickett, L.; P. Chu, P.; Lee, C.W.; Srivastava, R.K; Laudal, D.; Thompson, J.; Wocken, C. "Power Plant Evaluation of the Effect of SCR on Mercury," presented at the Combined Power Plant Air pollutant Control Mega Symposium, Washington, DC, May2003.
11. Galbreath, K.C.; Zygarlicke, C.J. *Fuel Process. Technol.* **2000**, 65-66, 289-310.
12. Ghorishi, S.B.; Lee, C.W.; Kilgroe, J.D. "Mercury Speciation in Combustion Systems: Studies with Simulated Flue Gases and Model Fly Ashes," presented at the 2nd

Annual Meeting of Air and Waste Management Association, St. Louis, MO, June 1999.

13. Lee, C.W.; Srivastava, R.K.; Ghorishi, S.B; Hastings, T.W.; Stevens, F.M. "Study of Speciation of Mercury under Simulated SCR NO<sub>x</sub> Emission Control Conditions," presented at the Combined Power Plant Air Pollutant Control Mega Symposium; Washington, DC, May 2003.

14. Method D 6782-02. "Standard Test Method for Elemental, Oxidized, Particle-bound and Total Mercury in Flue Gas Generated from Coal-fired Stationary Sources (Ontario Hydro Method)." American Society for Testing and Materials, 2002.

5. Brown, T.D.; Smith, D.N.; Hargis, R.A., Jr.; O'Dowd, W.J. *J. Air & Waste Manage. Assoc.* **1999**, 49, 628-640.

16. Hisham, M.W.M.; Benson, S.W. *J. Phys. Chem.* **1995**, 99, 6194-6198.

### **KEY WORDS**

Mercury speciation, Selective catalytic reduction, Coal combustion, Elemental mercury, Oxidized mercury, hlorine content