Mercury Speciation at Power Plants Using SCR and SNCR Control Technologies

by Dennis L. Laudal, Jeffrey S. Thompson, John H. Pavlish, Lynn Brickett, Paul Chu, Ravi K. Srivastava, C.W. Lee, and James Kilgroe

Coal combustion by electric utilities is a significant source of anthropogenic mercury emissions in the United States, according to the U.S. Environmental Protection Agency (EPA). Recent data indicate that mercury emissions from coal-fired power plants in the United States total 45 t/yr. Consequently, EPA views mercury from coal-fired utilities as a potential public health concern. Based on the capabilities of currently available analytical methods, mercury emissions from coal-fired boilers can be empirically classified into three main forms: elemental mercury (Hg$^0$), oxidized mercury (Hg$^{2+}$), and particle-bound mercury (Hg$_p$). The level of concentration of Hg$^0$, Hg$^{2+}$, and Hg$_p$ largely depends on coal composition/type and combustion conditions. During combustion, Hg$^0$ is liberated from coal. Depending on the coal type, a significant fraction of the mercury can be oxidized and become associated with the fly ash particles in the postcombustion environment of a coal-fired boiler, making capture difficult. Relative to Hg$^0$, Hg$^{2+}$ and Hg$_p$ are generally more easily captured using conventional pollution control systems, such as flue gas desulfurization (FGD) systems, fabric filters, and electrostatic precipitators (ESPs). Therefore, the identification of a process for converting Hg$^0$ to Hg$^{2+}$ and/or Hg$_p$ could potentially improve the mercury removal efficiencies of existing pollution control systems.

In addition to mercury, coal-burning power plants are a significant anthropogenic source of nitrogen oxides (NO$_x$) emissions. The 1990 Clean Air Act Amendments require specific reductions, depending on the size and type of boiler, of NO$_x$ emissions from coal-fired electric utilities. The most common NO$_x$ control technology currently in use is low-NO$_x$ burners. These burners are capable of reducing NO$_x$ emissions by 40–60%. However, with the possible enforcement of stricter fine particulate matter (PM$_{2.5}$), regional haze, and ozone regulations, there is increased incentive for utilities to reduce NO$_x$ emissions to a level below what can be currently achieved using low-NO$_x$ burners. Thus, selective catalytic reduction (SCR) technology, which can help reduce NO$_x$ emissions by more than 90%, is becoming an attractive alternative. It is estimated that 80–90 U.S. utilities are planning to install SCR units within the next five years.

SCR units achieve lower NO$_x$ emissions by reducing NO$_x$ to N$_2$ and water, using ammonia (NH$_3$) as the reductant. The SCR process is generally performed on metal oxide catalysts, such as titanium dioxide (TiO$_2$)-supported vanadium pentoxide catalysts (V$_2$O$_5$). These units are operated at temperatures of 340–399 °C (650–750 °F). Laboratory-scale testing indicates that metal oxides, including V$_2$O$_5$ and TiO$_2$, promote the conversion of Hg$^0$ to Hg$^{2+}$ and/or Hg$_p$ in relatively simple flue gas mixtures. In addition, mercury speciation measurements conducted at European coal-fired boilers
equipped with SCR reactors indicate that SCR catalysts promote the formation of Hg$^{2+}$. Consequently, it has been hypothesized that the use of SCR technology to reduce NO$_x$ emissions may also improve the mercury control efficiency of existing air pollution control devices by promoting Hg$^{2+}$ and/or Hg$_{np}$ formation.

**PILOT-SCALE TESTS**

In an attempt to evaluate the effects of SCR and NH$_3$ on mercury speciation, pilot-scale tests were conducted by the Energy & Environmental Research Center (EERC) in Grand Forks, ND. Tests were conducted firing four different coals: three bituminous coals and one Powder River Basin (PRB) subbituminous coal. The results indicated that while SCR and NH$_3$ might enhance mercury capture, it appeared that the impact was highly coal-specific. Because of the inherent concerns related to small pilot-scale tests—including surface area-to-volume ratios, different flue gas chemistries, and time and temperature profiles—it was decided that it was necessary to conduct sampling at full-scale power plants. EPRI, the U.S. Department of Energy (DOE), and EPA jointly funded a project with EERC to conduct full-scale mercury sampling at six power plants operating different types of air pollution control devices. These included four plants using SCR, one using selective noncatalytic reduction (SNCR), and one using NH$_3$ and sulfur trioxide (SO$_3$) for flue gas conditioning. For a 10–12-day period, sampling was conducted before and after the SCR unit or NH$_3$ injection using both the wet-chemistry Ontario Hydro (OH) method and near-real-time continuous mercury monitors (CMMs). Mercury variability, speciation, and concentration were evaluated. The units tested ranged from 160 to 1300 MW in size. The coals burned at the plants included two PRB coals, five eastern bituminous coals, and a blended PRB-eastern bituminous coal. The types of air pollution control devices

![Figure 1](image1.png) **Figure 1.** Results showing the effect of SCR on mercury at site S1.

![Figure 2](image2.png) **Figure 2.** Results showing the effect of SCR on mercury at site S2.
in use included SCR reactors, an SNCR injection system, ESPs, a wet scrubber, and a Venturi scrubber. Information about each of the plants is provided in Table 1. The coal analysis for each unit tested is shown in Table 2. Additional sampling involved the use of EPA Method 26A to test for chlorides, a selective condensation method to measure SO$_3$, and EPA Method 27 for NH$_3$ slip. Fly ash and coal samples were also collected to obtain the mercury balance across the control devices.

**EXPERIMENTAL APPROACH**

The overall objective of the project was to determine the effects of SCR operations on mercury speciation and the removal efficiencies for a variety of coal types. To achieve this objective for each unit/coal, a sampling plan was developed for various operating conditions so that the effects of the catalyst and the NH$_3$ injection could be determined separately. The mercury measurements were conducted using the manual OH method and CMMs. The tests were set up to obtain samples at the exit of the boiler (prior to NH$_3$ injection), at the stack, and between each of the air pollution control devices. The testing conducted at each power plant is described below.

At the four sites with SCRs (S1–S4), the plants were tested as follows:

- SCR operated under normal conditions;
- SCR operated with the NH$_3$ turned off; and
- SCR bypassed.

The one exception was site S2, where tests could not be conducted with and without NH$_3$, so tests were done under normal SCR conditions and with the SCR bypassed only. At site A1, which employs NH$_3$ and SO$_3$ conditioning to improve ESP performance, tests were conducted for two different coals with and without NH$_3$ injection (SO$_3$ conditioning only). At
site A2, which operated an SNCR system (urea injection), tests were conducted firing two different eastern bituminous coals; sampling was conducted with and without urea injection for both coals.

**MERCURY RESULTS AND DISCUSSION**

**Site S1**

The mercury results for site S1 are summarized in Figure 1. At the SCR inlet, mercury was present primarily in the gas phase and as Hg0. The fly ash generated at site S1 resulted in more than 60% of the mercury being Hg0 at the ESP inlet for all three tests conditions. This is a relatively high level of Hg0 for a PRB coal and may have been caused by a high level of unburned carbon (15%) in the fly ash. The mercury oxidation at the SCR inlet and outlet indicated that normal SCR operation increased the percentage of Hg2+ from 6 to 26%, yielding a 20% increase. However, comparing the mercury speciation results at the stack, with SCR and without SCR, there was little “net” improvement in the percentage of Hg2+ at site S1; 20% of the mercury was oxidized with SCR, compared to 28% without SCR. Similarly, the Hg0 was also comparable. This small difference (8%) is probably not significant. When the NH3 was turned off to the SCR reactor (but the flue gas was still passing through the SCR reactor), there was no significant effect of SCR on Hg2+. Mercury removal across the ESP was estimated by comparing the total ESP inlet mercury to that obtained at the stack:

- 78% when SCR was operating normally;
- 67% when SCR was operating without NH3; and
- 60% when SCR was bypassed.

As shown above, there was a small increase in mercury when the SCR was operating normally. However, the data set is small for PRB coals and it is not known if this is real or simply data variability.

**Site S2**

The results for site S2 are summarized in Figure 2. As can be seen, there was a significant effect of SCR on both Hg2+ and its

![Figure 7](image1.png)  
**Figure 7.** Results showing the effect of bypassing SCR (beginning at 18:20) on mercury at site S4.

![Figure 8](image2.png)  
**Figure 8.** Results showing the effect of adding NH3 to the flue gas at site A1, unit A.
subsequent removal in the wet scrubber. Comparing the mercury oxidation at the SCR unit inlet and outlet indicated that normal SCR operation increased the percentage of Hg\(^{2+}\) from 48 to 91%, yielding an increase of 43% across the SCR reactor. Comparing the mercury speciation results at the ESP inlet, with and without SCR, showed that 97% of the mercury was Hg\(^{2+}\) with SCR, compared to 74% without (a net increase of 23%). This increase in Hg\(^{2+}\) led to increased mercury capture downstream in the wet scrubber. Mercury removal across the ESP/FGD is defined by comparing the total ESP inlet mercury concentration to total mercury at the stack. Note that the ESP outlet variability is likely due to sampling issues, and this uncertainty does not affect the conclusion. Overall, mercury removal increased from 51 to 88% with the SCR reactor in service. Figure 3 shows the total mercury results using a CMM. The CMM clearly shows the increase in mercury emissions at the stack when SCR was bypassed. Site S2, which operates a wet scrubber, represents an ideal scenario for mercury removal, in that there is clearly oxidation of Hg\(^0\) across the SCR reactor. The result is a reduction of approximately 90% reduction in mercury emissions at the stack.

**Site S3**

The mercury results for site S3 are shown in Figures 4 and 5. The CMM results are shown in Figure 5 and support the results of the OH mercury sampling. Figure 4 shows that SCR had little effect on overall mercury oxidation. With normal SCR operation, Hg\(^{2+}\) increased from 55 to 65% across the SCR reactor. Comparing the measured mercury speciation at the ESP inlet location both with and without SCR, Hg\(^{2+}\) and Hg\(^0\) were comparable. These results were somewhat

![Figure 9. Results showing the effect of adding NH\(_3\) to the flue gas at site A1, unit B.](image1)

![Figure 10. Coal 1 results showing the effect of adding urea to the flue gas at site A2.](image2)

![Figure 11. Coal 2 results showing the effect of adding urea to the flue gas at site A2.](image3)

![Figure 12. Comparison of a mercury monitor with the OH mercury sampling method at site A2.](image4)
surprising, considering the relatively high chlorine and sulfur content of the coal. One possible contributing factor to the low mercury oxidation across the SCR reactor was that the space velocity of the SCR reactor was at 3930 hr⁻¹, which is nearly double the space velocity for sites S1, S2, and S4. Space velocity is inversely proportional to residence time, and recent studies have shown that residence time may impact mercury oxidation. In addition, the inlet mercury concentration was more than double the concentration of the other SCR sites tested. Comparing the total ESP inlet mercury concentration to those obtained at the stack for each of the test conditions gives the following ESP mercury removal results:

- 13% when SCR was operating normally;
- 10% when SCR was operating without NH₃; and
- 16% when SCR was bypassed.

These results are essentially the same; therefore, based on these measurements, it was concluded that the SCR reactor did not have a significant impact on mercury emissions at site S3.

**Site S4**

The mercury results for site S4 are shown in Figures 6 and 7. At site S4, there was significant mercury oxidation and removal by the FGD as a result of SCR operation. Comparing the mercury speciation results (Figure 6) at the air heater outlet (Venturi scrubber inlet) with and without SCR shows that 87% of the mercury is oxidized with SCR in service, compared to 56% without SCR, yielding a net increase of 31%. There was also significant oxidation across the SCR reactor when the NH₃ was turned off, with overall oxidation increasing to 93% (air heater outlet). The mercury oxidation increased from 90% at the SCR inlet to 80% at the SCR outlet. This increased mercury oxidation also led to increased mercury removal in the Venturi scrubber. Comparing the total air heater outlet mercury concentrations to those obtained at the stack gives the following mercury removal results:

- 90% when SCR was operating normally;
- 85% when SCR was operating without NH₃; and
- 46% when SCR was bypassed.

Figure 7 shows the total mercury results using a CMM. The results clearly show the increase in mercury emissions at the stack when the SCR reactor was bypassed. Like site S2, this facility represents an ideal scenario for effective mercury removal, in that there is clearly oxidation of Hg⁰ across the SCR reactor and the plant’s FGD system removes a high percentage of Hg²⁺.

**Site A1**

Measurements were conducted at two sister units (A and B) at site A1. The results for unit A (50:50 PRB–bituminous blend) are shown in Figure 8. Both with and without NH₃ addition, there is a high percentage of mercury in the particulate phase. The addition of NH₃ increased the particulate mercury by 29% (79%, compared to 50%). This increase in particulate mercury led to increased mercury removal in the ESP. The resulting mercury removal efficiencies of the ESP were 66% with NH₃ addition, compared to 46% without NH₃ addition. The mercury results for unit B (100% PRB coal) are shown in Figure 9. The mercury was predominately Hg⁰ both with and without NH₃ injection (77% and 69%, respectively). The ESP removal efficiency for the two test conditions was only 21% with NH₃ injection, compared to 10% without NH₃ injection.

**Site A2**

The mercury results for site A2 are shown in Figures 10 and 11. As shown in Figure 10, the addition of urea appeared to result in less mercury oxidation at the ESP inlet (62%, compared to 81% without urea). However, both with and without urea injection, there was little, if any, mercury removal across the ESP. For the test using the second coal, shown in Figure 11, there was little, if any, effect of urea injection on mercury speciation or removal. The CMM data generated for this test, as shown in Figure 12, support the results of the OH mercury sampling.

**COMPARISON OF RESULTS**

Hg²⁺ and Hg⁰ are more easily controlled with conventional air pollution control devices than is Hg⁰; therefore, it is important to examine the percentage of nonelemental mercury species (the sum of Hg²⁺ + Hg⁰) in the flue gas upstream of the particulate control device (PCD). A summary of the nonelemental mercury species percentages is presented in Table 3. The data from Table 3 show that there is a significant amount of nonelemental mercury even at the economizer outlet (SCR/AH inlet) for some coals. This appears to correlate with the amount of chloride in the coal. For sites S1, S4, and A1–2, where the coal contained less than 700 µg/g Cl, the nonelemental mercury averaged 8% at the SCR inlet (or air heater inlet). For the remaining sites where the coals contained greater than 700 µg/g Cl, the nonelemental mercury averaged 50% at the SCR inlet/air heater inlet. The data also show that all four sites with SCR systems showed greater than 87% nonelemental mercury at the PCD inlet, with an average of 92%. When the SCR reactor was bypassed, only two of the four sites (S1 and S3) showed greater than 87% nonelemental mercury at the PCD inlet. For two of the sites (S2 and S4), significant oxidation of mercury was shown across the SCR reactor. It is interesting to note that these are the plants that showed less than 85% nonelemental mercury at the PCD inlet when the SCR was bypassed. Hg⁰ was only a factor at two of the sites tested (S1 and A1) and only appeared after the air heater (temperature drop). Additionally, these two sites generated high loss on ignition ashes (>10%).

The potential contributing factors that can affect mercury oxidation across the SCR reactor include reaction with the catalyst, increased residence time, change in flue gas chemistry (including but not limited to the reduction in NOₓ concentration),
and reaction with NH$_3$. It appears that the addition of NH$_3$ does not have a significant effect on mercury oxidation across the SCR reactor. This also means that the change in flue gas chemistry related to the reduction of NO$_x$ also did not significantly affect mercury oxidation. This leaves reaction with the catalyst, an increase in residence time, and other changes in flue gas chemistry as the contributing factors to the increase in oxidation seen across some of the SCR reactors. Unfortunately, the data generated from this project do not allow the determination of these variables separately.

**CONCLUSIONS**

The following observations can be made from the results of the full-scale tests:

- It appears that SCR systems can assist in converting Hg$^{0}$ to Hg$^{2+}$. However, the effect on mercury speciation and removal appears to be coal-specific and, possibly, catalyst-specific. Significant oxidation of mercury across the SCR reactor was shown for two of the sites tested, with nonelemental mercury being greater than 90% at the PCD inlet.
- For the two sites with downstream FGD systems, 94–99% of Hg$^{0}$ was removed across the PCD/FGD systems.
- For the two sites with significant particulate-bound mercury, 99% of the Hg$^{0}$ was removed across the ESPs.
- For the two SCR sites with only minimal increase in mercury oxidation across the SCR, the results showed greater than 85% nonelemental mercury at the PCD inlet. Site S1 burned a PRB coal in a cyclone boiler and produced a high level of unburned carbon fly ash, which may not be representative. The SCR system at site S3 operates at a space velocity of 3930 hr$^{-1}$, which may explain the lower oxidation results.
- NH$_3$ injection, whether directly as a gas or indirectly as urea, did not appear to have a significant effect on mercury speciation.

It should be noted that the data set presented here is small, so the reader should exercise caution in extrapolating the results until further data can be obtained to develop a robust database to verify these observations. Although laboratory analyses and data interpretation are still ongoing, preliminary results seem to indicate that SCR technology can assist in converting elemental mercury to oxidized mercury. However, the effect largely appears to be coal-specific and, possibly, catalyst-specific. NH$_3$ injection, whether directly as a gas or indirectly as urea, did not appear to have a significant effect on mercury speciation and removal.

**FUTURE TESTS**

Based on a review of these test results, there remain numerous data gaps and uncertainty. Several other power plants are currently being tested to help fill in some of the data gaps. Further tests are planned to evaluate the effect of SCRs on mercury speciation for a power plant firing a low-sulfur compliance coal, as well as a plant using a PRB coal in a pc-fired boiler. There are also plans to retest the two “high-performing” SCR sites (S2 and S4) once the SCR system has had an additional year of service to evaluate the effect of catalyst age. Finally, it is important to note that all of the measurements provided here represent only short-term measurements, lasting several hours to several days. Additional measurements are planned to characterize mercury emissions for up to one month by placing more reliance on continuous monitors.

**REFERENCES**