Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low Rank Fuels

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Abstract

This is the seventh Quarterly Technical Report for DOE Cooperative Agreement No: DE-FC26-03NT41728. The objective of this program is to measure the oxidation of mercury in flue gas across SCR catalyst in a coal-fired power plant burning low rank fuels using a slipstream reactor containing multiple commercial catalysts in parallel. The Electric Power Research Institute (EPRI) and Argillon GmbH are providing co-funding for this program. This program contains multiple tasks and good progress is being made on all fronts. During this quarter, a model of Hg oxidation across SCRs was formulated based on full-scale data. The model took into account the effects of temperature, space velocity, catalyst type and HCl concentration in the flue gas.

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Executive Summary

This project received funding from the Department of Energy under Cooperative Agreement No: DE-FC26-03NT41728. The Electric Power Research Institute (EPRI) and Argillon GmbH are providing co-funding for this program. This project has a period of performance that started February 19, 2003 and continues through September 30, 2004.

Under a separate program (cooperative agreement DE-FC26-00NT40753), Reaction Engineering International (REI) has been funded by the Department of Energy to carry out research and development on NO_x control options for coal-fired utility boilers. The objective of one of the tasks in the NO_x-control program is to evaluate and model SCR catalyst deactivation. REI will be responsible for six-month testing of multiple commercial catalysts simultaneously in a power plant slipstream reactor. This multi-catalyst reactor provides an ideal test bed for advancing the state of knowledge regarding mercury oxidation by SCR catalysts, with a focus on low rank fuels.

In this program, REI is using the multi-catalyst slipstream reactor to determine oxidation of mercury across six separate SCR catalysts at AEP's Rockport Unit 1. During the six-month testing under the existing NO_x-control program, two week-long sampling campaigns for mercury speciation will be carried out: at the beginning of the six-month period and at an intermediate point. URS will conduct the one-week campaigns to measure gaseous mercury speciation at the inlet and at the outlet of each catalyst chamber.

The specific project tasks are:

- Task 1 Test Preparation
- Task 2 Test Plan
- Task 3 Field Measurements of Mercury Speciation
- Task 4 Data Analysis and Validation
- Task 5 Management and Reporting

During the last three months, our accomplishments included a model of Hg oxidation across SCRs was formulated based on full-scale data. The model took into account the effects of temperature, space velocity, catalyst type and HCl concentration in the flue gas.

Experimental Methods

Within this section we present in order, brief discussions on the different tasks that are contained within this program. For simplicity, the discussion items are presented in the order of the Tasks as outlined in our original proposal.

Task 4 - Data Analysis and Validation

As discussed in the quarterly report for April to June 2004, laboratory¹⁻³ and pilot-scale⁴⁻⁷ data have been collected on the behavior of mercury in SCR catalysts, in addition to the pilot-scale data obtained in this program. Data have been collected from measurements of mercury speciation across SCRs in six full-scale power plants under funding by DOE NETL and EPRI^{8,9}, from other utility data and from other data reported in the literature.¹⁰ The quarterly report for April to June 2004 provides details of the design and operating conditions, and the measured mercury speciation and oxidation in these catalysts. Further information can be found in References 8 through 10. The ammonia-to-NO ratios for these full-scale systems are not given; however, since the full-scale data all come from operating electric utility boilers, the NO_x reductions achieved by the SCR catalysts would be of a similar magnitude.

Results and Discussion

Task 4 - Data Analysis and Validation

In previous quarterly reports, laboratory, pilot and full-scale data have been reviewed. These data will be summarized briefly here before presenting the rationale for a global mercury oxidation model.

It has been noted previously that mercury appears to be adsorbed by SCR catalysts under certain circumstances.^{2,3} Hocquel² demonstrated in a laboratory experiment the adsorption of elemental mercury by a commercial SCR catalyst and showed that with increasing concentration of HCl in the flue gas, the amount of elemental mercury adsorbed decreased. One explanation for this observation might be that HCl can be adsorbed on the same site as Hg^0 and can displace adsorbed Hg^0 .

Data from the multicatalyst slipstream reactor at Rockport showed considerable loss of mercury across the commercial catalysts when the catalyst was relatively fresh as illustrated by CEM measurements shown in Figure 1. CEM measurements were made at the inlet to the slipstream reactor and at the outlet of the catalysts. Catalyst C1 was a blank cordierite honeycomb with no active catalyst.

Figure 1. Total Mercury as a function of time from first test series at Rockport, space velocity ~3,000, no ammonia, 600-630°F.

The blank catalyst showed the same amount of mercury at the outlet as at the inlet. Most of the other catalysts, however, showed a loss of mercury across the catalyst. With ammonia on, there was also loss of mercury noted across the commercial catalysts (Figure 2), but not across the blank catalyst C1. This suggests that the catalyst formulation, whether it is in plate or honeycomb form, was responsible for adsorption of mercury. The adsorption was not, however, observed in the second test series after the catalysts had been exposed to flue gas for approximately 2200 hours (Figure 3). Catalysts C5 and C3 oxidized mercury at about the same rate in August as in March/April, whereas catalysts C2, C4 and C6 showed less mercury

Figure 2. Total Mercury as a function of time from first test series at Rockport, space velocity ~3,000, ammonia to NO ratio ~5, 575-600°F.

oxidation in August. The ability of the catalysts to adsorb elemental mercury (or lack thereof) did not seem to be related to the ability of the catalyst to oxidize mercury.

Since adsorption of elemental mercury was observed in laboratory settings and the loss of total mercury (presumably by adsorption) was observed in pilot-scale catalyst, it is reasonable to determine if this phenomenon has been observed at full scale. Figure 4 contains full-scale data on mercury speciation in which the change in elemental mercury across the catalyst is plotted against the change in oxidized mercury. Little or no particulate-bound mercury was reported in the full-scale measurements. Thus, if elemental mercury is oxidized across the SCR, there should be an increase in oxidized mercury that corresponds to the decrease in elemental mercury; the line in the figure denotes this. Most of the full-scale points lie close to the line. There are, however, some full-scale points that lie below the line, suggesting that there may be some adsorption of mercury across the catalysts for certain measurements.

Figure 2. Total Mercury as a function of time from first test series at Rockport, space velocity ~3,000, no ammonia, 555-600°F.

Figure 4. Change in elemental mercury across full-scale SCR compared with change in oxidized mercury.

The oxidation of elemental mercury across SCR therefore does not require a net adsorption of elemental mercury by the catalyst, which could mean that adsorption of elemental mercury is not

the rate-limiting step in the process. Since HCl displaces adsorbed mercury (in laboratory experiments), perhaps HCl and Hg^0 are adsorbed on the type of same site.

Laboratory, pilot and full-scale data reviewed in previous quarterly reports have shown that the presence of ammonia reduces the oxidation of elemental mercury. Ammonia binds to the vanadium sites on the catalyst as part of the NO reduction process. Therefore, it seems likely the mercury oxidation process also takes place at the vanadium sites and involves HCl. At this point, there is not enough evidence to determine the detailed mechanism. Two alternatives can be proposed:

1. Hg^0 binds to a vanadium site; HCl binds to an adjacent vanadium site; the reaction takes places between the two bound species.
2. Hg^0 competes with HCl for binding to a vanadium site; bound HCl reacts with gaseous Hg^0 .

Distinguishing between these alternatives (or elucidating another mechanism) will require detailed laboratory studies.

In the previous quarterly report, thermochemical equilibrium calculations were carried out for flue gas compositions and the speciation of mercury at the inlet and outlet of SCRs was compared to equilibrium predictions. This quarter an error was discovered in the way the previous calculations were set up. The dependence of mercury speciation on HCl concentration was computed incorrectly. Figure 5 shows the corrected equilibrium calculations for the typical bituminous and subbituminous concentrations shown in Table 1.

Figure 5. Mercury speciation from thermochemical equilibrium calculations for flue gas compositions from Table 1.

Table 1. Flue gas compositions used for equilibrium calculations.

	Subbit.	Bit.
N ₂ [vol%]	70.6	75.4
CO ₂ [vol%]	13.9	14.6
H ₂ O [vol%]	12.3	6.8
O ₂ [vol%]	3.0	3.0
SO ₂ [ppm]	350	1000
HCl [ppm]	1.75	31
Hg [ppb]	0.2	0.2

At the inlet to the SCR, the mercury in the flue gas is far from equilibrium, as shown in Figure 6, which compares the fraction of elemental mercury at the inlet to the SCR with the equilibrium predictions for various temperatures as a function of the molar chlorine to mercury ratio in the coal. Based on gas-phase kinetic calculations, mercury is not expected to be in equilibrium at the economizer exist. Figure 7 shows the outlet speciation from the same full-scale SCRs. The SCR catalyst has had the effect of rendering mercury at the outlet closer to equilibrium, Yet in full-scale SCRs, mercury in the flue gas does not come to equilibrium.

Figure 6. Percentage of mercury as elemental at inlet to SCR: full-scale data compared to equilibrium predictions.

Figure 7. Percentage of mercury as elemental at outlet to SCR: full-scale data compared to equilibrium predictions.

Clearly, a kinetic model is required to describe mercury oxidation across full-scale SCR catalysts. Since the detailed data are not currently available to develop a fundamental reaction mechanism, a global kinetic model will be created and tested against the full-scale data. There is a body of pilot-scale data in the literature⁴⁻⁸, but it details like the inlet mercury concentrations and speciation are not always reported in the literature.

What factors should be incorporated into the global kinetic model? Temperature and space velocity have been shown to be important in laboratory and pilot-scale data discussed in previous quarterly reports. The full-scale data show a correlation between mercury oxidation and temperature as shown in Figure 8. As observed in pilot-scale data, mercury oxidation decreases with increasing temperature. The scatter in the data suggests that there are other important factors.

HCl concentration is also an important factor, based on laboratory experiments. In Figure 9, the importance of chlorine (as expressed by the coal chlorine content) can be seen for oxidation across full-scale SCRs.

Figure 8. Mercury oxidation across full-scale SCRs as a function of inlet temperature.

Figure 9. Mercury oxidation across full-scale SCRs as a function of coal chlorine content.

Ammonia has been shown to be important, as discussed above. The available full-scale data contain few measurements without ammonia. Most full-scale SCRs are operated at similar inlet ammonia to NO ratios and with similar amounts of NO removal. Ammonia concentration varies along the length of the reactor and this variation in ammonia will, effectively, be built into the global kinetics.

The full-scale SCR is essentially a plug-flow reactor. As such, integral reactor analysis¹¹ can be used to develop a global kinetic expression. The conversion of elemental mercury across the SCR is expressed as:

$$X = \frac{[Hg^0]_{in} - [Hg^0]_{out}}{[Hg^0]_{in}} \quad (1)$$

where $[Hg^0]$ is the concentration of elemental mercury in the flue gas in mol/m^3 . The rate of conversion of mercury per gram of catalyst, R , is:

$$F_{in}X = -R dW \quad (2)$$

where F_{in} is the molar flux of elemental mercury in to the SCR and W is the weight of catalyst in grams. The integral form of Eq. 2 is:

$$\frac{W}{F_{in}} = \int_0^X \frac{dX}{-R} \quad (3)$$

Given an equation for the rate R , Eq. 3 can be integrated to give the conversion at the reactor exit. Based on the evidence discussed previously, the chemical reaction appears to be between Hg^0 and HCl , mediated by active catalyst sites. The simplest rate equation can be written as

$$-R = k[HCl][Hg^0] \quad (4)$$

Substituting Eq. 4 into Eq. 3 and integrating gives:

$$k \frac{W[HCl][Hg^0]_{in}}{F_{in}} = \ln\left(\frac{1}{1-X}\right) \quad (5)$$

In doing so, the concentration of HCl has been assumed to be constant across the SCR. Considering the large excess of HCl with respect to mercury, this seems reasonable. Thus, if we

plot the quantity $\frac{W[HCl][Hg^0]_{in}}{F_{in}}$ against $\ln\left(\frac{1}{1-X}\right)$, the slope should be equal to the rate

constant k . This plot is shown in Figure 10. Full-scale data have been included that were taken with the ammonia on and for which the loss of total mercury across the catalyst was less than 20 per cent. That is, if there was an apparent loss of total mercury across the catalyst, then the data should be considered suspect. The data points have been divided into temperature ranges. Table 2 gives the values of the slopes of the lines. For three of the four temperature ranges, reasonable fits to the data were obtained. Figure 11 displays the data points without ammonia. Although the fitted rate constant without ammonia is higher than the rate constant with ammonia for the same temperature range, there appears to be overlap in the data points. It is difficult to conclude that the two sets of data points are different. More full-scale data without ammonia are needed.

Table 2. Rate constants derived from full-scale data.

T, °F	616-631	642-659	667-681	693-702	667-681*
$k, (m^6/mol^2)/(g-s)$	3.25E+09	4.86E+09	6.05E+09	4.35E+09	7.98E+09
r^2	0.544	-3.102	0.325	0.565	0.610

* No ammonia

Figure 10. $\frac{W[HCl][Hg^0]_{in}}{F_{in}}$ vs. $\ln\left(\frac{1}{1-X}\right)$ from full-scale data with ammonia.

Figure 11. $\frac{W[HCl][Hg^0]_{in}}{F_{in}}$ vs. $\ln\left(\frac{1}{1-X}\right)$ from full-scale data with and without ammonia, 667-681 F.

Based on full-scale data, a global kinetic model has been created for mercury oxidation. This model is applicable to full-scale SCRs that inject ammonia at NH_3/NO ratios that are typical of commercial experience. Figure 12 shows two examples of how the model could be used.

(a) Effect of load changes

Changing load in the boiler decreases the amount of flue gas, increasing the residence time in the SCR, and drops the temperature in the SCR. Both will have an effect of Hg oxidation across the catalyst. Assume a plant burning a bituminous coal with $800 \mu\text{g/g Cl}$ and $0.011 \mu\text{g/g Hg}$. The SCR is a plate catalyst. At full load, the space velocity is 2000 hr^{-1} and the temperature is 700°F . Assume that at 70% load, the space velocity is 1500 hr^{-1} and the temperature is 675°F . Under these conditions, the model predicts an increase in Hg oxidation from 70 per cent to 90 percent.

(b) Effect of blending

When the primary fuel for a boiler is a subbituminous or lignite coal, a potentially inexpensive way to increase the HCl in the flue gas is to blend in a higher chlorine bituminous coal. Assume that the SCR design and operation are the same as in example (a). The subbituminous coal has $25 \mu\text{g/g Cl}$ and $0.011 \mu\text{g/g Hg}$, while the bituminous coal is the same as in example (a). Blending bituminous coal with subbituminous coal increases mercury oxidation, in this example, from about 5 percent up to 40 percent (at 60% subbituminous coal).

Figure 12. Calculated Hg oxidation across full-scale SCRs; see text for details.

Task 5 - Management and Reporting

Results from portions of this research program have been reported to industry through technical presentations at conferences. One paper was presented at DOE/NETL's Mercury Control Technology R&D Program Review, July 14-15, 2004, Pittsburgh, PA:

- Connie Senior and Temi Linjewile, "Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low-Rank Fuels"

A paper was accepted for presentation at Power-Gen International, November 29 to December 1, 2004 in Orlando, Florida:

- Connie Senior and Temi Linjewile, "Understanding Oxidation of Mercury Across SCR Catalysts in Power Plants Burning Low Rank Coals"

Conclusions

A review of the available data on mercury oxidation across SCR catalysts from small, laboratory-scale experiments, pilot-scale slipstream reactors and full-scale power plants was carried out. SCR catalysts are, under certain circumstances, capable of driving mercury speciation toward the gas-phase equilibrium values at the SCR temperature. However, evidence suggests that mercury does not reach equilibrium at the outlet of SCR catalysts. Some of the other factors that have been shown to affect mercury chemistry across SCR catalysts are the space velocity and the presence of ammonia. There may be other factors, such as the sulfur content of the coal, that become apparent as more data become available. Catalyst properties may be important, including: the mix between vanadium oxides and other oxides in the catalyst; the pore size distribution; and catalyst deactivation with time.

A model of Hg oxidation across SCRs was formulated based on full-scale data. The model took into account the effects of temperature, space velocity, catalyst type and HCl concentration in the flue gas. The results of this analysis suggest strategies for maximizing the amount of oxidized mercury at the exit of SCR catalysts. The chief of these is to increase the chlorine content of the flue gas, either through blending low-chlorine coal with high-chlorine coal or additives. Lowering the temperature is another option, but this may not be practical in many utility boilers. Furthermore, NO reduction across SCR catalysts decreases with temperature.

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