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Effects of Chlorine and Other Flue Gas Parameters on Selective Catalytic Reduction Technology for Mercury Oxidation and Capture

Effects of Chlorine and Other Flue Gas Parameters on Selective Catalytic Reduction Technology for Mercury Oxidation and Capture

1020591

Final Report, December 2009

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This report was prepared by

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

The report is a corporate document that should be cited in the literature in the following manner: *Effects of Chlorine and Other Flue Gas Parameters on Selective Catalytic Reduction Technology for Mercury Oxidation and Capture.* EPRI, Palo Alto, CA: 2009. 1020591.

PRODUCT DESCRIPTION

Selective Catalytic Reduction (SCR) technology—the technology of choice for meeting stringent nitrogen oxides (NOx) emission limits for coal-fired electric generating plants—has potential for oxidizing mercury, which would provide enhanced removal in downstream systems. Catalyst behavior is relatively well understood for deNOx and SO_2 oxidation, but less is known about mercury oxidation behavior. This test program was designed to determine general behavior of typical SCR catalysts on mercury oxidation and capture with respect to various operating flue gas parameters. The program also determined if all catalysts behaved in a similar manner or if significant behavioral differences were present.

Results & Findings

The project showed a clear beneficial effect in terms of mercury oxidation and capture when levels of chlorine are increased. Overall, increased temperature had a negative effect on both SCR mercury oxidation and mercury capture. This effect is opposite from most catalytic reactions, including the deNOx reaction, which increases as temperature increases. Flow rate had very little direct effect on either mercury oxidation across the SCR or on mercury capture across the electrostatic precipitator (ESP). The data also showed that ammonia has an inhibiting effect on mercury oxidation across the SCR. In terms of ESP capture, an increase in ammonia, which creates a decrease in SCR mercury oxidation, had the counterintuitive effect of improving capture. Overall the project has shown that conventional SCR catalysts behave similarly with respect to chlorine level, temperature, flow rate, and ammonia level. Thus, the data can be applied with some confidence to the domestic SCR catalyst fleet as a whole, assuming that the catalyst is of conventional type and is relatively new.

Challenges & Objective(s)

The test program evaluated the mercury oxidation performance of multiple types of conventional SCR catalysts as a function of changes in various parameters, including chlorine level, deNOx rate, flow rate, and temperature.

Applications, Values & Use

By capitalizing on the potential of SCR technology to oxidize mercury and provide enhanced removal in downstream systems, new or retrofitted facilities utilities could potentially develop highly effective, low-cost methods of mercury removal primarily using equipment already in place. This would be an extremely attractive option compared to dedicated mercury removal methods. In general, project data will help full-scale facilities determine what methods could be used to improve mercury oxidation and capture and also help determine what beneficial or detrimental effects may occur due to a proposed change in certain boiler operating parameters.

EPRI Perspective

The program demonstrates a clear beneficial effect in terms of mercury oxidation and capture when levels of chlorine are increased. All catalysts tested demonstrated similar responses to chlorine level. Flue gas highly depleted in chlorine will see very strong incremental improvements in mercury oxidation across the SCR with increased chlorine. The potential capture of oxidized mercury across a wet flue gas desulfurization (FGD) system is of particular interest, and actual benefits of chlorine injection with respect to capture will need to be validated by measurements across an actual-full scale unit.

Approach

The project team evaluated four commercial SCR catalysts under the test program, all from different types and formulations. Testing was conducted at Gulf Power's Mercury Research Center (MRC), a 5-MW equivalent pilot-scale reactor located in Pensacola, Florida. Speciated mercury data, flue gas constituents, and operational data were acquired on a continuous basis throughout the test program. Mercury measurement locations included the SCR inlet and outlet, and ESP outlet. Flue gas modified parameters included chlorine levels, temperature, flow rate, and ammonia levels.

Keywords

Mercury oxidation
Selective catalytic reduction (SCR)
DeNOx catalyst
Chlorine injection

ABSTRACT

Although catalyst behavior is relatively well understood with respect to deNOx and SO_2 oxidation, relatively little is known about mercury oxidation behavior. The subject test program sought to evaluate mercury oxidation performance of four (4) conventional Selective Catalytic Reduction (SCR) catalysts as a function of changes in flue gas, including chlorine level, deNOx rate, flow rate, and temperature. The facility for this project was Gulf Power's Mercury Research Center (MRC), a 5-MW slip-stream facility. The available equipment for speciated mercury measurements made the facility extremely well suited for the test program. Host boiler coals fired during testing were consistent with Eastern bituminous low-chlorine coals.

Results from the test program showed that there is a clear beneficial effect in terms of mercury oxidation and capture when levels of chlorine are increased. All catalysts tested demonstrated similar responses to chlorine level. Project data show that, on average, SCR mercury oxidation could be increased from 50% to 90% (a relative improvement of 90%) with chlorine levels up to 350 ppmv in the flue gas. As the overall chlorine level increased, incremental beneficial effects leveled. Findings apply most directly to artificial adjustment of chlorine through direct injection of HCl upstream of the SCR. Chlorine level may, of course, also be changed via a fuel switch. For a fuel switch, it is cautioned that other parameters, in addition to chlorine, also may affect mercury oxidation and capture.

Data show that increased temperature has a negative effect on both SCR mercury oxidation and mercury capture. Flow rate appeared to have very little direct effect on either mercury oxidation across the SCR or on mercury capture across the electrostatic precipitator (ESP)—this finding was consistent for all catalysts tested. Data clearly show that ammonia has an inhibiting effect on mercury oxidation across the SCR; however, the inhibiting effect seems to be most apparent at low levels of chlorine (50 ppmv). At higher levels of chlorine (100 ppmv), the adverse effect on SCR mercury oxidation is much more muted. For the lower-chlorine data, where the response was most apparent, the SCR mercury oxidation decreased by 18% absolute (22% relative) across the deNOx range of 0% to 90%.

EXECUTIVE SUMMARY

Selective Catalytic Reduction (SCR) technology has become the technology of choice for meeting stringent Nitrogen Oxides (NOx) emission limits for coal fired electric generating plants. Industry data have indicated that along with NOx reduction, SCR technology has the potential for oxidizing mercury, thereby providing enhanced removal in downstream systems. By capitalizing on this oxidation behavior, utilities could potentially develop highly effective, low cost methods of mercury removal primarily using equipment already in place. This would be an extremely attractive option compared to dedicated mercury removal methods, such as activated carbon injection.

Although catalyst behavior is relatively well understood with respect to deNOx and SO_2 oxidation, relatively little is known about mercury oxidation behavior. The subject test program sought to evaluate the mercury oxidation performance of multiple types of conventional SCR catalysts as a function of changes in various parameters, including chlorine level, deNOx rate, flow rate, and temperature. Four commercial SCR catalysts were evaluated under the test program. The purpose of the test program was not to compare directly the absolute levels of mercury oxidation exhibited by the various catalysts tested. Rather, the test program was devised to determine the general behavior of typical SCR catalysts with respect to various operating flue gas parameters. Conclusions from the program offer end-users guidance as to the expected behavior of the catalysts in the domestic fleet as a whole, and highlights the similarities, or differences, in catalyst behavior with respect to mercury oxidation that the various commercial catalysts may possess. The data also provide a methodology for predicting how a change in certain operating parameters will affect mercury oxidation and capture relative to some base-line performance for a particular installation.

The facility utilized for this project was the Mercury Research Center (MRC), located near Pensacola, Florida. The MRC is a 5 MW slip-stream facility, with a 75 MW T-fired host boiler. The facility is extremely well designed for the test program, having equipment fully representative of a full-scale facility, as well as complete control over operating conditions. In addition, the available equipment for speciated mercury measurements, made the facility extremely well suited for the test program. The host boiler coals fired during the testing were consistent with eastern bituminous low-chlorine coals. The coals cannot be considered surrogates for PRB coals, however, even though the chlorine levels may be similar. Thus, the data should not be extrapolated to include PRB fired facilities. The research program was conducted over an extended period of time. Preliminary testing for the project began on August 9, 2007, and testing was completed on June 3, 2009.

The data show that there is a clear beneficial effect in terms of mercury oxidation and capture when levels of chlorine are increased. All of the catalysts tested demonstrated similar responses to chlorine level. The project data show that, on average, SCR mercury oxidation could be increased from 50% to 90% (a relative improvement of 90%), ESP capture could be increased from 60% to 80+% (a relative improvement of roughly 33%). These improvements are for the tested chlorine range, which was < 5 to 350 ppmv for SCR oxidation, and < 5 to 150 ppmv for capture. Very strong incremental improvements in mercury oxidation across the SCR were noted when the overall chlorine level was low (< 100 ppmv). As the overall chlorine level increased, the incremental beneficial effects were minimal. In terms of ESP capture, there was roughly a linear improvement with respect to chlorine across the entire range tested. The findings apply most directly to the artificial adjustment of chlorine, through direct injection or fuel additives. The chlorine level may, of course, also be changed via a fuel switch. For a fuel switch, it is cautioned that other parameters, in addition to chlorine, may also affect mercury oxidation and capture. This fact should be considered when making assumptions as to the effects of a fuel switch on mercury behavior.

The data show that increased temperature has a negative effect on both SCR mercury oxidation and mercury capture. All of the catalysts tested had a very similar response to increases in temperature, with the average decrease in SCR mercury oxidation at about 12% absolute (86% to 74% at the SCR outlet) for a temperature change of 625°F to 750°F. In terms of ESP capture, the decrease in captured mercury was roughly 13% absolute (16% relative), consistent with the decrease in SCR mercury oxidation. However, the response of ESP capture to temperature was not consistent with all four catalyst data sets. Thus, this average decline in ESP capture should be applied with caution, with the understanding that individual sites may experience very different responses. The reasons for the variability are unknown. These findings are associated with an independent change in temperature. If a temperature change comes about as a result of a load change, then other parameters may influence mercury oxidation and capture as well.

Flow rate appeared to have very little direct effect on either mercury oxidation across the SCR or on mercury capture across the ESP – this finding was consistent for all of the catalysts tested. This is based on the relatively narrow flow rate range tested, which was equivalent to a unit reducing load to 60% of design. For full-scale units which routinely have larger turn-downs, the effect of flow may become more apparent. Also for full scale units, flow rate changes are usually the result of a load change, which may also be accompanied by a temperature change. If so, lower temperatures would improve mercury oxidation and capture, thus a load decrease would generally improve mercury oxidation and capture more than what may be indicated by the flow rate data alone.

The data clearly show that ammonia has an inhibiting effect on mercury oxidation across the SCR. This general effect is consistent for all of the catalysts tested in the program. However, the inhibiting effect seems to be most apparent at low levels of chlorine (50 ppmv). At higher levels of chlorine (100 ppmv), the adverse effect on SCR mercury oxidation is much more muted. The confidence in this finding is somewhat limited, however. For the lower chlorine data, where the response was most apparent, the SCR mercury oxidation decreased by 18% absolute (22% relative) across the deNOx range of 0% to 90%. In terms of ESP capture, the increase in ammonia injection, which produced a decrease in SCR mercury oxidation, had the counterintuitive effect of improving capture. As with the SCR oxidation data, ESP capture

response appeared to be different depending on the chlorine level. ESP capture improved only slightly for high chlorine conditions, but the improvement was marked for low-chlorine conditions (increasing by roughly 20% absolute or 40% relative).

Overall the project has shown that conventional SCR catalysts behave similarly with respect to chlorine level, temperature, flow rate, and ammonia level. Thus, the data can be applied with some confidence to the domestic SCR catalyst fleet as a whole, assuming that the catalyst is of conventional type and is relatively new. The data averages based upon the project data offer a basis for determining both qualitatively and semi-quantitatively the relative effects of variations in the parameters on mercury oxidation through the SCR, and mercury capture through an ESP (within limits). It is cautioned that the data can be applied only to fuels and chlorine levels consistent with those tested in the program. It should also be noted that ESP capture is highly variable and is a function of many parameters in addition to those tested in the program. Thus, the average values for ESP capture experienced in the test program cannot necessarily be applied to any single full-scale unit. In general, the data will help full-scale facilities to determine what methods could be used to improve mercury oxidation and capture, and also help to determine what beneficial or detrimental effects may occur due to a proposed change in certain parameters. For new facilities, or those being retrofitted, the data show how various parameters affect mercury oxidation and capture, and thus would aid designers in optimizing mercury oxidation and capture.

ACKNOWLEDGEMENT

The authors would like to thank the participating catalyst suppliers for their contribution of catalyst material, as well as their technical support for this project. We would also like to especially thank the operators of the Mercury Research Center, Particulate Control Technologies, Inc., for their unflagging commitment to the success of the project, and also Mr. Randy Merritt, of Randy Merritt Consulting, for his dedication to the difficult task of accurately measuring speciated mercury. Special thanks also go to Ms. April Sibley of Southern Company Services, Inc. for her technical and administrative support during the course of the project. In addition, the authors would like to acknowledge Dr. Ramsay Chang from EPRI for providing valuable and timely input in all areas of mercury controls, providing useful guidance through the course of the project and reviewing the draft reports.

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Background

Selective Catalytic Reduction (SCR) technology has become the technology of choice for meeting stringent Nitrogen Oxides (NOx) emission limits for coal fired electric generating plants. Industry data have indicated that along with NOx reduction, SCR technology has the potential for oxidizing mercury, thereby providing enhanced removal in downstream systems. By capitalizing on this oxidation behavior, utilities could potentially develop highly effective, low cost methods of mercury removal primarily using equipment already in place. This would be an extremely attractive option compared to dedicated mercury removal methods, such as activated carbon injection.

Project Objectives

Although catalyst behavior is relatively well understood with respect to deNOx and SO_2 oxidation, relatively little is known about mercury oxidation behavior. The subject test program sought to evaluate the mercury oxidation performance of multiple types of SCR catalyst as a function of changes in various flue gas parameters, including chlorine level, deNOx rate, flow rate, and temperature. Four commercial SCR catalysts were evaluated under the test program. The purpose of the test program was not to compare directly the absolute levels of mercury oxidation exhibited by the various catalysts tested. Rather, the test program was undertaken to determine SCR catalyst oxidation trends with respect to various operating conditions, and to determine if all catalysts behaved in a similar manner, or if significant behavioral differences were present. The conclusions from the program offer end-users guidance as to the expected behavior of the catalysts in the domestic fleet as a whole, and highlights the similarities, or differences, in catalyst behavior with respect to mercury oxidation that the various commercial catalysts may possess. The data also provide a methodology for predicting how a change in certain operating parameters will affect mercury oxidation and capture relative to some base-line performance for a particular installation.

Test Facility

The facility utilized for this project was the Mercury Research Center (MRC), located near Pensacola, Florida. The facility is extremely well designed for the test program, having equipment fully representative of a full-scale facility, as well as complete control over operating conditions. In addition, the available equipment for speciated mercury measurements, as well as other flue gas parameters, made the facility extremely well suited for the test program.

2
DETAILED FACILITY DESCRIPTION AND TEST PLAN

Mercury Research Center Design

The Mercury Research Center (MRC) is located at Gulf Power's Plant Crist, near Pensacola, Florida. The facility was designed as a research platform for various pollution control processes, especially mercury, and has been in operation since April of 2006. The MRC operates as a 5 MW-equivalent slip stream facility, utilizing flue gas extracted from points both upstream and downstream of the host unit's economizer. The variation in temperature at these two extraction points allows for primary temperature control of the facility. The design flue gas flow rate is 50,500 lb/hr (23,990 acfm @ 700°F). Figure 2-1 shows the MRC configuration with respect to the host boiler (Unit #5).

The facility is equipped with all the major pollution control devices common to the domestic fleet of coal-fired boilers including: an SCR, electrostatic precipitator, pulse-jet fabric filter, and a wet FGD. A variable speed, standard design, Ljungstrom-type air preheater is utilized to cool the flue gas prior to it reaching the downstream equipment. Note that the FGD only processes a portion of the total MRC flue gas flow and was not typically in operation during the testing for this project. Also included in the facility are systems for activated carbon injection and systems for the injection of SO_2, SO_3, HCl, and bromine solution (boiler feed). Figure 2-2 shows a schematic of the MRC major equipment and flow paths. Figure 2-3 shows a photograph of the MRC with major equipment annotated. Note that this photograph was taken prior to the completion of the installation of ductwork insulation to better show the ductwork configuration.

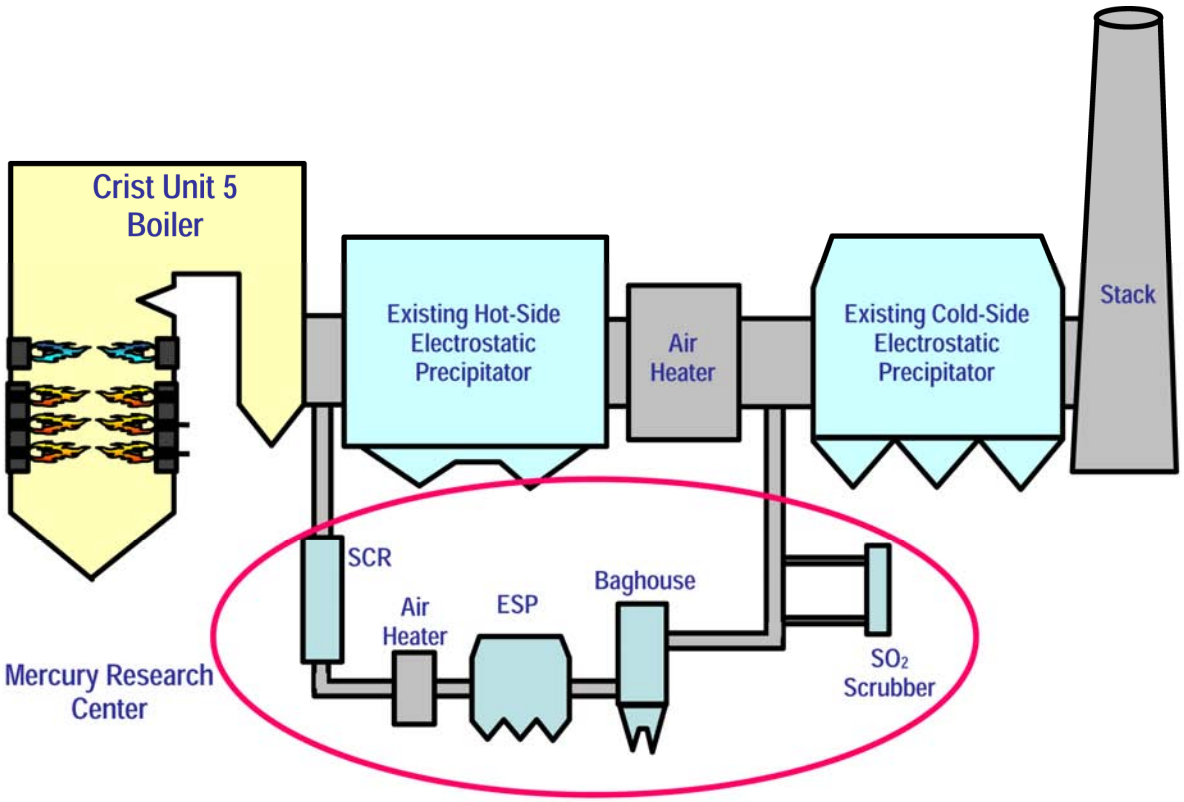

Figure 2-1
Mercury Research Center Configuration with Respect to Host Boiler

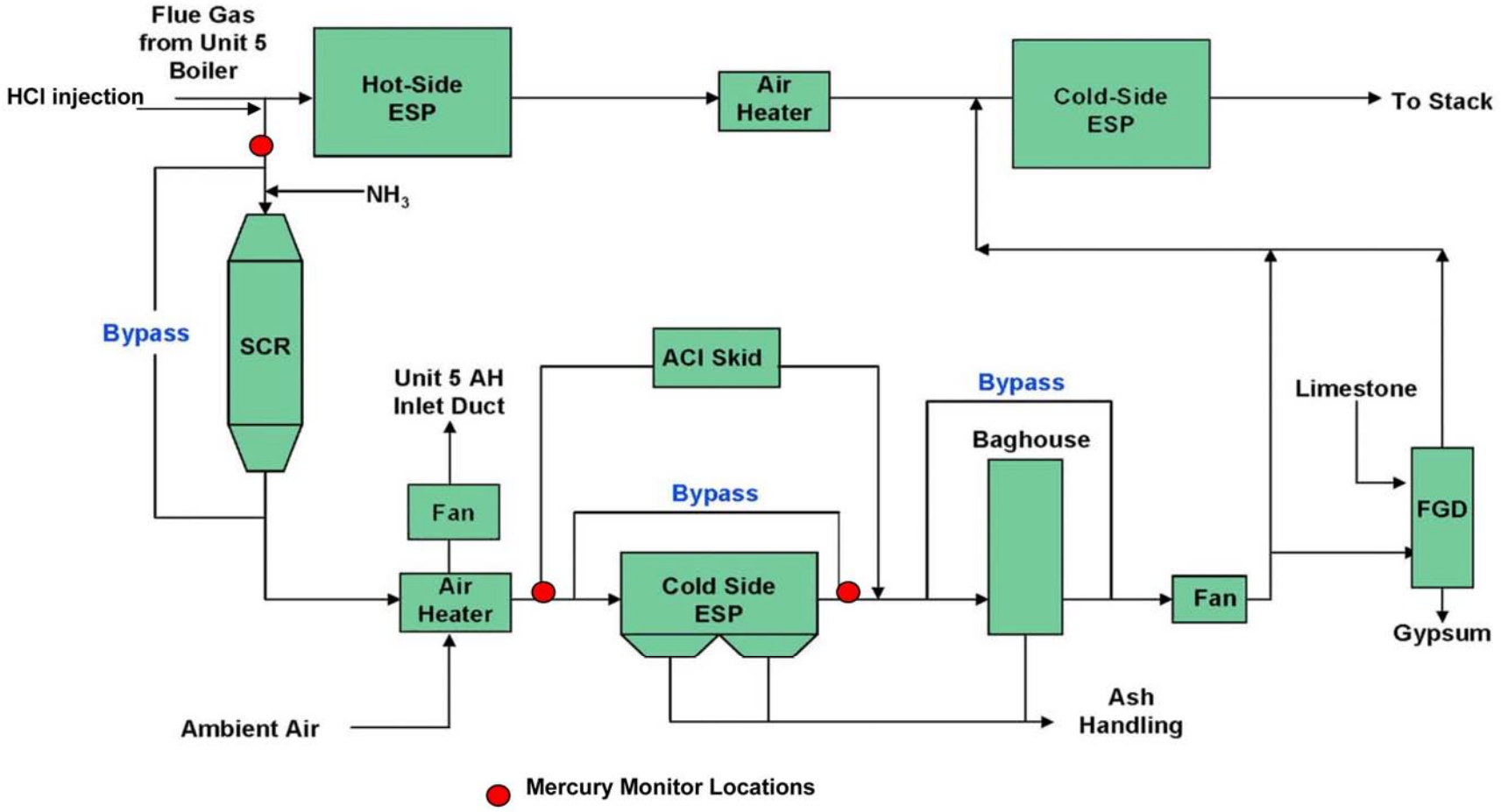

Figure 2-2
Mercury Research Center Schemati

Figure 2-3
Photograph of the MRC with Major Equipment Annotated

SCR Reactor and Catalyst Design

Table 2-1 shows the basic design parameters for the SCR, which also served as the nominal design parameters for the catalysts. The design of the SCR at the MRC is consistent with typical design parameters for the domestic coal-fired fleet as a whole.

The SCR operates with diluted anhydrous ammonia injected via a grid, upstream of turning vanes and a flow straightening device at the reactor entrance. Each catalyst layer is designed to hold roughly 4 m^3 of catalyst (in terms of gross module dimensions), depending on catalyst height. The SCR design allows for three (3) catalyst layers to be installed, if required.

Table 2-1
SCR and Catalyst Design Parameters

Parameter	Value
Reactor Interior Dimensions (nominal)	2 X 2 m (6.5 X 6.5 ft)
Available Catalyst Layers	3
Ammonia Type	Anhydrous
Cleaning	Sonic horns (one per layer)
Flow Rate (nominal baseline)	23,990 acfm @ 700°F
Temperature (nominal baseline)	700°F
NOx Removal	90%
Ammonia Slip	< 2 ppmv
SO_2 Conversion	Not specified

Catalyst Design Philosophy

As previously discussed, the purpose of the test program was not to compare in absolute terms the efficacy of the various catalysts utilized in the test program, but to gain some confidence about the general behavior of the catalyst fleet as a whole with respect to mercury oxidation, and their relative/qualitative response to various operational parameters. As a result, the participating catalyst suppliers were given latitude in their design, as would be the case for offerings for full-scale commercial installations. Thus the catalyst suppliers considered such factors as volume, cost, pressure drop, life, SO_2 conversion, slip, and fouling in their design, seeking to provide an optimum offering balancing the catalyst life cycle cost with performance. Since this design method does not provide for any sort of "normalization" of the catalyst in terms of cost, volume, reactor potential, performance, etc., the reader is cautioned that the data should not be evaluated on a direct comparison basis in terms of quantitative mercury oxidation. The data should be used in a qualitative fashion to describe the way the tested catalysts performed with respect to changes in the various operating parameters. In fact, since the catalysts were tested consecutively, with many months elapsing between the parametric series, a large number of variations were present which would make quantitative direct comparison of mercury oxidation between the various catalysts impossible. Further, in some cases catalyst was removed from the reactor after initial start-up, resulting in less volume than originally supplied to lower the overall mercury oxidation so that responses to various parameters would be more apparent. Thus absolute comparative mercury oxidation would not provide a meaningful analysis, and the data is presented in such a way as to prevent erroneous conclusions from be reached related to absolute mercury oxidation. The data do provide a reasonable basis for predicting how a particular full-scale installation will respond, in terms of mercury oxidation and capture to various parametric changes, in a relative sense. In other words, if a baseline level of oxidation or capture is known for a particular installation, the data provide a basis for determining how that same facility will respond to a change in operating parameters, such as chlorine level, temperature, etc.

Catalyst Properties

Table 2-2 shows the nominal catalyst properties of the four catalysts used in the test program. The catalysts are listed in no particular order. The four catalysts consisted of two plate type catalysts, one honeycomb type catalyst, and one corrugated type catalyst. The data are provided to show that the characteristics of the catalysts were consistent with conventional coal-fired catalysts. Note that as-tested, only one catalyst utilized three layers, but these layers were relatively short compared to the other catalysts utilized, making the volume for this catalyst actually lower than the other offerings. The exposure times listed represent the exposure time when the laboratory testing occurred, after all pilot testing was completed.

Table 2-2
Nominal Catalyst Properties

Parameter	A	B	C	D
Number of Layers	2	2	3	2
Approx. Total Catalyst Volume (m^3)	6.8	6.7	5.9	8.4
Approx. Exposure Hours	2,000	2,000	8,000	16,000
K (m/h)	40.1	44.7	38.7	29.4
SO_2 Conversion (%)	0.33	0.33	0.12	0.86

Mercury and Flue Gas Measurements

Speciated mercury was measured at the MRC at three points utilizing three discrete identical Thermo-Electron Model 80i Analyzers equipped with Model 83 inertial separation probes. The measured locations included fixed points at the facility inlet and SCR reactor outlet, and one mobile point, which could be located either at the ESP inlet or the ESP outlet. For the reported testing, the mobile point was located at the ESP outlet, unless troubleshooting or special testing was being conducted. These primary mercury measurement points were augmented occasionally with a manual system consisting of a Tekran monitor with an Apogee QSIS probe. This additional probe was utilized at the interlayer SCR location (between catalyst layers) for occasional assessment of mercury speciation at this location.

Additional flue gas parameters including NOx, CO_2, and SO_2, were measured at the MRC inlet and SCR outlet using two continuous CEMS-type dilution systems. These systems provided continuous documentation of the flue gas constituents entering the MRC, as well as gave primary control information for the NOx reduction across the SCR. Oxygen values were measured at various locations throughout the facility using Yokogawa in-situ oxygen probes with zirconium oxide sensors. In the latter part of the test program, chlorine concentrations were measured

continuously using an in-situ FTIR system at the facility inlet. Occasional manual measurements were made for SO_3, HCl, and HBr, as well.

Host Unit and Fuel

The host unit for the MRC is a 75 MW, T-fired unit firing pulverized coal. The unit is equipped with a hot-side and cold-side precipitator. Extraction points for the MRC are located upstream of the unit's economizer section and upstream of the unit's hot-side precipitator. The coal for the plant as a whole is delivered by barge, and multiple low-sulfur fuels are burned. Fuel was purchased off of the spot market and included South American, Western bituminous, and various fuel blends during the project testing. This fuel variability was a major source of variability in the general flue gas conditions at the MRC, especially in terms of native chlorine which ranged from less than 10 ppmv to over 100 ppmv. High levels of native chlorine would obviously preclude testing at conditions which called for lower chlorine levels. This variability in chlorine was a challenge for the research program, as will be discussed in detail.

Table 2-3 shows representative ultimate coal analyses for the range of coals fired at the plant during the test period. Ash mineral analyses are also shown. Note that these analyses are based upon laboratory prepared ash samples, and should not be confused with ash samples as collected from the ESP or other field location. Trace analyses of the fuels are shown in Table 2-4. The vast majority of the coals fired during the early testing corresponded to coals A or B (or similar). For later testing, blends of coals A or B with F or G were utilized, which gave higher overall levels of chlorine, since coals F and G were quite high in chlorine compared to A and B. Coals C, D, and E were only fired sporadically. All of the fuels had BTU values in the range of roughly 12,500 to 13,500 BTU/lb, and had ash constituents consistent with traditional eastern bituminous fuels, with the exception of fuel C, which had higher calcium in the ash (although this fuel was rarely fired). Chlorine levels ranged from a very low 40 ppmw to slightly over 4,000 ppmw. Table 2-4 shows the approximate predicted flue gas chlorine level (ppmv) based upon the fuel chlorine (ppmw). These calculations are made assuming that the particular fuel was fired without blending. As mentioned above, coals F and G were typically blended with lower chlorine coals, thus the actual experienced chlorine level was not as high as that indicated by the calculation. In addition, the calculated flue gas levels corresponding to the coals are very rough, and use a single conversion factor. Sulfur levels varied from roughly 0.5% with the very low chlorine fuels, to over 1% with the higher chlorine fuels, but again, due to the blending, the actual experienced sulfur concentrations were not as high as indicated by the individual coal analyses.

Table 2-3
Representative Coal Analyses – Ultimate

Coal ID	A	B	C	D	E	F	G
State	Colombia, SA	Colombia, SA	UT	WV	WV	IL	IL
ULTIMATE ANALYSIS (%, dry basis)							
Total Moisture	12.39	9.77	6.54	5.63	5.75	11.89	11.39
Ash	7.03	6.92	10.05	16.03	14.46	8.2	7.26
HOC (Btu/lb)	13003	13366	13325	12612	12785	13570	13656
Total Sulfur	0.65	0.59	1.3	0.66	0.94	1.75	1.18
Carbon	73.63	77.94	76.95	72.01	74.12	76.87	78.49
Hydrogen	4.94	4.94	4.78	4.49	4.62	4.98	4.85
Nitrogen	1.49	1.56	1.56	1.3	1.31	1.75	1.84
Oxygen	12.26	8.05	5.36	5.51	4.55	6.45	6.38
Volatiles	37.47	37.12	35.22	31.22	30.12	34.32	32.32
Fixed Carbon	55.5	55.96	54.73	52.75	55.42	57.48	60.42
Ash Fusion IT (°F)	2196	2368	2060	2541	2800	2046	2154
Ash Fusion ST(°F)	2378	2574	2134	2510	2800	2134	2260
Ash Fusion HT(°F)	2438	2652	2158	2645	2800	2238	2238
Ash Fusion FT(°F)	2532	2728	2260	2662	2800	2340	2534
Grindability Index	40	44	45	46	44	53	52
ASH CONSTITUENTS (%, as ashed in laboratory)							
Al_2O_3	20.94	20.31	18.28	29.4	29.46	19.88	22.42
Fe_2O_3	7.13	7.48	4.37	3.75	4.4	17.13	11.85
CaO	2.49	1.23	10.51	1	0.67	2.07	1.91
MgO	1.32	1.01	3.26	1.1	0.82	0.93	1.07
MnO_2	0.03152	0.0461	0.03018		0.0164	0.03108	0.03288
P_2O_5	0.32	0.28	0.16		0.17	0.55	0.36
K_2O	1.81	1.52	1.25	2.98	2.77	2.48	2.66
SiO_2	59.62	64.72	43.63	63	59.14	52.67	55.26
Na_2O	1.49	0.56	4.57	0.346	0.2	1.06	1.28
SO_3	3.21	1.55	11.69	0.636	0.59	1.81	1.82
TiO_2	1	1	1.08	1.75	1.66	1.25	1.31

Table 2-4
Representative Coal Analyses – Trace

Coal ID	A	B	C	D	E	F	G
TRACE CONSTITUENTS (ppmw, dry)							
As	3.7	2.4	1.5	3.86	5.5	23	9.6
Ba	190	120	730	102	90	40	30
Be	0.4	0.5	0.7	2.34	2.5	1.5	1.3
Cd	0.19	0.19	0.11	0.091	0.11	0.2	0.11
Cl	40	39	336	624	1173	4047	4011
Co	1.9	2.6	3	9.85	10.5	6.2	6.3
Cr	6.5	6.7	5	19.4	22.2	11.6	9.8
Cu	6.7	5.6	13.6	19.3	20.5	8.6	7.1
F	70	73	58	100.3	75	37	50
Hg	0.085	0.058	0.05	0.085	0.099	0.027	0.081
Mg	0.056	0.042	0.198	0.078	0.071	0.046	0.047
Mn	14	20.2	19.2	17.6	15	16.1	15.1
Na	0.078	0.029	0.341	0.024	0.022	0.065	0.069
Ni	5	5.7	3.9	17.2	15.6	19.2	17.4
Pb	2.1	2.4	2.5	7.31	7.1	57.9	18.7
Sb	1	1.2	0.2	0.406	1.4	1.3	0.8
Se	5.6	4.84	1.2	5.1	4	1	1.1
V	19.8	21.2	17.7	37.8	36.4	20.8	20.1
Zn	9.3	10	10.4	15.6	16.2	33.2	24.6
Approx. Flue Gas Chlorine ppmv w/o blending	2	2	20	38	72	247	245

Test Plan

A parametric sequence was devised to examine the effect of several parameters on the degree of mercury oxidation exhibited by the catalysts, as well as to investigate the rate of mercury capture across the ESP. Table 2-5 shows the nominal parametric sequence, which served as a guideline for testing. However, during actual testing, a number of additional conditions were examined, including transients, and some preliminary testing that included tests with the SCR reactor in by-pass, and with the SCR in service, but with the ammonia off. Note that the actual conditions obtained for any particular test condition may have deviated from those shown in the table as a function of operational convenience and limitations. Most notably, the higher chlorine fuels precluded the examination of chlorine levels below the native chlorine levels created by the fuel. Further, the fourth catalyst test was abbreviated, such that the parametric sequence for this catalyst did not include all of the parametric conditions examined with the previous three catalysts.

Speciated mercury data, flue gas constituents, and MRC and host boiler operational data were acquired continuously throughout the parametric testing, with an average for the various parameters being calculated for the steady-state operation of the facility at each of the parametric conditions. These average values corresponding to the particular parametric conditions constituted the "data set" for each catalyst, and provided the basis for the data and analyses presented in this report.

Testing Methodology

During the preliminary testing, it was determined that for many conditions, such as variations in chlorine level or deNOx rate, the system reached equilibrium quite quickly. This allowed for multiple conditions to be reached in a single day of testing. These relatively short test durations also helped to minimize inherent variability that might be present as a function of boiler operation and fuel inconsistency. As a result of these inherent variabilities, data points separated over long periods of time could not be compared directly with much confidence. This is especially true when comparing absolute mercury levels. Thus the data presented showing effects of the parameters were typically obtained during a single test day. By nature, the adjustment of temperature required a relatively long stabilization time due to thermal mass of the system. Therefore, in the case of temperature, it was only possible to obtain two temperature conditions within a single day of testing. Overall, there appears to be a high degree of consistency in the data, and there is great confidence in the relative effects demonstrated by the data. Thus there is high confidence in the overall conclusions reached.

Table 2-5
Nominal Parametric Design Sequence

Test ID	1	2a	2b	2c	3a	3b	3c	4a	4b	4c	4d	5a	5b	5c	5d
Description	**Base-line Reference Test**	**Flow Rate Effect**			**Temperature Effect**			**Chlorine Effect**				**Ammonia Effect**			
Flow Rate (% of Design)	100%	125%	100%	75%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°F)	700	700	700	700	625	700	750	700	700	700	700	700	700	700	700
DeNO$_x$ Level	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%	0%	50%	90%	95%
Chlorine Level (ppmv HCl)	< 5[1]	50	50	50	50	50	50	< 5[1]	50	100	150	50	50	50	50

[1] Rough estimated baseline chlorine level, without additional injection, based upon the "low" chlorine fuel. Other fuels dictated different minimum values and may have precluded the examination of certain other chlorine levels depending on the exact level of native chlorine present.

3
SPECIAL TESTS AND TRANSIENTS

Background

This report section describes various tests that were performed which were outside of the normal parametric test sequence. These tests provide supplemental data to that acquired during the parametric testing, and in most cases are not catalyst-specific.

Effect of Chlorine – SCR Bypassed

Limited amounts of data were taken with the SCR in by-pass which showed the effect on mercury oxidation and ESP capture with respect to chlorine injection without the effect of an SCR catalyst. For these tests, only two mercury measurement locations were utilized: the air preheater inlet and the ESP outlet. The residence time between chlorine injection and the air preheater inlet measurement point was approximately one second. Measurement of the mercury at the ESP outlet location allowed for the capture of mercury across the ESP to be determined.

Figure 3-1 shows these data, where the chlorine level was increased from the native level of roughly < 5 ppmv chlorine to 50 ppmv via HCl injection. Over this chlorine range, the oxidized mercury increased from roughly 14% to 20%. However, given the normal variability in the data, it is difficult to say with confidence that the increased chlorine had much influence on mercury oxidation with the SCR in by-pass.

Figure 3-2 is a complimentary plot for the same tests, showing ESP capture. The trend of the two plots is similar, with the ESP mercury capture being slightly higher with higher chlorine levels. Total ESP mercury capture was 64% with 5 ppmv chlorine concentration, and 68% with 50 ppmv chlorine. Again, given the normal variability, there does not appear to be much impact due to chlorine on ESP capture with the SCR in by-pass.

The effect of chlorine at levels higher than 50 ppmv was not explored, but an improvement in oxidation and capture would be expected as the chlorine level is increased, up to some maximum level, after which little or no improvement would likely be noted. The point at which the increased levels of chlorine ceased to be beneficial was not explored. Overall, these data serve as a baseline to demonstrate that without the presence of an SCR catalyst, chlorine does not have a significant impact on elemental mercury oxidation.

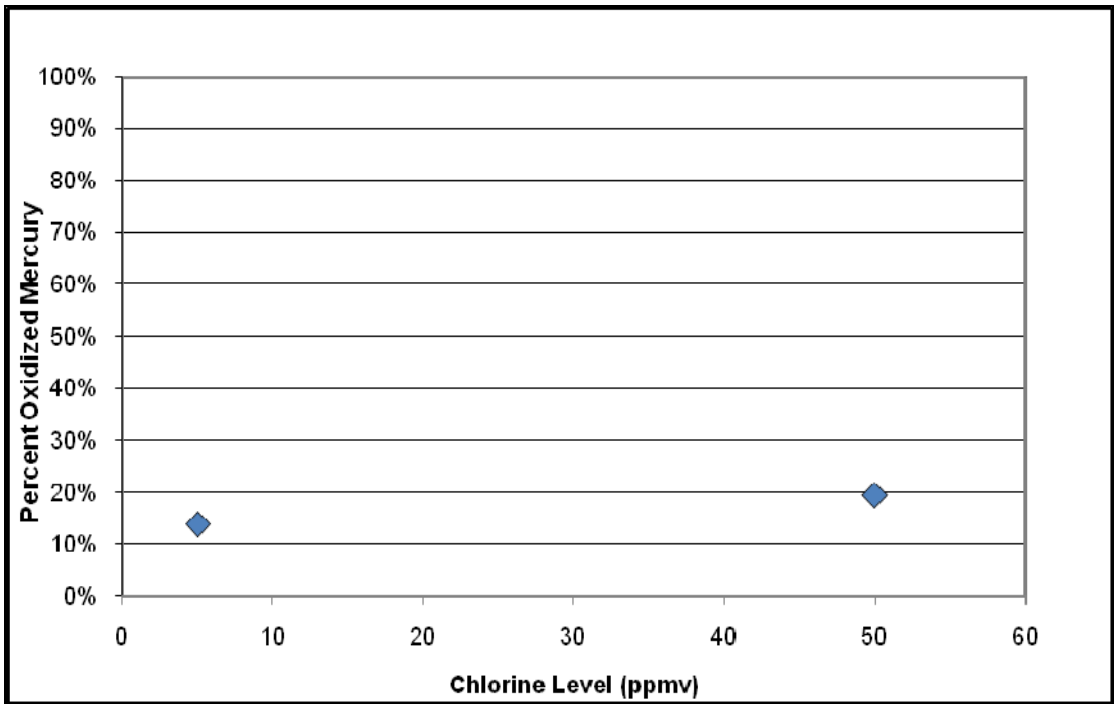

Figure 3-1
Effect of Chlorine on Mercury Speciation – APH Inlet, SCR in By-Pass

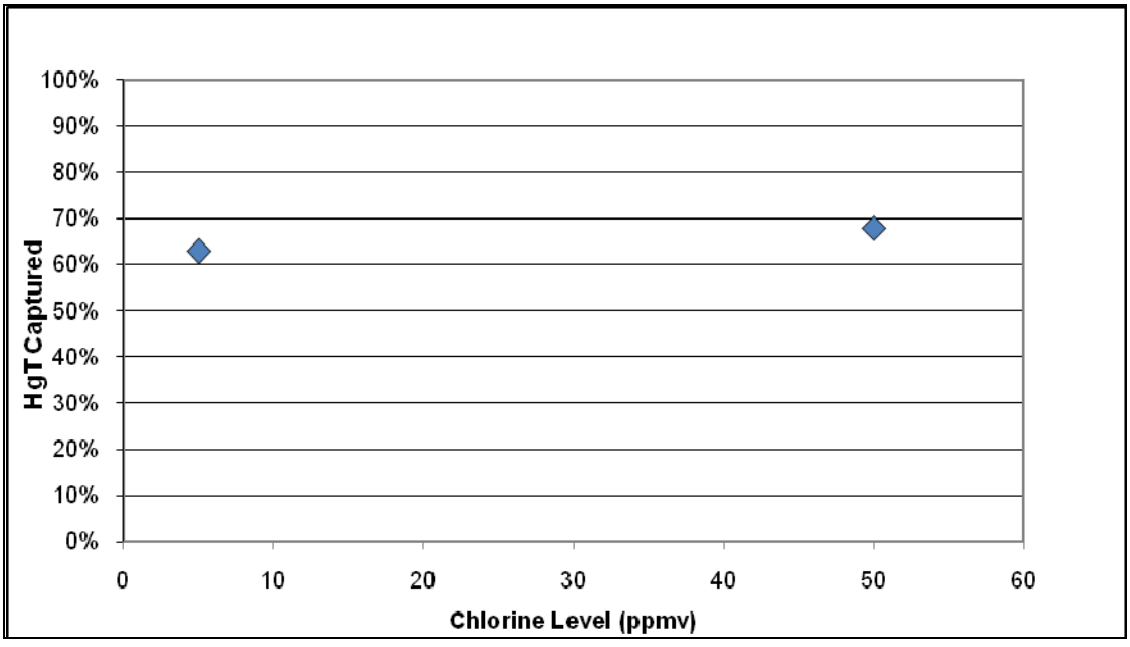

Figure 3-2
Effect of Chlorine on Total Mercury Capture Across the ESP, SCR in By-Pass

Behavior of Native Chlorine versus Chlorine Injected as HCl

One underlying question with the overall research approach is whether injected chlorine behaves in a similar manner to native chlorine (i.e. fuel chlorine), with respect to mercury oxidation. (This is of course not an issue for facilities considering injecting chlorine in a similar manner to what was done at the MRC, but for facilities utilizing the data to determine the effects of native fuel chlorine, the issue is important.) Obtaining meaningful data to answer the question is somewhat difficult, since fuel chlorine cannot be varied completely independently of other fuel parameters. For example, one might conceive of a test program where low-chlorine fuel is being fired, and chlorine is being injected to achieve 50 ppmv in the flue gas. This could then be compared to a fuel having a native chlorine level of 50 ppmv. Ostensibly, this scenario would give a comparison of the mercury oxidation effects of native versus injected chlorine. The concern is that other fuel characteristics which change along with the native chlorine level may also affect mercury oxidation; this includes physical parameters, such as grindability, and chemical characteristics such as sulfur content, bromine content, and ash level and mineral composition, etc. Thus, the isolation of a single parameter, chlorine, is impossible when considering the nature of coal. This limits the degree of confidence for which the above test approach can be applied.

Notwithstanding the above concerns, a testing opportunity did present itself which followed the above approach. On a single day of testing, fuel was being fired which created 50 ppmv of native chlorine in the flue gas (as measured by FTIR). On this day, the SCR was operated at two baseline conditions, one at no deNOx, and one at the standard 90% deNOx. This allowed for a comparison of this native 50 ppmv chlorine to other days at similar operating conditions, for which a much lower chlorine fuel was being fired and for which chlorine was injected to create 50 ppmv of chlorine. (Note that for these days of low chlorine fuel, the native chlorine was on the order of 5 ppmv or less, thus the injected chlorine was 45+ ppmv.) A representative analysis for the two coals is shown below in Table 3-1. These analyses show that the coal was similar in its characteristics as an eastern bituminous coal, but that the chlorine level was markedly different. The sulfur content also varied in tandem with the chlorine content, and some other differences were noted, such as total ash level and slightly higher ash silicon to aluminum ratio with the high-chlorine fuel.

Table 3-1
Coal Analyses for Chlorine Source Comparison

Parameter	Low-Chlorine Coal	High-Chlorine Coal
Dry Basis Proximate Analysis (% dry basis)		
Ash (%)	7.89	12.24
Volatile (%)	39.15	37.20
Fixed Carbon (%)	53.96	50.56
Sulfur (%)	0.51	1.68
BTU/Lb	12,810	12,865
Ultimate Analysis (% dry basis)		
Carbon	73.64	73.09
Hydrogen	4.84	4.89
Nitrogen	1.43	1.55
Ash	7.89	12.24
Sulfur	0.51	1.68
Oxygen	11.69	6.55
Ash Mineral Analysis (% ignited basis)		
Silicon Dioxide	55.29	66.30
Aluminum Oxide	21.72	13.38
Titanium Dioxide	0.96	0.68
Calcium Oxide	3.29	5.04
Potassium Oxide	1.77	0.94
Magnesium Oxide	1.69	1.56
Sodium Oxide	2.69	0.46
Phosphorus Pentoxide	0.24	0.55
Ferric Oxide	8.23	5.24
Sulfur Trioxide	3.74	5.08
Barium Oxide	0.23	0.10
Manganese Dioxide	0.03	0.02
Strontium Oxide	0.12	0.08
Trace Elements (µg/g dry basis)		
Bromine	< 5	< 5
Chlorine	**14**	**381**[2]
Mercury	0.064	0.055
Selenium	6.2	1.4

[2] The benchmark measurement for actual chlorine level in the flue gas was the FTIR reading which showed 50 ppmv for this coal, or at least coal from this same location. The level of coal chlorine measured for this coal sample would predict a flue gas level less than 50 ppmv. However, differences in sampling times and potential non-representativeness of the coal sample chlorine may be responsible for the discrepancy.

Figure 3-3 shows a comparison of the oxidization of mercury across the SCR for the native vs. injected cases, at two levels of deNOx. Note that one comparative point (injected chlorine) was available at the zero deNOx condition, while three comparative points were available for the 90% deNOx condition. At the zero deNOx condition, the native chlorine compares almost exactly to the injected chlorine, offering confidence that the two sources of chlorine behave similarly. At the 90% deNOx condition, there is much more scatter in the data, which is expected given normal variability. The average of the data for injected chlorine at 50 ppmv showed about 70% oxidized mercury, compared to the single data point of native chlorine which showed about 88% oxidized mercury. Based upon the average, one might conclude that native chlorine produced more oxidation than injected chlorine. However, the native chlorine data point is reasonably consistent with the injected-chlorine points, given the variability that is apparently present, as demonstrated by the three data points for the injected chlorine case. A more rigorous test series would have to be developed to conclusively compare the differences between native chlorine and injected chlorine.

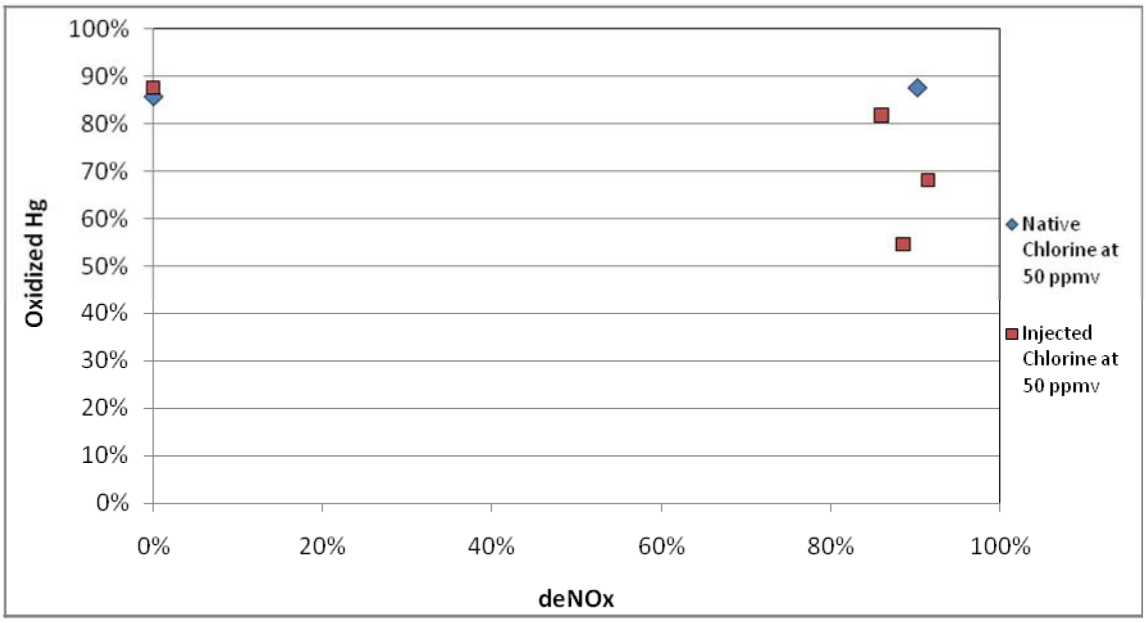

Figure 3-3
Oxidized Mercury at SCR Outlet vs. deNOx and Chlorine Source

Similar data are shown in Figure 3-4, but for the SCR inlet. Again, the data compare very well at the zero deNOx condition and relatively well at the 90% deNOx point. There is one outlier at the 90% deNOx condition, however. Given that this particular data point is at odds with virtually all inlet data (as demonstrated in subsequent report sections), it can be excluded from the comparison with some confidence. Given this exclusion, the data again compare very favorably. (At the SCR inlet, oxidized mercury was 29% with 50 ppmv native chlorine concentration, and 33% with 50 ppmv added chlorine concentration.)

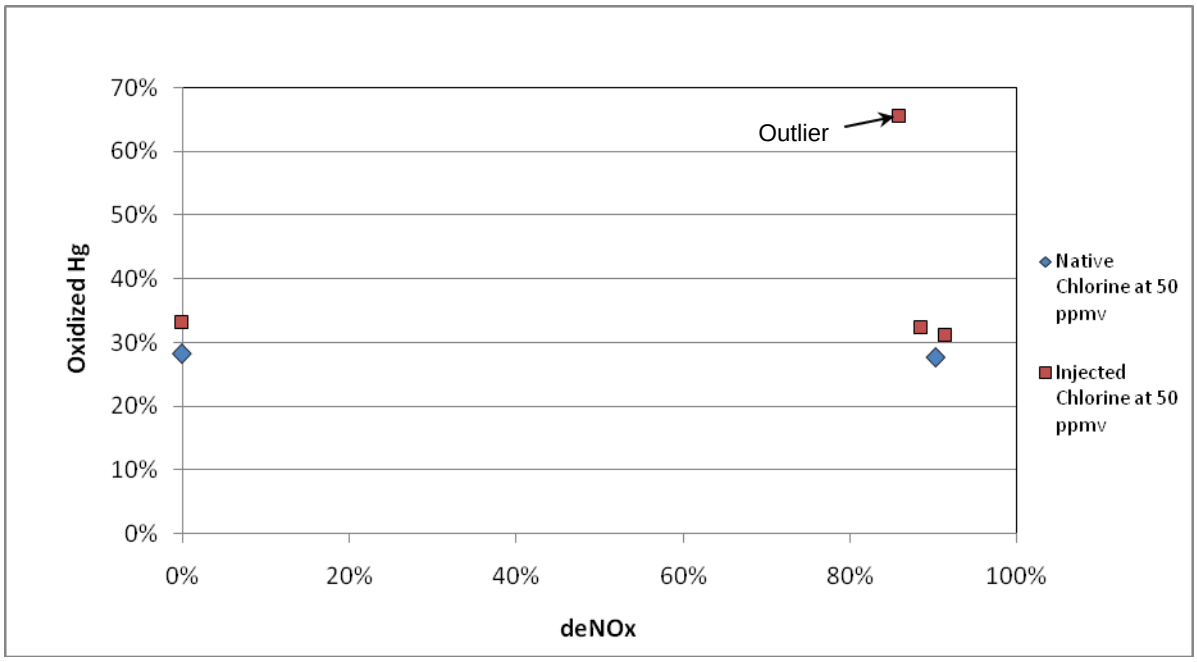

Figure 3-4
Oxidized Mercury at SCR Inlet vs. deNOx and Chlorine Source

The comparative mercury capture data are shown in Figure 3-5. These data show some variation at the zero deNOx point, but compare very favorably at the 90% deNOx point, where the average for the injected chlorine cases was roughly 60% removal, compared to the native chlorine case, which showed about 52% removal. Given that ESP mercury capture is especially susceptible to variations due to coal parameters, such as LOI, ash fineness, composition, etc., these data are surprisingly consistent. A meaningful hypothesis is difficult to establish which would dictate a difference at zero deNOx, but not at 90% deNOx, however. Therefore ESP mercury capture behavior remains inconclusive and additional research is needed in this area.

Overall, as a result of these analyses, within the limitations of the data, mercury oxidation across SCR catalyst may slightly favor native chlorine concentrations compared to injected HCl, but again, the confidence in this finding is relatively low.

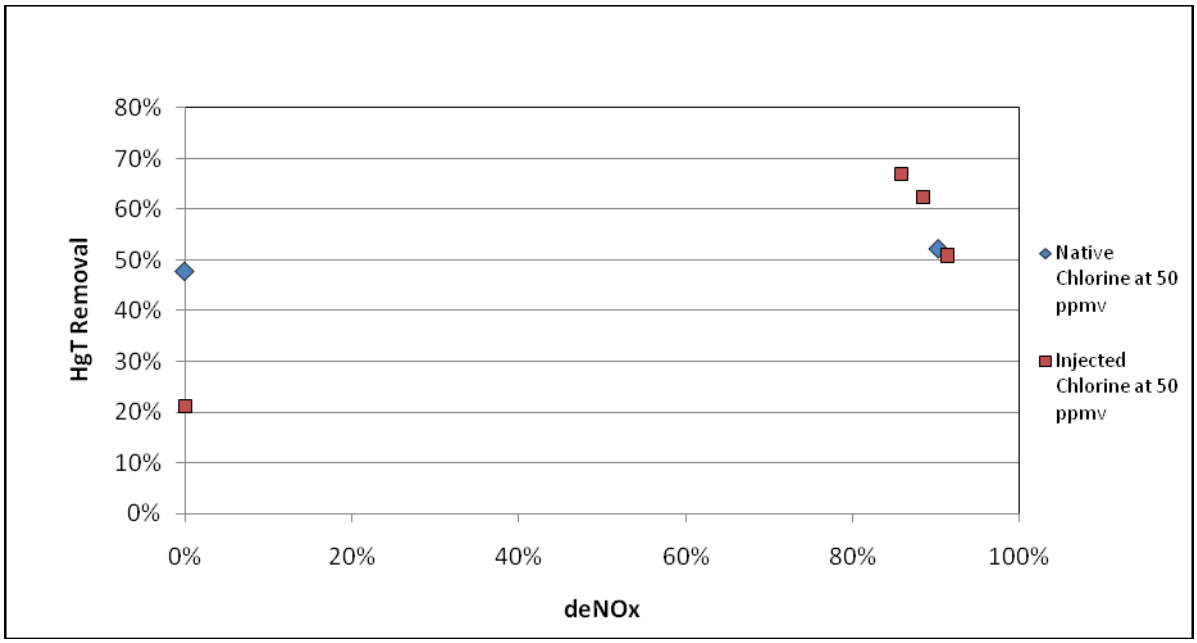

Figure 3-5
Mercury Capture vs. deNOx and Chlorine Source

Transient Data

A number of operational changes in the SCR/MRC operating conditions produced transients which are of interest in determining the behavior of the catalysts. In particular, step changes associated with initiation of ammonia and chlorine injection are of interest and are discussed below.

Transient Due to Ammonia Injection

Figure 3-6 shows an example of the mercury speciation at the SCR outlet after the initiation of ammonia injection. The start of ammonia represented a step change from no ammonia injection, to an alpha of roughly 0.9 (consistent with a target of 90% deNOx). This step change occurred at approximately 11:08, just after a probe blow-back period, for which a gap in the data is noted. Within a few minutes of the initiation of ammonia injection, an upward trend in total mercury is noted, spiking at roughly 11:16, after which the total mercury levels off to the prior steady-state level. This spike in total mercury is due primarily to oxidized mercury. After this spike, the speciation change can clearly be seen, where the oxidized mercury decreases, and the elemental mercury increases. After reaching steady-state, it is clear that the relative level of oxidized mercury has decreased substantially due to the negative impact of the ammonia on oxidized mercury. These data correspond to a low chlorine level of approximately 5 ppmv and standard operating conditions. It is important to note that the transient profile may be different for other flue gas conditions, especially with respect to chlorine level.

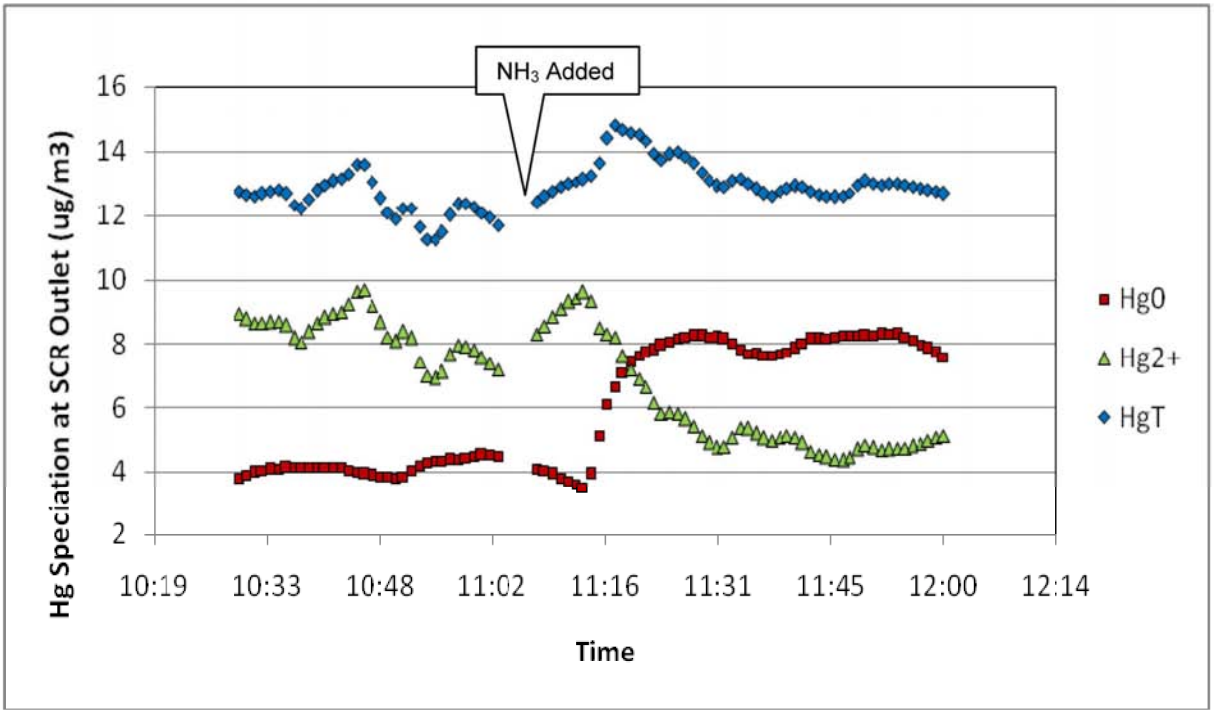

Figure 3-6
Transient in Mercury Speciation at SCR Outlet after Ammonia Injection

Transient Due to Chlorine Injection

Figure 3-7 shows the transient in mercury speciation at the SCR outlet after the initiation of chlorine injection. Here the chlorine had a native level of roughly 10 ppmv, and at approximately 13:35 chlorine was injected to give a total of roughly 50 ppmv. This increase from the very low native level represents a substantial increase in available halogens, and thus produced a more definitive change in mercury speciation than would chlorine increases at higher overall halogen levels. The data show a very clear initial spike in total mercury, which was due solely to a spike in oxidized mercury. One would conclude from this that oxidized mercury was adsorbed onto the catalyst, and released as a function of the change in chlorine level (additional work would be required to fully understand this desorption effect). After steady-state had once again been reached, the dramatic increase in the proportion of oxidized mercury exiting the reactor could be noted. It is notable that this transient was very quick, with most of the response being noted within a 10 minute period. The new steady-state values were essentially reached within 20 minutes.

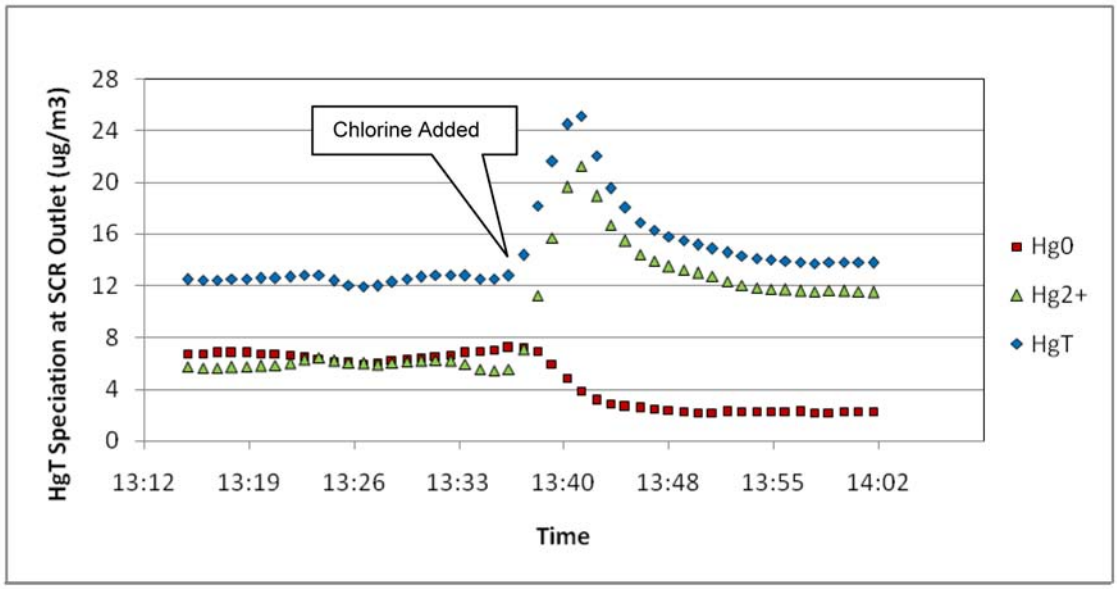

Figure 3-7
Transient in Mercury Speciation at SCR Outlet after Chlorine Injection

4
EFFECT OF CHLORINE

Background

One of the principal purposes of the test program was to determine the effect that changes in the flue gas chlorine level had on mercury oxidation and capture. Initially, the very low level of native chlorine in the coal allowed for a wide range of flue gas chlorine concentrations to be explored. As the project progressed, however, the coal chlorine level became more variable, and generally higher. In particular, the data for the last catalyst to be tested in the program had substantial limitations due to native chlorine levels which were generally around 100 ppmv. This limited the ability to explore low levels of chlorine, as well as hindered the ability to compare data from all the catalysts over the lower chlorine range. It is also important to note that chlorine levels were not typically measured on a continuous basis during the early phases of the research program due to the very steady nature of the coal chlorine concentration (resulting in flue gas levels consistently < 5 ppmv). However, as more variability in the coal chlorine was experienced, an in-situ FTIR device was utilized to provide continuous flue gas chlorine values. This assisted in determining the native level of chlorine in the flue gas, as well as in setting the desired overall flue gas chlorine levels when chlorine was being injected. With this approach, the chlorine injection level could be continuously adjusted, if required, to maintain a steady flue gas chlorine level.

Testing Approach

For the subject test program, chlorine was injected as HCl gas directly into the flue gas just downstream of the MRC primary extraction point. The injection location allowed for complete mixing of the HCl prior to reaching the SCR reactor entrance. Bottled HCl gas was used for this purpose, which was regulated using a simple manual valve system equipped with a rotameter. This injection location allowed for approximately 0.5 seconds of residence time prior to reaching the MRC inlet mercury analyzer. In practice, chlorine could be introduced into the flue gas or boiler in a number of ways, including using additives to the coal feed. The previous report section discussed the comparability of the native chlorine contained in coal versus chlorine injected as HCl in the flue gas, in terms of the relative effect on mercury speciation. It is important to note that the chlorine effect data were acquired for each catalyst during a single day of testing. This helped to remove some of the day to day variability from the data.

This testing approach was aimed at <u>independently</u> modifying the flue gas chlorine level. This allowed the effect of chlorine to be isolated, and the data obtained would be consistent with a full-scale facility that added chlorine in some fashion to augment mercury oxidation and capture. It should be cautioned that if the chlorine level in the flue gas is varied by fuel blending or switching, this does not necessarily represent an <u>independent</u> change in chlorine level. In other

words, in this case, many parameters associated with the fuel change may change in addition to the chlorine level change, such as boiler operation, flue gas composition, ash characteristics, etc. These changes may in fact outweigh any changes in mercury oxidation and capture due specifically to the change in chlorine. Thus one should be cautious in assuming that a fuel switch which created higher chlorine levels would necessarily be of benefit in terms of mercury oxidation and capture, especially if the chlorine level change is minor.

Effect of Chlorine at the MRC Inlet

Any effect from chlorine injection at the MRC inlet would presumably be due to gas-phase or fly ash catalyzed mercury oxidation as a function of chlorine. As stated above, the residence time between the chlorine injection point and the mercury measurement point was only 0.5 seconds. Intuitively one would not expect a significant effect due to chlorine injection at the MRC inlet.

Figure 4-1 shows the effect of chlorine on inlet oxidized mercury as a function of chlorine for the four catalysts tested. Note that the range of chlorine for one of the catalysts was substantially higher than for the others, due to coal differences. Each set of data has been fit with a second order polynomial curve.[3] In general, the data as a whole produce a "family" of curves which show a moderate response to chlorine (increase in oxidized mercury level), with the exception of one data set that showed a flat response. Note that on one data set, the final data point appears to be an outlier and has been removed from the polynomial curve fit. Most interesting is the day to day variability in the absolute levels of oxidized mercury, which ranged quite broadly (2% to 40%). It is clear that boiler or fuel differences created differences in the level of oxidized mercury that exited the boiler, but that the addition of chlorine produced additional oxidation over and above the oxidation levels that were present from the native chlorine level. These data help support the caution that day to day variability in the system is significant, and data points taken over several days of operation can not necessarily be compared in a meaningful manner.

[3] For this plot, and all other plots containing multiple data sets, linear or polynomial fits have been applied to the data to help the reader visually identify the different trends that are present. In many cases, especially with linear fits, care should be taken not to assume that the response is necessarily identical to that indicated by the line, especially when there are large gaps in the data.

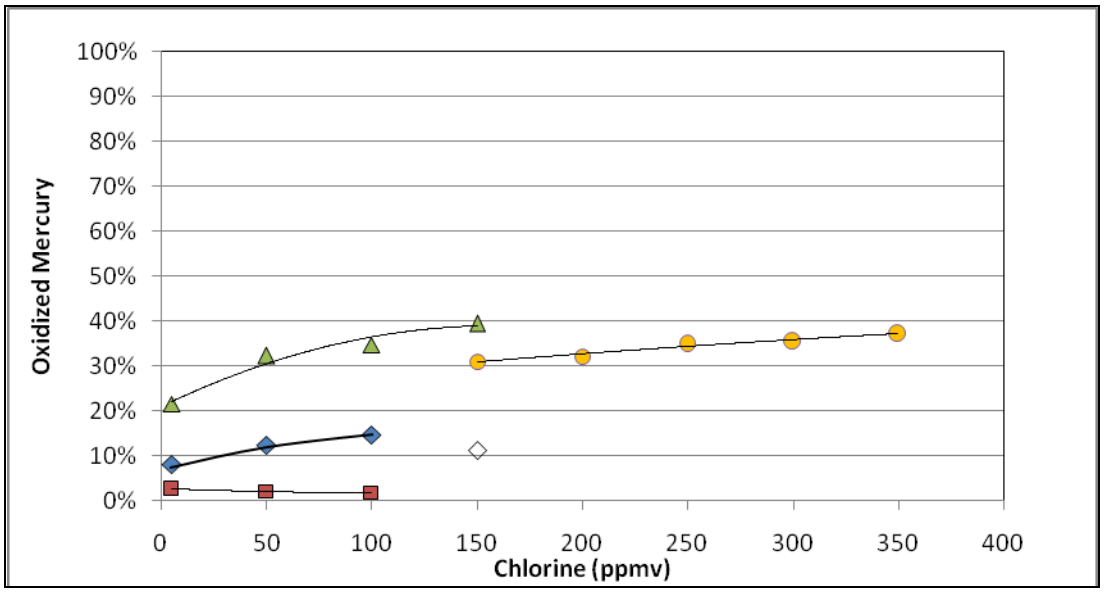

Figure 4-1
Oxidized Mercury vs. Chlorine – MRC Inlet

Effect of Chlorine at the SCR Outlet

The data of the most interest are, of course, associated with the SCR outlet, since they include the effects of the four catalysts tested.

The data are presented in such a way as to preclude comparison of the absolute levels of mercury oxidation between the four catalysts. As discussed in some detail prior, this has been done to prevent any misunderstanding in how the data should be evaluated – the data should be used to determine how the catalyst fleet as a whole would be expected to respond to increased levels of chlorine as a function of some baseline level of mercury oxidation that was being achieved at the facility. These data are necessarily subject to variability associated with boiler operation and fuel composition, as demonstrated in the inlet speciation data – this variability precludes a direct comparison of absolute levels of mercury oxidation between the catalysts. This is especially true since the catalysts were not "normalized" in any way, such as by having constant area velocity, reactor potential, etc.

The first plot to be presented, Figure 4-2, is based upon the average of all the available data to create a polynomial fit response curve. This allows the general response of the catalysts to be discussed in terms of various "regions" with respect to chlorine. This is valuable to help in the understanding of the effects of chlorine injection at different absolute levels.

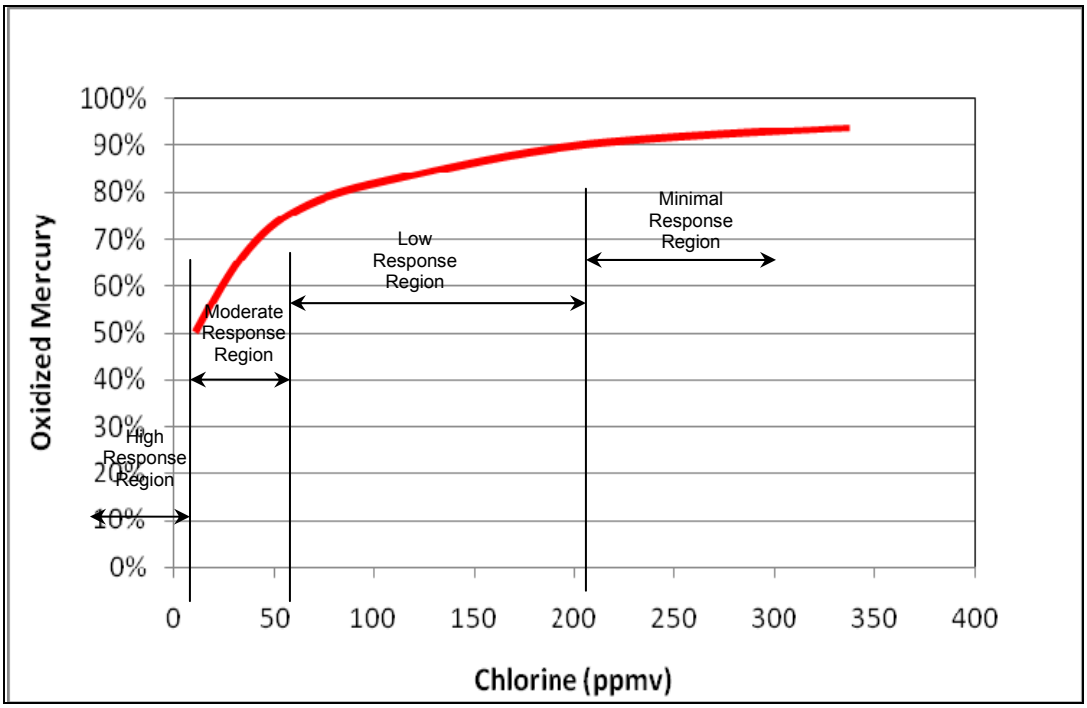

Figure 4-2
Generalized Effect of Chlorine Based on Average of All Data

The first region noted on the plot, labeled the "high-response" region, displays a very strong response to changes in chlorine level. In fact, over the range of chlorine in this region, from roughly 5 ppmv to 50 ppmv, the average mercury oxidation level increased from 50% to 73%, this is a 23% increase in absolute mercury oxidation, or from a relative standpoint, the mercury oxidation was increased by almost 50% compared to the 5 ppmv chlorine condition. This is a marked improvement in mercury oxidation, and demonstrates the dramatic improvement in oxidation that can be gained even by a relatively small amount of chlorine being added to severely halogen-depleted flue gases. In particular, for extremely low levels of chlorine, less than 5 ppmv, the response is dramatic, with just a few ppmv making a relatively marked difference in mercury oxidation.

The second region shown in the plot is considered a "moderate-response" region, and ranges from roughly 50 ppmv chlorine to 100 ppmv chlorine. In this region, the improvement in mercury oxidation with chorine is still appreciable, but not nearly as dramatic as with lower chlorine levels. From the average data, one can see that the absolute level of mercury oxidation improved by only about 10%, increasing from roughly 73% to 82% oxidation. In relative terms the mercury oxidation was only increased by roughly 12%.

The next range of chlorine levels shown on the plot is considered a "low-response" region, representing values from roughly 100 ppmv to 250 ppmv. In this region, the improvement in mercury oxidation varied from 82% to 93%. This is a relatively muted response considering the broad range in chlorine level.

The final range of chlorine levels, above 250 ppmv, is considered the "minimal-response" region. In this region, there are only marginal improvements in mercury oxidation, thus there is a point of diminishing returns when chlorine is increased above 250 ppmv. The research program did not investigate at what point there was a maximum in mercury oxidation with respect to chlorine level, but it is clear that mercury oxidation improved across the entire test range utilized in the program, albeit a very small improvement at high chlorine levels.

The previously described plot utilized the average of all the data to describe the general effects of chlorine on mercury oxidation across the catalysts, and to describe the various regions of response that would be expected for conventional catalyst. The plot does not, however, convey the differences between the various catalysts (and other operational parameters) in terms of the absolute levels of mercury oxidation that were noted during the testing. To help convey this information, Figure 4-3 was prepared, which shows the individual data points for each chlorine level tested, again based on the average of all the data acquired. In addition, the ranges of the data are included, showing the high and low values of absolute mercury oxidation that were measured for the four catalysts tested. Again, it is important to note that the range that is shown is due not only to differences in the catalyst design (including deNOx activity, SO_2 conversion, etc.) and volume, but also differences due to fuel characteristics (other than chlorine) and boiler operation. These ranges should provide, however, some feel as to what the SCR fleet as a whole might experience in terms of ranges.

In looking at the figure, it is notable that at very low levels of chlorine the range is quite broad, ranging from 40% to almost 70% oxidation. This mirrors to some degree the large variability noted with the inlet speciation. As the chlorine levels increase, the ranges of the measured values decreased, becoming much narrower, with the range at 150 ppmv of chlorine being only 10% mercury oxidation absolute. The reasons for this are unclear, but it may indicate that at high levels of chlorine, intrinsic differences in the catalyst designs (including volume), as well as boiler operation and fuel characteristics become less of a factor. *It is important to note that for chlorine levels above 150 ppmv, that only one catalyst was tested. Thus no range could be applied to this data. Therefore the lack of a range on these data should not be construed as meaning that all four catalysts had the same level of absolute mercury oxidation.* It is interesting to note that since the data at chlorine levels above 150 ppmv are based upon a single catalyst, that these data match so well the averages at the lower chlorine levels. In other words, there is no disjoint in the curve at this point. The fact that there is not a disjoint in the trend may be somewhat of a coincidence, although the narrowing of the range at higher chlorine levels would dictate that the oxidation for any one catalyst at these high chlorine levels would be fairly similar to the average of all other catalysts.

Overall, these data show that all of the catalysts tested behave similarly with respect to chlorine level in the flue gas. No catalyst had a markedly increased or decreased response to chlorine. In other words, the slope of the curve in response to chlorine was similar for all of the catalysts tested. However, the absolute level of mercury oxidation varied as a function of catalyst, presumably due to differences in intrinsic catalyst characteristics and volume, as well as boiler and fuel differences. Based upon the averages, the absolute level of mercury oxidation at the reactor increased by roughly 45% absolute, from roughly 50% oxidized mercury, to roughly 95% oxidized mercury. This is a relative increase in mercury oxidation of about 90%, or in other words, the level of oxidized mercury almost doubled over the chlorine range of < 5 ppmv to 350 ppmv.

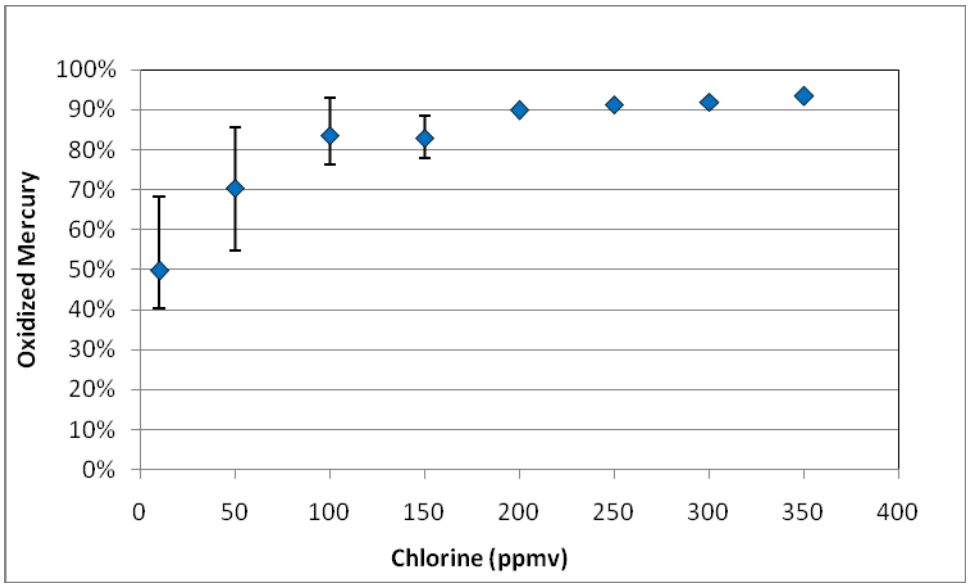

Figure 4-3
Average and Ranges of Mercury Oxidation vs. Chlorine – SCR Outlet

Effect of Chlorine on ESP Mercury Capture

Mercury capture was measured as the difference between total mercury at the ESP outlet and the MRC inlet corresponding to the test conditions of the previous graphs. However, the data taken for the single catalyst operated at the high chlorine levels was determined to be erroneous, and thus no data are available at the high chlorine levels (above 150 ppmv). Therefore, the averages shown associated with mercury capture are for the three catalysts tested at the lower chlorine range.

Figure 4-4 shows the general effect of chlorine level on mercury capture based upon the average of the data for the three catalysts for which data are available. The data for all catalysts showed very similar trends, with a roughly linear response to chlorine, as depicted on the plot. This is an interesting result if one assumes that mercury capture across the ESP is directly related to the proportion of oxidized mercury entering the ESP. If that assumption is made, then one would expect the mercury capture curve to be very similar in shape to the shape of the curve of oxidized mercury exiting the SCR. But this is not the case, and in general, one can see that the mercury capture across the ESP is not as low as one might expect given the shape of the curve for the SCR outlet.

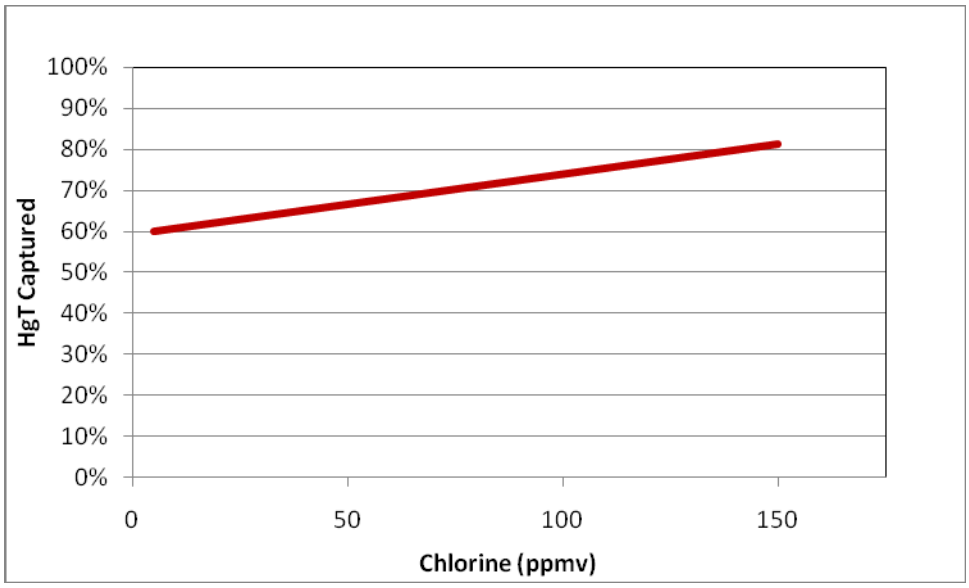

Figure 4-4
General Behavior of Total Mercury Capture with Respect to Chlorine

A closer analysis of the individual data[4] actually shows that the level of oxidized mercury exiting the SCR is not a good indicator for absolute mercury capture. In fact, the catalyst test series that produced the highest overall level of oxidized mercury actually showed the lowest ESP capture rate. Conversely, the catalyst test series that produced the lowest level of oxidized mercury produced the highest level of ESP capture. From this finding, it is readily apparent that ESP capture is strongly a function of parameters in addition to mercury speciation, presumably such as unburned carbon in the fly ash, ash loading, ash chemistry, etc.

Figure 4-5 helps to show some of the variability that was experienced in terms of mercury capture across the ESP. The range bars as shown on the figure demonstrate a very wide variation in mercury capture, much larger than the range in mercury oxidation that was present. This is an immediate indication that other factors that contribute to variability were at play. And, as mentioned above, one might expect that the data for the highest capture (the top of the range) would correspond to the test series which had the highest SCR outlet oxidation – this was not the case. Thus, overall ESP capture levels are expected to vary widely from facility to facility, even if the level of oxidized mercury exiting the SCR is comparable. It is clear, however, *that for any specific facility, the relative capture of mercury across the ESP will improve with the addition of chlorine*, at least over the ranges of chlorine tested. On average, the ESP capture increased by roughly 20% absolute, from just above 60% to just above 80%. This is a relative improvement in mercury capture of roughly 33%, which is substantial.

[4] The reader is not privy to the individual data corresponding to the different catalysts tested, due to concerns over anonymity and the possibility of making inappropriate conclusions related to the intrinsic mercury oxidation capability of the catalysts.

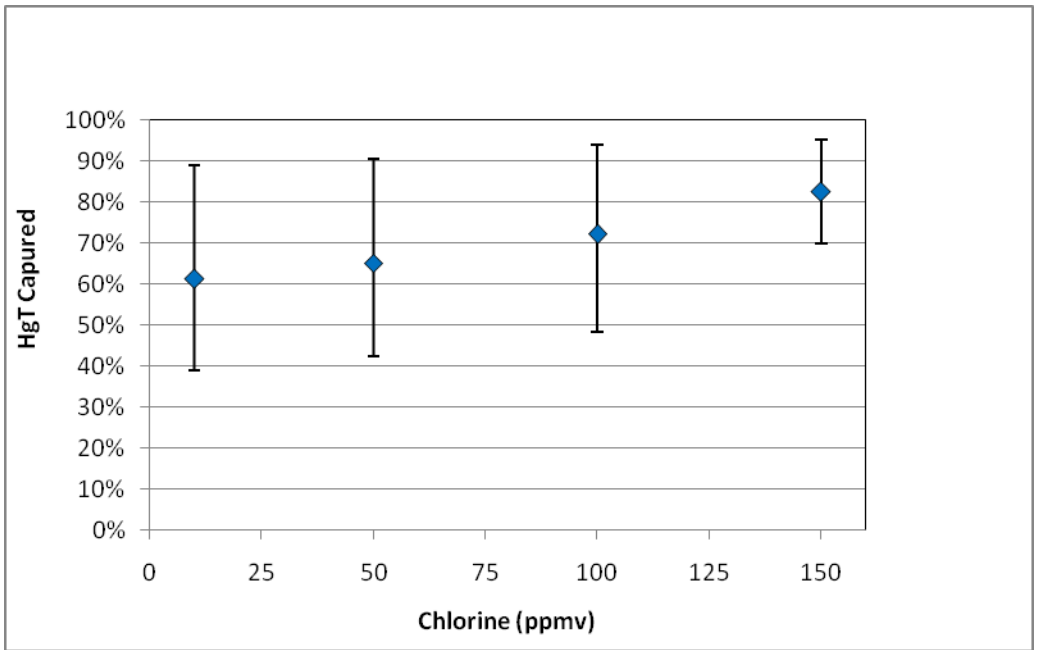

Figure 4-5
Average and Ranges of ESP Mercury Capture vs. Chlorine

The prior discussions related to ESP capture are particularly important for facilities not equipped with any additional downstream pollution control devices, such as wet or dry FGDs. These facilities would rely solely upon mercury capture through the ESP as the principal means of mercury control. Facilities equipped with FGDs will have an additional potential for mercury capture and will, in general, be able to realize mercury capture rates higher than those described for ESP capture alone, as indicated by the previous plots. The additional capture of mercury through a wet FGD, in particular, is largely dependent on the amount of oxidized mercury entering the FGD, and therefore available for capture, since wet FGDs typically capture elemental mercury poorly. Thus in considering the data in conjunction with facilities equipped with FGDs, the speciation of the mercury exiting the ESP is of particular interest.

Conclusions and Implications for Full-Scale Facilities – Effect of Chlorine

There is a clear, beneficial effect in terms of mercury oxidation and capture when levels of chlorine are increased. If all other factors are equal, then fuels having higher chlorine will likely exhibit better mercury oxidation than their lower-chlorine counterparts. It is important to note that these findings are relative in nature, however. In other words, higher levels of chlorine will improve mercury oxidation and capture with respect to the same fuel and operating conditions at lower levels of chlorine. On average, the data show that the level of oxidized mercury exiting the SCR can almost be doubled, to a high of almost 95% oxidized mercury by increasing the chlorine level from a very low < 5ppmv to roughly 350 ppmv. This is roughly a 90% improvement in mercury oxidation across the SCR. Mercury capture data also show marked improvements across the available test range of 5-150 ppmv Cl. These data show that on average, ESP capture improved from roughly 60% to 80%, equivalent to a relative improvement of 33%.

Although the above findings are relative to the specific fuels utilized at the MRC, they offer some confidence as to the marked benefit that facilities which typically fire very low chlorine coals can realize by increasing the chlorine level of the flue gas. These findings apply most directly to the artificial adjustment of chlorine, through direct injection or fuel additives. If chlorine level is adjusted due to a fuel change, many other parameters, in addition to chlorine, are likely to change. Thus, there is no guarantee that a coal, for instance, which generates 100 ppmv of chlorine in the flue gas will necessarily provide more mercury oxidation and capture than coal which generates 75 ppmv of chlorine in the flue gas. This is because many other parameters which affect mercury oxidation may also change. However, there is a general sense from the data that higher chlorine fuels will indeed result, on average, in higher mercury oxidation and capture, at least over the ranges of chlorine tested (up to roughly 350 ppmv).

For flue gas chlorine levels less than roughly 100 ppmv, the effect of increased chlorine is quite marked on mercury oxidation across the SCR. The effect is especially marked at chlorine levels under 50 ppmv. Above 100-150 ppmv chlorine, the beneficial effects of additional chlorine are less apparent, although still appreciable. Above 200-300 ppmv, the effect becomes much more muted, and thus the incremental beneficial effects are only slight. In terms of ESP mercury capture, the beneficial effect of increased chlorine is linear across the range for which data are available (roughly 10 ppmv to 150 ppmv Cl). The slope of the response is quite steep, thus significant benefits in terms of ESP capture would be realized across the entire tested range. The data are insufficient to determine at what point the incremental beneficial effects of chlorine on ESP capture decline or cease.

Overall, for facilities operating with very low chlorine coal (< 50 ppmv chlorine in the flue gas or roughly < 800 ppmw of chlorine in the coal), there would be a marked benefit in artificially increasing the flue gas chlorine level by means such as flue gas injection or chlorine addition to the fuel. The incremental benefits decline as the overall chlorine level increases, however. The chlorine level may also, of course, be increased by a change in the fuel (via fuel blending or a total fuel change), but again, there is the caution that a fuel change will affect many parameters in addition to the chlorine level. Thus, the relative response in terms of mercury oxidation and capture may not abide by the same response curves shown in this report when a fuel change is made, since these other fuel factors may also affect mercury oxidation. Still, there is some confidence that with fuel blending, especially in cases where the overall coal characteristics are only changed marginally (by adding a small percentage of very high chlorine coal, for instance) that the beneficial effect of the increased chlorine will outweigh any negative effects from the fuel change. In any event, one must be certain in the case of a fuel change that an attempt to adjust any one parameter, such as chlorine level, does not have unintended consequences due to changes in other parameters.

5
EFFECT OF TEMPERATURE

Background

Catalytic processes are often strongly affected by temperature, depending on the relative contributions of kinetics and mass transfer as related to the reactants. Although the effect of temperature on the deNOx and SO_2 conversion reactions for SCR catalysts are quite well understood, the effect of temperature on mercury oxidation and capture is not. The effect of temperature is a complicated issue, since many factors are affected by a change in SCR operating temperature, including the kinetic reaction rate, the system volumetric flow rate, diffusion and mass transfer, etc. For a full-scale facility, temperature is usually linked to unit load, which will in turn affect flue gas mass flow rate. Load will also affect flue gas constituents to some degree, as well as SCR reactor performance in terms of ammonia slip. Thus a full-scale facility will not experience an independent temperature change, for which all other factors remain constant.

The relationship of temperature and unit load is strongly a function of the boiler and downstream equipment design. The flue gas temperature leaving the boiler, in fact, may not affect the operating temperature of the SCR, since installations equipped with economizer by-pass systems may be able to adjust the SCR temperature independently, to some degree. In these cases, the SCR temperature may be load independent over some loads (at low loads for instance, where only SCR minimum operating temperature is being maintained), while it may fluctuate at other loads. Furthermore, temperature changes at the boiler exit may not, in fact, result in a temperature change for systems downstream of the air preheater, depending on facility operations. For example, the air preheater outlet temperature may be held steady regardless of the inlet temperature, thus temperature changes at the SCR would not be mirrored by temperature changes at the outlet of the air preheater, cold-side-ESP, or FGD inlet and outlet. However, as stated above, other changes may occur, such as flow rate changes, due to changes in unit load.

Notwithstanding the above issues with the independence of the temperature variable for full-scale systems, industry data indicates that mercury oxidation across the SCR itself is suppressed to some degree by increasing temperature. This effect is opposite from many classical catalytic processes, where the reaction rate increases with temperature.

Testing Approach

The general approach of the testing was to isolate the SCR temperature effect as much as possible. This was done by holding the mass flow rate constant (i.e. constant scfm) while varying the operating temperature of the SCR by adjusting the relative flow of flue gas from the MRC economizer by-pass line. This allowed for a reasonably independent adjustment of

temperature, but it should be noted that mass transfer parameters would still be affected due to an increase in volumetric flow rate (i.e. acfm) due to the temperature change. *An important point to note is that the air preheater outlet temperature was held constant for all tests. Thus, given that the mass flow rate was also held constant, the ESP flow rate and temperature remained unchanged due to changes in the SCR operating temperature.* Presumably, the primary effect on ESP capture due to an SCR temperature change would therefore be only due to changes in mercury speciation entering the ESP. As stated previously, for an actual commercial SCR, the temperature and flue gas mass flow rate would be interlinked under most operating conditions, as a function of boiler load.

In terms of all of the parameters investigated during the project, the time required to reach equilibrium was greatest for a temperature change. This was due primarily to the thermal mass of the system. As a result, only two temperature conditions could be reached in a single operating day.[5] For almost all cases, therefore, the data presented represent a single operating day for during which low (625°F) and high (750°F) temperature conditions were tested. Testing in this manner prevented having to compare data that were acquired on different days, which would be subject to the variability previously discussed. One of the limiting factors in the data set is the fact that the four test series were performed at different levels of chlorine, two at 50 ppmv chlorine, and two at 100 ppmv chlorine. This was due to fuel changes in the later part of the program that precluded testing at levels lower than 100 ppmv chlorine. In subsequent discussions, when appropriate, the data are separated into subsets of 50 ppmv chlorine data and 100 ppmv chlorine data.

Effect of Temperature at the MRC Inlet

The effect of SCR operating temperature on the inlet mercury speciation would, of course, be unrelated to the catalyst installed, but there are two other potential sources that could produce a change in inlet speciation. The first is the relative speciation between the economizer by-pass flue gas and the economizer exit flue gas. Since the temperature for the SCR was adjusted by modulating the flow rates between the economizer by-pass and outlet, any speciation difference between these two sources would result in a change in the composite speciation entering the MRC/SCR. The second source of potential inlet mercury speciation variability is due to differences in surface or fly-ash catalyst mercury reactions as a function of temperature. If these reactions were strongly affected by temperature, they could conceivably affect the measured mercury speciation since some residence time is present prior to the measuring of the mercury. It is also possible that the change in flue gas temperature affected the mercury monitoring system, creating a bias. It is not possible to determine from the available data which of these effects, or some unknown effect, were responsible for the noted change in inlet mercury speciation.

[5] In one case, the temperature data were acquired over two days. For the two test days, the design temperature was tested to provide a common data point. In other words, on one day temperatures of 625° and 700°F were tested, and on the following day, temperatures of 700° and 750°F were tested. This allowed for the data to be corrected to account for the day to day variability. This methodology required only a small adjustment, and the overall data set and findings are not affected by the utilization of this correction method.

Figure 5-1 shows the MRC inlet mercury speciation as a function of temperature for the four test series. Note that a straight line has been fit to the two data points for each test series, allowing the slope of the data points to be determined easily from a visual perspective. *It is important to note that there are insufficient data to determine if the temperature effect is indeed linear, and the reader is cautioned against making that assumption. This is the case for all subsequent temperature dependency plots as well.* For three of the four test series, there is a small, but apparent, increase in mercury oxidation with respect to temperature. The remaining test series showed a virtually flat response. This finding is interesting and somewhat counterintuitive, since catalytic reaction data indicate a decrease in mercury oxidation would be expected. Further, gas phase equilibrium would not favor an increase in oxidized mercury with an increase in temperature. Variability was noted in the absolute mercury levels from test to test, with the inlet oxidized mercury proportion ranging from a low roughly 15% to a high slightly over 40%. Some of this variability would presumably be due to differences in chlorine levels between the tests series.

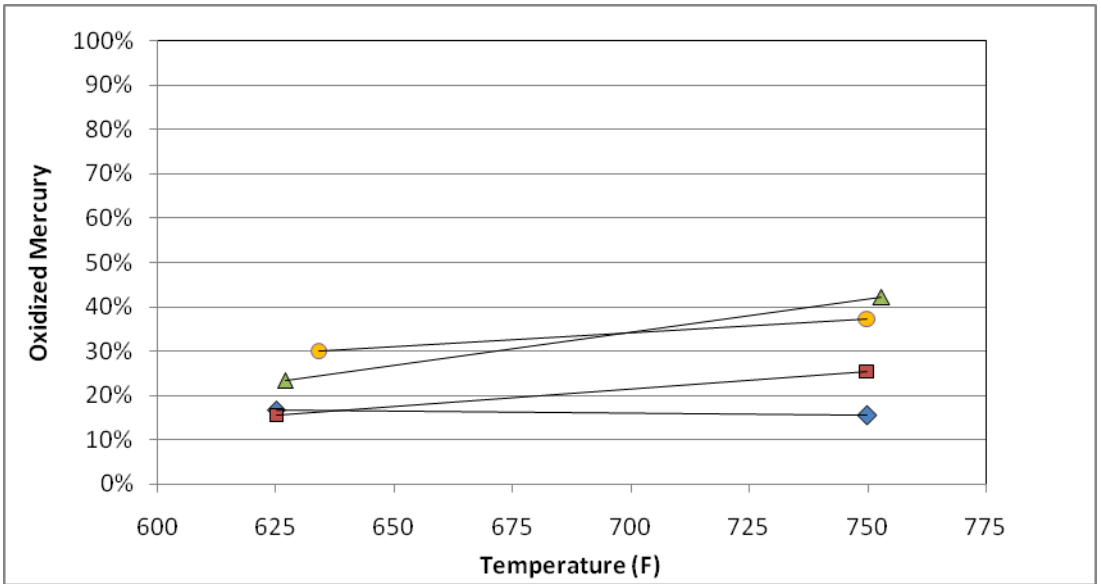

Figure 5-1
Effect of Temperature on MRC Inlet Mercury Speciation

Effect of Temperature at the SCR Outlet

Figure 5-2 shows the effect of temperature on the SCR outlet mercury speciation. The two points shown represent the average of all of the data (four catalysts), while the upper and lower ranges are shown by the bars. The ranges for these data were in general quite narrow, and the slope of the temperature effect line for each catalyst was virtually identical. This offers some confidence that temperature affects most conventional SCR catalysts in approximately the same way, at least in a relative sense. From a global perspective, it is apparent that increases in temperature adversely affect SCR oxidation. The oxidized mercury level decreased by 12% absolute, on average, for the catalysts tested over the temperature range of 625° to 750°F. This is a relative decrease in mercury oxidation of approximately 15% across the temperature range.

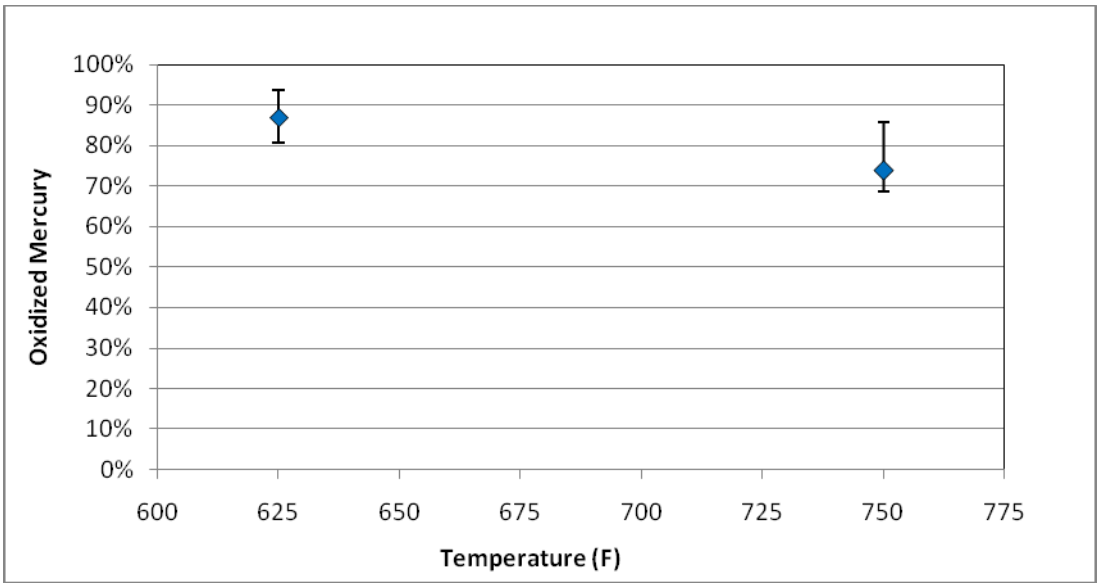

Figure 5-2
Effect of Temperature on SCR Outlet Mercury Speciation

Effect of Temperature on ESP Mercury Capture

As previously stated, the operating philosophy for the tests resulted in the ESP operating temperature and flow rate remaining constant for a variation of temperature at the SCR. Figure 5-3 shows the ESP capture response to temperature for each of the four test series, with the chlorine conditions for the tests noted in the legend. The data show a marked difference in the slope of the response from test to test. On two tests there was a small to moderate decrease in mercury capture, while on two tests there was a marked decrease. As previously mentioned, two test series were run at 50 ppmv chlorine and two at roughly 100 ppmv chlorine. This chlorine difference could conceivably be a source of the differences in capture behavior, but the data are inconsistent with respect to chlorine, as noted on the plot, and one could conclude that chlorine is not governing the response. Intraday variability (due to changes in ash parameters, such as LOI, for example) could be a major contributor, at least for the two test series that show the most marked change in capture, but this degree of intraday variability has not been seen with the other test data. Overall, the data are consistent in that a decrease in ESP capture will be experienced with respect to SCR operating temperature - the magnitude of that decrease, however, is inconsistent for the available data.

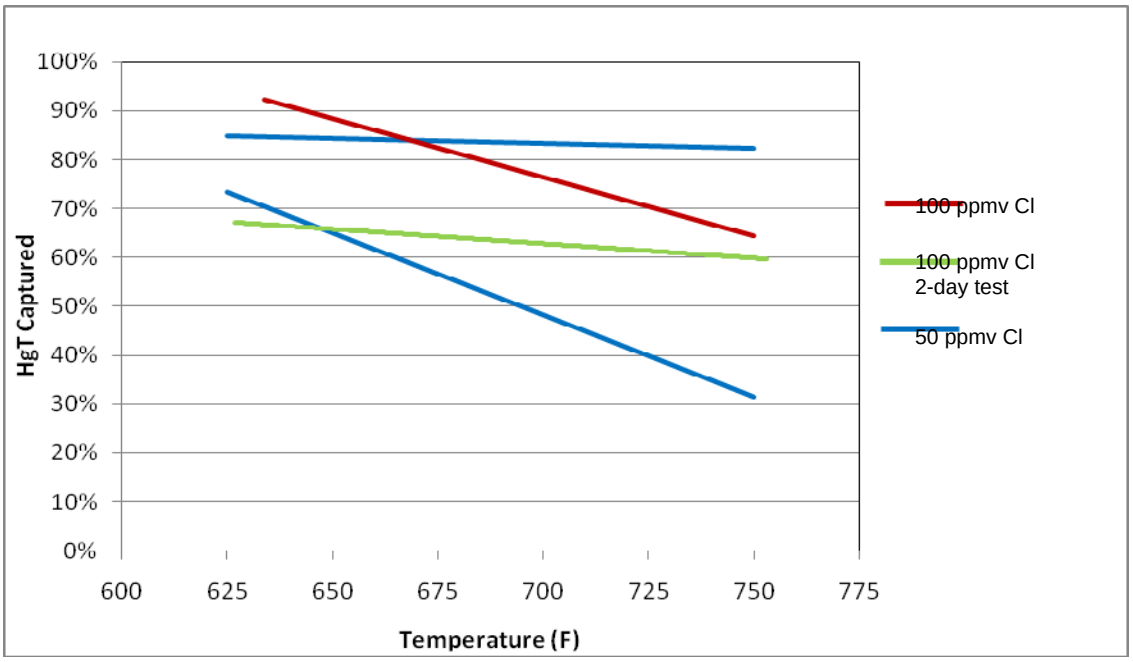

Figure 5-3
ESP Mercury Capture Response to Temperature – Individual Test Series

Figure 5-4 shows the data in terms of the average of all the data, with high and low ranges applied. The wide range at the 750°F is apparent, as indicated by the previous plot. Figure 5-4 shows that on average, the mercury capture decreased by 13% absolute (equivalent to a relative decrease in mercury capture of about 16%). Interestingly, this is almost identical to the decrease in absolute oxidized mercury exiting the SCR as described in the prior section. In light of the previous plot and discussions, one is cautioned against utilizing this average value with too much confidence, however.

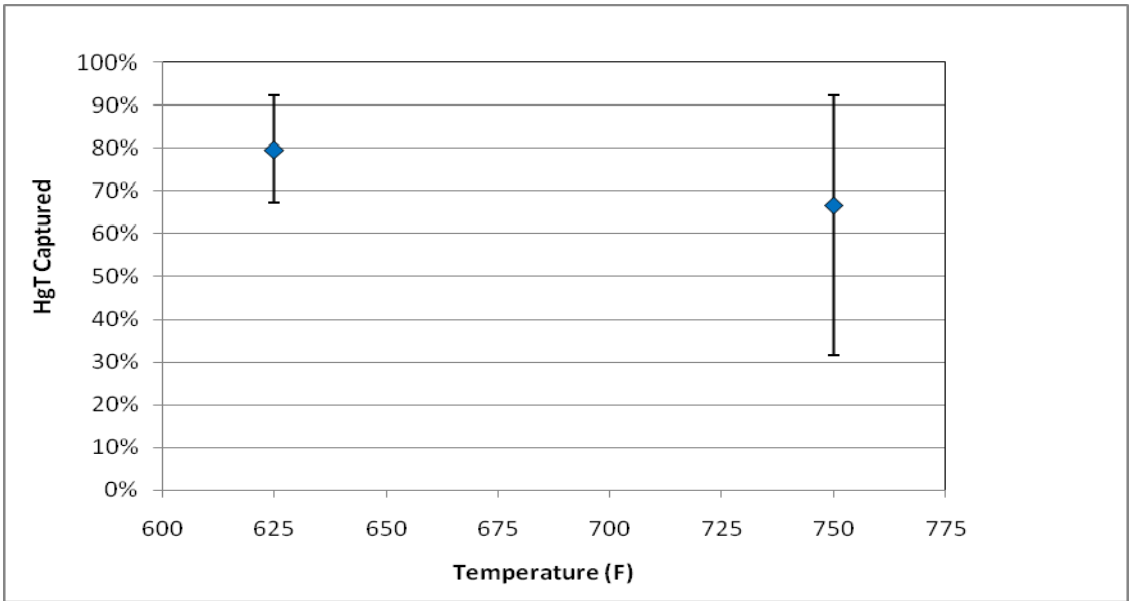

Figure 5-4
Average and Ranges of ESP Mercury Capture vs. Temperature

Conclusions and Implications for Full-Scale Facilities – Effect of Temperature

Overall, increased temperature has a negative effect on both SCR mercury oxidation and mercury capture. All of the catalysts tested had a very similar response to increases in temperature, with the average decrease in SCR mercury oxidation at about 12% absolute (15% relative). In terms of ESP capture, the decrease in captured mercury was roughly 13% absolute (16% relative) on average, consistent with the decrease in SCR mercury oxidation. However, this average value for ESP capture is somewhat misleading, since the individual test series showed quite a large variability. The source of this variability in response is unknown.

The above findings are associated with an independent change in temperature, since the mass flow rate (scfm) and air preheater outlet temperature were held constant for these tests. If temperature was the result of a load change, then a change in other parameters, such as flow rate or air preheater outlet temperature, may impact the response, especially in terms of mercury capture.

For full-scale facilities, lower temperature operation of the SCR is generally beneficial at least in terms of SCR mercury oxidation. For retrofit facilities, lowering the operating temperature via boiler operating practices, or boiler back-end modifications, will help to maximize SCR mercury oxidation and capture. For green-field installations, a boiler/SCR design which provides for generally lower SCR temperatures will help to maximize the achievable mercury oxidation through the SCR, at least with conventional catalysts. Lower operating temperatures also have potential benefits in terms of SO_2 oxidation, and this may, in fact, contribute to the improved mercury capture across the ESP. Of course the benefits of lowering the SCR temperature, in terms of increased mercury oxidation, must be weighed against the potential loss in reactor potential for NOx removal.

6
EFFECT OF FLOW RATE

Background

SCR systems are affected by flow rate due to changes in the mass throughput of the reactor, as well as changes in mass transfer parameters. Increased flow rate through the SCR results in higher ammonia slip or lowered deNOx, if slip is held constant. The rate of SO_2 conversion through the SCR will generally vary inversely proportionate to flow rate. The effect on mercury oxidation, however, is not clearly understood in terms of full-scale systems.

As with temperature changes, flow rate changes have multiple effects on the system as a whole, including residence time effects, mass-transfer effects, and ammonia slip effects associated with the SCR. Flow rate changes will affect the temperature profile within the air preheater and will have the potential to affect ESP and FGD capture due to residence time and mass transfer differences.

Testing Approach

The effect of flow rate was examined by varying the flow rate through the MRC while holding the other operating conditions constant. As mentioned in the temperature discussions, this is somewhat different from a full-scale commercial SCR where flow rate and temperature are likely to be interlinked. The design flow rate differed slightly from catalyst to catalyst, thus the flow rate conditions were selected based on percent of design. In general three flow rate conditions were utilized: 75%, 100%, and 125% of design, and the three flow tests were typically conducted over a single day of testing. However, in some cases, primarily early on in the project, the flow tests were done over more than one day of testing. This decreases the confidence in those data, although the data appear to be consistent for all of the test series. One additional mitigating factor is that the coal variability was much lower during the early phases of the project, helping to bolster the confidence of the early data, even though they were acquired over separate test days.

It is important to note that data are only available for three test series. This is due to the final test series being truncated due to time and budget concerns. In addition, data at the design flow condition are not available for one of the test series, due to erroneous mercury speciation data. This loss of a single data point does not significantly affect the overall data set.

Effect of Flow Rate at the MRC Inlet

Theoretically, the flow rate through the MRC should have little effect on the inlet mercury speciation, since the variation in flow will cause minimal changes to other parameters, except for a slight change in residence time prior to the inlet mercury speciation being measured.

Figure 6-1 shows the effect of flow rate on the MRC inlet mercury speciation for the three test series for which data are available. These data show virtually no change in speciation as a function of flow rate, as one would expect. This offers some confidence that the global operating conditions for the boiler remained constant throughout the test periods.

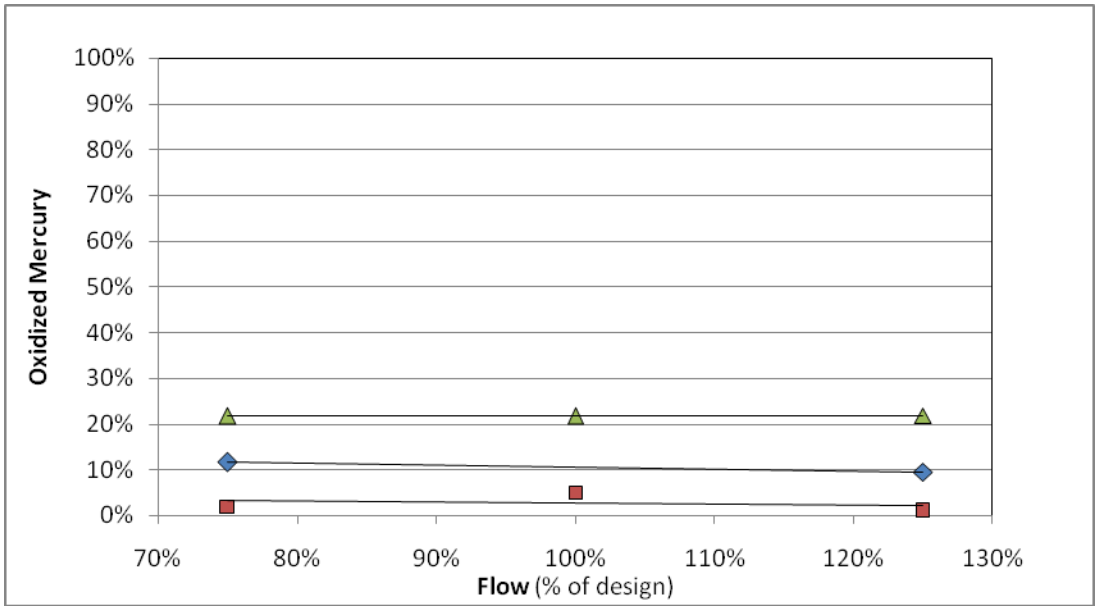

Figure 6-1
Effect of Flow Rate on MRC Inlet Mercury Speciation

Effect of Flow Rate at the SCR Outlet

Figure 6-2 shows the effect of flow rate on the SCR outlet mercury speciation for the three test series, based upon the average of all data and the high and low ranges. The variability between test series is quite small, and *all catalysts behaved in generally the same manner, with very little effect due to flow rate.* Thus, the response indicated by the averages shown on the plot is consistent with all of the catalysts' individual responses. This is an interesting finding, since intuitively one might expect that the lower residence time and higher reactor mass flow would reduce the capability of the catalyst to oxidize mercury. Mass transfer will be slightly improved due to the increased flow through the reactor, which would help to improve oxidation, but the beneficial mass transfer effect should not be particularly large. The data may indicate that an equilibrium is being reached, and thus additional residence time is not advantageous, but the data should not be used to conclusively make this assumption.

It is also important to note that the range of flows tested is equivalent to a boiler turn-down to 60% of full load. Actual boilers may have turn-downs much greater than this, and therefore may see a greater effect across the actual load range. And, as discussed, a boiler load change would also likely affect temperature, thus the actual mercury speciation effect would be greater than that indicated by Figure 6-2 in cases where a load change is made. One important note is that based on the available data, the effect on mercury oxidation across an SCR due to a boiler load change will be primarily due to the temperature change, not the flow rate change. Thus, the temperature dependency, as described previously, could be used to some degree as a surrogate for load change dependency, at least for the mercury oxidation behavior across the SCR, and for moderate changes in load.

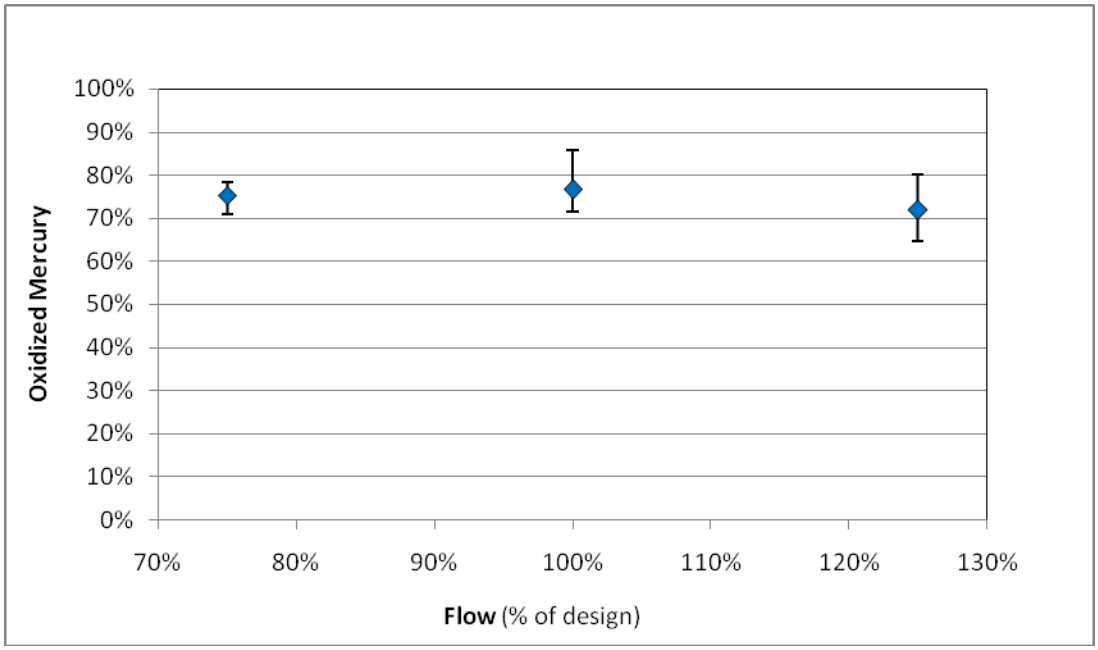

Figure 6-2
Effect of Flow Rate on SCR Outlet Mercury Speciation

Effect of Flow Rate on ESP Mercury Capture

A change in flow rate for the MRC inlet results in a commensurate change in flow rate through the ESP, since all temperatures were held constant. Thus, the residence time through the ESP would decrease with increasing flow rate. The decreased flow rate may also lead to some changes in mass transfer parameters. Given that there was very little effect on the SCR outlet mercury speciation due to flow rate, one could assume that any effect noted with the ESP capture would be due primarily to this residence time change (both through the ESP and air preheater), as well as a slightly different temperature profile through the air preheater.

Figure 6-3 shows the ESP capture data for the flow rate variation, again as a function of the average of all of the data, and the high and low ranges. As with the SCR data, all tests series showed approximately the same behavior, with the average values being a good indicator of the individual behaviors. Thus, very little effect was noted on ESP capture due to flow rate changes.

This is surprising since intuitively one might expect that the changes in residence time would affect ESP capture noticeably. Looking at the ranges of data, it is apparent that the absolute capture between the test series varied widely. Again, the response to flow rate was flat for all test series, but in some test series the overall capture was very high, while in others, the capture was very low. This is partly due to differences in the oxidation levels exiting the SCR, but in looking at the prior plot, the ranges of speciation exiting the SCR were miniscule compared to the ranges in capture. Thus, one could conclude that other parameters, such as LOI, were governing the absolute levels of mercury capture across the ESP.

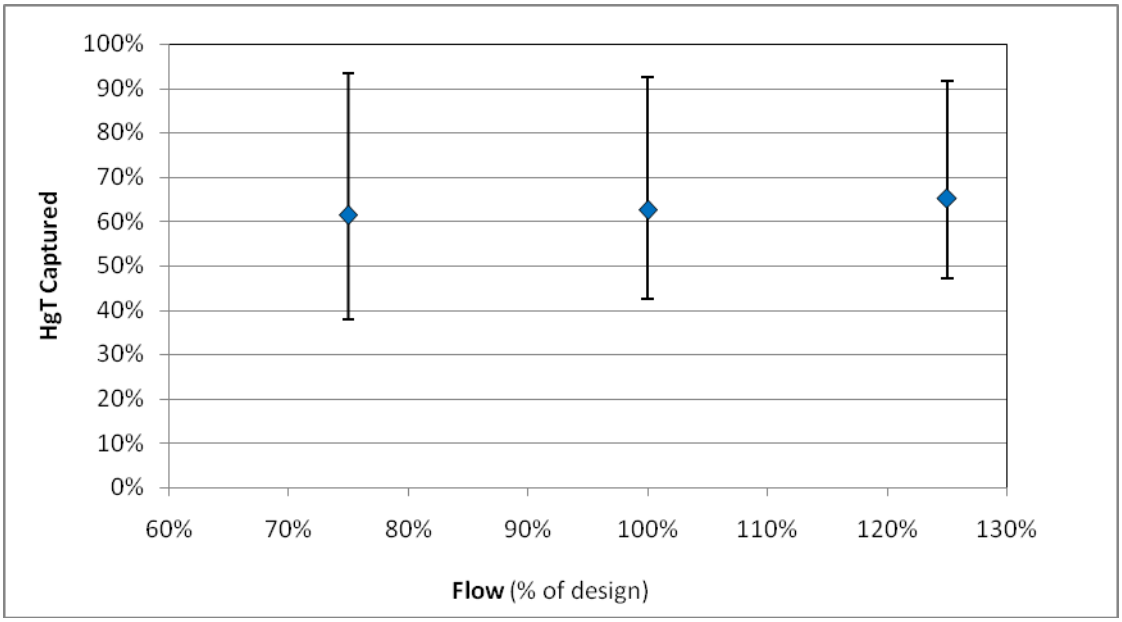

Figure 6-3
Effect of Flow Rate on ESP Mercury Capture

Conclusions and Implications for Full-Scale Facilities – Effect of Flow Rate

Flow rate appeared to have very little direct effect on either mercury oxidation across the SCR or on mercury capture across the ESP. This is, of course, based on the relatively narrow flow rate range tested, which was equivalent to a unit reducing load to 60% of design. For full-scale units, which routinely have larger turn-downs, the effect of flow may become more apparent.

The data are based on an independent change in flow rate (i.e., all other operating parameters were held steady). For a full-scale unit, flow rate changes are usually, primarily the result of a load change, which may also be accompanied by a temperature change. As discussed prior, lower temperatures improve mercury oxidation and capture, thus a load decrease would generally improve mercury oxidation and capture more than what may be indicated by the flow rate data alone.

7
EFFECT OF AMMONIA

Background

Industry data indicates that the presence of ammonia has an inhibiting effect on mercury oxidization across SCR catalysts. This effect is presumably due to the ammonia competing for sites that are active for mercury oxidation, but other more complex mechanisms may be involved. Only rarely are SCRs operated without any ammonia injection, so the investigation of low levels of ammonia (low deNOx) is somewhat academic, but it does provide useful data from a theoretical standpoint. The mercury oxidation response of a catalyst to varying higher levels (near design) of ammonia is an important parameter, since many parameters affect the ammonia profile in the reactor, such as temperature, flow rate, inlet NOx level, desired deNOx level, as well as catalyst activity, volume, age, and deactivation rate. Furthermore, the general health of an SCR system in terms of distributions, fouling, etc., will greatly affect the ammonia profile through the reactor.

Testing Approach

The general testing approach, with respect to ammonia, was to vary the level of deNOx and measure the resultant effects on mercury oxidation and capture. As the deNOx was varied, the ammonia profile through the reactor would of course change, as would the potential for ammonia slip. Ammonia slip, in particular, may be an important parameter for mercury capture, and it is important to note that ammonia slip was not measured directly – it can only be inferred from the deNOx data. Various parameters, such as maldistributions, catalyst activity, volume, etc., will all have an effect on ammonia slip in addition to the deNOx level, and this certainly may be the source of some of the differences that were noted between the various test series. To fully understand the effects of ammonia slip on mercury capture, testing would need to be conducted which measured the ammonia slip directly, rather than inferring it from the deNOx level.

For the first three test series, deNOx was varied across the range of 0% to 90%, and in some cases higher. For the final truncated test series, data at 0% and 90% deNOx were acquired, but data were not acquired for values in between these levels. Thus, the final data set is not as extensive as the previous three. It is important to note that two catalysts were tested at 50 ppmv chlorine, while the remaining two catalysts were tested at 100 ppmv chlorine. The differences in chlorine level were due to fuel changes at the host boiler, which precluded testing at the lower chlorine level during certain periods of the test program. These differences in chlorine level may impact the way in which the system responds to deNOx variations, as discussed in detail below.

Effect of Ammonia at the MRC Inlet

Theoretically, there should be no effect on the MRC inlet mercury speciation due to variation in the SCR deNOx level. This is because the inlet speciation is measured prior to the ammonia injection. Therefore, any variability noted in the inlet data would be strictly the result of speciation variations created by the boiler itself.

Figure 7-1 shows the variation in MRC inlet oxidized mercury at the testing conditions. As expected there is no clear trend with respect to deNOx, and as previously stated, any variability noted is attributable to the native speciation exiting the boiler. MRC inlet oxidized mercury ranged between 10% and 45%. The relatively steady nature of the inlet mercury speciation (within a particular test series) offers some confidence that the boiler was operating at constant conditions (including fuel, etc.).

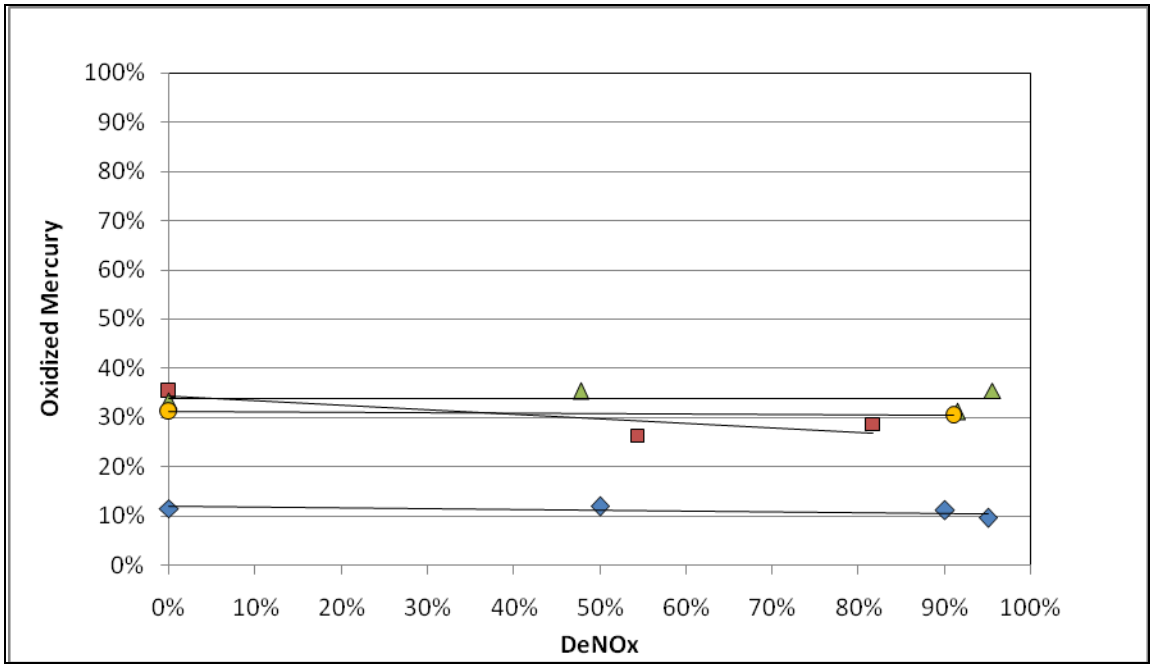

Figure 7-1
Effect of DeNOx on MRC Inlet Mercury Speciation

Effect of Ammonia on SCR Outlet Mercury Speciation

The effect of ammonia level on the SCR outlet mercury speciation is more difficult to analyze compared to the previously discussed parameters due to the variation in behavior that was noted for the different test series/catalysts. Figure 7-2 shows the average and ranges of the data, similar to previous plots. The range at the higher level of deNOx becomes quite large (with the exception of the last data point, where very little data were available). This large range indicates a difference in behavior between the various test series.

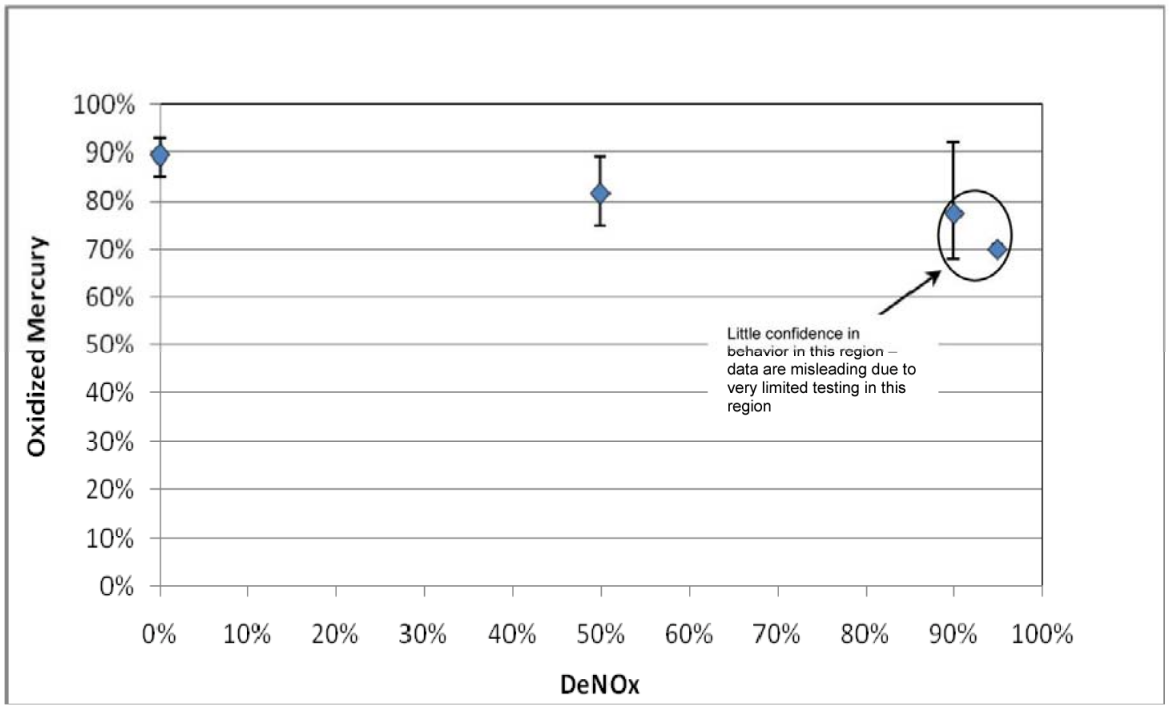

Figure 7-2
Effect of DeNOx on SCR Outlet Mercury Speciation – Average of All Data and Ranges

There were two general responses noted, one type of response was flat and was exhibited by two catalysts, and the other type of response was relatively steep and exhibited by the other two catalysts. By separating the data into two response types, the behavior can be better noted, as shown in Figure 7-3. In this figure, the upper line represents all data from the two catalysts which showed a relatively flat response, which were in fact tested at roughly 100 ppmv chlorine. The lower line on the plot was created from all available data from the two remaining catalysts, for which a more dramatic effect is noted. These two catalysts were tested at 50 ppmv chlorine. The data are probably insufficient to confidently state that the chlorine level controls the response to deNOx, but there is at least an indication that this may be occurring. The differences in the two response regimes are quite marked, with the high-chlorine regime showing very little effect due to deNOx, while the low-chlorine regime shows a marked effect due to deNOx, with the absolute mercury oxidation falling by almost 18% across the deNOx range of 0% to 90%. This is a relative decrease of roughly 22%. All data in both regimes do indicate a roughly linear response to deNOx although the exact nature of the response at very high deNOx levels (90%-95%) is difficult to determine from the limited data.

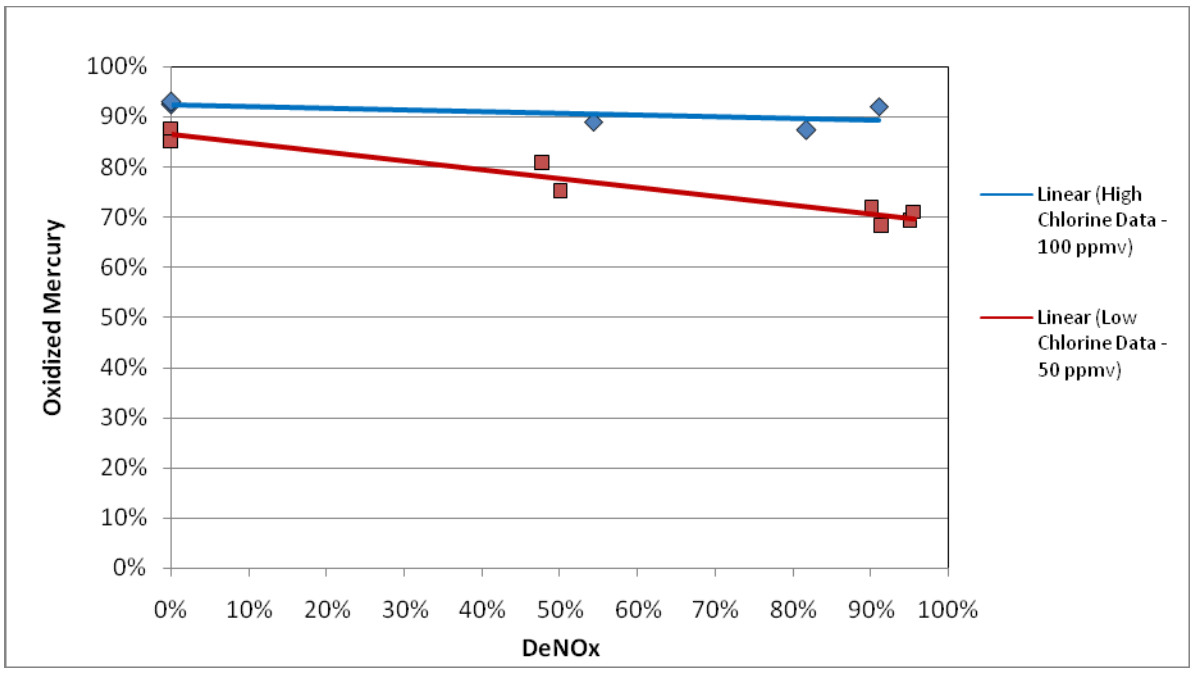

Figure 7-3
Effect of DeNOx on SCR Outlet Mercury Speciation – Responses Grouped based on High and Low Chlorine

Overall given the limitations of the data there will be a minor to marked negative effect on mercury oxidation due to ammonia injection. The data indicate that the chlorine level may impact the way a catalyst responds to deNOx, but this cannot be established with absolute confidence. It appears that the response to deNOx will be linear in all cases up to roughly the design level of deNOx. The behavior at very high deNOx levels is unclear and may deviate from the linear response seen at lower deNOx levels. Severely deactivated catalysts, or SCR systems that are operating outside of normal design parameters, may exhibit behaviors that are very different from that indicated by this data. Additional tests on deactivated SCR catalyst would help understanding the impacts of overall reactor potential on elemental mercury oxidation.

Effect of Ammonia on ESP Mercury Capture

The data, with respect to ESP mercury capture, are somewhat similar to that for the SCR outlet oxidized mercury in that two distinct groups of behavior were noted, again partitioned according to the chlorine level. First, the averages and ranges of the capture data are shown in Figure 7-4, which combines all of the data to show the trend. Thus the trends of the data as a whole show a gradual increase in mercury capture with respect to deNOx, with a relatively sharp uptick in the very high deNOx region.

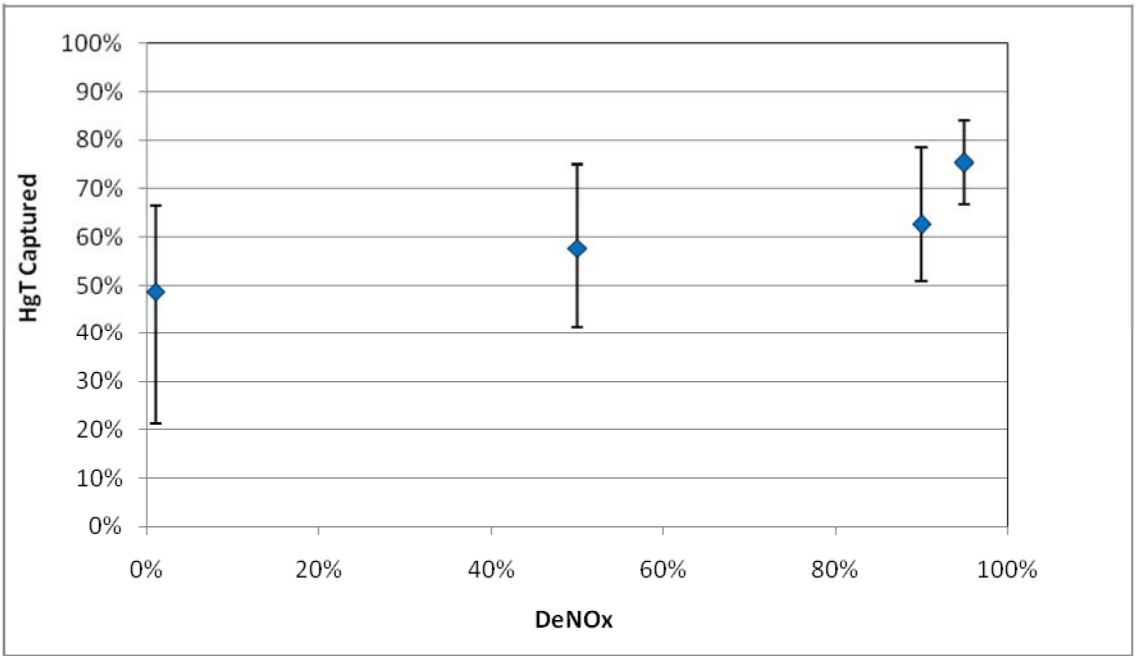

Figure 7-4
Effect of DeNOx on ESP Mercury Capture – Average of All Data and Ranges

However, as before, the previous data are somewhat misleading, as can be seen from Figure 7-5. In this figure, the data are averaged according to two groups, high and low chlorine, for which the behavior was almost identical. In the high-chlorine group, as in the previous report section, there was very little effect with respect to deNOx. One might expect this given the flat nature of the response in SCR outlet mercury oxidation (all other factors being equal). For the low-chlorine data, there was a marked improvement in mercury capture with respect to deNOx, showing an increase in ESP capture of roughly 20% absolute (nearly 40% relative). *This is counterintuitive, since for this group of catalysts, one might expect the mercury capture to decrease with deNOx, since the level of oxidized mercury decreased rather sharply across the range.* Further, for this subset of data, there is a noticeable uptick in mercury capture between 90% and 95% deNOx. This uptick was very consistent for the two catalysts tested at low chlorine levels. *A similar uptick was not noted in the high-chlorine data, but this was generally due to a lack of data in this region – thus it is unclear if chlorine plays a role in the presence of this uptick or not.*

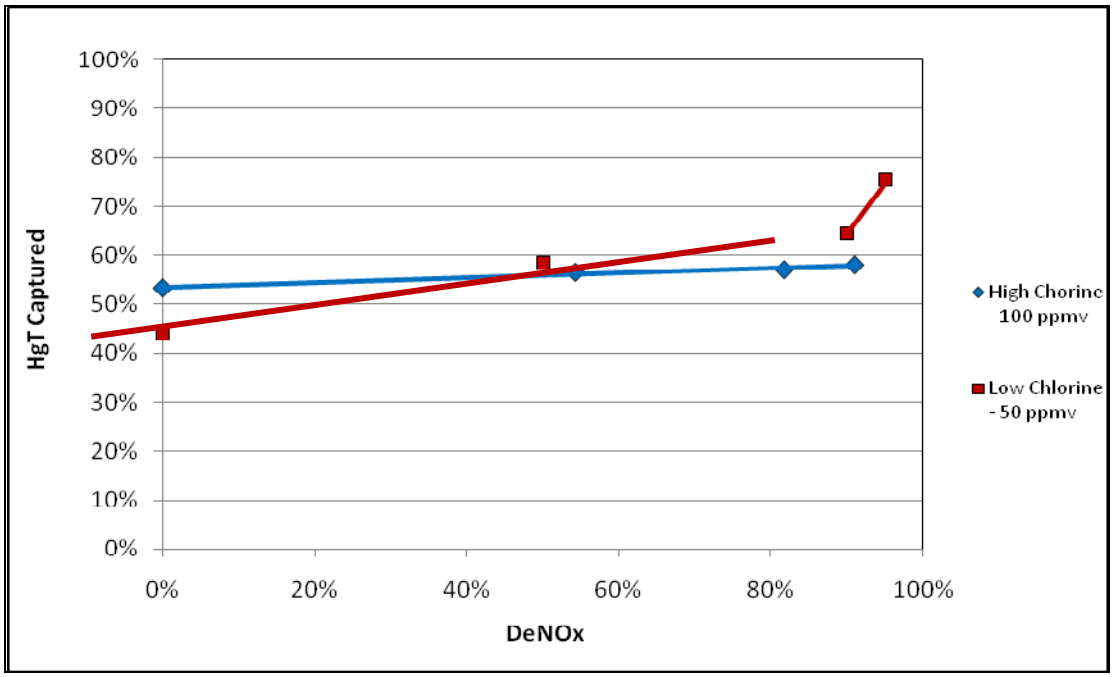

Figure 7-5
Effect of DeNOx on ESP Mercury Capture – Responses Grouped based on High and Low Chlorine

The improvement in ESP mercury capture in spite of a general decrease in oxidized mercury exiting the SCR (especially for the low-chlorine cases) is a surprising behavior, as one would expect a decrease based upon the SCR speciation data. Taken at face value, the data would indicate that this effect is more pronounced at lower levels of chlorine. One prevailing theory explaining the response of ESP capture to deNOx is that ammonia slip, which increases with deNOx, may be scavenging SO_3, which in turn helps to maximize mercury capture on ash active sites, since SO_3 generally acts as an inhibitor for that capture. More testing would be required to fully understand the response of ESP capture to deNOx, as well as the interrelationship of chlorine and deNOx/ammonia on SCR mercury oxidation and ESP capture.

Conclusions and Implications for Full-Scale Facilities – DeNOx Effect

The effect of deNOx on mercury oxidation and capture is somewhat academic, especially at very low levels of deNOx, since it seems unlikely that a full-scale facility would heavily adjust deNOx specifically for the purpose of mercury oxidation and capture. However, the data do offer some insights related to the mechanism of mercury oxidation and capture. In addition, the data provide some basis for developing some practical guidance related to catalyst aging, ammonia distribution, etc.

The data clearly show that ammonia has an inhibiting effect on mercury oxidation across the SCR. This effect is consistent for all of the catalysts tested in the program. However, the inhibiting effect seems to be most apparent at low levels of chlorine (50 ppmv), where an absolute decrease in SCR mercury oxidation of roughly 18% (22% relative) was noted for the range 0% to 90% deNOx. At higher levels of chlorine (100 ppmv), the adverse effect on SCR

mercury oxidation was much more muted. The confidence in this finding is somewhat limited in that only two catalysts were tested at the low chlorine condition, and two at the higher chlorine condition – more data would be necessary to fully understand the interrelationship of chlorine and deNOx with respect to the behavior of the catalysts when the deNOx level is changed.

In terms of ESP capture, the decrease in SCR mercury oxidation is not adverse since ESP capture actually improves with deNOx. This is counterintuitive. As with the SCR oxidation data, ESP capture response appears to be different depending on the chlorine level. ESP capture improves only slightly for high chlorine conditions, but the improvement is marked for low-chlorine conditions.

The counterintuitive effect on ESP capture requires additional testing to fully determine the sources of the effect, but it is clear that increased deNOx levels will not have an adverse effect for units relying solely on ESP capture as a means of mercury control – at least for facilities that have fuels and equipment designs similar to those of the test program.

If ammonia slip is the controlling factor in the improved ESP capture rates, then facilities relying solely on ESP mercury capture would not experience adverse effects from very high deNOx conditions (greater than design). This is also potentially true for catalyst aging, which typically leads to higher slip levels. Maldistributions leading to higher slip may also result in improved ESP mercury capture. It is important to note, however, that all of these statements are predicated on ammonia slip being the underlying cause for the improvement in ESP capture. If slip is not the cause, then these statements may or may not hold.

8
INTERLAYER MERCURY MEASUREMENTS

Background

One of the goals of the research program was to examine the speciation of mercury between catalyst layers. This analysis helps to determine the effects of ammonia on mercury oxidation (since upper catalyst layers will have a higher ammonia level than lower layers). The data are also valuable in better understanding the reaction mechanisms, as well as the interrelationship of variables, such as chlorine and ammonia.

Testing Approach

The testing approach was to use a semi-continuous Tekran mercury system to determine the interlayer mercury speciation. This system utilized a wet impinger system to determine the mercury speciation. This system is of course different from the continuous dry Thermo-Electron systems utilized for the other mercury measurements. There is always a concern of bias when two different instruments or analytical methodologies are utilized for comparative mercury measurements, so the confidence in the data is somewhat diminished by this fact. In addition, the interlayer mercury measurements typically involved conditions of very high ammonia compared to the SCR inlet and outlet locations. This high level of ammonia could conceivably adversely affect the interlayer measurements due to interferences.

Interlayer measurements were only made during one test series, owing to the difficulties and costs associated with making these types of measurements. Further, and perhaps most importantly, very poor spike recoveries made the confidence in the data extremely limited. (These very poor recoveries were mainly obtained after the first interlayer test series – the data reported had modest recoveries, for which the data are thought to be reasonably accurate.) Given the difficulties, costs, and poor data quality of the interlayer measurements subsequent to the first test series, the interlayer testing was ultimately abandoned, and thus data are available for only one test series. This particular catalyst for which the interlayer data are available had three layers, and the interlayer measurement location was between the second and third catalyst layer. Thus, the interlayer measurements were taken downstream of two-thirds of the catalyst.

The data presentation generally follows that of the previous sections in that interlayer data are presented on the basis of the variable being examined, i.e. chlorine, temperature, flow rate, and deNOx.

Interlayer Mercury Measurements – Effect of Chlorine

The first set of interlayer measurements to be reported is from the chlorine test series. Again, these data are from a single test series, corresponding to a single catalyst. The data were taken downstream of the second of three layers of catalyst.

Figure 8-1 shows the mercury speciation data for four levels of chlorine at the MRC inlet, SCR interlayer, and SCR outlet locations. Note that the data representing the lowest chlorine level (native chlorine at roughly 5 ppmv), was taken on the day prior to all of the other data. These data appear to be relatively consistent with the other data, however, at least based on the MRC inlet mercury level. The data were acquired at roughly 90% deNOx, 700°F, and design flow. Polynomial fits have been applied to all of the data to help visually determine the shape of the response curve. All of the data are roughly linear, as plotted, but it is important to note again that the SCR interlayer measurement was taken downstream of two-thirds of the catalysts. Thus for a perfectly linear plot, the data would show that the first two-thirds of the catalyst accomplished roughly the same amount of oxidation that the final one-third of catalyst did (in terms of the increase in the absolute level of oxidized mercury present). Given that these data are approximately linear, one can conclude that the final layer of catalyst was oxidizing elemental mercury at a higher rate than the previous two catalyst layers, especially considering the fact that the overall elemental level was lower at the final catalyst layer. (Thus a much higher percentage of this elemental mercury would have to be oxidized to give the same absolute increase in oxidized mercury percentage.) This finding is consistent with other project data which shows suppression of oxidation due to ammonia, since of course the upper layers of catalyst would have relatively high ammonia levels compared to the final layer. One may be tempted to make conclusions that relate the fine details of the shape of the response curves to chlorine level. The reader is cautioned against making such conclusions, since the absolute accuracy in the interlayer measurement is probably not great enough to make such conclusions with any confidence.

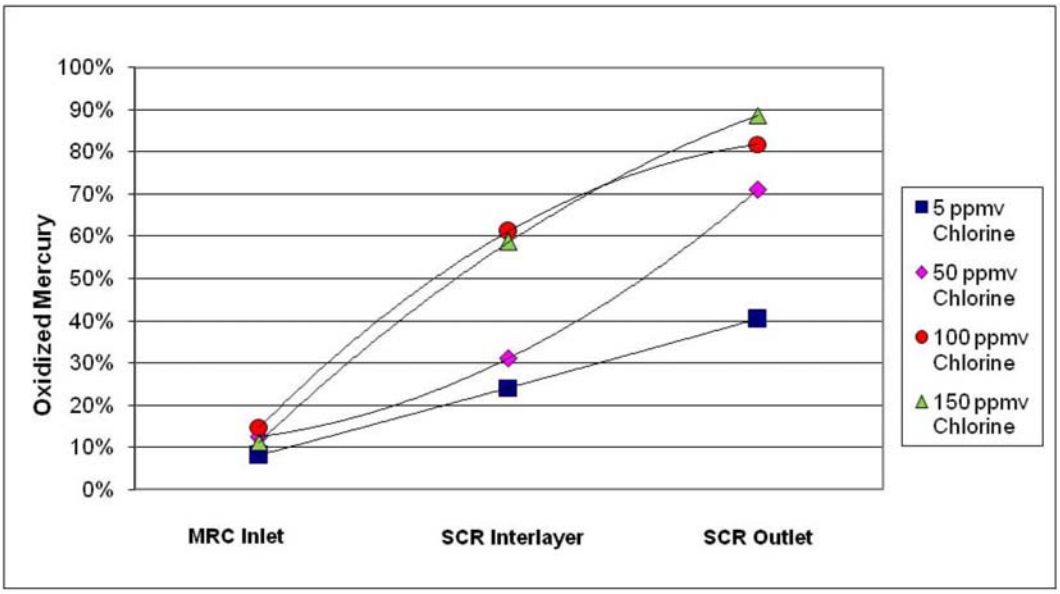

Figure 8-1
Mercury Speciation vs. Location and Chlorine Level

Interlayer Mercury Measurement – Effect of Temperature

Similar data to that shown in the prior plot is shown in Figure 8-2, but as a function of temperature. These data were acquired at approximately 90% deNOx, 50 ppmv chlorine, and design flow. The mid-temperature data are similar to that shown previously, with the data as plotted being roughly linear, indicating that the first two-thirds of catalyst increased the oxidized mercury level by roughly the same amount that the final layer of catalyst did. At face value, the high-temperature data shows very little oxidation occurring across the first catalyst layer, thus virtually all of the oxidation that is noted occurred across the last catalyst layer. For this high-temperature condition, there appears to be a very strong suppression of mercury oxidation across the upper catalyst layers having high levels of ammonia, at least according to this data. The low temperature data also shows more suppression than the mid-temperature data, but not to the degree that the high-temperature data does. An examination of the inlet speciation, however, shows that for the low and high-temperature data, the proportion of oxidized mercury entering the SCR was higher. Thus this parameter may, in fact, be the controlling factor in the shape of the response curve. This brings into question the quality of the data, in that there is no clear trend in the response with respect to temperature, and there are inconsistencies in the inlet speciation. Caution should be taken, therefore, in applying any conclusions with too much confidence, as the accuracy of a very few interlayer measurement data points is critical to the analysis. Additional data would be required before one could confidently determine that there was trend in interlayer mercury oxidation suppression with respect to temperature.

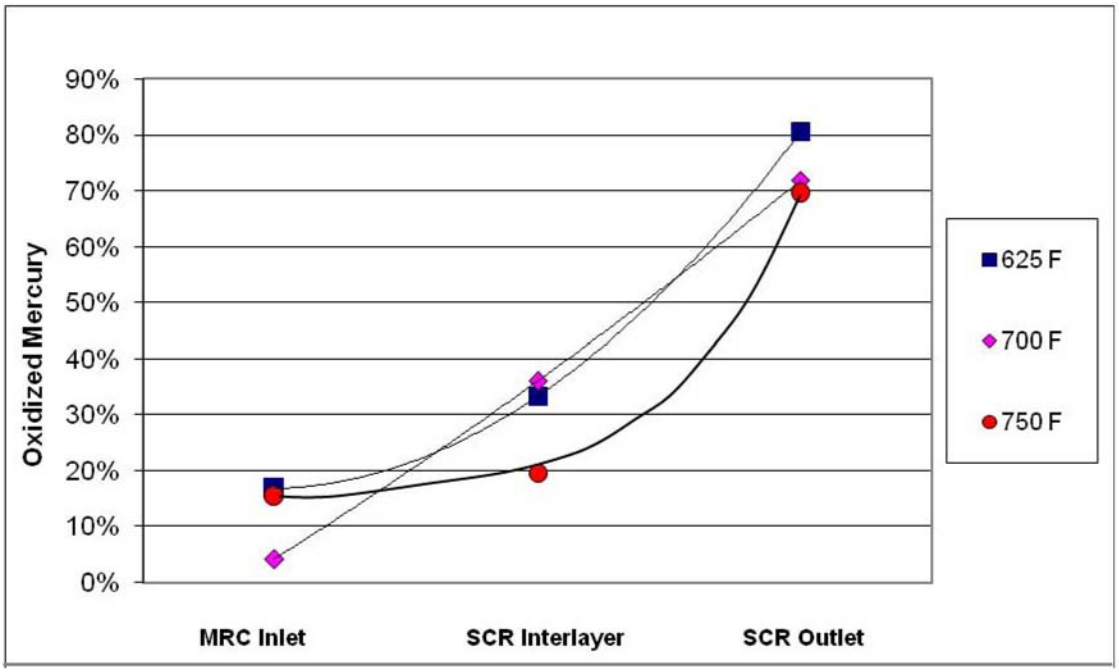

Figure 8-2
Mercury Speciation vs. Location and Temperature

Interlayer Mercury Measurement – Effect of Flow Rate

Similar data to that shown in the prior plots is shown in Figure 8-3, but as a function of two flow rates: design and 75% of design. Interlayer data for the high flow condition are not available, due to a malfunction of the analyzer. The 75% flow condition shows virtually a straight line response, similar to many of the previously shown conditions. The design flow condition shows much more mercury oxidation suppression for the upper two layers of catalyst. As with the previous plot, it is difficult to make any firm conclusions since the data are limited. At face value, one might conclude that at low flow, the final layer of catalyst is more depleted in ammonia than it would be at higher flow rates, thus the mercury oxidization is more apparent across the final layer of catalyst for this low flow rate condition, thereby giving the pronounced curve as shown in the plot. However, as stated before, it may be just as likely that the variation in inlet oxidation level affects the shape of the response curve. In any event, it is clear that on an absolute basis, the mercury oxidation is higher across the final layer of catalyst than it is across each of the first two layers.

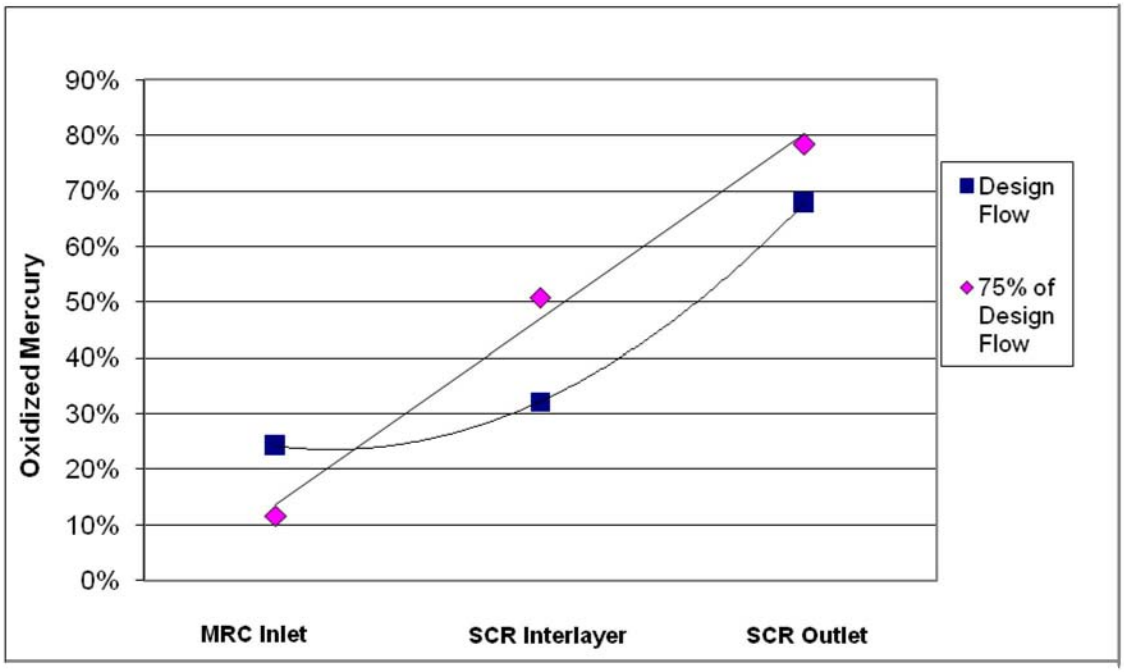

Figure 8-3
Mercury Speciation vs. Location and Flow Rate

Interlayer Mercury Measurement – Effect of DeNOx

The interlayer data based on deNOx level are shown in Figure 8-4 The data were taken at design flow, 700°F, and 50 ppmv Cl. The data are very consistent for all conditions above the minimum deNOx level of 16%. (Note that the actual ammonia level should have been closer to zero for this 16% condition – monitor bias may have created an erroneously high indication of deNOx.) They show the basic trend as found in most of the previous plots, where the final layer of catalyst

was clearly oxidizing more mercury, on an absolute basis, than each of the first two layers. With the low deNOx data however, there is a change in trend. These data indicate that the upper layers of catalyst are oxidizing more mercury than would be the case when ammonia is present in higher quantities. Keeping in mind that there are two layers of catalyst prior to the interlayer measurements, one can see that these two layers increased the absolute level of oxidized mercury by roughly 70%, while the final layer increased it by only about 5%. This matches a first order reactor mechanism much better than the data at higher levels of ammonia, since a first order reaction mechanism dictates that more absolute oxidation would take place when the available elemental mercury concentration is higher. Taken at face value, these data help to show the inhibiting effect of ammonia very clearly.

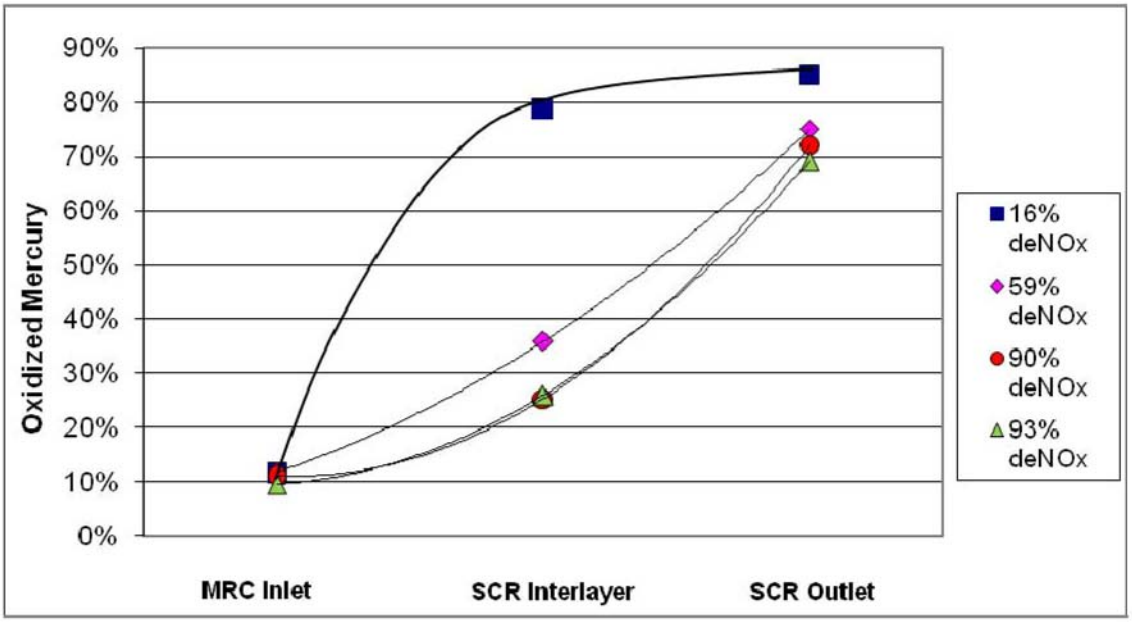

Figure 8-4
Mercury Speciation vs. Location and DeNOx

Conclusions– Interlayer Ammonia Measurements

The interlayer mercury measurements are perhaps most useful in a theoretical sense because they aid in the understanding of the mechanism of mercury oxidation as it relates to various parameters such as ammonia and chlorine. From a global standpoint, the data clearly show that mercury oxidation is suppressed over the upper catalyst layers, presumably due to the effect of ammonia. Figure 8-5 offers somewhat of a summary of this general finding, where all the available data at baseline conditions (90% deNOx, 50 ppmv Cl, 700°F, and design flow) are plotted. These data come from the various test series for a single catalyst (chlorine test series, flow test series, deNOx test series, and temperature test series). The fact that these four separate test runs give similar response curves gives some confidence to the global findings. Interestingly, the final mercury speciation at the reactor exit was very consistent, even though the inlet mercury speciation varied much more widely. This clearly shows that the oxidizing effect of the catalyst is not additive to the inlet oxidized mercury level, and in a sense, the catalyst

appears to create a sort of equilibrium level of oxidized mercury, relatively independent of the inlet speciation. Thus, the shape of the response curves (linear vs. curved, etc.) appears to be relatively strongly a function of the inlet speciation.

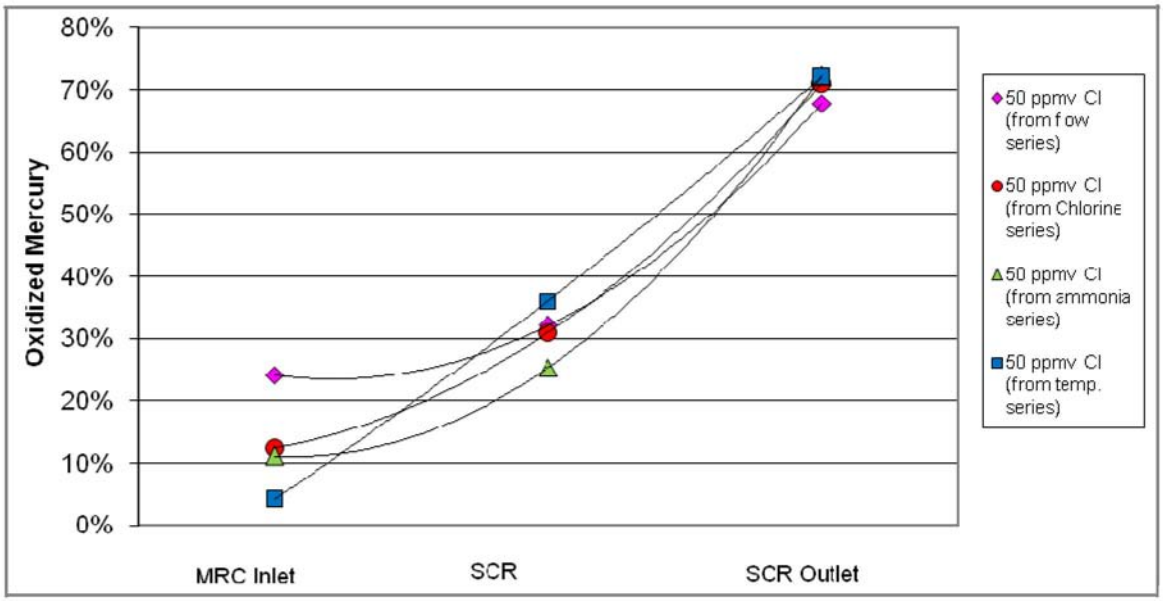

Figure 8-5
Mercury Speciation vs. Location at Design Conditions – Four Test Runs

Overall, the data show that a great deal of mercury oxidation occurs across the final layer of catalyst, especially considering that the available elemental mercury for oxidation is lower in this region. Thus the percentage of elemental mercury that is oxidized is much higher for the final layer of catalyst, than for the previous layers. This is strongly supportive of the theory that ammonia inhibits the mercury oxidation reaction, especially considering the data with and without ammonia. However, it is clear that the upper layers of catalyst do participate in mercury oxidation, just not to the same degree as the final catalyst layer.

9
VARIABLE COSTS OF CHLORINE INJECTION

Introduction

The project data demonstrate that by increasing flue gas chlorine levels, SCR mercury oxidation, and ESP mercury capture can be improved. This is especially true for flue gases that are severely depleted in halogens. Facilities which fire low-chlorine coals may opt to artificially increase flue gas chlorine levels by some means of chlorine injection. The following analysis provides some basic variable cost data associated with various reagents utilized to increase flue gas chlorine levels.

Basis and Assumptions

Table 9-1 shows the general design basis for the reagent cost calculations. A 500 MW coal-fired unit has been assumed, which seeks to increase the flue gas chlorine level from < 5 ppmv to roughly 100 ppmv of chlorine.

Table 9-1
Calculation Basis and Design Assumptions

Unit Size	500 MW
Coal BTU	12,000 Btu/lb
Coal Burn Rate	429,000 lb/hr
Flue Gas Mass Flow Rate (100% Load)	5,550,000 lb/hr
Flue Gas Molar Flow Rate (100% Load)	3,300 lb-mole/min
Assumed Capacity Factor	0.70
Native Flue Gas Chlorine Level	< 5ppmv
Target Flue Gas Chlorine Level	100 ppmv

Reagent Options and Costs

A number of reagent options are available for increasing flue gas chlorine levels. These include HCl (hydrochloric acid) and NH_4Cl (ammonium chloride) which would typically be injected into the flue gas downstream of the boiler, or $CaCl_2$ (calcium chloride) which could be fed along with the coal to the boiler. The reagents may be injected in pure form or in solution form, depending on costs and safety and design considerations. Table 9-2 shows the required amount of material

needed to increase the flue gas level to 100 ppmv as a function of reagent type, and based upon the design specifications given in Table 9-1. The reagent amounts and costs are based upon pure reagent. As stated, the reagent may be utilized in various forms including aqueous solutions. If solutions are utilized, then costs will vary according to the costs of the solutions themselves.

Table 9-2
Required Reagent Amounts and Approximate Costs

Reagent	HCl	NH_4Cl	$CaCl_2$
Amount of Pure Reagent Required (tons/yr)	2,210	3,250	3,370
Cost of Pure Reagent ($/ton)[6]	$240	$500	$300
Reagent Cost ($/yr)	$531,000	$1,624,000	$1,011,000
Offset	NA	$207,000[7]	Not Quantified[8]
Final Reagent Cost ($/yr)	$531,000	$1,417,000	$1,011,000

In the case of HCl, it is unlikely that pure HCl gas would be utilized due to safety and storage concerns. Commercial hydrochloric acid could likely be utilized, which typically is available as a 38% aqueous solution. For aqueous HCl, the reagent cost is calculated at approximately $500,000/year, utilizing the basis shown in Table 9-1. In the case of ammonium chloride, the ammonia contained in the compound would offset a portion of the amount of ammonia required for the SCR in terms of the deNOx reaction. This would represent a cost savings, which has been applied in Table 9-2 assuming anhydrous ammonia. This would give a total reagent cost for ammonium chloride of roughly $1,400,000/yr. (Note that the price utilized for ammonium chloride is a very rough estimate – exact ammonium chloride costs will depend on plant location, availability purity, and transport costs.) For calcium chlorine, the calcium contained in the compound may be beneficial in terms of limiting arsenic poisoning on the coal. The calcium chloride feed would be roughly 0.18% of the coal fee, equivalent to a calcium level of 0.06% in the coal. An exact value for this benefit is difficult to apply, however. Without applying any offset due to the benefits of calcium, the calcium chloride reagent cost is roughly $1,000,000/yr.

Overall, it appears that utilizing hydrochloric acid solution is the most cost-effective option for artificially increasing flue gas chlorine levels through direct reagent injection. This appears to be the case, even with offsets applied. It should be cautioned that in all cases, the analysis is highly dependent on the actual cost of the reagent as delivered to the plant site. The analysis does not include fixed costs associated with reagent storage and injection and handling systems. Furthermore, balance of plant issues may add significant to the costs of utilizing a particular reagent. Thus, the reagent costs data should not be utilized as a substitute for a rigorous cost-benefit analysis, which would of course be highly site specific.

[6] Based upon aqueous HCl solution at (38% conc.) @ $100/metric ton, pure NH_4Cl @ $550/metric ton, and $CaCl_2$ flake (77% purity) @ $250/metric ton.
[7] Value of ammonia offset for SCR feed, based on anhydrous ammonia @ $200/ton.
[8] Calcium may have value as an inhibitor of arsenic poisoning for facilities firing eastern bituminous or similar coals – exact value difficult to quantify.

10
DATA LIMITATIONS

It is important to first discuss the project objectives and data limitations to help set the context of any conclusions that are reached. First and foremost, the project was developed to examine the relative response of conventional catalysts to various parameters, in terms of their ability to oxidize mercury. No attempt was made to normalize the catalyst offerings in any way, thus the data cannot be used to evaluate the comparative intrinsic mercury oxidation capability of the various catalysts. The data can only be used to examine the differences in the various catalysts' responses to the parameters examined. In addition, day to day fluctuations in boiler operation and fuel would make it impossible to compare the catalysts' activity for mercury oxidation on an absolute basis, even if there was some basis for normalization. As a result, the data are most valuable in determining how a particular installation that is exhibiting a particular level of baseline mercury oxidation will respond to independent changes in variables such as chlorine level, temperature, flow rate, and ammonia level.

Another primary data limitation applies to the associated fuel for which the data were generated. The findings generally apply only to low and ultra-low chlorine coals which are similar to eastern bituminous fuels in terms of ash constituents and BTU values. Even though PRB or other sub-bituminous or lignite coals may have similar chlorine levels, the data cannot be applied with any confidence to these fuels, primarily due to the high alkalinity present on PRB fuels. Also, the data are only marginally applicable in a direct sense to high chlorine coals, so care must be taken to avoid applying the results too broadly in terms of fuel. The fuel ranges of chlorine varied up to 350 ppmv of chlorine in the flue gas (approximately 6,000 pppw in coal). The conclusions are based upon this range of chlorine. High-chlorine coals will not see the same responses, at least in terms of chlorine dependency, that are demonstrated in this report.

All of the catalysts tested were of conventional type, meaning that they were not specially formulated to maximize mercury oxidation. Thus, the data in terms of the shape of the response curves is generally thought to apply to most conventional SCR catalysts. The catalysts tested represent a reasonable range of deNOx activities and SO_2 conversions that are consistent with the domestic SCR fleet. However, as previously discussed, in two cases, catalyst was removed from the reactor to lower the overall mercury oxidation rate into a range where the response was more easily detected. This is likely, therefore, to artificially decrease the average level of mercury oxidation of the catalysts tested in the program compared to the domestic fleet as a whole. However, the catalysts tested were of course relatively fresh, where full-scale catalysts may be significantly aged. Catalyst aging is expected to decrease the mercury oxidation potential somewhat. Thus the young age of the catalyst utilized in the test program may artificially increase the average mercury oxidation that was noted compared to the domestic fleet as a whole. Therefore, the two factors: reduced catalyst volume and catalyst age tend to offset one another to some degree.

11
CONCLUSIONS

Effect of Chlorine

There is a clear beneficial effect in terms of mercury oxidation and capture when levels of chlorine are increased. All of the catalysts tested demonstrated similar responses to chlorine level. Flue gas highly depleted in chlorine (i.e. < 50 ppmv or roughly < 1,000 ppmw in coal) will see very strong incremental improvements in mercury oxidation across the SCR with increased chlorine.

The project data show that, on average, SCR mercury oxidation could be increased from 50% to 90% (a relative improvement of 90%), and ESP capture could be increased from 60% to 80+% (a relative improvement of roughly 33%). These improvements are for the tested chlorine range of ~5 to 350 ppmv (~ 100 to 6,000 ppmw in coal) for SCR oxidation, and ~5 to 150 ppmv (~100 to 2,500 ppmw in coal) for ESP capture.

The potential capture of oxidized mercury across a wet FGD is of particular interest. Although the data imply that FGD mercury capture will be improved, the actual benefits of chlorine injection with respect to capture will need to be validated by measurements across an actual unit, as re-emissions and measurement errors associated with mercury speciation measurements before the FGD may affect the actual mercury removal efficiency.

Effect of Temperature

Overall, increased temperature has a negative effect on both SCR mercury oxidation and mercury capture. This effect is opposite from most catalytic reactions, including the deNOx reaction, which increases as temperature increases. Based upon the project data, the average decrease in SCR mercury oxidation was about 12% for a temperature change of 625° to 750°F. In terms of ESP capture, the decrease in captured mercury was roughly 13% on average. Although all catalysts tested had a negative response to increases in temperature, there was some variability in the catalysts' sensitivity.

These findings are associated with an independent change in temperature. If a temperature change comes about as a result of a load change, then other parameters, such as flow rate and flue gas composition, may influence mercury oxidation and capture as well.

Effect of Flow Rate

Flow rate appeared to have very little direct effect on either mercury oxidation across the SCR or on mercury capture across the ESP – this finding was consistent for all of the catalysts tested. This is based on the relatively narrow flow rate range tested, which was equivalent to a unit reducing load to 60% of design. For full-scale units which routinely have larger turn-downs, the effect of flow may become more apparent.

The data are based on an independent change in flow rate. In other words, other operating parameters were held steady. For a full-scale unit, flow rate changes are usually primarily the result of a load change, which may also be accompanied by a temperature change. As discussed previously, lower temperatures improve mercury oxidation and capture, thus a load decrease would generally improve mercury oxidation and capture more than what may be indicated by the flow rate data alone.

Effect of Ammonia

The data clearly show that ammonia has an inhibiting effect on mercury oxidation across the SCR. This general effect is consistent for all of the catalysts tested in the program. However, the inhibiting effect seems to be most apparent at low levels of chlorine (50 ppmv). At higher levels of chlorine (100 ppmv), the adverse effect on SCR mercury oxidation is much more muted. The confidence in this finding is somewhat limited, however. For the lower chlorine data, where the response was most apparent, the SCR mercury oxidation decreased by 18% absolute (22% relative) across the deNOx range of 0% to 90%.

In terms of ESP capture, an increase in deNOx, which creates a decrease in SCR mercury oxidation, has the counterintuitive effect of improving capture. As with the SCR oxidation data, ESP capture response appears to be different depending on the chlorine level. ESP capture improves only slightly for high chlorine conditions, but the improvement is marked for low-chlorine conditions (increasing by roughly 20% absolute or 40% relative).

Interlayer data further showed the suppressive effects of ammonia on SCR mercury oxidation. For appreciable ammonia levels (deNOx > 50%) the final layer of catalyst will contribute far more to mercury oxidation than the upstream catalysts layers, although the upstream layers do participate to some degree.

Global Findings

Overall the project has shown that conventional SCR catalysts behave similarly with respect to chlorine level, temperature, flow rate, and ammonia level. Thus, the data can be applied with some confidence to the domestic SCR catalyst fleet as a whole, assuming that the catalyst is of conventional type and is relatively new. The data averages based upon the project data offer a basis for determining both qualitatively and semi-quantitatively the relative effects of variations in the parameters on mercury oxidation through the SCR and mercury capture through an ESP (within limits).

It is cautioned that the data can be applied only to fuels of similar type used in the program (consistent with eastern bituminous coals) and with chlorine levels consistent with those tested in the program. Generally, the data do not apply directly to PRB or lignite coals, even though they may have chlorine levels that are similar to those in the test program. It should also be noted that ESP capture is highly variable and is a function of many parameters in addition to those tested in the program. Thus, the average values for ESP capture experienced in the test program cannot necessarily be applied to any single full-scale unit. Furthermore, the relative response of ESP capture to the various tested parameters may be outweighed by changes in other parameters such as ash LOI levels. These factors undermine the confidence in which the data can be applied to ESP capture.

The data are valuable in determining how a particular installation will respond to a change in operational parameters with respect to SCR mercury oxidation and mercury capture. The data are not designed to predict the absolute level of mercury oxidation without some baseline value for the facility in question being known – the data can only predict relative changes. In practice, the absolute level of mercury oxidation and capture will be highly site specific and depend on the many parameters in addition to those tested in this program, including: boiler configuration and back-end equipment design, fuel, catalyst intrinsic properties, and catalyst volume, age, and reactor distributions.

In general, the data will help full-scale facilities to determine what methods could be used to improve mercury oxidation and capture, and also help to determine what beneficial or detrimental effects may occur due to a proposed change in certain parameters. For new facilities, or those being retrofitted, the data show how various parameters affect mercury oxidation and capture, and thus would aid designers in optimizing mercury oxidation and capture

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RECOMMENDATIONS AND RESEARCH NEEDS

Recommendations

The project findings show clearly that for low-halogen flue gases, increases in flue gas chlorine levels will have beneficial effects on SCR mercury oxidation and ESP capture. To capitalize on this effect, facilities may consider the artificial adjustment of chlorine, through direct injection or fuel additives. Alternately, if all other factors are equal, then fuels having higher chlorine will likely exhibit better mercury oxidation than their lower-chlorine counterparts (this finding holds at least for fuels producing less than 350 ppmv of chlorine in the flue gas, or having roughly less than 6,000 ppmw of chlorine in the coal). It should be cautioned that if the chlorine level is adjusted by making a fuel change, then many other parameters in addition to chlorine are likely to change and care must be taken that these parameters do not have over-riding adverse effects.

The project data show that lower temperature operation of the SCR will help to maximize SCR mercury oxidation and improve ESP capture. Thus in designing both retrofit and green-field facilities, lower SCR operating temperatures aid in mercury oxidation and capture. For green-field installations, boiler/SCR designs that provide for generally lower SCR temperatures will help to maximize the achievable mercury oxidation through the SCR, at least with conventional catalysts. Lower operating temperatures also have potential benefits in terms of SO_2 oxidation, but the benefits of lowering the SCR temperature must be weighed against the potential loss in reactor potential for NOx removal.

Independent changes in flow rate did not appear to have much effect on mercury oxidation or ESP capture. Thus in the case of a load change, the change in temperature is expected to have the greatest impact, rather than any effects due to flow rate. This holds for a moderate turn-down in load (roughly 60%). More extreme turndowns may see larger effects in which flow rate does play a significant role, but facilities should not assume that low-load conditions are necessarily beneficial in terms of mercury oxidation and capture, especially in cases where the flue gas temperatures do not change significantly.

The data indicate that any change in conditions that change the ammonia profile in the SCR are likely to change, at least to some degree, the amount of mercury oxidized through the SCR. This includes catalyst volume changes, maldistributions at the reactor inlet, reactor fouling, and catalyst aging/deactivation. If ammonia slip is the controlling factor in the improved ESP capture rates noted with increased deNOx, then facilities relying solely on ESP mercury capture would not experience adverse effects from very high deNOx conditions (greater than design). This is also potentially true for catalyst aging, which typically leads to higher slip levels. Maldistributions leading to higher slip may also result in improved ESP mercury capture. It is important to note, however, that all of these statements are predicated on ammonia slip being the underlying cause for the improvement in ESP capture. If slip is not the cause, then these statements may or may not hold.

Overall, the project data offer some guidance as to how changes in operating parameters will affect SCR mercury oxidation and ESP capture. The data can be used in a relative sense to determine how various operational changes will affect mercury-related parameters. End-users are cautioned that ESP capture (or potential wet FGD capture) does not always follow the trend of SCR oxidation, and in some cases the ESP capture response can be counterintuitive, as with the effect due to ammonia/deNOx. Further, ESP capture will be highly dependent on factors other than mercury speciation, temperature, and flow rate. Until ESP capture is better understood, facilities should not make assumptions about absolute levels of mercury capture across an ESP unless specifics are known about the facility in question. Similarly, the data do not offer a complete assessment for wet FGD-equipped facilities. Additional information is needed to fully integrate wet FGD performance with the current findings.

Research Needs

The following sections discuss specific research needs that have been identified associated with SCR mercury oxidation, as well as ESP and FGD mercury capture.

Evaluation of Mercury Oxidation Across Spent SCR Catalyst

The effect off catalyst aging is not well understood in terms of its effect on mercury oxidation. Although previous EPRI studies have sought to understand aging effects better, there is still a limited understanding of how catalyst aging affects both the absolute level of mercury oxidation, as well as how it affects the relative response to operating parameters. A more thorough understanding of catalyst aging on catalyst mercury oxidation would be very helpful in terms of long-term mercury compliance planning.

Evaluation of Mercury Oxidation Across Regenerated Catalyst

Catalyst regeneration has become a relatively common option as an alternative to new catalyst purchase. As with catalyst aging, EPRI has studied the effects of catalyst regeneration on mercury oxidation to some degree. However, the exact effects of catalyst regeneration, especially with respect to long-term performance, are not well understood. The industry would benefit greatly by studies which evaluated regenerated catalyst long-term performance with respect to mercury oxidation.

Impacts of Catalyst Design on Mercury Oxidation

The current project did not attempt to correlate specific catalyst physical and chemical design parameters to mercury oxidation properties. An improved understanding of how specific catalyst design parameters affect mercury oxidation would be of benefit, however. Common catalyst design parameters include such physical parameters as porosity and pore size distribution, surface area, wall thickness, and overall geometric configuration. Chemical design parameters include the relative amounts of active catalytic species and promoters, as well as their dispersion, etc. A better understanding of the intrinsic catalyst properties affecting mercury oxidation would help in both the design of catalysts, and in the evaluation of different catalyst formulations for their potential advantages in terms of mercury oxidation.

Impacts of Alkalinity on Halogen-Induced Mercury Oxidation

One of the primary limitations of the current study is that the data can only be applied directly to coals having low alkalinity. In contrast, some fuels such as PRB coals, have quite high levels of alkaline components, such as calcium. This high alkalinity can have strong effect mercury on oxidation and capture. Additional studies are needed to determine how halogens affect mercury oxidation and capture in a high-alkaline environment, especially with respect to various operating parameters, such as temperature and flow rate.

Mercury Capture Efficiency and Re-Emissions with Wet FGD Systems

The current project did not directly assess the impact on wet FGD performance with respect to the various halogen levels and other parameters that were investigated. FGD systems will respond to changes in operating parameters in addition to being affected by the absolute level and speciation of mercury entering the device. Thus, even though the effect on mercury speciation and ESP capture is known to some degree for the parameters investigated, the exact effects on overall capture efficiency with a wet FGD in place are not known with confidence. Additional studies which specifically examine FGD capture efficiencies and re-emissions as a function of operating conditions, including inlet mercury speciation, would be extremely helpful in predicting overall mercury capture for a facility that is FGD-equipped.

Effects of Flue Gas Properties on ESP Mercury Capture

In general, the current study showed that ESP mercury capture could be quite high, especially under certain conditions, offering a reasonably effective control option for facilities not equipped with devices such as wet FGDs. Under certain conditions, the mercury removal was over 90%. Depending on the regulatory environment, the optimization of ESP operation for mercury control could be a very valuable part of a utility's overall compliance strategy. To better understand ESP capture, the following specific research areas have been identified.

Effects of Ammonia on ESP Capture

The current study showed that increases in ammonia (deNOx) caused a decrease in SCR mercury oxidation. However, ESP mercury capture noticeably increased as ammonia was increased, rather than decreased as one might expect from the speciation at the exit of the SCR. This effect is very surprising and the exact reasons for this behavior are not known. One theory is that ammonia slip may scavenge SO_3 which in turn may improve the adsorption rate of mercury on carbon sites contained in the fly ash. Since an increase in deNOx typically creates an increase in ammonia slip, there would be a positive response in terms of ESP capture to increased deNOx. A similar ammonia-related theory is that the additional formation of acidic ammonium bisulfate across the air preheater due to increased levels of ammonia slip somehow improves mercury oxidation and capture. Testing which added ammonia before and after the air preheater at various levels would be very helpful in determining if indeed ammonia was influencing the ESP capture efficiency, and by what mechanism. This testing approach would allow ammonia to be varied independently of deNOx, and would also allow for a comparison of effects for ammonia injected upstream and downstream of the air preheater.

Effects of SO_3 on ESP Capture

SO_3 is thought to adversely affect ESP mercury capture efficiency by inhibiting adsorption sites on the fly ash particles, as mentioned above. SO_3 entering the ESP is a function of a number of parameters including fuel, boiler operation, SCR catalyst design, and air preheater operation. If a more detailed understanding of the effect of SO_3 can be determined, and across what ranges it has an impact, then optimization steps could be taken to minimize the adverse effects of SO_3.

Effects of Ash Properties on ESP Capture

The current study showed that the day to day variability in mercury capture across the ESP was very large, even for conditions which appeared to be nearly identical. One potential source of this variability is unburned carbon on the fly ash, which is known to have a strong effect on ESP mercury capture under some conditions. Other ash characteristics may also play a role, such as ash surface area and pore size distribution, ash loading, chemical composition, and surface chemistry (acid/base sites, etc.). Isokenetic ash sampling could be used to obtain representative ash samples which corresponded to ESP capture measurements. The ash characteristics could then be correlated to ESP capture. This would allow the fly ash parameters affecting ESP mercury capture to be identified, and hopefully would assist in optimizing ESP mercury capture.

A
TABULAR DATA

The following tabular data correspond to the data shown in the figures within the report.

Table A-1
Chlorine Dependency - Average and Ranges of All Catalysts

Cl (ppmv)	SCR in Oxid	SCR in Oxid. (high)	SCR in Oxid. (low)	Positive Range	Negative Range	SCR out Ox.	SCR out Ox. (high)	SCR out Ox. (low)	Positive Range	Negative Range	ESP Capture	ESP Capture (high)	ESP Capture (low)	Positive Range	Negative Range
10	11%	21%	3%	11%	8%	50%	68%	40%	19%	9%	62%	89%	41%	27%	21%
50	16%	**32%**	2%	17%	14%	70%	86%	55%	15%	16%	65%	91%	43%	25%	23%
100	17%	35%	2%	18%	15%	84%	93%	76%	9%	7%	72%	94%	48%	22%	24%
150	27%	39%	11%	12%	16%	83%	89%	78%	6%	5%	83%	95%	70%	13%	13%
200	32%	32%	32%	0%	0%	90%	90%	90%	0%	0%				0%	0%
250	35%	35%	35%	0%	0%	91%	91%	91%	0%	0%				0%	0%
300	35%	35%	35%	0%	0%	92%	92%	92%	0%	0%				0%	0%
350	37%	37%	37%	0%	0%	94%	94%	94%	0%	0%				0%	0%

Table A-2
Temperature Dependency - Average and Ranges of All Catalysts

Temp. (°F)	SCR in Oxid	SCR in Oxid. (high)	SCR in Oxid. (low)	Positive Range	Negative Range	SCR out Ox.	SCR out Ox. (high)	SCR out Ox. (low)	Positive Range	Negative Range	ESP Capture	ESP Capture (high)	ESP Capture (low)	Positive Range	Negative Range
625	21%	30%	16%	9%	6%	87%	94%	81%	7%	6%	79%	92%	67%	13%	12%
750	30%	42%	15%	12%	15%	74%	86%	69%	12%	5%	67%	92%	32%	26%	35%

Table A-3
Flow Dependency - Average and Ranges of All Catalysts

Flow (% of design)	SCR in Oxid	SCR in Oxid. (high)	SCR in Oxid. (low)	Positive Range	Negative Range	SCR out Ox.	SCR out Ox. (high)	SCR out Ox. (low)	Positive Range	Negative Range	ESP Capture	ESP Capture (high)	ESP Capture (low)	Positive Range	Negative Range
75%	12%	22%	2%	10%	10%	75%	78%	71%	3%	4%	61%	93%	38%	32%	23%
100%	12%	22%	5%	9%	7%	77%	86%	72%	9%	5%	63%	93%	43%	30%	20%
125%	11%	22%	1%	11%	10%	72%	80%	65%	8%	7%	65%	92%	47%	27%	18%

Table A-4
Ammonia Dependency - Average and Ranges of All Catalysts

DeNOx	SCR in Oxid	SCR in Oxid. (high)	SCR in Oxid. (low)	Positive Range	Negative Range	SCR out Ox.	SCR out Ox. (high)	SCR out Ox. (low)	Positive Range	Negative Range	ESP Capture	ESP Capture (high)	ESP Capture (low)	Positive Range	Negative Range
0	28%	35%	12%	7%	16%	90%	93%	85%	3%	4%	49%	67%	21%	18%	27%
50%	24%	35%	12%	11%	13%	82%	89%	75%	7%	7%	58%	75%	41%	17%	16%
90%	24%	31%	11%	7%	13%	77%	92%	68%	15%	9%	63%	78%	51%	16%	12%
95%	22%	35%	10%	13%	13%	70%	71%	69%	1%	1%	75%	84%	67%	9%	9%

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