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Effects of Chlorine and Other Flue Gas Parameters on SCR Catalyst Mercury Oxidation and Capture Efficiencies

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Technical Update, August 2008

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REPORT SUMMARY

Although catalyst behavior is relatively well understood with respect to deNOx and SO_2 oxidation, relatively little is known about mercury oxidation behavior. This test program seeks to evaluate the mercury oxidation performance of multiple types of Selective Catalytic Reduction (SCR) catalyst as a function of changes in various flue gas parameters, including chlorine level, ammonia level, flow rate, and temperature. This interim report describes the results from parametric testing on the first catalyst.

Background

SCR technology has become the technology of choice for meeting stringent NO_x emission limits for coal fired electric generating plants. Industry data have indicated that along with NO_x 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.

Objectives

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, ammonia level, flow rate, and temperature.

Approach

The project team tested the mercury oxidation performance of a commercial SCR catalyst as a function of changes in chlorine level, deNOx rate, flow rate, and temperature. They conducted the tests at the Mercury Research Center (MRC), located near Pensacola, Florida, using a Columbian coal, which, except for a very low chlorine level, has characteristics similar to eastern bituminous coals. The MRC 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 scrubber. The host unit for the MRC is a 75 MW, T-fired unit firing pulverized coal. The team gathered speciated mercury data at the SCR inlet, SCR intermediate layer, SCR outlet, ESP outlet, and scrubber outlet.

Results

The data showed a substantial, beneficial effect associated with increased chlorine levels above the very low native chlorine levels found in the flue gas. This effect was most dramatic up to very roughly 100 ppmv chlorine injection, after which the beneficial effects appeared to levelize somewhat, although improvements in mercury oxidation and capture were demonstrated across the entire range of increased chlorine tested in the program. The presence of additional chlorine

had the effect of improving the proportion of oxidized mercury exiting both the SCR and ESP and thus improving the ability of the wet scrubber to capture oxidized mercury.

The data show that the ammonia level can have a substantial effect on mercury oxidation across the SCR, with increased deNOx leading to lower rates of mercury oxidation. However, the percentage capture of oxidized mercury across the ESP appeared to actually improve with increasing deNOx levels, thus resulting in a net improvement in overall mercury capture as measured from boiler outlet to scrubber outlet.

An adverse effect on mercury oxidation through the SCR was associated with increases in both temperature and flow rate. Since an SCR will typically encounter both an increase in temperature and flow rate at higher boiler loads, overall mercury capture efficiency may be heavily impacted by boiler load.

EPRI Perspective

Overall, the project has been very successful in isolating and determining the effects of primary SCR/boiler operational parameters, including chlorine, on mercury oxidation and capture. These findings offer guidance to facility operators in terms of optimizing mercury oxidation performance, while providing important guidance on the use of chlorine injection as a method for improving mercury capture performance. Future project work examining additional catalysts will validate the conclusions reached thus far and provide much needed information related to the mercury oxidation performance of the catalyst fleet as a whole.

Keywords

Mercury
Mercury oxidation
Chlorine
Selective catalytic reduction
Electrostatic precipitators
NO_x control
Catalyst

ABSTRACT

SCR catalysts are known to oxidize mercury under certain conditions. For coals low in native chlorine, the addition of chlorine into the flue gas may be a viable option to improve mercury oxidation across the SCR. A test program has been devised to evaluate the mercury oxidation performance of four commercial SCR catalysts as a function of changes in chlorine level, deNOx rate, flow rate, and temperature. Included in the evaluation are ESP and scrubber mercury capture efficiencies. This interim report describes the results from the first catalyst tested. The test facility used in this project is the Mercury Research Center, located near Pensacola, Florida. The fuel selected for testing is a very low chlorine Columbian coal, which has characteristics similar to eastern bituminous coals, with the exception of chlorine level.

The data from the first catalyst tests show a substantial beneficial effect of increased chlorine levels. The effect is most dramatic up to about 100 ppmv, after which the beneficial effects appear to levelize. The added chlorine has the expected effect of increasing the proportion of oxidized mercury leaving the SCR and ESP, thereby improving the capture in the wet FGD. Investigations related to ammonia (deNOx) level show a lower level of mercury oxidation with increasing ammonia. However, the rate of mercury capture was higher across the ESP and outweighed the associated loss in oxidized mercury resulting in an increase in overall mercury capture. Increases in both temperature and flow rate had an adverse effect on mercury oxidation.

These findings offer guidance to facility operators seeking to optimize mercury oxidation performance and also provide important guidance related to the use of chlorine injection as a method for improving mercury capture performance for a given system. Future project work examining additional catalysts will provide valuable information adding confidence to the conclusions reached thus far and will provide much needed information related to the mercury oxidation performance of the catalyst fleet as a whole.

ACKNOWLEDGEMENT

The authors would like to thank the participating catalyst suppliers for their gracious 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. Thanks also go to Mr. Keith Harrison, Ms. April Sibley, and Mr. Nick Irvin for their administrative support during the course of the project.

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INTRODUCTION

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 Goals

Although catalyst behavior is relatively well understood with respect to deNOx and SO_2 oxidation, unfortunately relatively little is known about mercury oxidation behavior. The reported test program seeks to evaluate the mercury oxidation performance of multiple types of SCR catalyst as a function of changes in various parameters, including chlorine level, deNOx rate, flow rate, and temperature. Four commercial SCR catalysts will ultimately be evaluated under the test program, although this interim report only describes the results from the first catalyst tested. 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 offer some confidence in the general behavior of typical SCR catalysts with respect to various operating parameters. This philosophy will thus offer some confidence as to the expected behavior of the catalysts in the domestic fleet as a whole, and will hopefully highlight any dramatic differences in catalyst behavior with respect to mercury oxidation, if they are present.

Test Facility

The facility utilized for this project is the Mercury Research Center (MRC), located near Pensacola, Florida. The facility is extremely well designed for the test program, having numerous control devices, as well as complete control over operating conditions. In addition, the available equipment for speciated mercury measurements, as well as other flue gas parameters, makes the facility extremely well suited for the test program.

Project Schedule

The testing on the first catalyst was completed in mid-December 2007. Due to a scheduled unit outage, testing on alternate catalysts will not resume until early spring of 2008. Testing of all catalysts is expected to be completed by fall of 2008.

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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 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/h (23,990 acfm @ 700^{o}F). Figure 2-1 shows the MRC configuration with respect to the host boiler (Unit #5).

The facility is equipped with the 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 scrubber. 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 scrubber only processes a portion of the total MRC flue gas flow. 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.

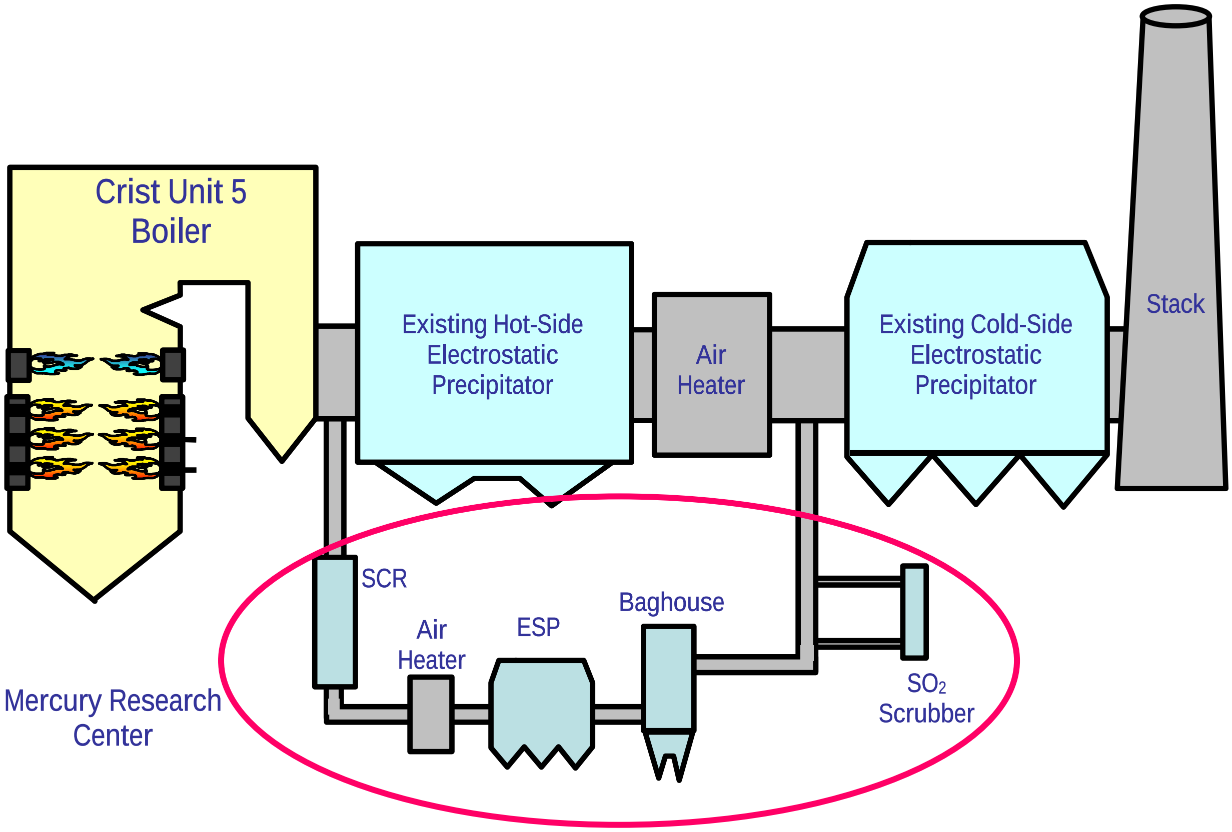

Figure 2-1
Mercury Research Center Configuration with Respect to Host Boiler

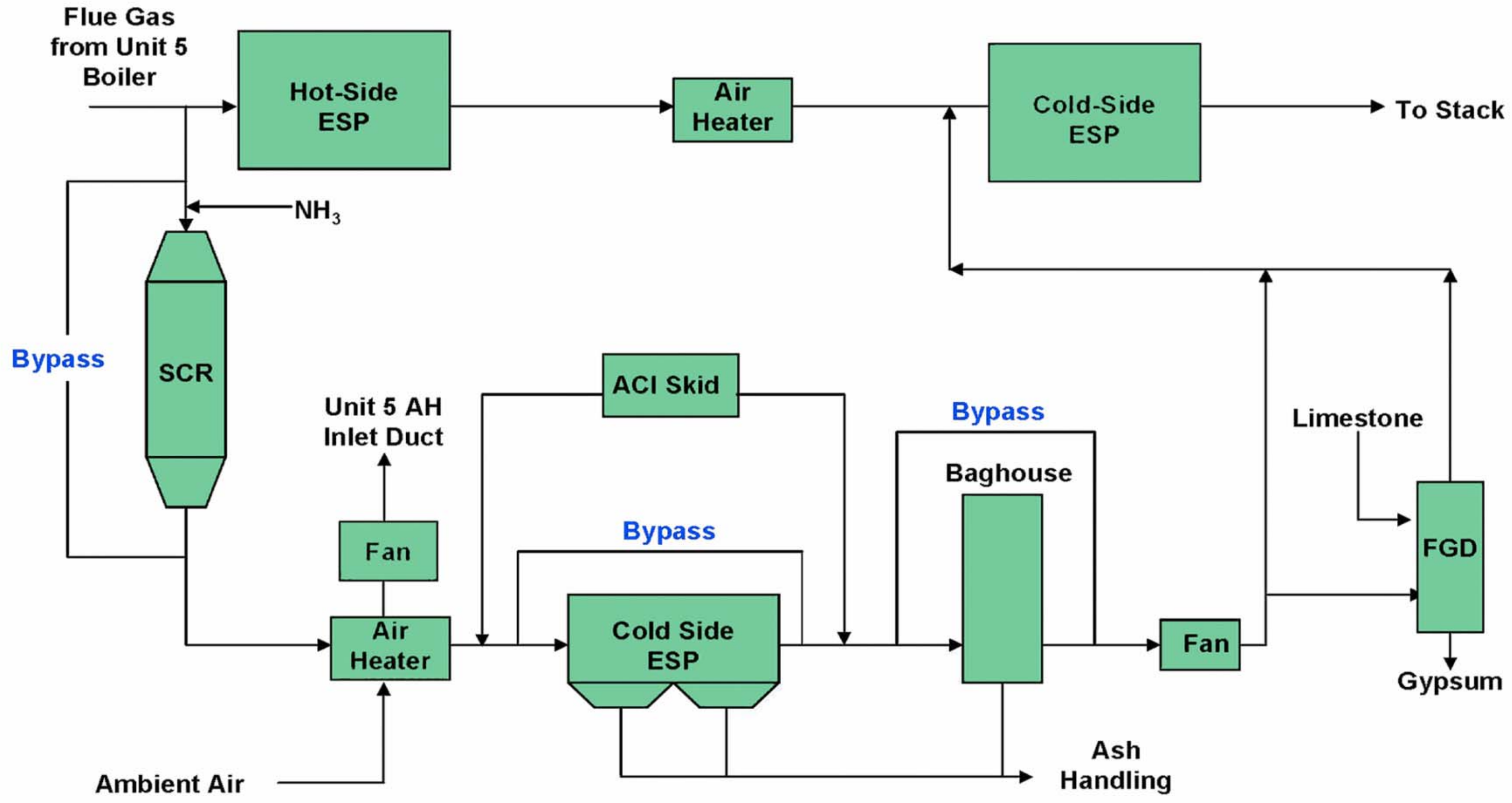

Figure 2-2
Mercury Research Center Schematic

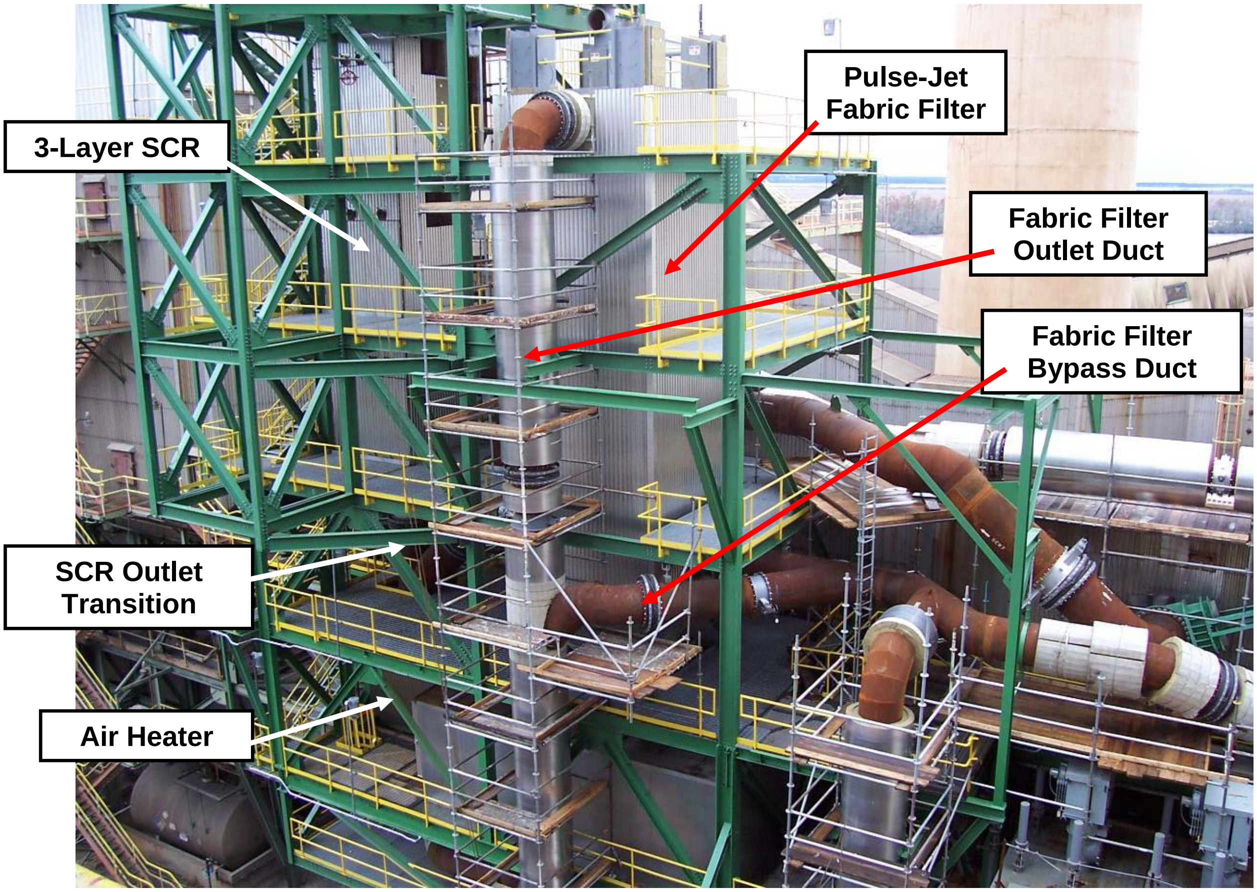

Figure 2-3
Photograph of the MRC with Major Equipment Annotated

SCR Reactor and Catalyst Design

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

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, 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)	2m X 2m (6.5 ft 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 ppm
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 catalyst 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. 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 will be tested consecutively, with many months elapsing between the parametric series, a large number of variations will be present which would make quantitative direct comparison of mercury oxidation between the various catalysts impossible. In any event, this interim report only describes the results of the first catalyst tested, and as a result, no qualitative comparisons of different catalysts can be made at present.

Mercury and Flue Gas Measurements

Speciated mercury is measured at the MRC routinely at three points. These points may include the following locations: SCR/facility inlet, SCR outlet, SCR bypass exit, ESP inlet, and ESP outlet. For the reported testing, the measurement points were located at the SCR/facility inlet, SCR outlet, and ESP outlet. These permanent points were measured using three identical Thermo Fisher Scientific speciated mercury monitors/probes. In addition, the SCR intermediate point and the scrubber outlet point were measured utilizing a Tekran system.

Primary flue gas components including CO_2, O_2, SO_2, and NOx were measured at the MRC using two continuous CEMS-type systems. These systems provided continuous documentation of the flue gas constituents entering the MRC, as well as gave primary control information for the reduction of NOx across the SCR and reduction of SO_2 across the scrubber.

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, typically South American, are burned. For the test program, a Columbian fuel with very low chlorine was selected. This fuel provided flue gas constituents and ash characteristics similar to an eastern bituminous coal, but offered very low baseline chlorine concentrations that allowed for maximum flexibility in parametric testing. Table 2-2 shows a representative proximate coal analysis of the Columbian fuel fired at the plant, as compared to a representative eastern bituminous fuel (Illinois Basin). Also included is an ash mineral analysis. Note that the fuels are quite similar in primary components and ash characteristics, although the chlorine level for the Columbian fuel is an order of magnitude lower. **Error! Reference source not found.** shows a representative trace analysis of the Columbian fuel. This analysis shows chlorine at 177 ppm, which corresponds roughly to 10-15 ppmv in the flue gas.

Table 2-2
Proximate Columbian and Comparative Eastern Bituminous Coal Analysis

Parameter	Columbian Average	Illinois Basin
BTU/lb	11,405	11,917
% Moisture	12.25	11.41
% Ash	6.04	7.63
% Sulfur	0.58	1.36
% Volatile	35.49	28.73
% Carbon	69.52	67.20
% Hydrogen	4.87	4.27
% Nitrogen	1.30	1.57
% Chlorine	0.02	0.322
Ash Mineral Analysis (%)		
Silica Dioxide	59.85	51.65
Alumina Oxide	20.98	20.99
Ferric Oxide	8.38	15.51
Calcium Oxide	2.88	2.78
Magnesia Oxide	1.71	0.98
Sodium Oxide	1.11	1.18
Potassium Oxide	1.58	2.34
Titania Dioxide	0.97	1.22
Manganese Oxide	0.03	0.04
Phosphorus Pentoxide	0.18	0.62
Sulfur Trioxide	1.66	2.63

Table 2-3
Representative Trace Analysis of Columbian Coal

Parameter	Value
Heat of Combustion, As Received (BTU/lb)	11,354
Moisture, Total (% By Weight)	13.48
Volatiles, As Received (% By Weight)	32.3
Ash, As Received (% By Weight)	5.810
Aluminum, As Received (% By Weight)	0.644
Antimony, As Received (mg/kg)	1.0
Arsenic, As Received (mg/kg)	2.9
Barium, As Received (% By Weight)	0.019
Beryllium, As Received (mg/kg)	0.4
Cadmium, As Received (mg/kg)	0.170
Calcium, As Received (% By Weight)	0.101
Chlorine, As Received (mg/kg)	177
Chromium, As Received (mg/kg)	4.8
Cobalt, As Received (mg/kg)	1.9
Copper, As Received (mg/kg)	4.0
Fluorine, As Received (mg/kg)	64
Iron, As Received (% By Weight)	0.356
Lead, As Received (mg/kg)	1.9
Magnesium, As Received (% By Weight)	0.049
Manganese, As Received (mg/kg)	14.7
Mercury, As Received (mg/kg)	0.074
Nickel, As Received (mg/kg)	4.2
Phosphorus, As Received (% By Weight)	0.005
Potassium, As Received (% By Weight)	0.092
Selenium, As Received (mg/kg)	4.85
Silicon, As Received (% By Weight)	1.557
Sodium, As Received (% By Weight)	0.084
Strontium, As Received (% By Weight)	0.006
Sulfur (lbs/MMBtu)	0.48
Sulfur, As Received (% By Weight)	0.55
Titanium, As Received (% By Weight)	0.034
Vanadium, As Received (mg/kg)	14.3
Zinc, As Received (mg/kg)	7.8

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 and scrubber. Table 2-4 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. 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.

Speciated mercury data were acquired at the following locations: SCR inlet, SCR intermediate layer, SCR outlet, ESP outlet, and scrubber outlet. As previously noted, the SCR inlet, outlet, and ESP outlet locations were measured using the MRC's permanent continuous mercury analyzers, while the SCR intermediate and scrubber outlet locations were measured using a Tekran system specifically set-up for the purpose. In addition to the data for speciated mercury, data were obtained which described the operation of the host boiler and MRC as a whole, including such parameters as flow rate, temperature, pressure, primary flue gas constituents, etc.

Table 2-4
Nominal Parametric Design Sequence

Test ID	1	2a	2b	2c	3a	3b	3c	4a	4b	4c	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%
Temperature (°F)	700	700	700	700	625	700	750	700	700	700	700	700	700	700
DeNOx Level	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%	0%	50%	90%	95%
Chlorine Level (ppm HCl)	15[1]	50	50	50	50	50	50	50	100	150	50	50	50	50

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[1] Estimated baseline chlorine level, without additional injection.

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TEST RESULTS AND ANALYSIS

Methodology

Data for the first catalyst type were acquired during late October and early November. In addition, a short series of preliminary tests was performed in August. During the preliminary testing, it was determined that for many conditions, such as variations in chlorine level or deNOx rate, that 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, the reader is cautioned against comparing data points separated over long periods of time. For instance, meaningful results would be difficult to obtain by comparing a low chlorine operating condition on one day, to a higher chlorine operating condition performed on another test day. This is especially true when comparing absolute mercury levels. Thus, the data presented showing effects of certain parameters were typically obtained during a single test day. In data presentations for which this is not the case, the data are annotated and the confidence in the comparative nature of the data is somewhat diminished.
By nature, the adjustment of certain parameters such as temperature requires a relatively long stabilization time. In these cases it was not possible to obtain a series of data during a single test day, and the confidence of the comparative data is limited by this fact. Overall, however, there appears to be a high degree of consistency in the data, and there is great confidence in the qualitative effects demonstrated by the data.

Test Results

For convenience, the test results are subdivided according to specific operational parameters. Included in these subdivisions are the effects on mercury oxidation across the SCR, as well as capture efficiency information associated with the downstream equipments. These data subdivisions include the following sections:

- Effect of Ammonia
- Effect of Chlorine
- Effect of Temperature
- Effect of Flow Rate

Effect of Ammonia

The effect of ammonia has been shown first since this parameter has the potential to influence data in subsequent sections. During the parametric tests NH_3/NOx ratios were varied between 0 and 0.95 to control reactor deNOx levels up to 94%. Subsequent data analyses will present deNOx levels to indicate the effects of ammonia on total mercury oxidation.

As will be demonstrated by the data in this section, the maintenance of a consistent level of deNOx is important to all data obtained in the test program. In subsequent data subdivisions, data are noted where the deNOx level was inconsistent with other data points presented. Note that the NOx data for low/no ammonia conditions showed some apparent NOx reduction (roughly 16%). This is thought to be a bias in the monitoring system, where calibrations were poor for the high outlet NOx values under these test conditions. Although the data are reported as measured, the low deNOx level is thought to be zero, rather than 16% as actually noted by the monitors.

Figure 3-1 shows percent oxidized mercury as a function of deNOx level. These data were taken during preliminary testing. There is a relatively marked decrease in the proportion of oxidized mercury at the SCR outlet, as the deNOx level is increased. Note that these data were obtained at a moderate level of injected chlorine (50 ppmv). The inlet oxidized mercury proportion was relatively constant during these tests at roughly 10%, and total mercury was on the order of 10 $\mu g/Nm^3$.

Figure 3-2 shows similar data taken during the final testing sequence. These data show the same general trend as the preliminary data, with the proportion of oxidized mercury at the SCR outlet falling markedly with increasing ammonia injection or deNOx levels. There appeared to be a disproportionately large decrease in oxidized mercury at very high deNOx levels, from roughly 90% to 94% deNOx. This effect will be examined in more detail during future testing. One discrepancy in the data between the preliminary and final tests is the level of oxidized mercury at mid-level deNOx. The preliminary data does not show a decrease in oxidized mercury at roughly 50% deNOx, while the final data does. The source of this discrepancy is unclear and will be investigated in future testing. The question is somewhat academic, however, since it would be unlikely that an SCR would be operated at roughly 50% of its design deNOx on a normal basis.

Figure 3-3 shows the level of oxidized mercury as a function of ammonia increase (deNOx increase) at different SCR locations (inlet, intermediate layer, and outlet). The intermediate location corresponds to the location between the second and third catalyst layers. With the exception of the low/no ammonia case, there is an approximate linear increase in oxidized mercury through the SCR reactor. For the low/no deNOx case, the vast majority of the mercury oxidation exhibited at the reactor exit occurs across the first layer of catalyst. Overall, these data clearly indicate the suppressive nature of ammonia on mercury oxidation.

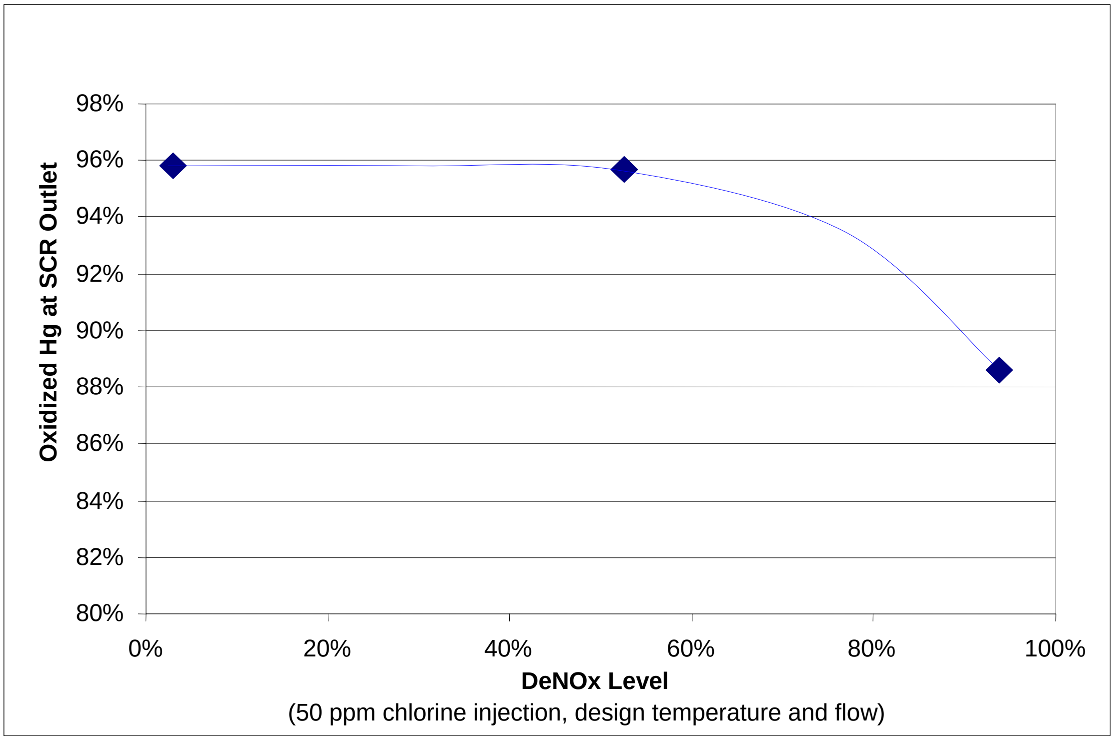

Figure 3-1
Oxidized Mercury vs. DeNOx (preliminary data set)

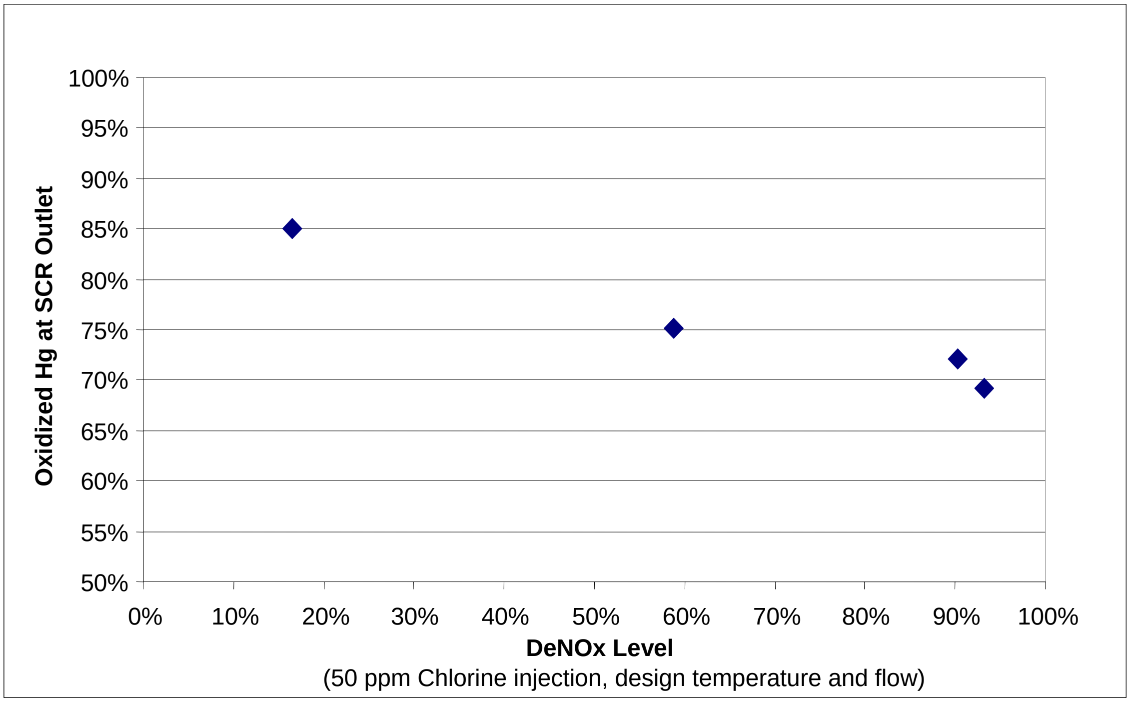

Figure 3-2
Oxidized Mercury vs. DeNOx

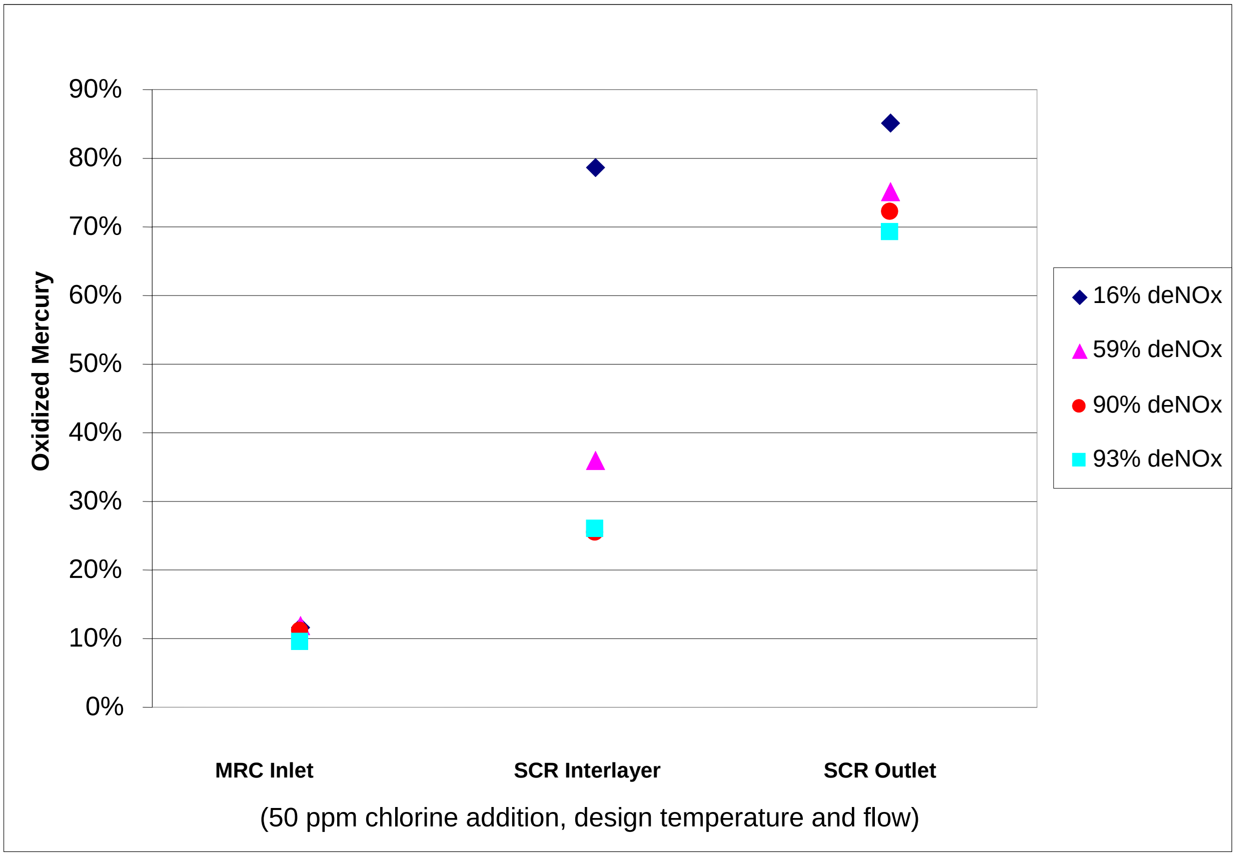

Figure 3-3
Oxidized Mercury vs. SCR Location and DeNOx Level

The rate of mercury capture at the ESP and scrubber outlets, as a function of deNOx level, was examined. Figure 3-4 shows the overall rate of total mercury removal between the MRC inlet and the ESP outlet. Interestingly, although the proportion of oxidized mercury exiting the SCR decreased with increasing ammonia injection, the total mercury capture at the ESP actually increased. Virtually all of this improvement in mercury capture was due to an increase in the efficiency of removal of oxidized mercury. This effect is demonstrated in Figure 3-5 and Figure 3-6, where Figure 3-5 shows the increasing rate of oxidized mercury capture across the ESP itself, while Figure 3-6 shows the relatively stable rate of elemental mercury capture across the ESP.

The effect is opposite from what one might expect intuitively, where one would assume that decreased oxidized mercury levels would lead to lower total capture rates. In essence, the improvement in oxidized mercury capture across the ESP associated with increased deNOx levels outweighed the loss in oxidized mercury entering the ESP. A number of possible hypotheses could be developed to explain this effect. One attractive hypothesis is that the presence of increasing amounts of ammonia lead to increased ammonia slip, which then acted as a scavenger for SO_3. If the ash was acting as a mercury sorbent, similar to conventional activated carbon, then the lowered SO_3 levels may have enhanced its ability to adsorb mercury. This hypothesis is based on the known detrimental effect of SO_3 to conventional activated carbons under certain conditions. In an optimally operating SCR, however, one would expect little, if any, ammonia slip to occur at lower deNOx levels, and thus a relatively linear increase in mercury capture with deNOx level would not be consistent with the expected ammonia slip (i.e., ammonia slip may only become evident at high deNOx rates). However, an SCR operating non-ideally (with catalyst by-pass, non-ideal distributions, etc.) may indeed exhibit increasing slip across the entire deNOx range, and thus the hypothesis would be consistent with the data in this case.

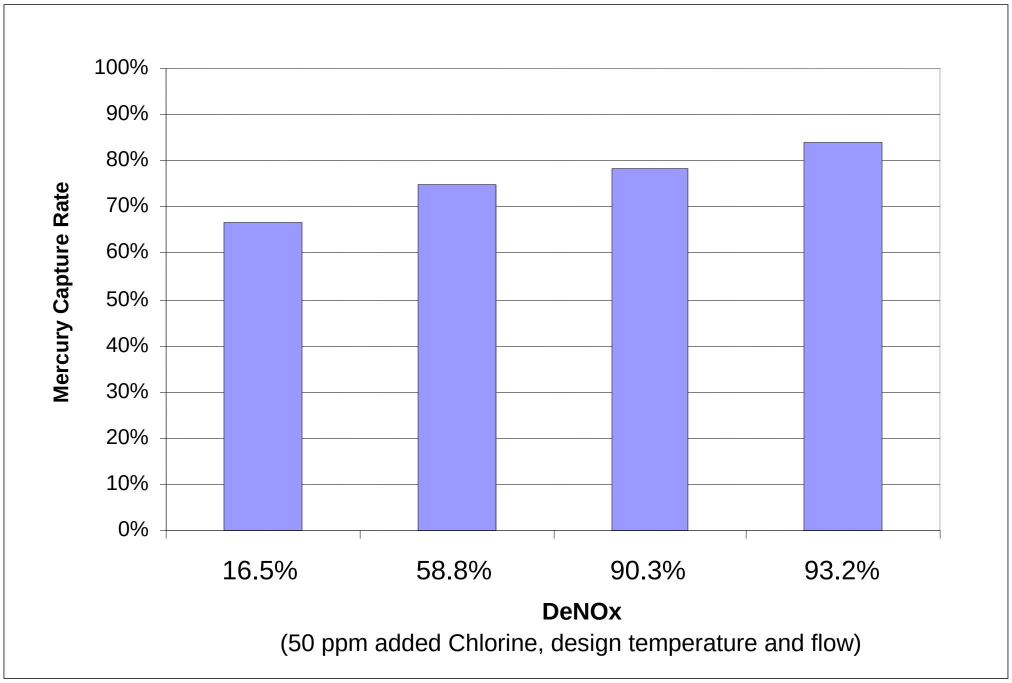

Figure 3-4
Hg^T Capture Rate – MRC Inlet to ESP Outlet vs. DeNOx Level

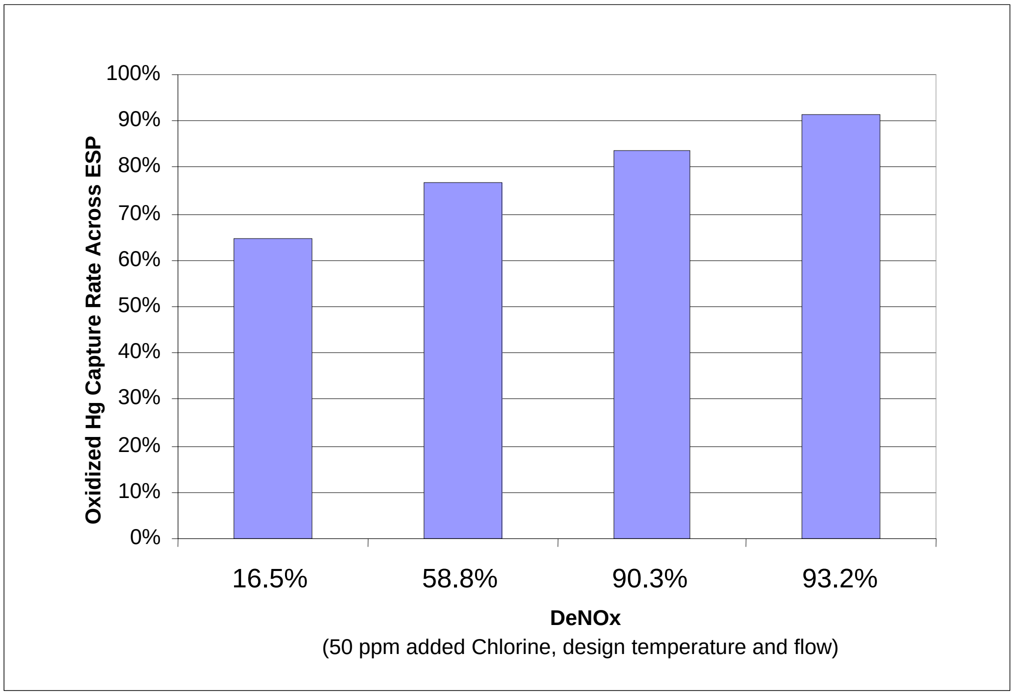

Figure 3-5
Hg^{+2} Capture Rate – SCR Outlet to ESP Outlet vs. DeNOx Level

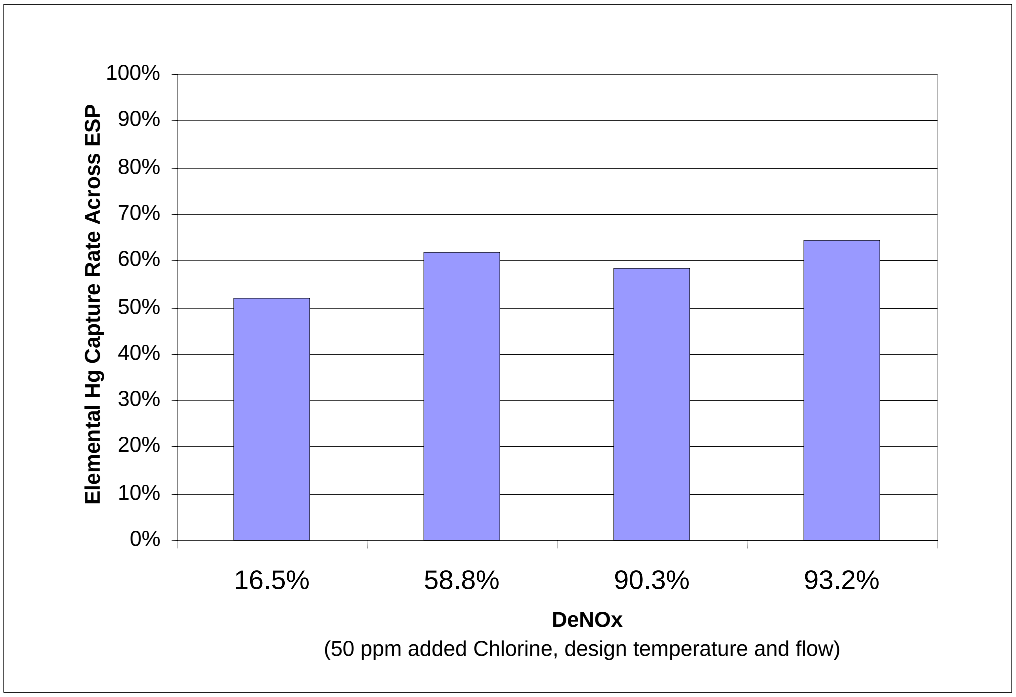

Figure 3-6
Hg^{0} Capture Rate – SCR Outlet to ESP Outlet vs. DeNOx Level

Examining similar data at the scrubber outlet yields results more consistent with intuitive expectations. Figure 3-7 shows the overall mercury capture rate (MRC inlet to scrubber outlet) as a function of SCR deNOx level. In this data set, a clear decrease in overall mercury capture is noted as the ammonia injection level is increased.

This is consistent with the decrease in the proportion of oxidized mercury exiting the SCR with increases in deNOx. The data do show a slight improvement in capture efficiency at the highest deNOx level (93%) over that of the 90% deNOx condition, but this finding is likely a data anomaly rather than a valid effect. The overall reduction in mercury capture rate was not as sharp as was the decrease in oxidized mercury at the SCR outlet, however. In other words, the oxidized mercury fell 15% absolute across the deNOx range, while the capture efficiency at the scrubber outlet only fell about 8% absolute across the same range. Much of this off-set in overall capture rate is due to the improved ESP capture rate with increasing deNOx. As shown in Figure 3-8, the oxidized mercury capture efficiency across the scrubber itself was unchanged at roughly 93% for all deNOx levels, thus any effects noted for total mercury removal are due to relative speciation changes through the SCR and ESP and varying ESP capture rates. Similar data for elemental capture rates across the scrubber are difficult to interpret due to the low absolute levels of elemental mercury (roughly 1 µg/Nm^3), making relative errors quite large, and thus the calculation of percent elemental mercury removal highly uncertain.

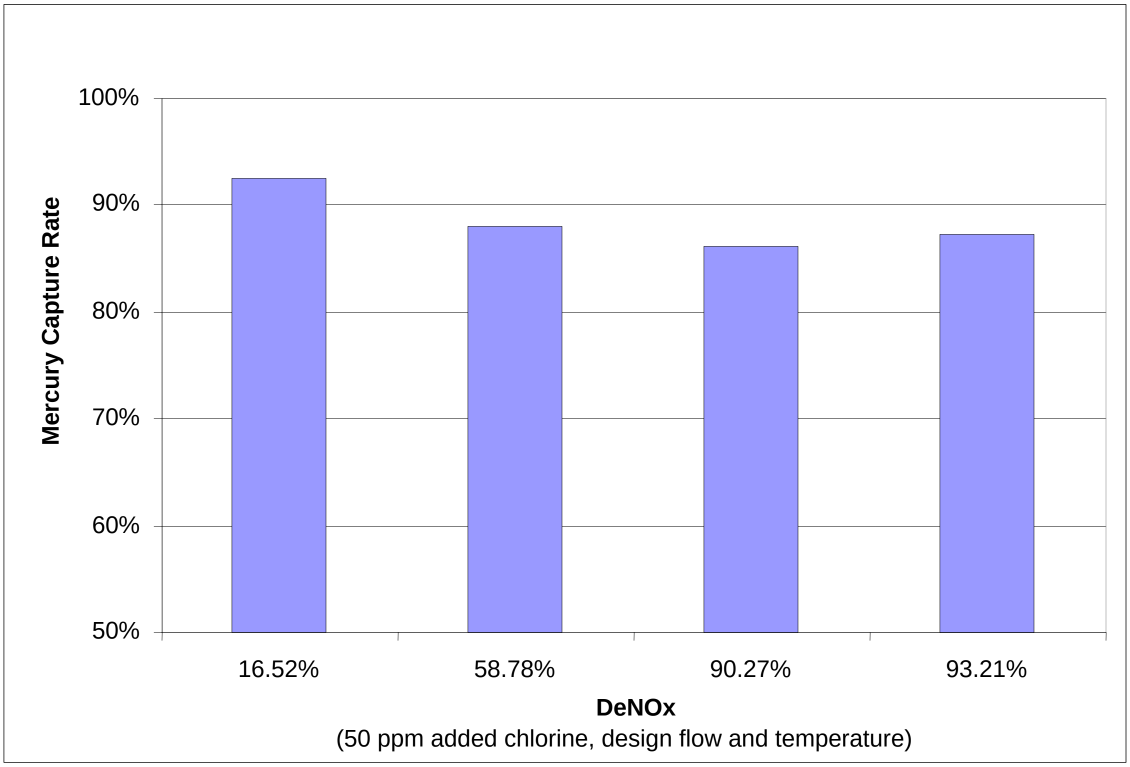

Figure 3-7
Hg^T Capture Rate, MRC Inlet to Scrubber Outlet vs. DeNOx Level

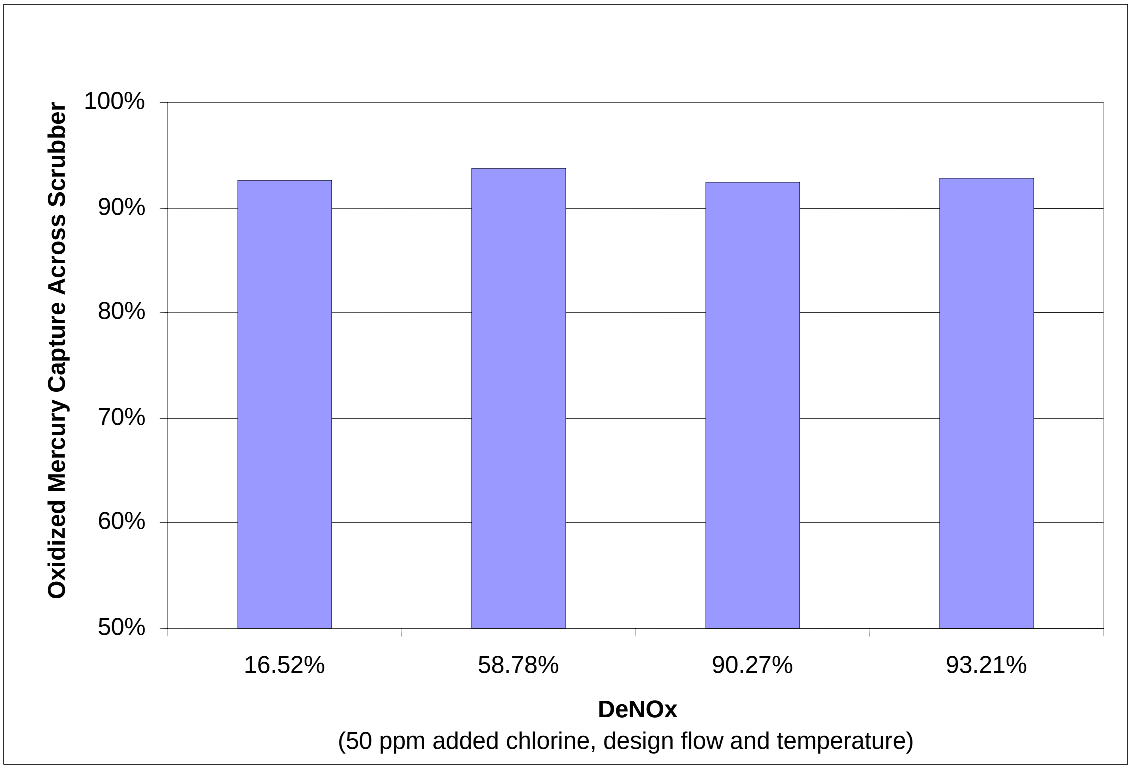

Figure 3-8
Hg^{+2} Capture Rate, ESP Outlet to Scrubber Outlet vs. DeNOx Level

As a way of summarizing the data, Figure 3-9 shows absolute speciated mercury as a function of location and deNOx level. The data show the marked decrease in absolute mercury levels at the ESP outlet and scrubber outlet, and show the relative decrease in oxidized mercury at most locations as the deNOx level increases.

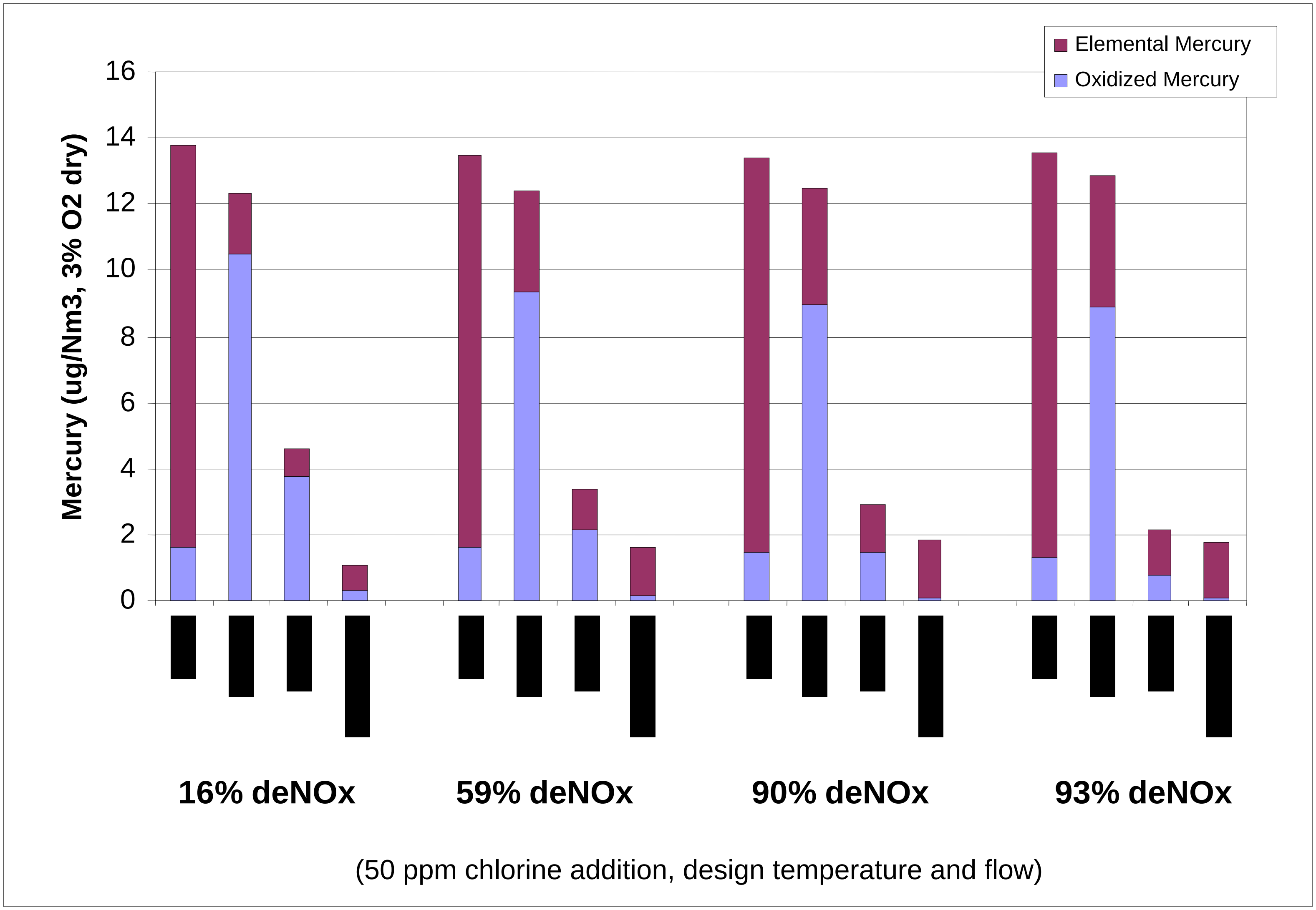

Figure 3-9
Speciated Mercury versus Location and DeNOx Level

Effect of Chlorine

One of the principal purposes of the test program was to determine the effect of flue gas chlorine levels on mercury speciation and capture. The very low level of native chlorine in the coal allowed for a wide range of flue gas chlorine concentrations to be explored. It is important to note that the findings associated with chlorine injection are specific to coals having very low native chlorine levels. Typical eastern bituminous fuels, having moderate to high native chlorine levels, would not see the benefits of chlorine injection as demonstrated by this data, at least at the levels of chlorine utilized in this project.

For the parametric testing on the current project, 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.

Figure 3-10 shows mercury speciation at the SCR outlet as a function of injected chlorine level, based upon the preliminary test data. The data demonstrate a marked improvement in mercury oxidation across the SCR as the chlorine in the flue gas was increased. Above roughly 100 ppmv chlorine injection, the improvement in mercury oxidation diminishes.

Figure 3-11 shows similar data to that previously shown, but from the final parametric test series. These data show a continued improvement in SCR outlet mercury oxidation with increased chlorine levels above 100 ppmv, but the overall effect is similar to that shown in Figure 3-10. Note that all of the data points are somewhat higher in Figure 3-10 than in Figure 3-11, especially the data corresponding to zero chlorine injection. Presumably, differences in boiler operating conditions and fuel are the source of these differences. This provides an excellent example of the difficulty in comparing data that are separated substantially in time and cautions against selecting data points from many different run days to develop any conclusions (without validating the comparability of the data in terms of inlet mercury levels and speciation).

Figure 3-12 shows both SCR intermediate layer and outlet oxidized mercury proportion at two different chlorine injection conditions, 0 ppmv and 50 ppmv. The data corresponding to 0 ppmv chlorine injection show a linear oxidized mercury profile through the reactor, similar to the data shown previously (for 90% deNOx). However, when chlorine is introduced, there is a sharp up-tick in mercury oxidation across the last catalyst layer. Several sets of data are available to show this phenomenon, corresponding to data obtained for parametric test series examining effects of flow, temperature, and chlorine. These data indicate that the majority of the mercury oxidation attributable to increased chlorine levels occurs across the last layer of catalyst.

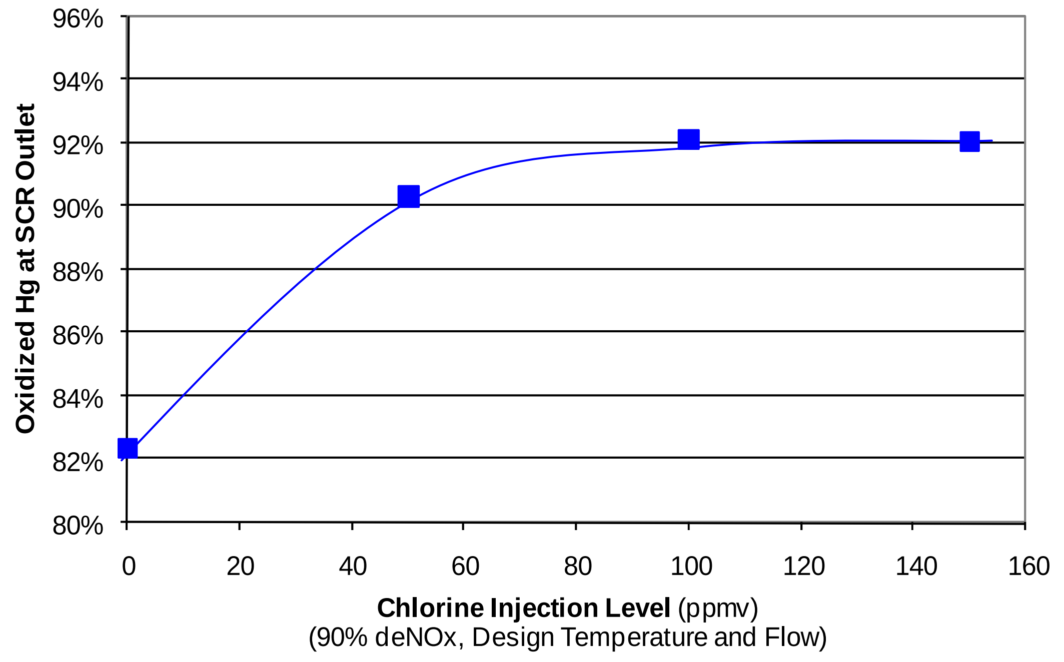

Figure 3-10
Oxidized Mercury at SCR Outlet vs. Injected Chlorine (preliminary data series)

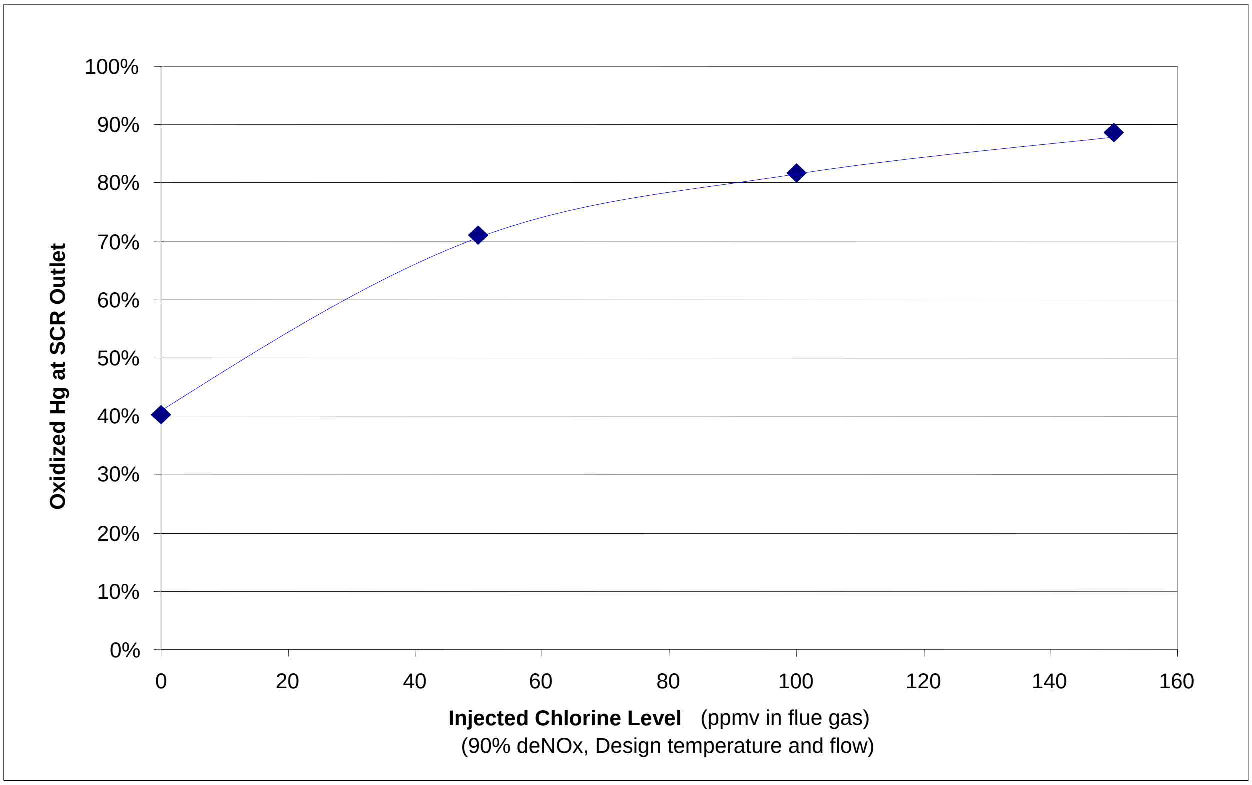

Figure 3-11
Oxidized Mercury at SCR Outlet vs. Injected Chlorine (final data series)

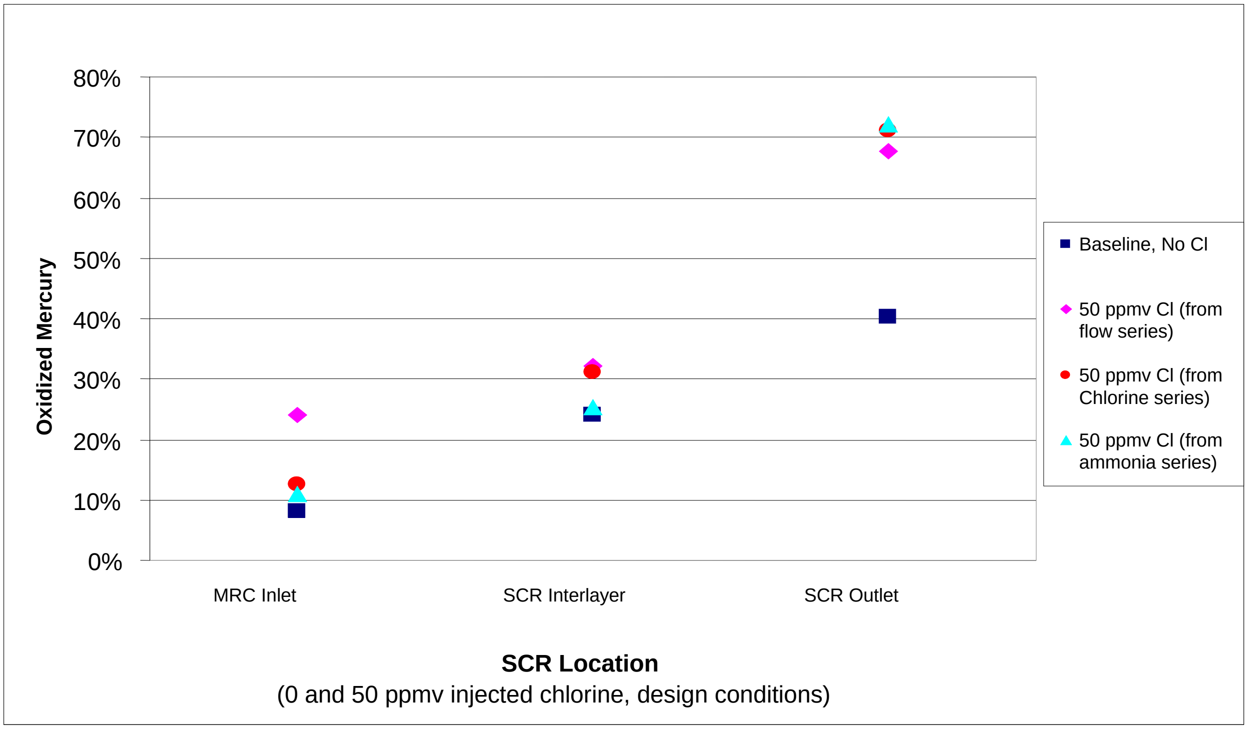

Figure 3-12
Oxidized Mercury vs. SCR Location and Chlorine Level

Figure 3-13 shows the capture rate of total mercury through the ESP (MRC inlet to ESP outlet). These data are limited due to the lack of data for the 150 ppmv chlorine injection case. Given the limitations, however, a clear improvement in mercury capture at the ESP outlet is noted. The data are not clear as to the source of improvement, that is, whether the improvement is solely due to the increase in quantity of oxidized mercury entering the ESP, or if improved capture efficiency of the oxidized mercury also occurs.

Figure 3-14 shows the overall capture efficiency of mercury, from the MRC inlet to the scrubber outlet, as a function of injected chlorine level. Note that similar data were not available corresponding to the ESP outlet due to equipment problems, although the limited data available did show an improvement in mercury capture measured at the ESP outlet with the injection of chlorine. Although the mercury capture rates are quite high for all conditions, there was still a clear improvement with increasing levels of chlorine. The data demonstrated an improvement in total mercury capture (MRC inlet to scrubber outlet) from roughly 88% without any chlorine injection, to roughly 95% with 150 ppmv chlorine injection. Note that higher chlorine levels will likely be explored during future testing.

Figure 3-15 shows the scrubber capture efficiency of oxidized mercury across the scrubber itself (ESP outlet to scrubber outlet). There is a clear improvement in oxidized mercury capture with increasing chlorine level (0 chlorine injection point data not available). This is an interesting finding because it demonstrates that the presence of chlorine not only improves the oxidized mercury proportion leaving the SCR and ESP, but also improves the oxidized mercury capture percentages across the scrubber itself. Thus, increased chlorine levels have multiple, beneficial effects.

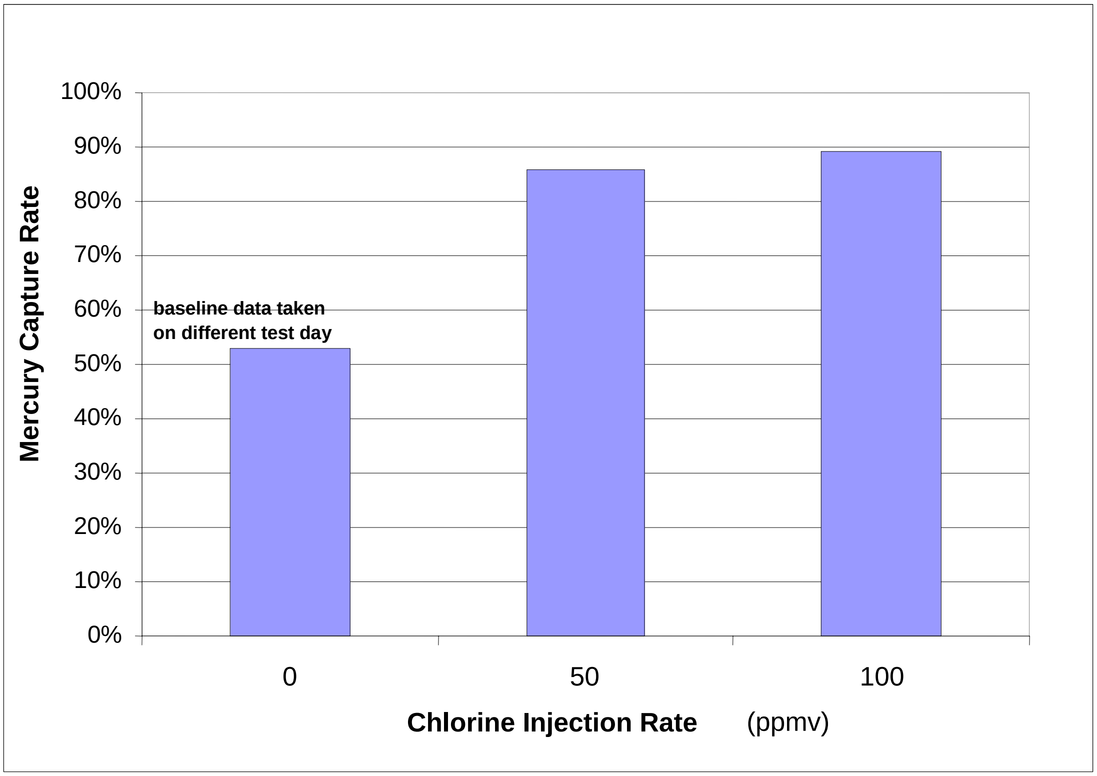

Figure 3-13 Hg^T Capture Rate, MRC Inlet to ESP Outlet vs. Chlorine Level

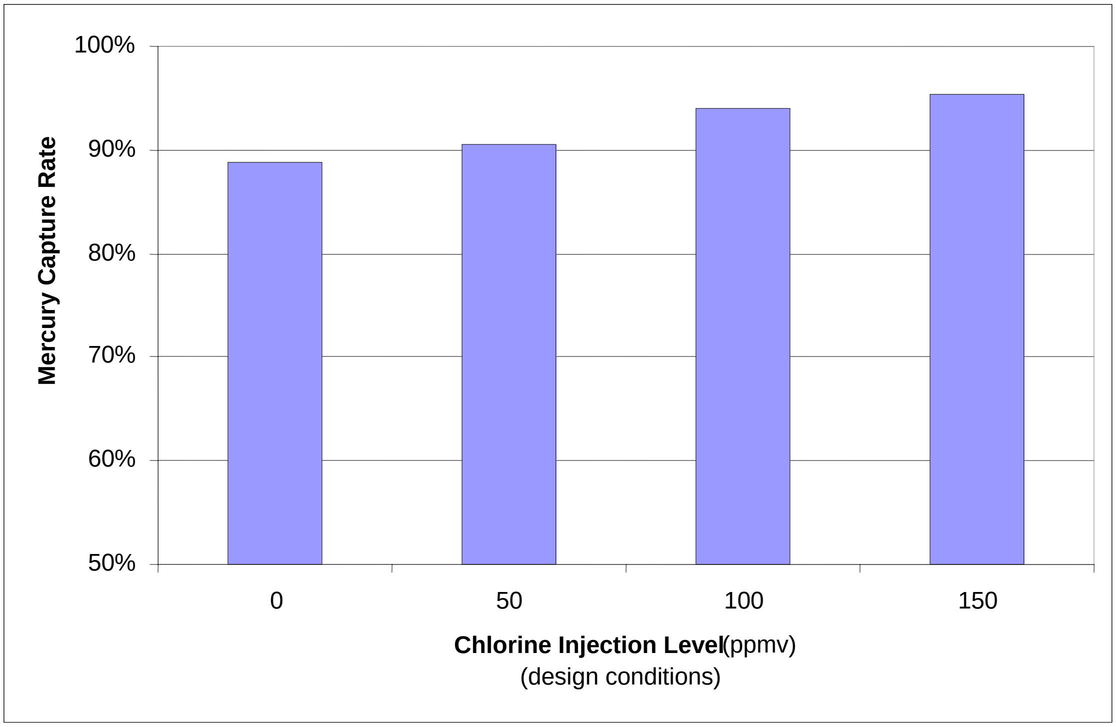

Figure 3-14 Hg^T Capture Rate, MRC Inlet to Scrubber Outlet vs. Chlorine Level

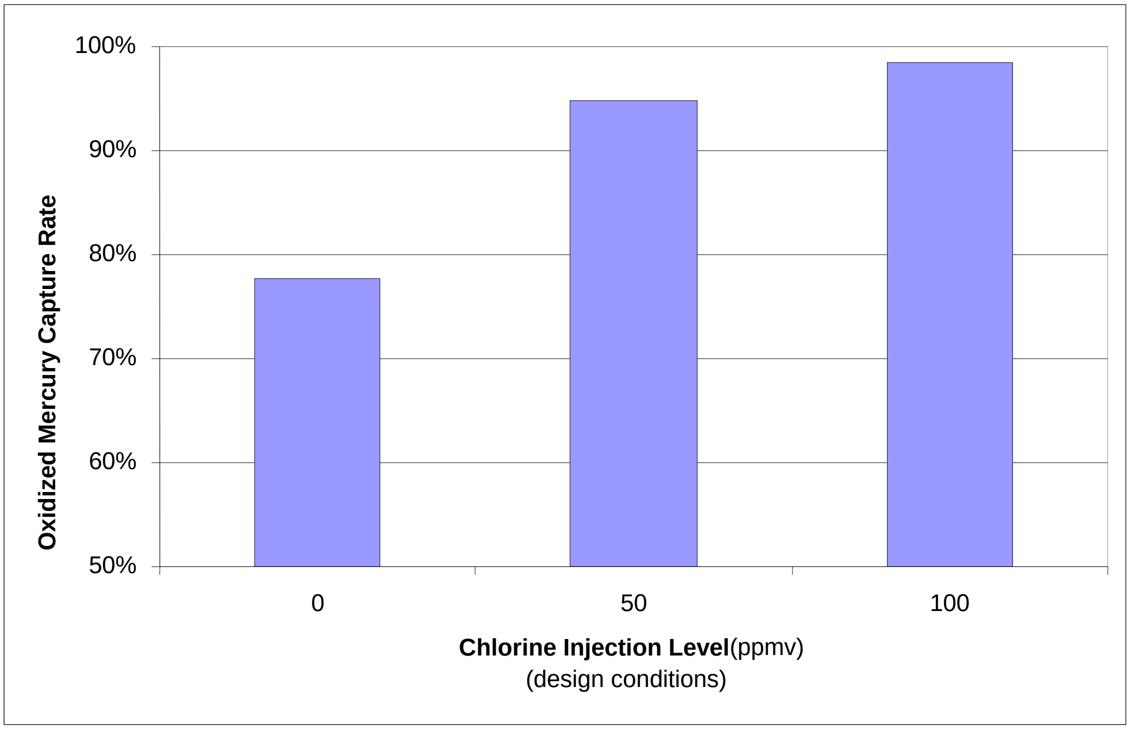

Figure 3-15 Hg^{+2} Capture across Scrubber (ESP outlet to Scrubber Outlet)

The following figures provide summary data showing the effects of chlorine as a function of location. Figure 3-16 shows data for the oxidized mercury percentage, while Figure 3-17 shows absolute elemental mercury. Figure 3-18 shows total mercury. Note that the data corresponding to 0 ppmv chlorine addition were taken on a day previous to the test day when chlorine injection was conducted. Thus, this data is somewhat suspect in terms of offering a firm comparative baseline. Also, note that no ESP outlet data are available for the 150 ppmv chlorine injection condition. The graphs show the clear increase in the percentage of oxidized mercury at the SCR inlet, SCR intermediate, and SCR outlet locations, as well as at the ESP outlet. Elemental mercury levels fall dramatically for all locations with increasing chlorine level (with the exception of the SCR inlet). The reductions in total mercury level are also apparent with increasing chlorine. A final summary is shown in Figure 3-19 with a bar chart indicating the absolute level of elemental and oxidized mercury as a function of chlorine level and location.

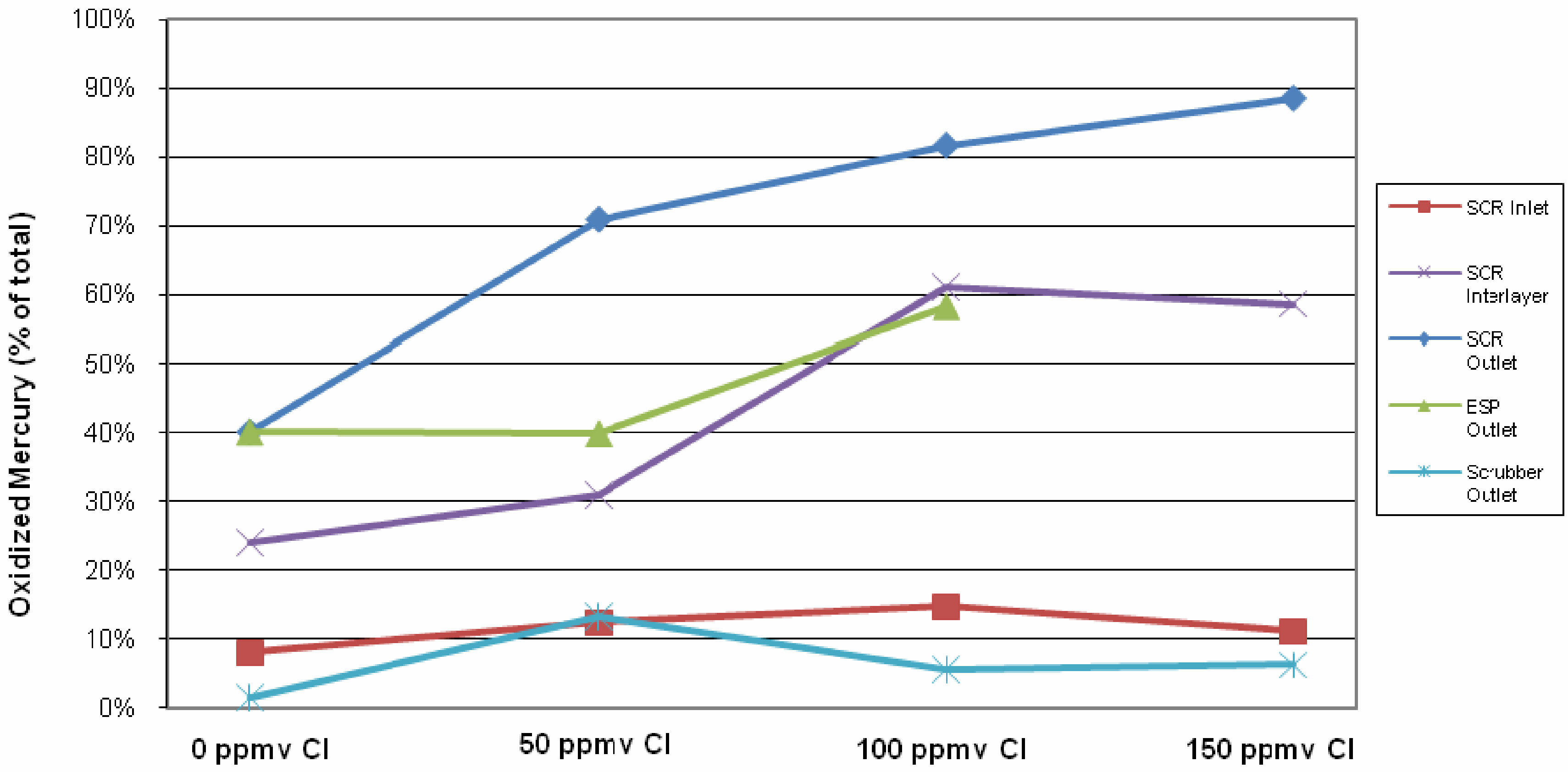

Figure 3-16 Oxidized Mercury Percentage as a Function of Chlorine Level and Location

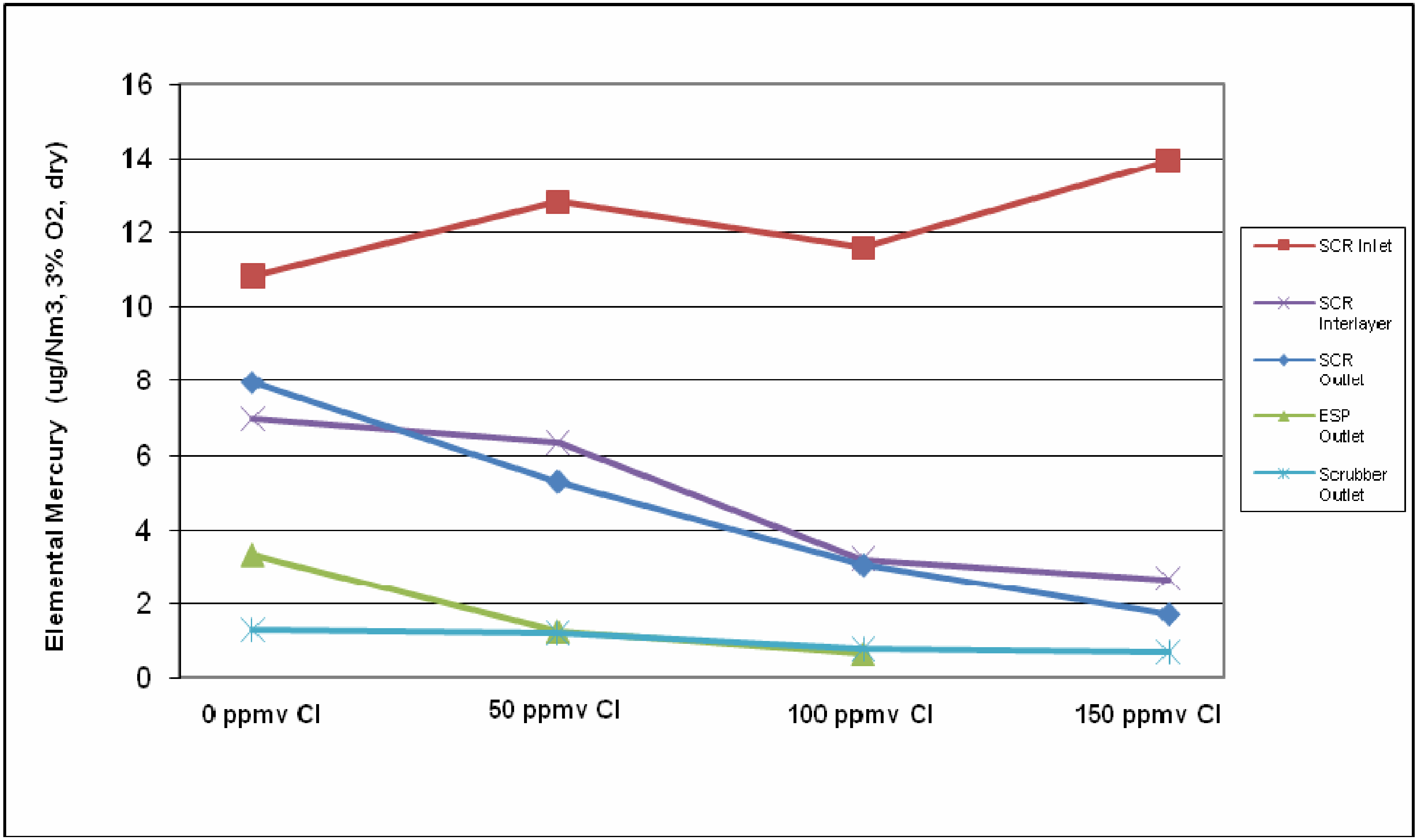

Figure 3-17 Elemental Mercury as a Function of Chlorine Level and Location

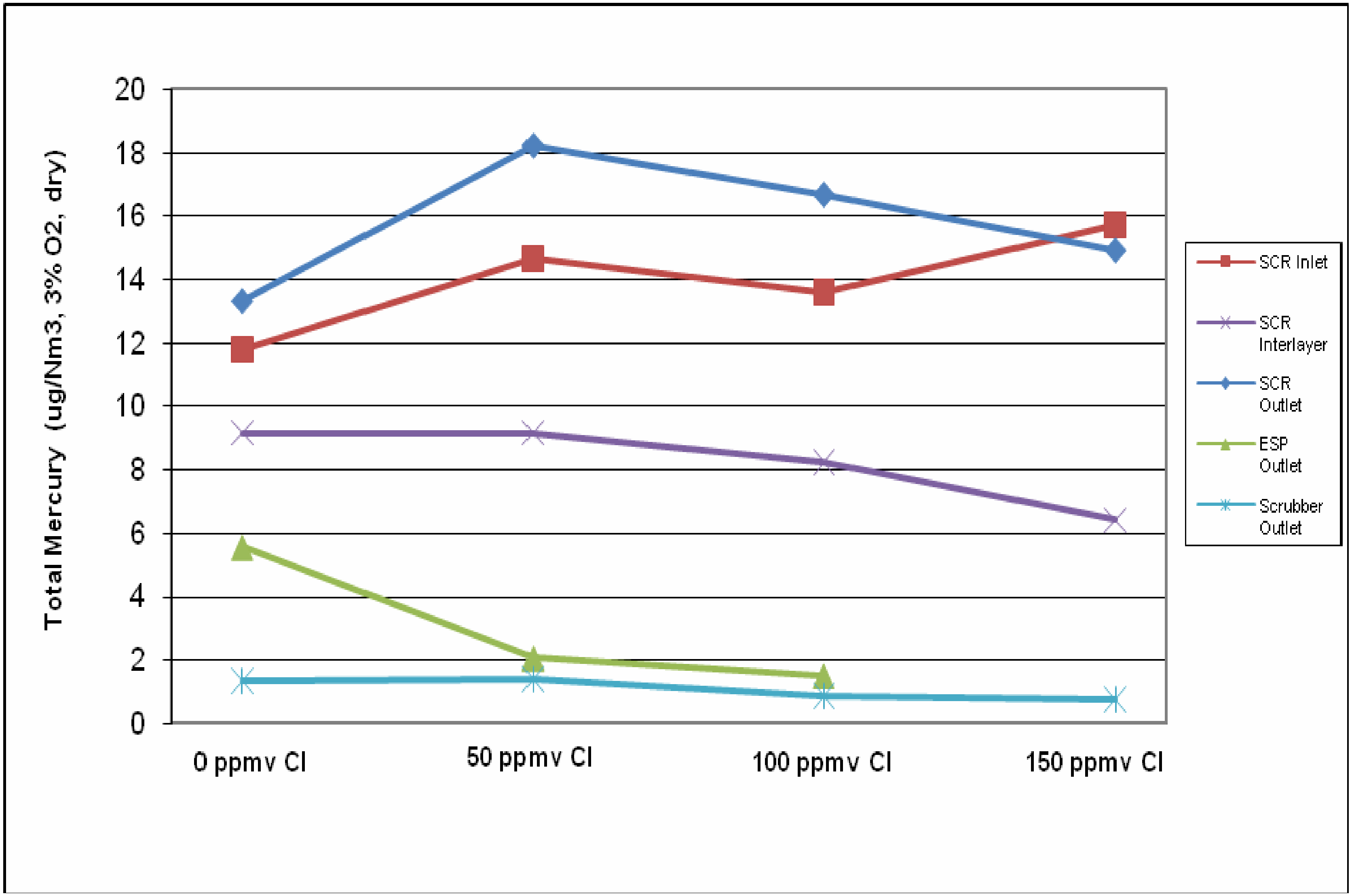

Figure 3-18 Total Mercury as a Function of Chlorine Level and Location

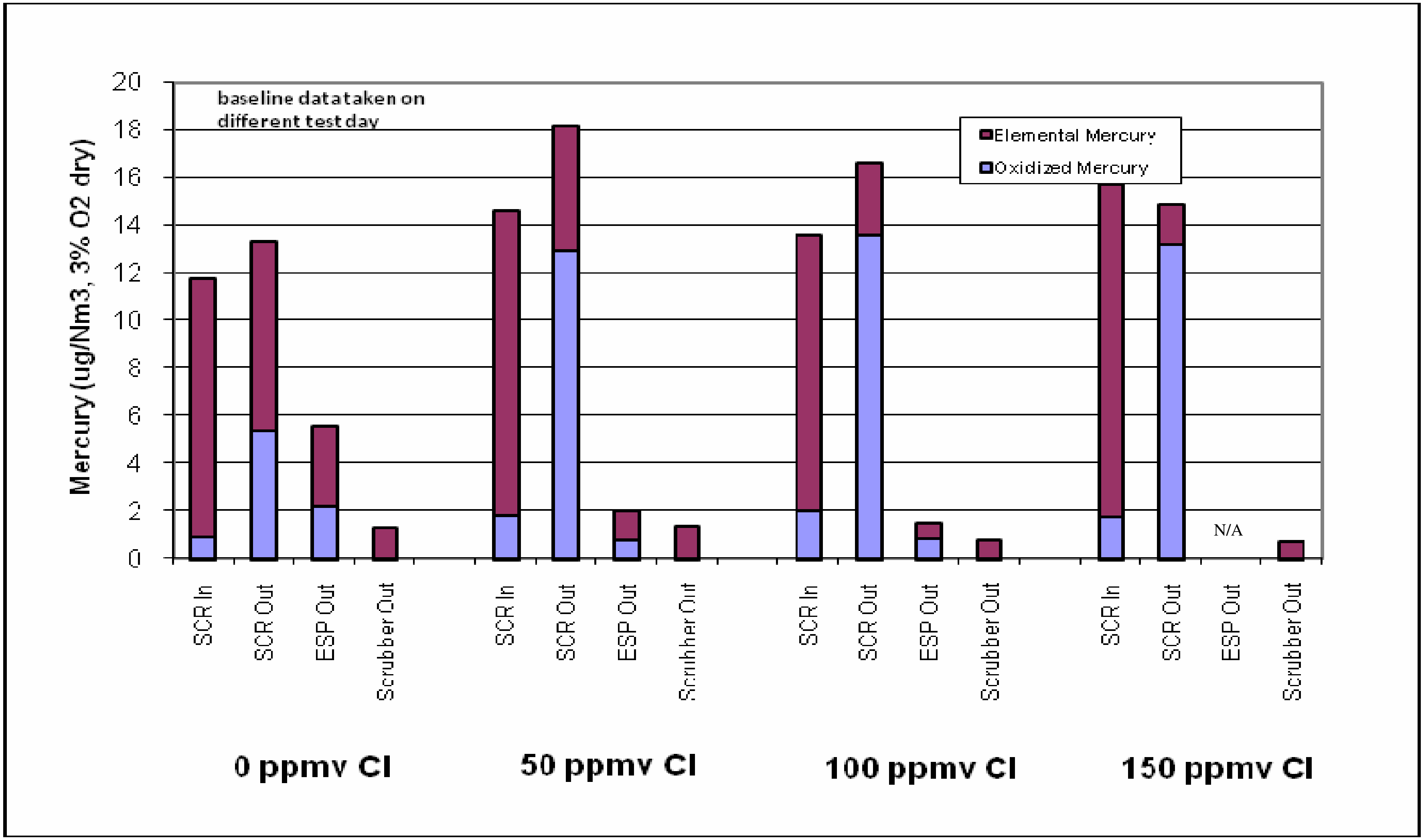

Figure 3-19 Chlorine Effect Summary Data Showing Absolute Mercury Speciation

Effect of Temperature

The effect of temperature is of course an important consideration with any chemical reaction process. For SCR catalysts, as temperature increases, deNOx efficiency generally improves, although SO_2 conversion also increases. The specific behavior of any particular catalyst with respect to these two reactions is a function of many parameters, thus the relative behavior to temperature change may be quite different from catalyst to catalyst. For a constant standard flow rate of flue gas, temperature changes also result in changes in actual volumetric flow through the SCR reactor. This affects the mass-transfer characteristics of the reaction system. Thus, a temperature change can have a complicated and marked effect on a catalytic system. Although the effect of temperature on the deNOx and SO_2 conversion reactions are quite well understood, with respect to overall SCR system performance, the effect is less clearly understood for mercury. Thus, the parametric test series involving temperature offers important data describing the effect of temperature on mercury oxidation and capture.

An important point to note relative to temperature changes at the MRC is that when a temperature change is made, the actual volumetric flow rate through the reactor will vary accordingly, since the mass or standard, flow rate is held constant. However, the volumetric flow rate will not change for equipment downstream of the air preheater, since the air preheater outlet flue gas temperature is typically held constant, regardless of the temperature within the SCR reactor. In an actual commercial SCR, the temperature and flue gas mass flow rate are interlinked under most operating conditions as a function of boiler load.

Figure 3-20 shows two sets of data corresponding to a low and high temperature operating condition. These data were acquired during the preliminary testing. The chlorine injection rate was varied for both of these temperature conditions. The data show a decline in mercury oxidation with increased temperature for all conditions where chlorine was being injected. Note that the data are confounded by two factors. One is that the two data sets were acquired on two different test days (a necessity given the equilibrium times required for the MRC to reach new steady state temperature conditions). The second confounding factor is that the deNOx rate was slightly different for the two data series. For the high-temperature condition, the deNOx rate was slightly lower than that of the low-temperature condition (85% deNOx for the 755°F condition and 88% deNOx for the 666°F temperature condition). The lower deNOx rate will tend to improve mercury oxidation slightly, as previously shown. As a result, the figure understates slightly the adverse effect of increasing temperature.

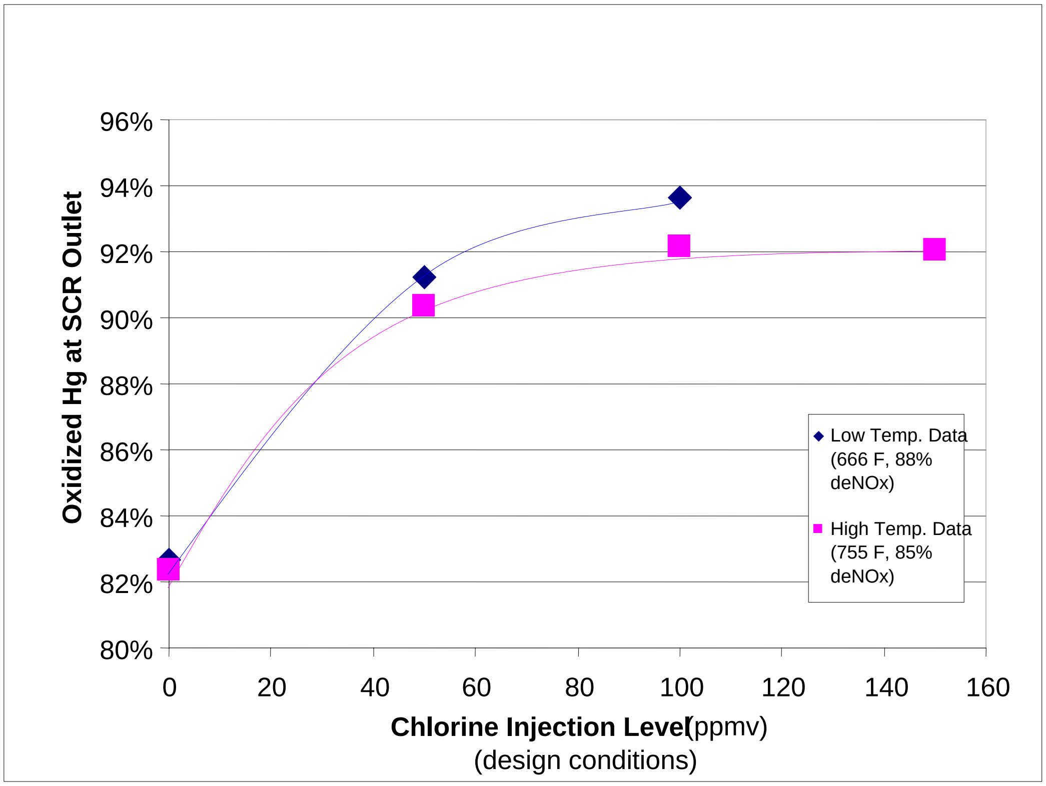

Figure 3-20 Effect of Temperature on SCR Hg Oxidation at Multiple Chlorine Levels (preliminary data)

Figure 3-21 shows additional temperature effect data taken during the final test series. These parametric tests were designed to hold all operational parameters constant with the exception of temperature. However, as with the previously shown data, variations in deNOx level confound the data. This is due to operational difficulties with the ammonia injection system which prevented a constant 90% deNOx level to be maintained throughout the testing. These data show a decline in SCR outlet oxidized mercury with increasing temperature, but the deNOx level also consistently increased along with temperature. This prevents a clear determination of how much oxidation loss is attributable to increased temperature, and how much is attributable to increased deNOx level. The previous data showing the effect of deNOx on mercury oxidation revealed roughly a 4-5% drop (absolute) in oxidized mercury from roughly 80% deNOx to 92% deNOx. Figure 3-21 shows roughly a 10-12% drop (absolute) in oxidized mercury for both the change in deNOx and the change in temperature. Thus, if one assumes that 4-5% of the drop in oxidized mercury is due to the increasing deNOx level, then one could assume that roughly half of the adverse effect as shown in Figure 3-21 is due to the temperature effect. This is a very rough analysis, but it is generally consistent with the data shown in Figure 3-20. (An additional confounding factor in this analysis is that the catalyst will be more efficient in terms of deNOx at higher temperatures, thus affecting slip. Consequently, utilizing the deNOx data to evaluate the current data is further limited by this fact.) Overall, the data show that while there is an adverse temperature effect, it is not particularly marked. Testing on future catalysts will hopefully elucidate the temperature effect more clearly.

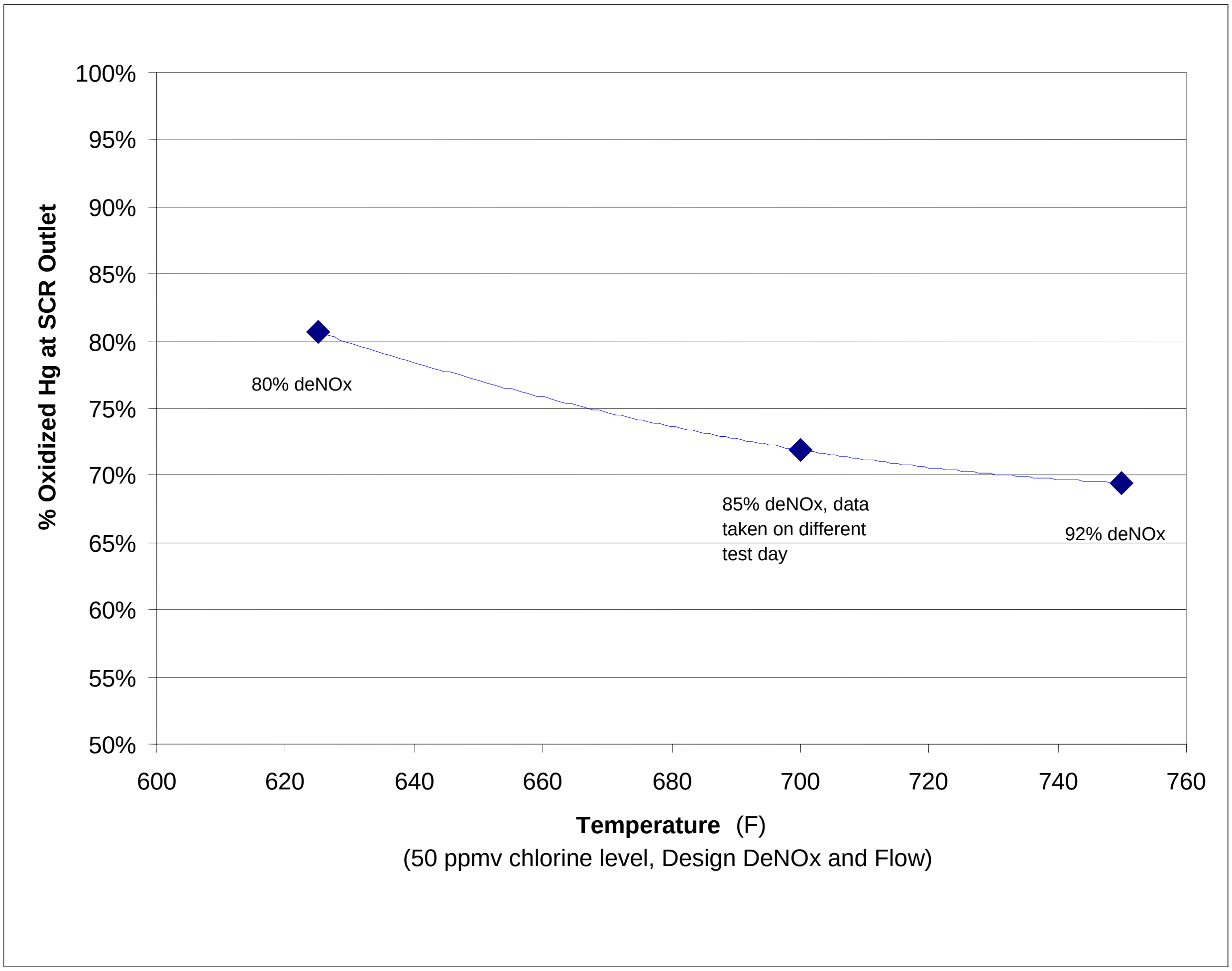

Figure 3-21 Temperature Effect on SCR Outlet Hg Oxidation

Figure 3-22 shows the effect of temperature on the mercury capture rate as measured between the MRC inlet and the ESP outlet. Note that the data corresponding to 700°F is not considered valid for this comparison, since this data point was acquired on a different test day and does not appear to be consistent with the data set as a whole. Also note that, as before, the variation in deNOx confounds the data. However, it was previously shown that an increase in deNOx actually produced an improvement in ESP outlet mercury capture. Thus, this phenomenon would tend to offset some of the adverse impacts associated with temperature in the data set as shown in Figure 3-22. In other words, the data as shown tend to minimize the adverse impact of temperature on ESP outlet capture. One might conclude that the majority of the loss in mercury capture associated with increasing temperature occurs as a result of the loss in mercury oxidation through the SCR and perhaps loss of oxidation and/or capture through the air preheater. No corresponding scrubber outlet capture data were available due to monitor problems.

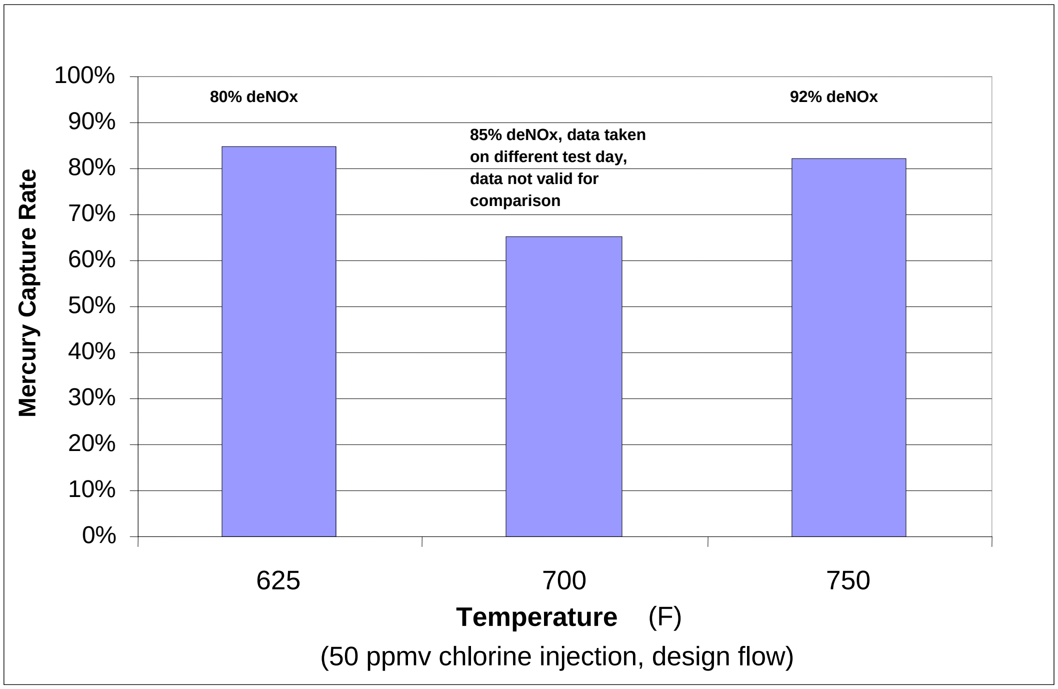

Figure 3-22 Hg^T Capture Rate, MRC Inlet to ESP Outlet vs. Temperature

Effect of Flow Rate

The effect of flow rate was examined by varying the flow rate through the MRC while maintaining the other operating conditions at a constant level. As previously mentioned, this is somewhat different from a full-scale commercial SCR where flow rate and temperature are likely to be interlinked. 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. In addition, flow rate changes will affect the temperature profile within the air preheater.

Note that since the MRC scrubber operates as a slip stream of the MRC primary gas flow, the flow through the scrubber did not vary with changes in the MRC flow rate. This is fundamentally different than would be the case in a full-scale scrubber. Consequently, any effects associated with mercury capture across the scrubber alone would be solely due to differences in flue gas chemical characteristics and not scrubber residence time/throughput.

Figure 3-23 shows the effect of flow rate on mercury oxidation across the SCR. Note that although these data were taken on different test days, they appear to be internally consistent. In addition, the inlet mercury levels for these days were quite consistent at roughly 12 to 15 µg/Nm^3. As one would intuitively expect, increases in flow rate produced a decrease in oxidized mercury exiting the reactor. This is probably the result of multiple factors, including lowered residence time for the oxidation reaction to occur, and an increase in the concentration of ammonia throughout the reactor.

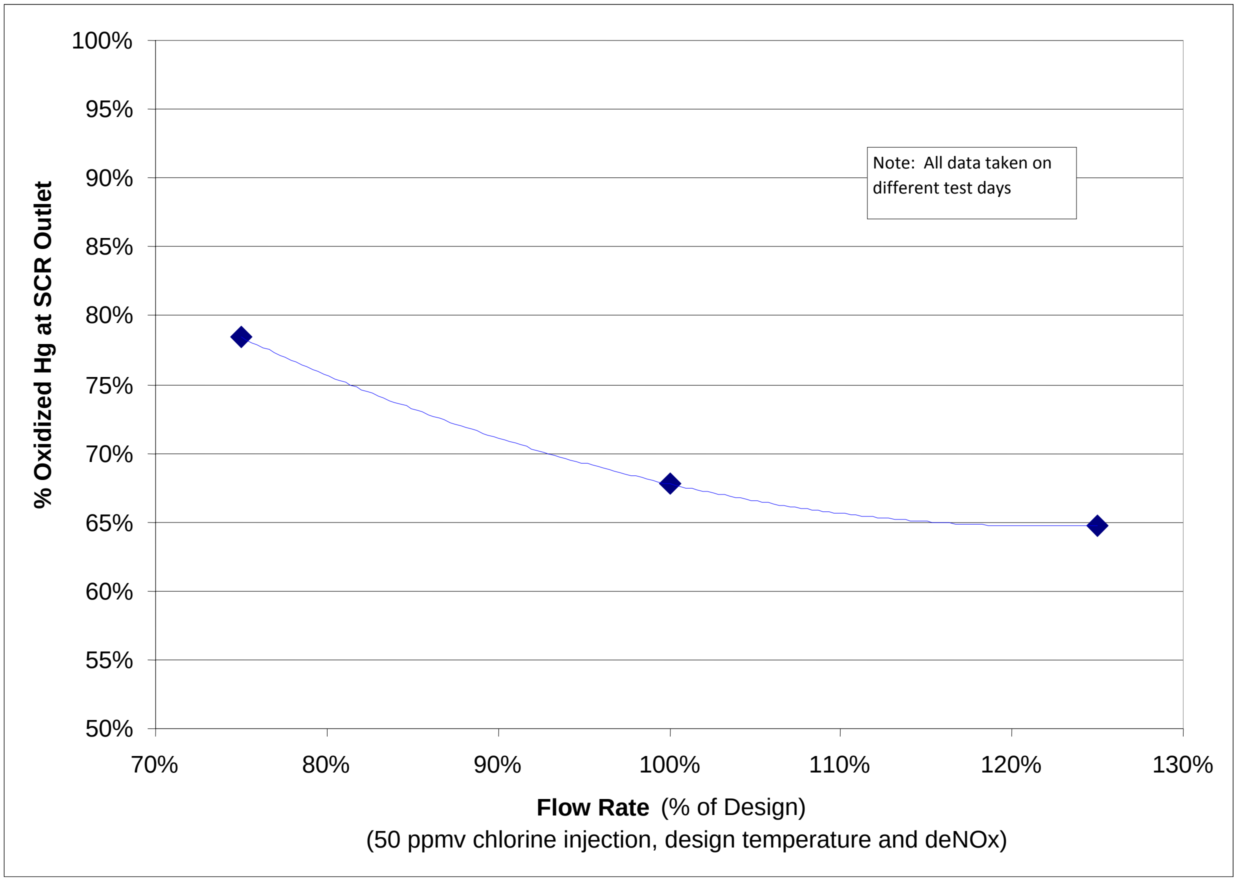

Figure 3-23 Effect of Flow Rate on SCR Outlet Mercury Oxidation

In terms of mercury capture, Figure 3-24 shows the flow rate effect as measured between the MRC inlet and the ESP outlet. The data are difficult to analyze because they are internally inconsistent, showing an improbable response to flow rate. This is thought to be a data anomaly, the source of which is unclear. The data for the 75% and 125% of design flow conditions show a clear loss in overall mercury capture with increasing flow rate, as would be expected. The effect is likely a combination of decreased residence time through the air preheater and ESP, as well as a reduction in the proportion of oxidized mercury entering these devices.

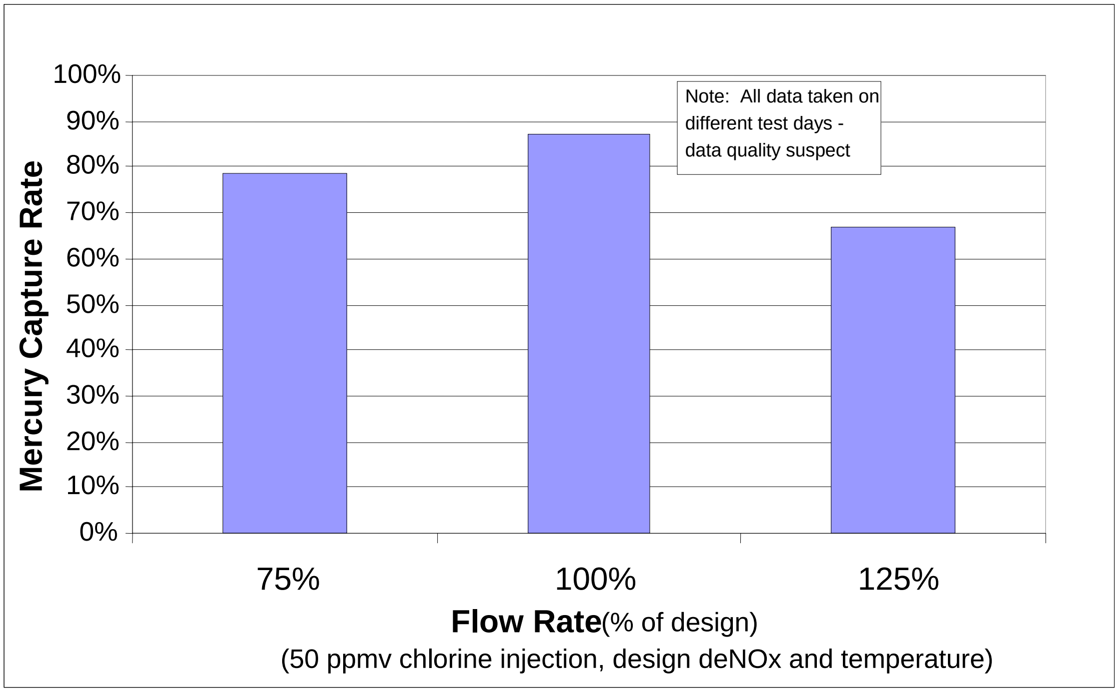

Figure 3-24 Hg^T Capture Rate, MRC inlet to ESP outlet vs. Flow Rate

Figure 3-25 shows the effect of flow rate on total mercury capture, MRC inlet to scrubber outlet. As previously discussed, the flow rate through the scrubber itself did not change due to this testing, since the scrubber operated as a slip stream, processing only a portion of the MRC flow. Thus, any effects noted would be the result of a combination of several effects including residence time in the SCR, air pre-heater, and ESP (but not the scrubber), changes in oxidized mercury proportion at the SCR outlet, and changes in overall flue gas chemistry due to ammonia level and other constituents that may change with flow rate. In any event, the decrease in mercury capture noted between the 75% and 125% of design flow data points, mirrored that shown for the ESP outlet. For a full-scale facility where scrubber flow rate increased commensurately with SCR and ESP flow rate, the effect might be more marked, due to the lower residence time of the flue gas through the scrubber.

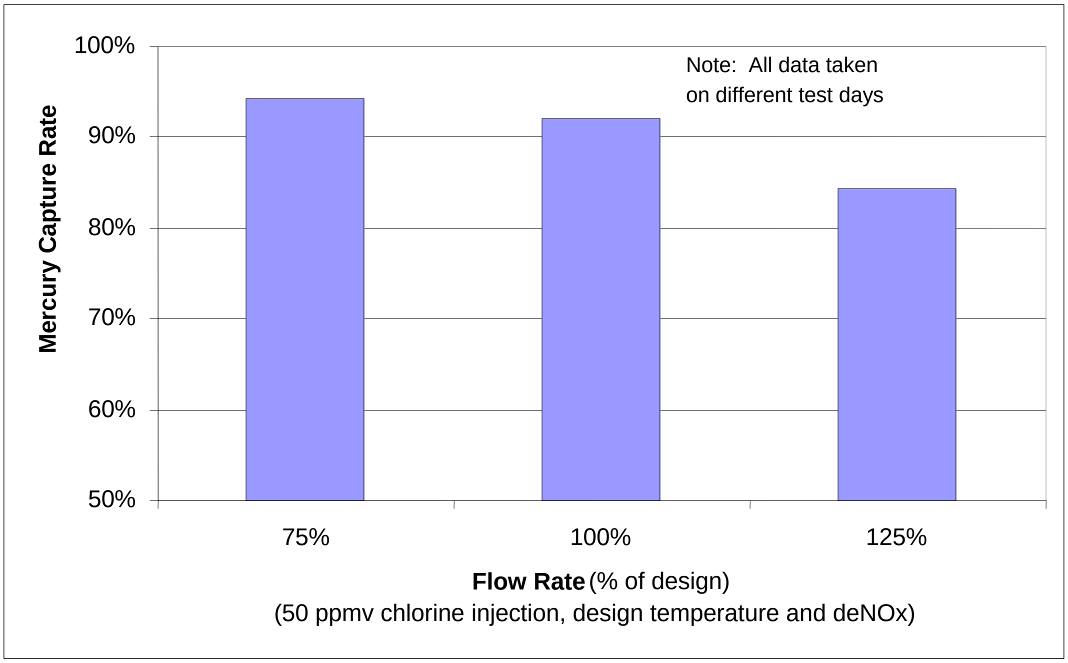

Figure 3-25 Hg^T Capture Rate, MRC Inlet to Scrubber Outlet vs. Flow Rate

Figure 3-26 shows summary data in terms of absolute mercury speciation at various locations for different flow rates. The increase in total mercury at the scrubber outlet is clearly evident, along with the decreasing proportion of oxidized mercury at the SCR outlet with increasing flow rate. The anomalous decrease in ESP outlet total mercury at the 100% of design flow condition is also apparent.

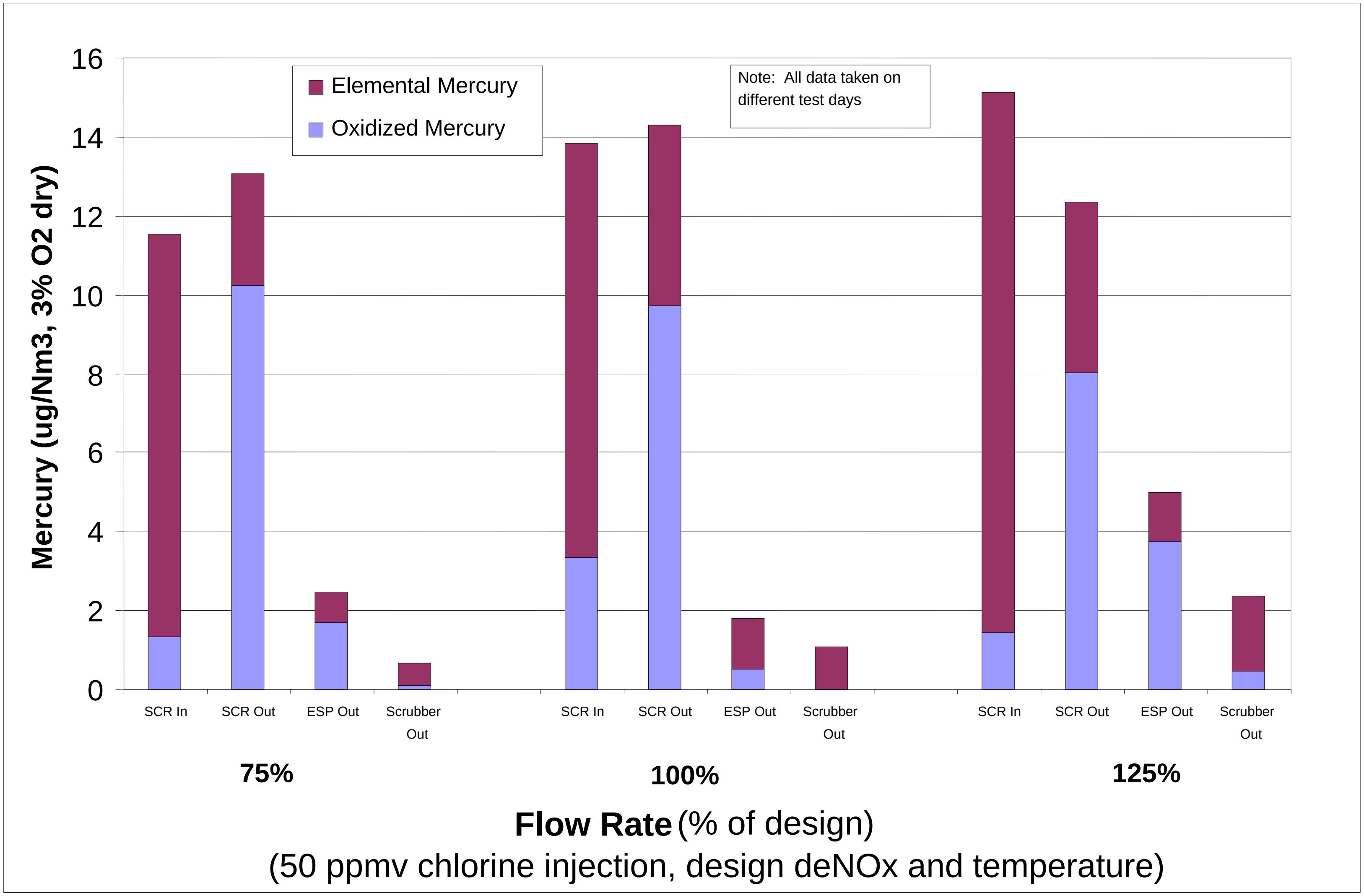

Figure 3-26 Flow Effect Summary Data Showing Absolute Mercury Speciation

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CONCLUSIONS

The data of course are limited by the fact that only a single catalyst has been tested thus far in the research program. As a result, any conclusions reached are catalyst-specific. Although one might intuitively expect the qualitative response of various catalysts to be similar, this assumption has yet to be demonstrated by the project. As such, the reader is cautioned against globally applying the findings of the reported tests to the commercial catalyst fleet as a whole.

The primary focus of the project was to investigate the response of SCR catalyst mercury oxidation to variations in flue gas chlorine level. The data showed a substantial, beneficial effect associated with increased chlorine levels above the very low native chlorine levels found in the flue gas. This effect was most dramatic up to very roughly 100 ppmv chlorine injection, after which the beneficial effects appeared to levelize somewhat, although improvements in mercury oxidation and capture were demonstrated across the entire range of increased chlorine tested in the program. The presence of additional chlorine had multiple effects, apparently improving the proportion of oxidized mercury exiting both the SCR and ESP and improving the ability of the wet scrubber to capture oxidized mercury. The combined effect of these phenomena, resulted in a rather marked improvement in overall mercury capture when chlorine was injected.

The effect of ammonia levels (deNOx) was investigated in some detail during the parametric testing. The data show that the deNOx level can have a substantial effect on mercury oxidation across the SCR, with increased deNOx leading to lower rates of mercury oxidation. The limited data available indicate that the effect may be quite sharp at very high deNOx levels, but this behavior needs to be investigated further before a definitive conclusion can be reached about the sensitivity at very high ammonia levels. The percentage capture of oxidized mercury across the ESP appeared to actually improve with increasing deNOx levels. Thus, a net improvement in overall mercury capture (boiler outlet to scrubber outlet) was exhibited (the improvement in oxidized mercury capture across the ESP outweighed the reduction in the proportion of oxidized mercury entering the ESP). These findings do have implications associated with catalyst aging and non-optimal SCR operation, since these phenomena result in ammonia profiles similar to operation at high deNOx.

An adverse effect on mercury oxidation through the SCR was associated with increases in both temperature and flow rate. Increasing temperature produced a moderate reduction in mercury oxidation across the SCR, although the data were somewhat confounded by variations in deNOx which occurred along with the temperature variations. Of course, an increase in temperature also results in an increase in volumetric flow through the SCR when total mass flow rate is held constant, so the exact underlying reasons for the reduction in mercury oxidation may be quite complicated. The adverse effect associated with flow rate was more dramatic than for temperature, where one would surmise that the loss in residence time through the SCR resulted in lowered mercury oxidation. Still, the effects of flow rate changes are quite complicated since mass transfer parameters are also affected when flow rate is changed. In practice, both temperature and flow rate will likely be interlinked over much of the operating range for full-scale commercial boilers. At higher boiler loads, the SCR will typically encounter both an increase in temperature and an increase in flow rate. This may substantially lower the proportion of oxidized mercury exiting the SCR, and will potentially lower the capture rate of the oxidized mercury in the ESP and scrubber. Thus, the data imply that overall mercury capture efficiency may be heavily impacted by boiler load.

Overall, the project has been very successful in isolating and determining the effects of primary SCR/boiler operational parameters, including chlorine, on mercury oxidation and capture. These findings offer guidance to facility operators in terms of optimizing mercury oxidation performance, as well as provide important guidance related to the use of chlorine injection as a method for improving mercury capture performance for a given system. Future project work, examining additional catalysts, will provide valuable information adding confidence to the conclusions reached thus far, and will provide much needed information related to the mercury oxidation performance of the catalyst fleet as a whole.

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