

Mercury Oxidation Behavior of a New Advanced Selective Catalytic Reduction Catalyst Formulation

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Technical Update, July 2011

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ABSTRACT

Industry data have indicated that along with NOx reduction, selective catalytic reduction (SCR) technology has the potential for oxidizing mercury, providing enhanced removal in downstream systems. In recent years there has been an incentive to develop SCR catalyst formulations that maximize mercury oxidation while retaining their deNOx and SO₂ conversion properties. The subject test program sought to evaluate the mercury oxidation performance of Hitachi's new Triple Action Catalyst (TRAC) as a function of flue gas parameters and as compared to conventional catalysts. The test program compared three SCR catalyst configurations: two layers of TRAC catalyst, two layers of CX catalyst, and an SCR filled with one layer of TRAC and one layer of CX catalyst (hybrid configuration). Gulf Power's Mercury Research Center, a 5-MW slipstream facility, was used for this project.

Results from the test program showed that the TRAC catalyst is likely to have less chlorine dependency than conventional catalysts. The data, however, are limited to chlorine concentrations higher than 100 ppmv. Additional testing would be required to reach any final conclusions related to ultra-low chlorine levels. With respect to flue gas temperature effects, current findings indicate that the TRAC catalyst is likely to have less temperature dependency than conventional catalysts. With respect to bromine injection, at chlorine concentrations higher than 100 ppmv, no significant differences at the SCR outlet were noted among all three catalyst configurations.

Keywords

Selective catalytic reduction SCR Catalyst Mercury oxidation NOx control Co-benefits

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1 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.

In recent years there has been an incentive to develop SCR catalyst formulations which maximize mercury oxidation, while still retaining their deNOx and SO₂ conversion properties. It is of special interest to develop catalysts which maximize mercury oxidation in low halogen environments, such as with low-chlorine eastern bituminous or PRB coals. One such catalyst (termed TRAC) has been developed by Babcock-Hitachi K.K. (supported by Hitachi America, Ltd. in the U.S.). This catalyst was tested in the subject research program and compared to conventional Hitachi catalyst.

Project Objectives

The subject test program sought to evaluate the mercury oxidation performance of Hitachi's new TRAC catalyst, as a function of changes in various parameters, including chlorine and bromine levels, deNOx rate, flow rate, and temperature. The test program compared three catalyst configurations:

- SCR reactor filled with two layers of conventional Hitachi catalyst (all-CX configuration)
- The first (top) layer filled with CX catalyst and the second (bottom) layer with TRAC catalyst (termed a hybrid configuration), and
- Both layers filled with TRAC catalyst (all-TRAC configuration).

In all three cases, two layers of catalyst were used. The test program was devised to determine the relative behavior of the catalysts with respect to various operating parameters.

The data and project conclusions offer information as to the behavior of the advanced TRAC catalyst, as well as the beneficial aspects of using the advanced catalyst formulation, and under what conditions those advantages become apparent. Although some conclusions can be reached about the absolute intrinsic capability of the various catalysts' ability to oxidize mercury, there are limitations, since the catalysts were tested consecutively, and various parameters, especially those associated with the fuel, changed in the course of the project.

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 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 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 SO₂, SO₃, 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

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 m³ 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 2-1SCR 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

The participating catalyst supplier was given design latitude, as would be the case for offerings for full-scale commercial installations. Thus the catalyst supplier 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. These design parameters were basically set based upon the CX formulation. The TRAC catalyst was then provided using the same volume and geometry as the CX, but the formulation of course differed. Table 2-2 shows the nominal SCR catalyst layer arrangement for each test.

Table 2-2Nominal Physical Catalyst Properties

Parameter	СХ	Hybrid	TRAC
Number of Lavors	2	1 CX +	2
Number of Layers	2	1TRAC	2

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, CO₂, and SO₂, 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. Chlorine concentrations were measured continuously using an in-situ FTIR system at the facility inlet. Occasional manual measurements were made for SO₃, 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 typically burned. 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 100 ppmv to roughly 170 ppmv. These relatively high native levels obviously precluded testing at very low levels of chlorine – this limits the findings of the project to some degree. In addition, the 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 testing corresponded to coal blends which were comprised of the very low chlorine coals (A and B) blended with higher chlorine coals (C and D). The native chlorine level was a function of the blending ratio of the fuels. All of the fuels had BTU values in the range of roughly 13,000 to 13,600 BTU/lb and had ash constituents consistent with traditional eastern bituminous fuels. Chlorine levels ranged from a very low 40 ppmw to slightly over 4,000 ppmw. Table 2-4 also 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 C and D were typically blended with lower chlorine coals A or B, 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 the individual coal analyses would indicate.

Table 2-3 Representative Coal Analyses – Ultimate

Coal ID	Α	В	С	D					
State/Region	Colombia, SA	Colombia, SA	IL	IL					
ULTIMATE ANALYSIS (%, dry basis)									
Total Moisture	12.39	11.39							
Ash	7.03	6.92	8.2	7.26					
HOC (btu/lb)	13003	13366	13570	13656					
Total Sulfur	0.65	0.59	1.75	1.18					
Carbon	73.63	77.94	76.87	78.49					
Hydrogen	4.94	4.94	4.98	4.85					
Nitrogen	1.49	1.56	1.75	1.84					
Oxygen	12.26	8.05	6.45	6.38					
Volatiles	37.47	37.12	34.32	32.32					
Fixed Carbon	55.5	55.96	57.48	60.42					
Ash Fusion IT (°F)	2196	2368	2046	2154					
Ash Fusion ST(°F)	2378	2574	2134	2260					
Ash Fusion HT(°F)	2438	2652	2238	2238					
Ash Fusion FT(°F)	2532	2728	2340	2534					
Grindability Index	40	44	53	52					
ASH COI	NSTITUENTS	(%, as ashed	in laborator	y)					
Al ₂ O ₃	20.94	20.31	19.88	22.42					
Fe ₂ O ₃	7.13	7.48	17.13	11.85					
CaO	2.49	1.23	2.07	1.91					
MgO	1.32	1.01	0.93	1.07					
MnO ₂	0.03152	0.0461	0.03108	0.03288					
P_2O_5	0.32	0.28	0.55	0.36					
K ₂ O	1.81	1.52	2.48	2.66					
SiO ₂	59.62	64.72	52.67	55.26					
Na ₂ O	1.49	0.56	1.06	1.28					
SO ₃	3.21	1.55	1.81	1.82					
TiO ₂	1	1	1.25	1.31					

Table 2-4Representative Coal Analyses – Trace

Coal ID	Α	В	С	D					
Trace Constituents (ppmw, dry)									
As	3.7	2.4	23	9.6					
Ba	190	120	40	30					
Be	0.4	0.5	1.5	1.3					
Cd	0.19	0.19	0.2	0.11					
Cl	40	39	4047	4011					
Со	1.9	2.6	6.2	6.3					
Cr	6.5	6.7	11.6	9.8					
Cu	6.7	5.6	8.6	7.1					
F	70	73	37	50					
Hg	0.085	0.058	0.027	0.081					
Mg	0.056	0.042	0.046	0.047					
Mn	14	20.2	16.1	15.1					
Na	0.078	0.029	0.065	0.069					
Ni	5	5.7	19.2	17.4					
Pb	2.1	2.4	57.9	18.7					
Sb	1	1.2	1.3	0.8					
Se	5.6	4.84	1	1.1					
V	19.8	21.2	20.8	20.1					
Zn	9.3	10	33.2	24.6					
Approx. Flue Gas Chlorine ppmv w/o blending	2	2	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 three catalyst configurations (SCR with all-CX catalyst, hybrid, all-TRAC catalyst), as well as to investigate the rate of mercury capture across the ESP. Table 2-5 shows the nominal parametric sequence, as originally designed, which served as a guideline for testing. Note that the actual chlorine levels differed from that shown in this test plan, based upon the native flue gas chlorine levels that were actually experienced at the time of testing. These native chlorine levels were generally around 100 ppmv, which obviously precluded testing at lower levels.

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 configuration and provided the basis for the data and analyses presented in this report.

Testing Methodology

During the preliminary testing, it was determined 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, 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 relatively high degree of internal 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, which focus on relative effects, rather than absolute values.

Table 2-5Nominal Parametric Design Sequence

Description	I	Effect of	Chlorine		Effect of Bromine					Effect of Temperature		Effect of Flow (TRAC ONLY)	
Test ID	1a	1b	1c	1d	2a	2b	2c	2d	2e	3a	3b	4a	4b
Standard Flow Rate	Design	Design	Design	Design	Design	Design	Design	Design	Design	Design	Design	75%	125%
(SCFM @ 32 F)													
Temperature (F)	700	700	700	700	700	700	700	700	700	625	750	700	700
DeNOx	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%	90%
CaBr₂ Injection (ppmw based on dry coal input)	0	0	0	0	0	5	5	25	50	5	5	5	5
Chlorine Level Supplement native chlorine to maintain indicated level	Native chlorine level	50	100	150	Native chlorine level	Native chlorine level	50	50	50	50	50	50	50

3 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 for the three catalyst configurations. The lowest level of chlorine that could be explored was, of course, dictated by the native flue gas chlorine level as a function of the coal being fired at the host boiler. The original intention of the project was to explore very low levels of chlorine (< 5 ppmv). This was based upon the coal being fired at the host plant at the project's conception. However, at the time of testing, the available coals had higher levels of chlorine, roughly 100 ppmv, which precluded testing at the very low chlorine levels that were originally desired. This limits the findings of the report to mid-to-high chlorine conditions, but not ultra-low chlorine conditions. Other flue gas and operating conditions could be adjusted without limitation.

Testing Approach

Chlorine levels in the flue gas were raised above the native flue gas chlorine level by injecting 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, and allowed for approximately 0.5 seconds of residence time prior to reaching the MRC inlet mercury analyzer. Bottled HCl gas was used for this purpose, which was regulated using a simple manual valve system equipped with a rotameter. In practice, chlorine could be introduced into the flue gas or boiler in a number of ways, including using additives to the coal feed. Previous EPRI studies at the MRC demonstrated that injecting chlorine in this manner was comparable to chlorine in the coal, at least in terms of its influence on mercury oxidation and capture. It is important to note that the chlorine effect data were acquired for each catalyst configuration during a single day of testing. This helped to remove some of the day to day variability from the data. All operating conditions, other than chlorine, were held at design (i.e. design flow rate, 90% deNOx, 700°F, no added bromine).

This testing approach was aimed at independently 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 independent 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 inlet to the MRC would be unrelated to the SCR catalyst and 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 this location.

Figure 3-1 shows the effect of chlorine on inlet oxidized mercury as a function of chlorine for the three catalyst configurations.¹ Note that in the case of the all-TRAC configuration, two test runs were completed. This was done to take advantage of a test day where the native chlorine was lower than usual, allowing the chlorine range to be slightly expanded. In general, the data as a whole produce a "family" of curves which show a small response to chlorine (increase in oxidized mercury level). Most interesting is the day to day variability in the absolute levels of oxidized mercury, which ranged quite broadly. It is clear that boiler or fuel differences created differences in the level of oxidized mercury that exited the boiler. These data help support the caution that day to day variability in the system was significant and data points taken over several days of operation can not necessarily be compared in a meaningful manner.



Figure 3-1 Oxidized Mercury vs. Chlorine – MRC Inlet

¹ For this plot, and other plots containing multiple data sets, linear or polynomial fits have typically 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 fit line, especially when there are large gaps in the data.

Effect of Chlorine at the SCR Outlet

The data of the most interest are associated with the SCR outlet, since they include the effects of the three catalyst configurations. These data are necessarily subject to variability associated with boiler operation and fuel composition, as demonstrated in the inlet speciation data. This variability limits the confidence with which a direct comparison of absolute levels of mercury oxidation between the catalyst configurations can be applied.

Figure 3-2 shows the SCR outlet proportion of oxidized mercury as a function of chlorine level and catalyst configuration. As noted with the previous plot, two separate runs were performed for the all-TRAC catalyst configuration. For the all-CX catalyst, there was a notable increase in mercury oxidation with increasing chlorine. This is consistent with other data taken for conventional catalysts at the MRC (refer to EPRI Report 1020591). The all-TRAC catalyst configuration, however, showed a basically flat response to chlorine level. This is a departure from the conventional catalyst behavior. As noted in Figure 3-2, chlorine in the flue gas varied between 100 ppmv and 350 ppmv, therefore the catalyst potential to oxidize mercury at chlorine levels below 100 ppmv remains inconclusive.

Data collected at the SCR outlet (Figure 3-2) shows a very small difference in overall mercury oxidation between all three catalyst configurations, suggesting that TRAC does not offer any advantages for mercury oxidation over the chlorine levels tested. However during TRAC testing, oxidize mercury at the SCR inlet (Figure 3-1) was relatively lower, showing greater oxidation efficiency. Additional testing at consistent SCR inlet mercury levels is needed to reach any solid conclusions.

Note that for Run #2 of the TRAC catalyst, an unusual upswing took place with the last two data points. This is considered to be a data anomaly and not a bona fide effect, considering the bulk of the data available for the TRAC catalyst.

Overall, data at lower chlorine levels would need to be acquired to fully determine any advantages that may exist with the all-TRAC and hybrid catalyst configurations. This is especially true for ultra-low chlorine levels, where the mercury oxidation for conventional catalysts is extremely sensitive to chlorine level.



Figure 3-2 Oxidized Mercury 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. Figure 3-3 shows these data. Note that no corresponding data to the all-CX catalyst configuration are available, due to monitoring difficulties during the test run.

In the case of the all-TRAC catalyst (two runs), there is a relatively flat response to chlorine level. This might be expected given that the oxidized mercury exiting the SCR also showed a flat response.² One important note is that day to day variability in ESP capture is very common, presumably due to differences in fly ash related parameters, such as LOI. Prior testing at the MRC has shown that even for identical catalysts and operating conditions, the day to day variability in ESP capture can be marked. Therefore, the data should not be used to make any determination about the absolute magnitude of potential ESP capture in relation to the specific catalyst configuration being tested. The data should only be used in a relative way to examine the trend of the capture response to chlorine level.

The data for the hybrid catalyst configuration is much more difficult to reconcile. These data, which show a relatively marked improvement at higher level of chlorine (i.e., the polynomial fit

 $^{^{2}}$ This statement is made with the assumption that the capture effect associated with chlorine is due only to the effect that chlorine has on mercury oxidation across the catalyst. This, in fact, is not quite true since previous studies have shown that chlorine has other beneficial capture effects. In other words, the mercury capture response is not identical to the mercury oxidation response with respect to chlorine.

is curved upward) is unusual, and has not been experienced with any of the prior testing at the MRC. A somewhat linear increase in capture might be expected for conventional catalyst, according to previous studies at the MRC, but not a response of the nature demonstrated here. One reason for this behavior may be intraday variability of fly ash characteristics, such as LOI. Although interday variability is known to be very significant at the MRC, intraday variability has not typically been a problem though. Thus, a drift in LOI for the boiler (or a switch in fuel) that occurred during the testing period could have accounted for the behavior demonstrated by the hybrid catalyst. It should be noted that during testing no ash samples were collected at the ESP, thus ash properties' effects on ESP mercury capture remain inconclusive.

Overall, the data are inconclusive with respect to mercury removal across the ESP as a function of chlorine content. This is particularly true for the data for the hybrid catalyst configuration. In order to better quantify the ESP potential to remove mercury, a more in-depth research program involving fuel and ash analyses is recommended. Therefore, the absolute levels of ESP mercury capture demonstrated here should not be used as an indicator of any particular full-scale facility's performance.



Figure 3-3 ESP Mercury Capture vs. Chlorine

Conclusions – Effect of Chlorine

Based upon the bulk of the data available, the all-TRAC catalyst and hybrid catalyst configurations appear to be less influenced by chlorine level than is the case for the all-CX catalysts. The data are limited in that very low levels of chlorine could not be explored, thus the findings cannot be directly applied to chlorine levels less than roughly 100 ppmv.

The ESP mercury capture response for the all-TRAC catalyst configuration is generally similar to the SCR oxidation response, with the ESP capture being relatively flat across the chlorine range tested. For the hybrid catalyst version, mercury capture across the ESP increased with chlorine content (170 ppmv to 330 ppmv). This increase in capture is unusual based on data previously obtained with other conventional catalyst. It is speculated that changes in boiler conditions, fuel, and ash characteristics contributed to the increase in capture. However, no ash samples were analyzed during testing, therefore ESP capture performance as a function of chlorine content remain inconclusive.

4 EFFECT OF BROMINE

Background

Bromine is known to strongly influence mercury oxidation behavior, especially when the overall level of halogens in the flue gas is low. Previous EPRI studies at the MRC demonstrated this effect well. In particular, when chlorine levels are quite low, less than roughly < 50 ppmv, the effect of adding bromine will be quite marked. As chlorine levels increase, the effect of bromine is less dramatic. Given that the chlorine levels for the subject testing were not extremely low; the impact due to bromine is expected to be somewhat muted, but still apparent. Considering that the TRAC catalyst was designed to perform well at low chlorine levels, its response to bromine is of special interest, and thus the current test plan was devised to determine comparative behavior for the three catalyst configurations: all-CX, hybrid, and all-TRAC.

Testing Approach

Bromine levels in the flue gas were modified by adding bromine directly to the coal feed for the boiler. The boiler is a T-fired configuration with four burner banks and four mills. The bromine was added as a 52% solution of calcium bromide which was added directly to the coal feed for a single mill. Given the rather high rate of mixing within a T-fired boiler, this injection method was thought to be reasonably representative of a boiler for which bromine was added with the entire coal feed. The calcium bromide solution was metered into the coal feed piping (situated vertically above the mill) using a peristaltic pump, with the metering rate being set manually as a function of the desired bromine level and unit load. Note that unit load was generally very consistent, at 82 MW (maximum continuous load). Also note that the following discussions are based upon bromine levels in terms of ppm by weight in the coal. This should not be confused with bromine concentration in the flue gas as ppmv. For this particular boiler and coal btu value, 10 ppmw of bromine in the coal would give roughly 0.27 ppmv of bromine (as HBr) in the *flue gas.* This equivalency value can be used to determine gas-phase bromine levels corresponding to the coal bromine levels discussed in the report, for those interested in this parameter. All operating conditions, other than bromine level, were held at design (i.e., native chlorine, 90% deNOx, 700°F, design flow).

Note that in all cases, the discussed bromine level is additive to the native bromine. Thus the total bromine in the flue gas would be a function of the native bromine in the coal plus the bromine being added. It is important to note, too, that the relatively high native coal bromine and chlorine levels may have suppressed to some degree the intensity of the response that was noted from adding bromine.

Effect of Bromine at the MRC Inlet

Any effect at the MRC inlet from bromine injection would be unrelated to the SCR catalyst and would be due to gas-phase or fly ash catalyzed mercury oxidation as a function of bromine. These reactions could occur within the boiler itself or during transport through ductwork from

the convective pass to the SCR inlet. Surface catalyzed reactions may also play a role. Compared with chlorine, the residence time was greater for bromine, since it was injected with the coal into the boiler.

Figure 4-1 shows the effect of bromine on inlet oxidized mercury for the three catalyst configurations. The coal for the hybrid configuration was different from the other two, and this may be the source for some of the variability in the absolute level of oxidized mercury entering the MRC. Also note that although the other two catalyst configurations had ostensibly the same coal, the chlorine levels did vary, denoting that some differences were present. This was probably a function of the blending ratios that were used. Further, it is clear that chlorine level was not controlling the response, since the all-CX test series actually had the lowest level of chlorine, but the highest level of oxidized mercury entering the MRC.



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

Effect of Bromine at the SCR Outlet

Figure 4-2 shows the effect of bromine injection at the SCR outlet up to 50 ppmw of added bromine (equivalent to roughly 14 ppmv added bromine in the flue gas). Note that the presence of relatively high levels of native chlorine during these tests apparently tended to suppress the sharp initial effects of bromine injection as seen with previous conventional catalyst testing at the MRC (when chlorine was very low).

All of the catalysts behaved virtually identically with respect to bromine injection, both in terms of the absolute level of mercury oxidation and the shape of the response curve. The hybrid catalyst did show slightly lower overall absolute levels of mercury oxidation, which may be due to the coal difference as previously discussed. Overall, injecting bromine from 0 to 50 ppmw increased mercury oxidation at the SCR outlet from 91% to 96%.



Figure 4-2 Oxidized Mercury vs. Bromine – SCR Outlet

Effect of Bromine on ESP Mercury Capture

Figure 4-3 shows the mercury capture data (capture as measured between the MRC inlet and the ESP outlet) corresponding to the previous two figures. These data are intuitive for the hybrid and all-TRAC catalyst configurations, showing an improvement in capture roughly consistent with the improvement in mercury oxidation with respect to bromine. The all-CX data are somewhat counterintuitive, as they show a slight decrease in mercury capture with increased bromine (even though the mercury oxidation increased as measured at the SCR outlet). As previously discussed, mercury capture effects across the ESP are influenced by other parameters, such as fuel properties and LOI. The incorporation of these parameters goes beyond the scope of this project. Therefore, additional work is needed to determine actual ash effects on ESP mercury capture.



Figure 4-3 ESP Mercury Capture vs. Bromine

Conclusions – Effect of Bromine

Based upon the bulk of the data available, all three catalyst configurations behaved in a similar relative way for mercury oxidation with respect to variation in bromine levels. Thus, no behavior differences were noted for the all-TRAC or hybrid configurations as compared to the all-CX configuration, at least for the chlorine and bromine levels tested here. Bromine injection from 0 to 50 ppmw (equivalent to roughly 14 ppmv in the flue gas) improved mercury oxidation at the SCR outlet from 91% to 96%, on average. The ESP mercury capture data were more difficult to interpret, thus no definitive conclusions about the relative behavior of the three catalyst configurations could be reached.

5 EFFECT OF TEMPERATURE

Background

Catalytic processes are often strongly affected by temperature, depending on the relative contributions of kinetics and mass transfer. 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 normally experience an independent temperature change, for which all other parameters 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 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 and cold-side-ESP. 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 fullscale 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 and economizer outlet ducts. 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 volumetric flow rate and temperature remained unchanged even when changes were made to the*

SCR operating temperature. Presumably, the primary effect on ESP capture due to an SCR temperature change would, therefore, only be 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. Therefore, the data presented represent a single operating day, during which low $(625^{\circ}F)$ and high $(750^{\circ}F)$ 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 testing on the three catalyst configurations was performed at slightly different levels of chlorine, as a function of the native level of chlorine that was being experienced. The chlorine variability further prevents the direct comparison of the different catalyst configurations on an absolute mercury oxidation basis. All tests related to the temperature response were performed at design flow rate (constant scfm), 90% deNOx, native chlorine, and <u>5 ppmw bromine</u> (added to the coal as with the bromine dependency testing).

Effect of Temperature at the MRC Inlet

The effect of SCR operating temperature on the inlet mercury speciation would 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 economizer outlet ducts, 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 catalyzed mercury reactions as a function of temperature. If these reactions were strongly affected by temperature, they could conceivably affect the measured mercury speciation. 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, if any, was responsible for the noted change in inlet mercury speciation.

Figure 5-1 shows the MRC inlet mercury speciation as a function of temperature for the three catalyst configurations. 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 (before the SCR catalyst) is indeed linear, and the reader is cautioned against making that assumption.* For the all-CX and hybrid catalyst tests, there was a small increase in mercury oxidation with respect to temperature. During the all-TRAC test, no changes in oxidized mercury were observed.

Variability was noted in the absolute mercury levels from test to test, as was the case for the other test series, with the inlet oxidized mercury proportion ranging from a low roughly 10% to a high slightly over 30%. Some of this variability would presumably be due to differences in chlorine levels between the tests series.



Figure 5-1 Oxidized Mercury vs. Temperature – MRC Inlet

Effect of Temperature at the SCR Outlet

Figure 5-2 shows the effect of temperature on the SCR outlet mercury speciation. In the case of the all-CX and hybrid catalyst configurations, there was a notable decrease in mercury oxidation as temperature increased. This finding is consistent with industry data, as well as data acquired for conventional catalysts previously tested at the MRC. The relative loss in mercury oxidation was nearly identical for the all-CX and hybrid configurations. Interestingly, the TRAC catalyst showed a flat response. This behavior deviates significantly from all other conventional catalyst tested at the MRC.



Figure 5-2 Oxidized Mercury vs. Temperature – SCR Outlet

Effect of Temperature on ESP Mercury Capture

Figure 5-3 shows the ESP mercury capture for the three catalyst configurations, as a function of temperature. As previously stated, the operating philosophy for the testing resulted in the ESP operating temperature and flow rate remained constant for a variation of temperature at the SCR.³ Given this, one might expect the mercury capture across the ESP to generally follow the trend of the mercury speciation at the SCR outlet. However, although the SCR mercury oxidation for the TRAC catalyst was flat across the temperature range, the capture data for the TRAC catalyst was very similar to the hybrid and all-CX configurations. This behavior was very similar to the previous MRC testing with conventional catalysts (although there was some variability in those data in terms of the magnitude of the decrease in capture with increasing temperature). Overall, this is a very interesting finding, and it is clear that the mercury oxidation response is not governing the ESP capture response.

In terms of the absolute level of capture, there were significant differences between the three test runs. Again, it is not unusual for absolute ESP capture to vary so markedly since other parameters, such as LOI, can strongly influence capture. Also, the chlorine level varied somewhat between tests, which could affect mercury capture. However, the data moved opposite to the chlorine level. In other words, the catalyst configuration with the highest chlorine level

³ ESP inlet temperature was held at 325 °F. Flow rate at this temperature was 16,750 acfm.



actually had the lowest capture, so it is clear that chlorine was not governing the absolute capture rate.

Figure 5-3 ESP Mercury Capture vs. Temperature

Conclusions– Effect of Temperature

The data show that the TRAC catalyst was relatively insensitive to temperature in terms of mercury oxidation, at least for the temperature range and levels of chlorine and bromine examined. The all-CX and hybrid configurations behaved in a manner similar to conventional catalysts in general, with mercury oxidation falling with increasing temperature. In terms of mercury capture across the ESP, all catalyst configurations behaved similarly, with a decrease in capture with respect to temperature. This behavior was generally consistent with conventional catalysts, as tested previously at the MRC (although the previous testing showed significant variability in the magnitude of the temperature effects). It is somewhat counterintuitive that the for the TRAC catalyst, the SCR oxidation behavior differed from the other two configurations, but the ESP capture response was virtually identical.

It is important to note that 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.

6 EFFECT OF AMMONIA

Background

Industry data indicates that the presence of ammonia has an inhibiting effect on mercury oxidation 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, and desired deNOx level, as well as catalyst activity, volume, and age. Furthermore, the general health of an SCR system in terms of distributions, fouling, etc., will greatly affect the ammonia profile through the reactor.

Another parameter directly linked to deNOx level is ammonia slip. Slip may be an important parameter for mercury capture, since it can potentially impact mercury adsorption on fly ash. Thus, deNOx level may have an impact on mercury capture over and above what would be expected based on its effect on SCR mercury oxidation. It is important to note that various parameters, such as maldistributions, catalyst activity, volume, etc., will all have an effect on ammonia slip. 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.

Testing Approach

The effect of ammonia/deNOx was not measured in detail, since a full parametric sequence with respect to deNOx was not performed. However, as a matter of course in the testing, data were taken that corresponded to no ammonia injection (0% deNOx) and to design deNOx (90%). This allowed for a very rudimentary evaluation of the effect of ammonia. All of the reported tests were performed at design flow rate, 700°F and native chlorine, with no bromine injection.

Effect of Ammonia at the MRC Inlet

Theoretically, there should be no effect on the MRC inlet mercury speciation due to variations 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, including the coal being burned.

Looking at the SCR inlet speciation in Figure 6-1, one can see that the inlet oxidized mercury was stable during the all-CX and hybrid test runs, as expected, but that it increased with the all-TRAC test run. This may be a clue that the flue gas changed somewhat between the tests for the TRAC catalyst.



Figure 6-1 Oxidized Mercury vs. DeNOx – MRC Inlet

Effect of Ammonia on SCR Outlet Mercury Speciation

In terms of the SCR outlet speciation, as shown in Figure 6-2, there was little effect due to ammonia for all catalyst configurations. The TRAC catalyst showed a slight improvement in oxidation with the addition of ammonia; however this slight improvement may in fact be a function of the inlet speciation, which also showed a slight increase in oxidized mercury between the two tests. In any event, all three catalyst configurations did not appear to be adversely affected by the presence of ammonia.

There may be some influence on the deNOx effect due to the chlorine level in the flue gas, the majority of the data in this project were acquired at higher levels, ranging between 100 ppmv and 150 ppmv. Overall, at face value, all three catalyst configurations appear to be insensitive to deNOx level. Additional testing would be required to more fully understand this behavior, especially at lower halogen levels.



Figure 6-2 Oxidized Mercury vs. DeNOx – SCR Outlet

Effect of Ammonia on ESP Mercury Capture

The ESP capture data are shown in Figure 6-3. These data are particularly difficult to reconcile, since the hybrid catalyst shows a notable improvement in capture with deNOx, while the other two catalysts show virtually no response. This is not consistent with the speciation shown in Figure 6-2. Previous data for conventional catalysts at the MRC showed an improvement in ESP capture with increased deNOx, so the data with respect to the hybrid catalyst tests is not unusual. However, it is unclear why this same trend was not demonstrated by the all-CX and all-TRAC catalyst tests. It should be noted that in previous project data, the improvement in ESP capture occurred in spite of a notable decrease in mercury oxidation at the SCR outlet with increasing deNOx. Since no decrease in oxidation at the SCR outlet was demonstrated with the all-CX and all-TRAC tests, one might expect the capture to be even more marked than in previous data, but this was not the case.

There are several theories that could explain the ESP capture data that was noted. For the previous data acquired at the MRC, it was theorized that ammonia slip may be playing a role in ESP capture. (If slip acted as a scavenger for SO₃, which in turn reduced the adverse effect of SO₃ on active carbon sites on the fly ash, then the deNOx effect as previously noted, would actually be due to ammonia slip.) If the three catalyst configurations tested in this program had particularly low levels of slip (or the reactor was operating in an optimized manner that minimized slip, i.e., good distributions, high reactor potential, etc.) across the entire ammonia range tested, then perhaps the data would not show an ammonia dependency as was noted before. A second theory is that chlorine levels were also be playing a role in the demonstrated

behavior, as discussed with the SCR outlet speciation data (although this does not necessarily explain the TRAC test series behavior). And finally, as previously discussed, ESP capture is particularly subject to variability. This variability may be confounding the data, making the data set as a whole difficult to interpret. It is not possible to determine which of these phenomenon, if any, were controlling the ESP capture behavior.

Overall, at face value, the data demonstrate a behavior that is a significant departure from data previously acquired at the MRC. Additional testing would be required to better confirm and understand the ESP capture response for these catalyst configurations with respect to ammonia.



Figure 6-3 ESP Mercury Capture vs. DeNOx

Conclusions – Effect of Ammonia

The effect of ammonia on mercury oxidation and capture is somewhat academic, especially at very low ammonia levels, since it seems unlikely that a full-scale facility would heavily adjust ammonia 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.

Contrary to data previously acquired at the MRC for conventional catalysts⁴, none of the catalysts tested in this study demonstrated an adverse impact due to the presence of ammonia in

⁴ Effects of Chlorine and other Flue Gas Parameters on SCR Catalyst Mercury Oxidation and Capture, EPRI, Palo Alto, CA: 2009. 102059.

terms of oxidation across the SCR. The tests were rather rudimentary in nature, since only two ammonia/deNOx levels were explored, but presumably since a very wide range of ammonia/deNOx was explored (0% and 90%), any effects would be apparent if indeed there was an influence from deNOx. The chlorine levels for the current testing were generally higher than was the case for the previous testing at the MRC on conventional catalyst. However, the TRAC catalyst, in particular, had a chlorine level that was consistent with some of the previous testing which showed adverse effects due to deNOx.

ESP capture data was particularly difficult to reconcile. The behavior for the all-CX and all-TRAC catalyst configurations did not match the previous testing at the MRC associated with conventional catalysts. The hybrid configuration did demonstrate an ESP capture response similar to the previous MRC testing, in spite of the fact that its SCR oxidation response was different from previous testing.

Overall, the data indicate that all three catalyst configurations behaved somewhat differently from previous experience. More detailed experiments would be required to more fully explore the ammonia/deNOx dependency behavior of these catalysts.

7 EFFECT OF FLOW RATE

Background

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 scrubber capture due to residence time and mass transfer differences. Increasing flow rate will generally reduce reactor potential for deNOx, and the rate of SO₂ 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.

Previous testing at the MRC with conventional catalysts showed very little effect due to flow rate on either SCR mercury oxidation or ESP capture. The current test plan, in an effort to conserve resources, therefore, focused only on the effect of flow rate on the TRAC catalyst, since its expected behavior was not known, and previous conventional catalyst testing would not necessarily be an indicator of its behavior. Thus, unlike the previous report chapters, only the flow rate effects for the TRAC catalysts are available.

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. Only two flow rate conditions were examined: 75% and 125% of design. These two tests were performed in a single day to help minimize interday variability in the data. *The tests were performed under native chlorine conditions which were 120 ppmv for the low flow rate condition, and 133 ppmv for the high flow rate condition (for an average of 125 ppmv). The change in chlorine level between the two tests was of course an undesirable variation, but based on the chlorine dependency testing, this variation is not expected to adversely affect the data to any significant degree. Other operating conditions were held at design (i.e., 90% deNOx and 700°F) and with 5 ppmw of bromine injection.*

Effect of Flow Rate at the MRC Inlet

Theoretically, the flow rate through the MRC should have little effect on the <u>inlet</u> 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. This may differ from a full-scale boiler, however, since a change in flow rate is usually due to a change in unit load, which of course does have the potential to change flue gas composition and temperature.

Figure 7-1 shows the inlet mercury speciation response to flow rate, which is flat as one would expect. The slight change in residence time between the two flow conditions did not, apparently,

have any effect on mercury speciation. This also offers some confidence that the global operating conditions for the boiler remained relatively constant throughout the test period. As mentioned, the chlorine levels were slightly different for the two tests, but this apparently had no effect on the inlet speciation.



Figure 7-1 Oxidized Mercury vs. Flow Rate – MRC Inlet – TRAC Catalyst

Effect of Flow Rate at the SCR Outlet

Figure 7-2 shows the effect of flow rate on mercury speciation at the SCR outlet, based upon the two test conditions (75% and 125% of design flow). The data show a slight reduction in mercury oxidation as a function of flow rate, with the level of oxidation reduced by about 5% absolute between the low and high flow rate conditions. As discussed, the chlorine level for the higher flow rate condition was approximately 133 ppmv, while the chlorine level for the lower flow rate condition was approximately 120 ppmv – thus chlorine level could not be the source of the decrease. This is a slightly more marked effect than has been seen previously with the testing at the MRC with conventional catalysts, where there was virtually no flow rate effect.

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 may be greater than that indicated by Figure 7-2 in cases where a load change is made (although the TRAC catalyst appeared to be unaffected by temperature according to the previously discussed data).



Figure 7-2 Oxidized Mercury vs. Flow Rate – SCR Outlet – TRAC Catalyst

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 change in flow rate may also lead to some changes in mass transfer parameters, as well as some changes to the temperature profile through the air preheater.

Figure 7-3 shows the mercury capture across the ESP as a function of flow rate. These data show an <u>increase</u> in mercury capture with flow rate. This is counterintuitive, since both the level of oxidized mercury exiting the SCR decreased with flow rate, and the residence time within the ESP decreased with flow rate. As with prior discussions, variations in other parameters, such as LOI, may actually be controlling the apparent ESP capture. However, previous data associated with conventional catalysts and at relatively high chlorine levels (50-100 ppmv) also showed an improvement in ESP capture with increased flow rate, even though there was no improvement in SCR outlet mercury oxidation. This offers some confidence that the effect is indeed genuine, although it is difficult to understand what mechanisms would cause this behavior. Given that the chlorine level for the high flow rate condition (133 ppmv) was slightly higher than for the low flow rate condition (120 ppmv), one might surmise that chlorine level was influencing the capture, but again, previous data showed a similar response in ESP capture even when chlorine levels were steady. One might surmise that the increase in flow rate through the SCR also leads to an increase in ammonia slip. If slip strongly influences ESP mercury capture, then this might be the underlying mechanism for the noted behavior.



Figure 7-3 ESP Mercury Capture vs. Flow Rate – TRAC Catalyst

Conclusions – Effect of Flow Rate

Data on flow rate effects are limited since flow effects were explored for the all-TRAC catalyst configuration only. The data are based on an independent change in flow rate (i.e., all other operating parameters were held steady), and only two flow rate conditions were examined: 75% and 125% of design. For full-scale units, flow rate changes are usually, primarily the result of a load change, which may also be accompanied by a temperature change. Unit load changes may create flow differences that are much broader than those tested here, resulting in flow effects that are more pronounced than those indicated by the range tested here.

Flow rate appeared to have very little direct effect on SCR inlet speciation. One might intuitively expect this, since MRC flow rate was not a function of boiler flow rate/load. In terms of the SCR outlet speciation for the TRAC catalyst, there was a decrease, albeit rather small, in the level of oxidized mercury exiting the reactor when the flow was increased. This occurred in spite of a slight increase in chlorine level at the higher flow rate condition.

Increased flow rate apparently caused an increase in ESP mercury capture, which is counterintuitive. The slight increase in chlorine level from low to high flow rates may have influenced this response, but this same response was noted with previous MRC testing on conventional catalysts, even when the chlorine level was steady. The mechanism of this counterintuitive response is not known.

8 CONCLUSIONS

Data Limitations

The project was developed to examine the relative response of the catalysts to various flue gas parameters, in terms of their ability to oxidize mercury. Day to day fluctuations in boiler operation and fuel made it difficult to compare the catalysts' intrinsic activity for mercury oxidation on an absolute basis. As a result, the data are most valuable in determining how the particular catalyst configurations will respond to independent changes in variables, such as chlorine level and bromine level, temperature, flow rate, and ammonia.

It is cautioned that the findings 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. Further, very low chlorine conditions were not explored due to limitations associated with the coals being burned at the MRC host boiler during the testing. Catalyst behavior at very low chlorine conditions (5-50 ppmv) were of specific interest, unfortunately testing at these conditions was precluded by the plant coals.

Mercury speciated data was collected at the ESP inlet and outlet to study any potential trends as a function of flue gas parameters. However, in general, ESP capture data was difficult to reconcile, since 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 extraneous parameters. These issues undermine the confidence in which the data can be applied to ESP capture. More detailed experiments would be required including ash analysis to more fully explore the SCR impacts on ESP mercury capture.

Effect of Chlorine

Based upon the bulk of the data available, the all-TRAC and hybrid catalyst configurations appear to be less influenced by chlorine level than is the case for conventional catalysts. The data are limited in that very low levels of chlorine could not be explored, thus the findings cannot be directly applied to chlorine levels less than roughly 100 ppmv.

The mercury capture response was generally similar to the SCR oxidation response, with the ESP capture being relatively flat across the chlorine range tested. There is an indication for the range of 100-150 ppmv chlorine that the all-TRAC and hybrid catalyst's lack of sensitivity to chlorine did help to improve ESP capture across this range as compared to conventional catalysts. Additional data would be required to fully assess the impact of the TRAC formulation on mercury oxidation and capture for chlorine levels below roughly 100 ppmv.

Effect of Bromine

Based upon the bulk of the data available, all three catalyst configurations behaved in a similar relative way for mercury oxidation and capture with respect to bromine. The data show marginal improvements with respect to increases in bromine (up to 50 ppmw on the coal) for all the parameters explored: inlet speciation, SCR outlet speciation, and ESP capture. The data do not show high bromine sensitivity at low bromine injection levels (< 10 ppmw) as was generally the case with previously tested conventional catalysts. This may be due, at least in part, to the relatively high levels of chlorine and/or bromine found natively in the coal.

Effect of Temperature

The data show that the all-TRAC catalyst was relatively insensitive to temperature in terms of mercury oxidation, at least for the temperature range and levels of chlorine and bromine examined. The all-CX and hybrid configurations behaved in a manner similar to conventional catalysts in general, with mercury oxidation falling with increasing temperature. In terms of mercury capture across the ESP, all catalyst configurations behaved similarly, with a decrease in capture with respect to temperature increases. This behavior was consistent with conventional catalysts in general, as tested previously (although the previous testing showed quite a lot of variability in the magnitude of the temperature effects).

Effect of DeNOx/Ammonia

Data previously acquired at the MRC for conventional catalyst showed that ammonia has an inhibiting effect on mercury oxidation across the SCR (refer to EPRI report 1020591). However, the inhibiting effect was most apparent at lower chlorine concentrations (50 ppmv). At higher levels of chlorine (100 ppmv), the adverse effect on SCR mercury oxidation was much more muted.

The chlorine levels for the current testing ranged between 100 ppmv and 150 ppmv. At these levels, there was a little effect due to ammonia for all catalyst configurations. Additional testing would be necessary to more fully understand the effects of catalyst activity, specially at lower halogen concentrations.

ESP capture data was particularly difficult to reconcile with respect to ammonia. This behavior did not match the previous testing at the MRC, and the behavior is somewhat counterintuitive given the mercury speciation data for the SCR outlet. Overall, the data indicate that all three catalyst configurations behaved somewhat differently from previous experience. More detailed experiments would be required to fully explore the ammonia/deNOx dependency behavior of these catalysts.

Effect of Flow Rate

Data on flow rate effects and conclusions are limited since flow rate effects were explored for the all-TRAC catalyst configuration only. Flow rate appeared to have very little direct effect on SCR inlet speciation as would be expected. In terms of the SCR outlet speciation, there was a decrease, albeit rather small, in the level of oxidized mercury exiting the reactor with an increase in flow rate.

Increased flow rate apparently caused an increase in ESP mercury capture, which is counterintuitive. The slight increase in chlorine level from low to high flow rates may have influenced this response, but this same response was noted with previous MRC testing on conventional catalysts, even when the chlorine level was steady. The mechanism of this counterintuitive response is not known.

Conclusions Summary and Global Findings

- Overall the project has shown that there are some differences in behavior between the all-TRAC catalyst configuration and the all-CX and hybrid configurations. This appears to be especially true with respect to the influence of flue gas temperature on the mercury oxidation across the SCR. No significant differences at the SCR outlet were noted with respect to bromine and ammonia injection.
- The current findings indicate that the TRAC catalyst is likely to have less chlorine dependency than conventional catalysts, but additional data are necessary to fully explore this finding and to determine at what ranges of chlorine the findings hold true.
- The behavior of the TRAC catalyst at ultra-low levels of chlorine is of great interest. Additional testing would be required to reach any final conclusions related to ultra-low chlorine levels.
- The all-TRAC configuration appeared to be relatively in-sensitive to temperature, as compared to the all-CX and hybrid configurations (which had a behavior generally consistent with previously tested conventional catalysts).

No adverse effects were noted with any of the three catalyst configurations as a function of ammonia level. This differs from the behavior of previously tested conventional catalysts.

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