

Effects of SCR Catalyst and Wet FGD Additive on the Speciation and Removal of Mercury within a Forced-Oxidized Limestone Scrubber*

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ABSTRACT

The Babcock & Wilcox Company (B&W) conducted a full-scale mercury test program at Dominion Power's 1,662-megawatt Mount Storm Power Station in Grant County, West Virginia. This is a bituminous-coal-fired power plant. The goals of this test program were to evaluate the impacts of selective catalytic reduction (SCR) catalyst and B&W's wet FGD process (injection of a sulfur-donating compound) on the speciation and removal of mercury within a limestone forced-oxidized wet FGD system. Cormetech conducted a follow-on comparative study of the field data with its internally-developed SCR mercury oxidation model, including agreement of the model predictions with the field data, projected unit performance curves, and the identification of key operating and design parameters for accurate predictive capability.

It was demonstrated that, in the absence of the SCR system, the implementation of B&W's wet FGD technology can result in an increase in mercury removal efficiency through the wet FGD unit (from 71% to 78%). In the absence of B&W's patented additive injection system, a 15% increase in the elemental mercury (Hg^0) concentration across the wet FGD was observed. The presence of the sulfur-donating compound suppressed the re-emission of Hg^0 and improved the overall Hg control capability of the wet FGD.

This test program further demonstrated that the presence of the SCR catalyst can significantly impact mercury speciation profile. In the absence of the SCR system, the extent of oxidation of Hg^0 at the inlet of the FGD was about 64%. The presence of the Cormetech SCR catalyst that had operated for one full ozone season improved this oxidation to levels greater than 95%. Predictions from Cormetech's proprietary SCR Hg oxidation model accurately matched the observed plant data. It was significant that nearly all of the oxidized mercury generated by the SCR catalyst was captured by the wet FGD system. For the combustion of this coal, the combination of the SCR system and the wet FGD constituted a very good Hg control technology.

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INTRODUCTION

Provisions of the Clean Air Act Amendments of 1990 (CAAA) have resulted in the intensive study of hazardous air pollutants (HAPs) by federal and state agencies, academic and independent research organizations, and private industry.¹⁻⁶ One outcome of this work was the December, 2000, decision by the U.S. Environmental Protection Agency (EPA) that it was “appropriate and necessary” to regulate HAPs from coal- and oil-fired electric generating stations. EPA concluded that mercury and its compounds were of greatest concern for coal-fired utility plants.

In addition to SO₂ control, wet scrubbing has the potential of providing a reliable and cost-effective mercury control. The most important factor influencing mercury control emission by wet scrubbers is the form of mercury in the flue gas. Mercury appears in coal combustion flue gases in both the solid and gas phases (particulate-bound mercury and vapor-phase mercury, respectively). Particulate bound mercury is easily removed by particulate matter control devices such as electrostatic precipitators and baghouses. Vapor-phase mercury can appear as elemental mercury (Hg⁰, metallic mercury vapor) or as oxidized mercury (Hg²⁺, vapor-phase species of various volatile compounds of mercury). Hg⁰ is nearly insoluble in water, whereas Hg²⁺ compounds are highly soluble. The speciation of vapor-phase mercury depends on coal type and other factors. Eastern U.S. bituminous coals generally produce a higher percentage of oxidized mercury than do Western sub-bituminous and lignite coals. A loose empirical relationship exists between the chloride content of coal and the extent to which mercury appears in the oxidized form.^{3,7} The aqueous-based control technologies such as wet flue gas desulfurization (FGD) systems should be effective in controlling Hg²⁺ emissions.

The Babcock and Wilcox Company's (B&W) objectives throughout a twelve-year program have been to develop practical, low-cost, synergistic means for reducing mercury emissions from coal-fired power plants utilizing, whenever possible, existing pollution control devices. For example, B&W has developed techniques for achieving greater than 95% removal of oxidized mercury in wet flue gas desulfurization (FGD) systems. During work aimed at enhancing the mercury removal performance of wet FGD systems, B&W discovered that, under some circumstances, oxidized mercury initially captured in a wet FGD system can be re-emitted in elemental form.⁵ B&W subsequently developed several techniques for preventing this from happening. One very promising technique identified, and subsequently patented, was to add a trace amount of a sulfide-donating reagent to the wet FGD slurry. This technique was further tested in pilot- and full-scale facilities and proved to be a feasible approach.⁸

The total wet FGD mercury removal performance can be limited by the amount of elemental mercury present in the inlet flue gas. This underscores the importance of a viable mercury oxidation technology in obtaining high total wet FGD mercury removals. The presence of a selective catalytic reduction (SCR) unit can positively affect the speciation of mercury in the flue gas entering the wet FGD system. SCR technology is increasingly being applied for controlling NO_x emissions from coal-fired boilers due to

its high NO_x emission control efficiency (>90⁺%). Recent field and pilot studies conducted in the U.S. have found increases in oxidized mercury across the SCR reactors.⁹⁻¹¹ Additional bench-scale studies on SCR catalysts further demonstrated the activity of these systems toward oxidation of elemental mercury.^{12, 13} Utilization of SCR catalysts for the oxidation of Hg⁰ (in addition to their primary role of NO_x reduction) in conjunction with wet FGD systems can ultimately present the coal industry with a viable and cost-effective combination for total mercury control.

The goal of this project was to assess the role of SCR and B&W's enhanced wet FGD technology on the overall mercury control performance of such systems in coal-fired utility boilers. To this end, B&W conducted this full-scale test program to gain a better understanding of Hg speciation changes at the inlet of wet FGD resulting from SCR and the resultant changes in Hg control across the wet scrubber with and without an additive for the FGD. The main objectives of this test program were to evaluate the individual and cumulative impacts of SCR catalyst, ammonia (NH₃) injection, and B&W's wet FGD process (injection of a sulfur-donating compound) on the speciation and removal of mercury within a limestone forced-oxidized wet FGD system. An additional objective was to verify that full-scale Hg oxidation behavior of field-aged SCR catalyst can be accurately predicted by Cormetech's proprietary Hg⁰ oxidation model. Since this model predicts the simultaneous NO_x reduction and Hg oxidation behavior of SCR catalyst, it was a further goal of this project to assess field measurement parameters and uncertainties that have an impact on accurately predicting SCR Hg oxidation behavior. Predictions of SCR behavior are important for SCR design, operational planning relative to regulatory requirements, and catalyst addition or replacement decisions.

APPROACH

The mercury control project was conducted at Dominion Power's 1,662-megawatt Mount Storm Power Station in Grant County, West Virginia (see Figure 1). Specifically, B&W's patented additive technology test was applied to the Unit 2 wet FGD system. The combustion system for Unit 2 is a controlled circulation, radiant reheat, divided furnace steam generator. Mt. Storm Unit 2 is equipped with a selective catalytic reduction (SCR) system for NO_x control (located downstream of the economizer). The SCR system consists of two parallel reactors containing V₂O₅•WO₃/TiO₂ SCR catalysts (manufactured by Cormetech Inc.). The catalytic reactors are designed to treat 5.82 million lb/hr of flue gas at 700 °F using a total SCR catalyst volume of 842 m³ installed in two layers and achieves 90⁺ % NO_x reduction. Following the SCR, the flue gases pass through an air heater and then enter an electrostatic precipitator (ESP; Research-Cottrell) for the removal of particulate matter. The division of flue gas flow between two ducts starting from the economizer outlet and continuing until the ESP outlet is shown in Figure 1. At the ESP outlet, the flue gases are combined in one common duct and are directed to the wet flue gas desulfurization (FGD) system. The Unit 2 wet FGD system is a limestone forced-oxidation system using dibasic acid for improved lime solubility and SO₂ capture. The absorber module is an open spray tower, and is 55 ft in diameter. The

tower is a tile-lined concrete tower with four slurry spray headers. General specifications for the wet FGD system are summarized in Table 1.

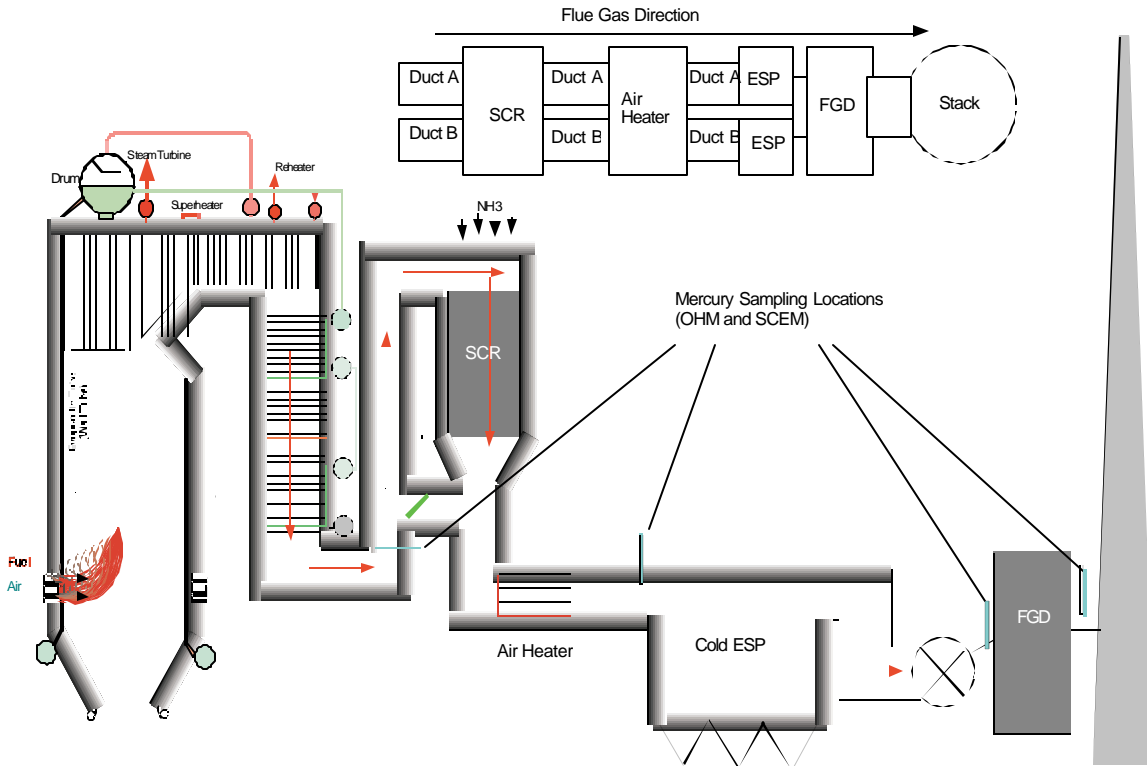


Figure 1- Schematic of duct configurations, flue gas flow direction, and sampling points at Mt. Storm Station, Unit 2

Dominion Power – Mt. Storm Station Unit 2	
FGD inlet SO ₂ concentration, ppmv, dry	1400
FGD reagent	Limestone
Recycle slurry pH	5.60
Recycle slurry total suspended solids, %	14 – 16
Recycle slurry operating level, ft	29.1
FGD liquid to gas ratio, gal/1000 acf	70
FGD forced-oxidation method	In situ – lance method
DBA concentration, ppm	294 – 557
Chloride concentration, ppm	35,000
Slurry dewatering – Primary	Hydroclone
Slurry dewatering – Secondary	Rotary drum vacuum filters
FGD purge	None, closed system
Gypsum use	Mine reclamation
De-foaming agent use	Yes, sporadically

Table 1- General Specification for Mt. Storm Unit 2 Wet FGD System

B&W's wet FGD mercury control enhancement process was implemented in the Mt. Storm's Unit 2 wet scrubber. The device employed is an additive (sulfur-donating compound) feed/metering system that is skid-mounted thus, minimal construction and set-up at the plant site was required. Chemical transfer hoses were used to connect the skid to the additive tank truck, plant water system, and wet FGD absorber recirculation piping. Stainless steel piping was used to connect the components on the skid. Two identical additive injection/metering pumps were mounted on the skid to accommodate a wide range of reagent flow rates. The pumps were equipped with variable frequency controllers that enable a 100:1 turndown ratio.

To address the main objectives of this test program, mercury sampling was performed at different locations of the power plant. Baseline mercury measurements were conducted under several scenarios including full flue gas bypass of the SCR as well as flue gas flow through the SCR both with and without NH_3 injection. After baseline testing, the scrubber additive (sodium hydrosulfide) was injected into the wet FGD absorber to evaluate its impact on oxidation and re-emission of Hg^0 . The additive injection was implemented for the two operational modes of SCR: full flue gas bypass and flue gas flow through the SCR. Ontario Hydro Method (OHM) sampling (see reference 19 for ASTM Method D 6782-02) and a number of on-line mercury speciation analyzers manufactured by PS Analytical Instruments were used to quantify mercury species in the flue gas stream at the economizer exit (SCR inlet), air heater exit (ESP inlet), wet FGD inlet (ESP outlet), and wet FGD outlet.

The mercury sampling activities in this test program were divided into four major categories. The first campaign was conducted from May 21st to May 24th, 2004. During this period the SCR catalyst was in the by-pass mode; the economizer outlet flue gas directly entered the air heaters. The first campaign included two distinctive sampling periods: 1) May 21st sampling period was conducted under a "FGD baseline" condition with no additive injection into the wet FGD and, 2) May 24th sampling period was conducted while implementing the B&W's additive injection system in the wet FGD. During the second campaign (May 25th through June 3rd) the SCR was on-line and its impact on Hg speciation and control was evaluated. No additive was injected in the wet FGD system during this period. The SCR was operated with ammonia injection upstream of the SCR catalysts during the second campaign except May 25th, when NH_3 was not injected in order to assess the effect of NH_3 on Hg^0 oxidation by the SCR catalyst. In the third sampling campaign (June 6th through 8th), and with the SCR on-line, the effect of the B&W's patented additive technology on mercury re-emission and control across the wet FGD was studied. Finally, in the fourth sampling period the conditions tested during the second campaign were reexamined. The objectives of the fourth sampling campaign were to confirm the role of SCR on Hg speciation and to further assess if there were any significant changes induced in the wet FGD system due to the injection of the additive during the first and the third campaign.

Cormetech performed modeling studies of the SCR Hg oxidation performance for comparison to the field data and for determining sensitivity to uncertainty in measured parameters. Cormetech has developed a proprietary model for simultaneous NO_x

reduction and oxidation of elemental Hg over SCR catalyst. This model is an integral reactor model that predicts concentration changes through the SCR catalyst by numerical integration of the governing differential equations for reaction kinetics. The model output includes predicted Hg oxidation and NO_x reduction with allowance for ammonia inhibition of SCR Hg oxidation, activity decline with catalyst age, thermodynamic limits on the extent of Hg oxidation (e.g. due to low coal chloride content), and actual field operating conditions. Regression constants for the model are based on extensive parametric studies on pilot scale using both fresh and field-aged catalyst samples including variation of catalyst properties (e.g. metals composition which is optimized for each plant site during the SCR design process).

The modeling studies involved several steps. Average and uncertainty were determined for field data properties relevant to SCR Hg oxidation modeling. The aged catalyst activity at the time of the Mt. Storm Unit 2 Hg field tests was determined by Cormetech in laboratory pilot tests on aged field samples taken after the preceding ozone season (i.e. the pilot tests were conducted at effectively the same catalyst age as the field studies since the SCR was off-line until May 25th). The non-SCR (i.e. APH plus ESP) contribution to observed Hg oxidation was estimated from the first campaign of the study with the SCR bypassed. Model runs were made at average field measurement values for input parameters. Model runs were also made with variation of input property values within statistical confidence limits for the field measurement data (or equivalent uncertainty estimates from propagation of error analysis for calculated properties). Combustion calculations were made to estimate chloride and moisture levels at the SCR location. The field data for Hg oxidation based on the OHM method were compared with the model predictions at the observed NO_x reduction level to verify the model's utility for predicting field performance of aged SCR catalyst for Hg oxidation. Key field parameter uncertainties for predictive modeling of SCR Hg oxidation were identified.

MERCURY SAMPLING RESULTS AND DISCUSSION

The flue gas mercury measurements results for the four major sampling campaigns are discussed in this section. Important observations and correlations between flue gas mercury concentration and other parameters such as power plant data, air quality control system (AQCS) configuration, coal analysis, and fly ash characteristics are outlined and conferred in detail.

Hg⁰ re-emission and control across the wet FGD without SCR in service

Results obtained during the 1st sampling campaign were used to assess the Hg⁰ re-emission and control across the FGD for the "SCR in by-pass mode" configuration. OHM results depicting this comparison are illustrated in Figure 2. The "test with additive" results were obtained while implementing the B&W's patented additive injection technology.

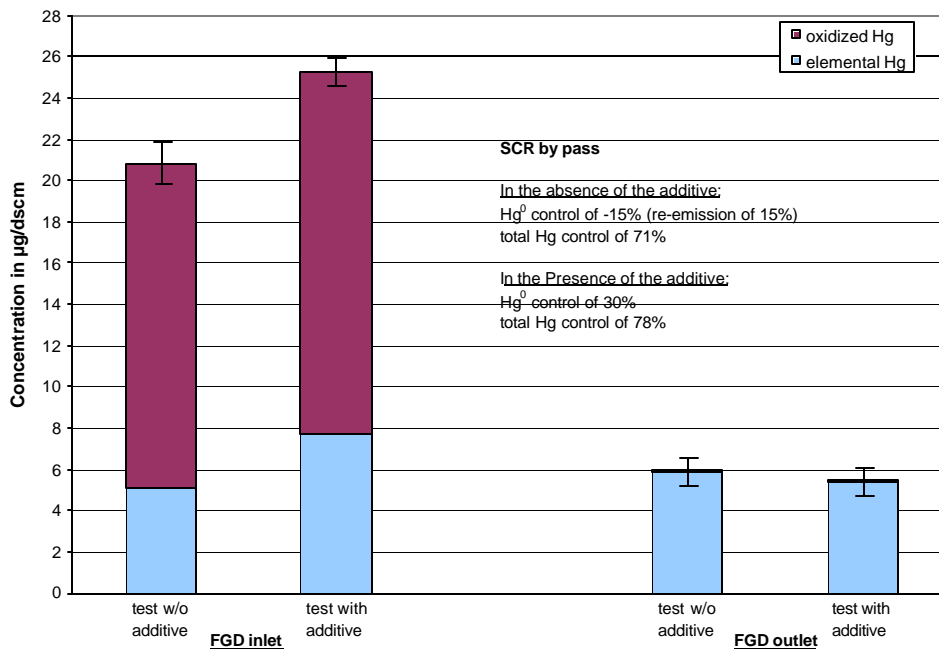


Figure 2- Effect of B&W’s additive injection on Hg^0 re-emission and control across the wet FGD (SCR was by-passed).

The total amounts of Hg at the FGD inlet were in the same range of those observed at the economizer outlet and the ESP inlet for both tests (not presented in Figure 2). For the test without the additive, the total Hg at the economizer outlet was $21.6 \pm 1.4 \mu\text{g}/\text{dscm}$ (triplicate measurements). Total Hg at the ESP inlet for Ducts A and B (see Figure 1) were 23.1 ± 1.4 and $26.9 \pm 2.1 \mu\text{g}/\text{dscm}$, respectively. The higher total Hg at the FGD inlet for the tests with the additive is related to the higher total Hg measured at the economizer outlet for these tests ($30.1 \pm 1.7 \mu\text{g}/\text{dscm}$). No significant removal of total Hg across air heater and ESP was observed. Rather large amounts of loss of ignition (LOI) and unburned carbon (UBC) were observed in the ESP fly ash (7-8%). No inorganic carbon was found in the samples; the LOI and UBC contents of the fly ash samples were thus, identical. ESP fly ash samples had a very low Hg content; they ranged from 0.1 to 0.28 ppm with an average of 0.21 ppm. This observation is in agreement with those obtained during the OHM sampling (no removal of Hg across ESP). Despite the rather high LOI/UBC in the fly ash, very little Hg was associated with particulate matter. The UBC in the fly ash did not induce significant capture of Hg in the ESP. Baghouse configuration (fixed-bed) is believed to be more effective in the capture of Hg by the fly ash’s unburned carbon. Also different types of UBC are believed to have different mercury sorption capabilities. The majority of mercury in this test program was in the vapor phase.

As shown in Figure 2, and in the absence of the SCR system, about 24-30% of the total Hg content of the flue gas was Hg^0 at the inlet of the FGD. The coal combusted in this test program was a rather low chlorine bituminous coal (Cl of 600 ppm). Previous analyses of the information collection request (ICR) data have shown the existence of a correlation between Hg speciation profile and Cl content of the coal.^{3, 7} In most cases, ICR results showed that combustion of coals with more than 1000 ppm chlorine (usually all bituminous) resulted in less than 20% of Hg^0 in the stack flue gas, whereas combustion of bituminous or subbituminous coals with lower levels of chlorine (100-1000 ppm) showed a higher and a wider range of Hg^0 in their flue gases (20-70%). The coal tested in this program falls into the latter category.

Firing of the bituminous coal used at Dominion Mt. Storm Unit 2 produced about 76% of Hg^{2+} at the inlet of the FGD as a percentage of total gaseous Hg. The high oxidation of Hg^0 in the bituminous coal flue gases has been related to the composition of the fly ash in addition to the flue gas chlorine content. The presence of high iron oxide (Fe_2O_3) and low calcium oxide (CaO) in bituminous coal fly ashes has been shown to be influential factors in determining the extent of Hg^0 oxidation.^{14, 15} The fly ash produced by the combustion of this coal had a high concentration of Fe_2O_3 (10.7 wt%) and low concentration of CaO (1.1 wt%).

Figure 2 also shows that Hg^{2+} control across the wet FGD was better than 95% for both cases: the baseline operation of the wet FGD and when the B&W's additive technology was in place. B&W's technology had no detrimental effect on Hg^{2+} removal by the wet FGD. However, in the absence of the additive, a 15% increase in the Hg^0 concentration was observed across the wet scrubber. Implementation of B&W's technology suppressed the Hg^0 re-emission; and it further induced about 30% removal of Hg^0 . Implementation of this technology resulted in an overall increase in the total removal of Hg across the wet FGD system (from 71 to 78%).

On-line Hg analysis (Hg CEM) results for this specific test campaign are illustrated in Figure 3. Rather large variations in the concentration of total and elemental mercury were observed especially at the wet FGD inlet. It should be noted that the on-line speciating mercury analyzers are still in their developmental stage; their results should be interpreted with great caution. No definite conclusion can be made as to the cause of these variations; as they could be process related or artifacts created by the analyzer. The SCMM results should be considered qualitative. The Hg CEM data presented in Figure 3 may show the decreasing trend in the concentration of Hg^0 at the outlet of the FGD when the scrubber additive injection system was implemented. As indicated in Figure 3, prior to the injection of the additive, outlet Hg^0 concentrations were equal or greater than inlet Hg^0 .

SO_2 concentration at the inlet of the wet FGD was steady during these two test campaigns (1344-1434 ppm). A better than 97% control of SO_2 was observed across the wet FGD system for both cases (with and without B&W additive). The implementation of B&W's technology had no adverse effect on the SO_2 removal by the wet FGD.

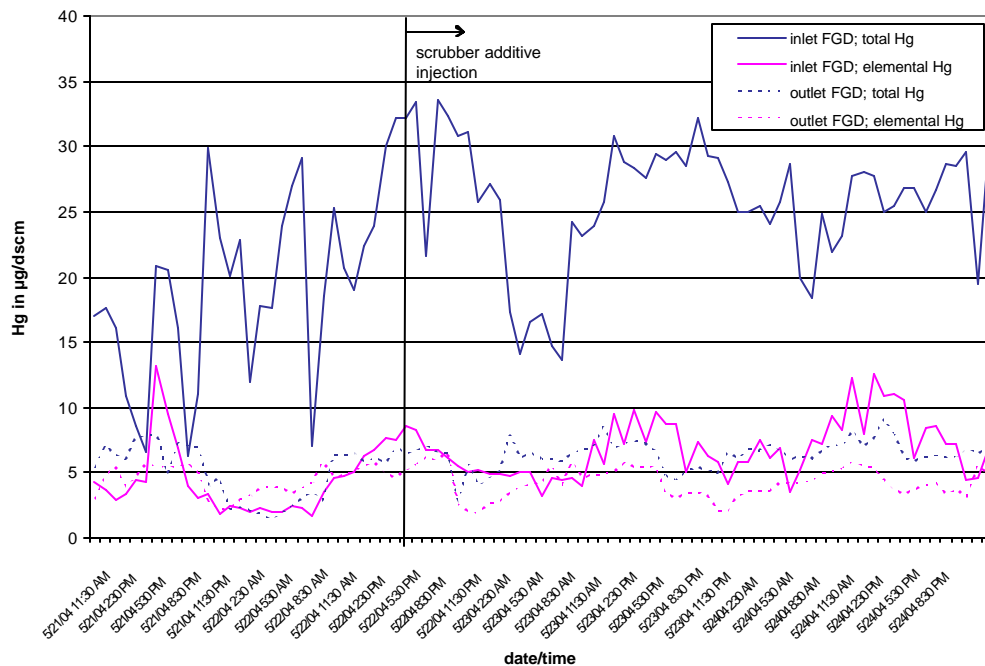


Figure 3- Hg CEM Results for the 5/21-5/24 test campaign, SCR was by-passed

Effect of SCR on Hg speciation and control across the wet FGD

The effect of SCR on Hg speciation was determined by comparing the results obtained during the first and the second Hg sampling campaigns. The SCR catalyst temperature was isothermal at 705-715 °F for the duration of the tests and B&W’s additive injection system was not operational during these periods. Hg speciation profiles at the economizer outlet, FGD inlet, and FGD outlet as measured by the OHM are shown in Figure 4. The presence of the SCR catalyst significantly impacted the Hg speciation profile at the inlet of the FGD system. In the absence of the SCR catalyst, the natural oxidation of Hg^0 in the coal combustion flue gas from the economizer outlet (upstream of the SCR) to the inlet of the FGD unit averaged about 64%. The presence of the SCR catalyst increased this oxidation to more than 98%. The heterogeneous oxidation of Hg^0 by conventional SCR catalysts has been observed previously.^{10, 12, 13} Those studies demonstrated that the presence of HCl in the flue gas is an essential component for the heterogeneous, catalytic oxidation of Hg^0 by the SCR systems. The bituminous coal used in this test program has sufficient chlorine content to produce significant quantities of HCl in the flue gas. EPA Method 26A (Code of federal Regulations, Title 40, Part 60, Appendix A, U.S. Government Printing Office, Washington DC, 1994) was used to measure HCl at the inlet of the wet FGD. HCl concentration at the inlet of the FGD was 34 ± 1 ppmvdc. The concentration of HCl should be high enough to thermodynamically allow high levels of heterogeneous oxidation of Hg^0 by the SCR

temperature and expected flue gas composition for Mt. Storm. The effect of HCl on Hg⁰ oxidation by the SCR catalyst is further illustrated in the SCR mercury modeling section.

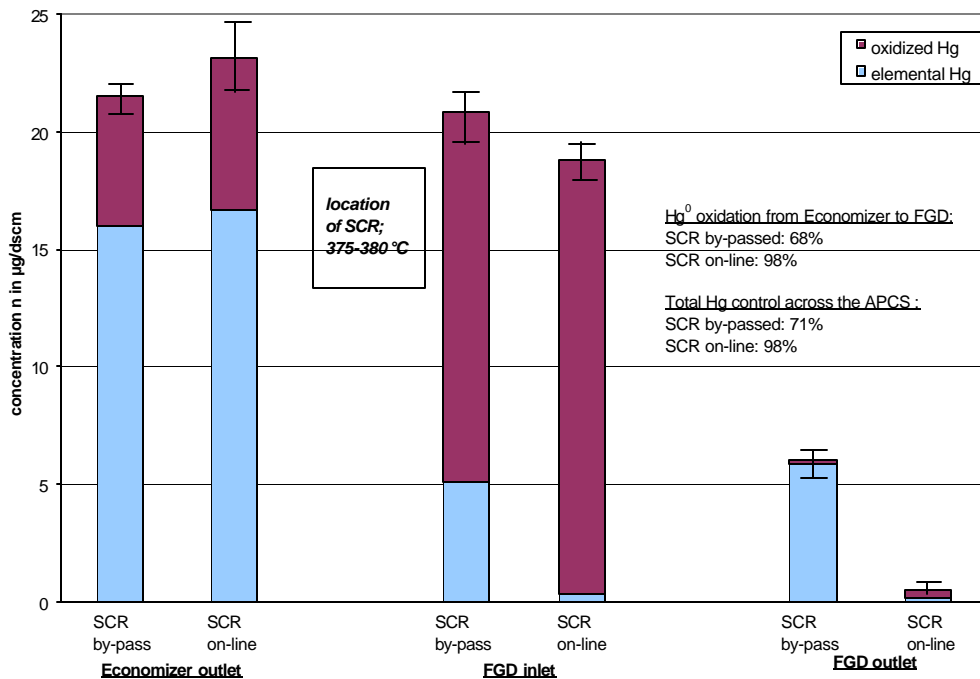


Figure 4- Effect of the SCR catalyst on Hg speciation and control across the air pollution control devices; no FGD additive was injected during these periods.

Also of significant importance were (a) the fact that nearly all of the oxidized Hg generated by the SCR catalyst was captured by the wet FGD system (>95% control of Hg²⁺) and (b) no re-emission of Hg⁰ was observed even in the absence of the patented B&W's additive system. For the combustion of this coal, the combination of the SCR system and the wet FGD constituted a very good Hg control technology (>95% total Hg removal). It should be noted that the SCR system at Mt. Storm power plant had approximately 3800 hours of operation. The potential effect of additional aging (i.e. operation over multiple ozone seasons) on Hg⁰ oxidation by this SCR system remains to be assessed. The modeling section illustrates the effects of catalyst aging as predicted by Cormetech's proprietary SCR mercury oxidation model.

Recent studies have shown that the presence of NH₃ may have an adverse effect on Hg⁰ oxidation by the SCR catalyst.^{13, 16} In order to infer the effect of NH₃ on Hg⁰ oxidation, and for a period of one day (5/25/04), no NH₃ was injected in the flue gas while the SCR was on-line. These results as obtained by the Hg CEM are shown in Figure 5. NH₃ had no discernable effect on the net observed oxidation of Hg⁰ through the SCR plus APH. A slight decrease in Hg⁰ at the inlet of the FGD is indicated in Figure 5. No firm conclusion as to the effect of NH₃ on the Hg⁰ oxidation could be made for the conditions

of this study. However, as discussed further in the SCR modeling section, (a) at Mt. Storm Unit 2 there was adequate catalyst capability present to enable high SCR Hg oxidation with NH₃ injection, (b) Cormetech's SCR Hg oxidation model predicted only a small increase in Hg conversion without NH₃ injection, and (c) the important role of NH₃ would be more evident in other situations such as lower HCl levels or for older catalyst.

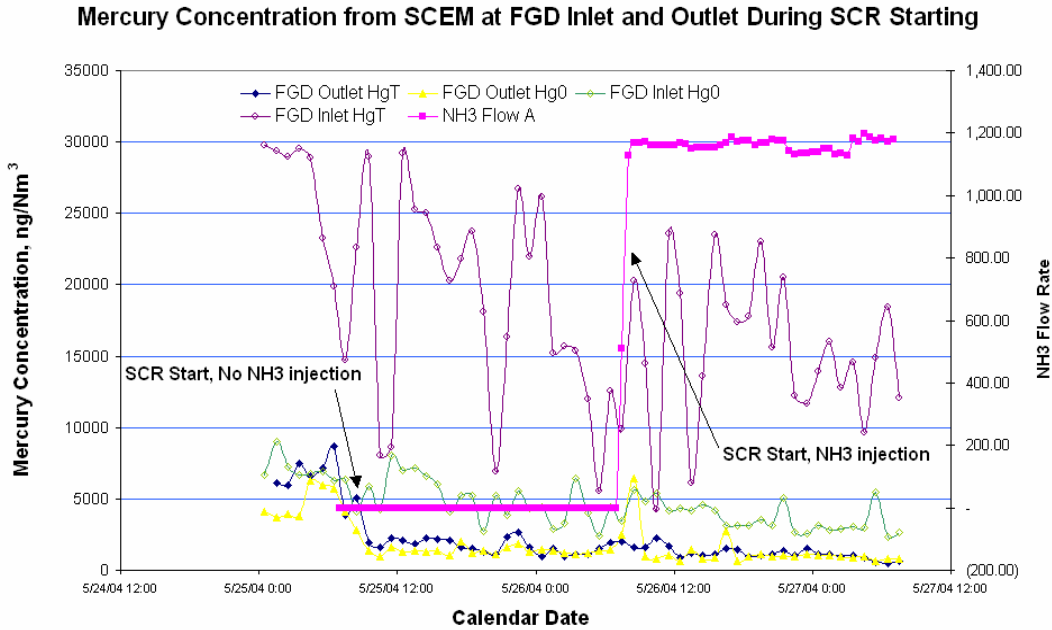


Figure 5- Effect of NH₃ on Hg⁰ oxidation by the SCR catalyst; 1000 ng/dscm is 1 µg/dscm

Hg⁰ re-emission and control across the wet FGD with SCR in service

The results discussed above (Figure 4) showed no re-emission of Hg⁰ from the wet scrubber. This observation indicates that the addition of the B&W's scrubber additive may not be needed when the SCR catalyst is in place. To further confirm this observation, the 3rd sampling campaign was implemented. During this test campaign the SCR system was kept on-line and the B&W additive injection system was put into operation. OHM results are shown in Figure 6. It is evident that with the SCR on-line, no re-emission of Hg⁰ occurred in the wet FGD; the implementation of B&W's patented technology for suppression of Hg⁰ re-emission may not be required when the SCR system is in operation. Literature data have indicated that the presence of the SCR catalyst may suppress the re-emission of Hg⁰ in wet FGD systems.¹⁰ Very little is known on this subject.

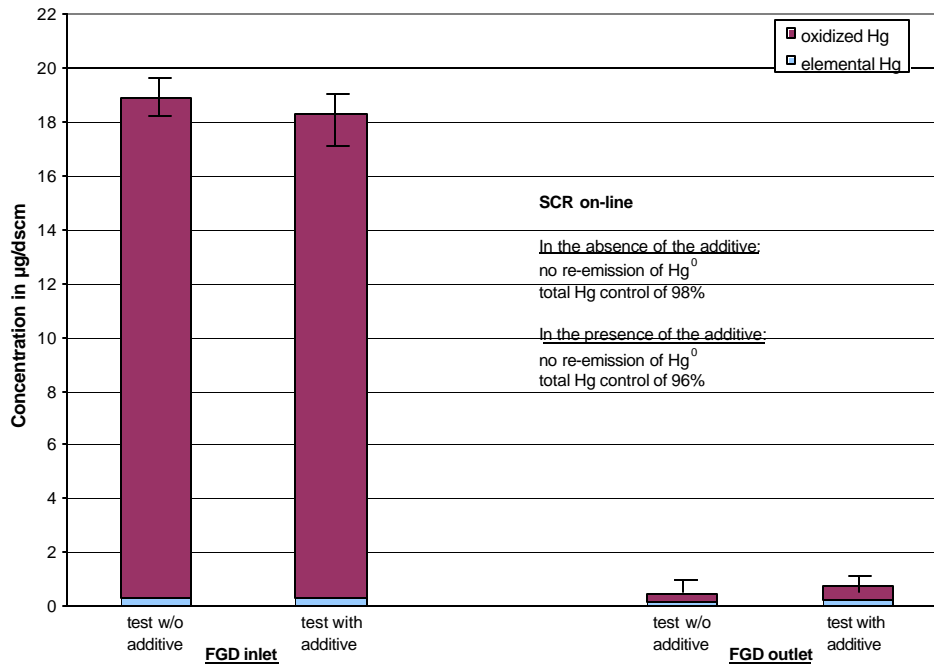


Figure 6- Effect of B&W’s additive injection on mercury speciation and control across the wet FGD; SCR system was in service.

Confirmation of the effect of SCR on Hg speciation and control across wet FGD; assessment of the effect of the additive on the operation of the wet FGD

At the end of the test program, another OHM flue gas mercury measurement sampling campaign was performed (4th campaign). The objective was to confirm the previously-observed effects of SCR on Hg⁰ oxidation and re-emission suppression from the wet FGD. Another objective was to determine if there were any significant system changes due to chemical injection during the preceding additive injection periods. During this sampling campaign the SCR was in service and no additive was injected in the FGD unit. The OHM results once again indicated that the presence of the SCR catalyst induced better than 98% oxidation of Hg⁰ at the inlet of the FGD. Only about 0.18 µg/dscm of Hg⁰ at the inlet of the wet FGD was measured. Moreover, no re-emission of Hg⁰ was observed across the FGD unit. Total mercury control across the FGD unit for this period was about 97%. All the observations made during the preceding, SCR-in-service sampling campaigns were further confirmed.

SCR MERCURY OXIDATION MODELING RESULTS AND DISCUSSION

Cormetech's modeling and data uncertainty assessment for the Mt. Storm Unit 2 SCR oxidation of elemental Hg are discussed in this section. A quantitative statistical comparison is made between predicted SCR Hg oxidation performance and the observed field data at Mt. Storm. Key field data uncertainties relevant to SCR Hg oxidation performance prediction are identified through model sensitivity analysis supplemented by general considerations for model usage.

Fractional conversion is defined as the absolute value of the change in species concentration divided by the inlet species concentration, and is often expressed as a percentage. An example of conversion relationship for elemental Hg conversion, η_{SCR} , across the SCR catalyst is provided in Equation (1) where C indicates concentration.

$$\eta_{SCR} = |C_{Hg, SCR outlet} - C_{Hg, SCR inlet}| / C_{Hg, SCR inlet} \quad (1)$$

Measurement uncertainties and confidence limits for an expanded uncertainty, as used herein, follow ISO guidelines.¹⁷ For example, a standard uncertainty might be multiplied by a "coverage factor" of 2 to give a statistical level of confidence of approximately 95% (similar to $\pm 2s$).

Separation of SCR and non-SCR contributions to observed Hg oxidation

For the SCR by-pass configuration without use of B&W's FGD additive, the observed non-SCR conversion of elemental Hg to oxidized Hg was 68.1% from the economizer outlet to the FGD inlet (ESP outlet) based on OHM measurements at both locations. Similarly, for the SCR by-pass configuration with the use of B&W's FGD additive, the observed non-SCR Hg conversion was 59.2%. The average non-SCR Hg conversion of these two data sets is 63.7% with a pooled standard uncertainty of 8.1% absolute.

This average value of 63.7% for the non-SCR conversion of elemental Hg is assumed to be valid for other portions of the field test program when the SCR is on-line. This assumption is based on field observations that there was no significant amount of Hg removed with the ESP fly ash, there was no significant change in total Hg, testing was always done at full load, and the coal being fired was unchanged.

Thus, for modeling of cases with the SCR on-line (not bypassed), it is assumed that an equal percentage as above (i.e. 63.7%) of the amount of elemental Hg leaving the SCR is oxidized by non-SCR mechanisms as the flue gas travels through the APH and ESP. The net observed fractional conversion of elemental Hg from SCR inlet to FGD inlet (denoted η_{net}), may be related to the SCR and non-SCR fractional conversions of elemental Hg as follows:

$$\eta_{net} = 1 - [(1 - \eta_{SCR})(1 - \eta_{non-SCR})] \quad (2)$$

Equation (2) is valid when the percent elemental Hg conversion downstream of the SCR remains constant when the configuration is changed from the SCR by-pass to SCR on-line configuration.

As a prime example, the SCR portion of the Hg conversion may be calculated from rearrangement of Equation (2) using the OHM data from June 1-3, 2004 during the second campaign of the field test program when the SCR was operating normally with NH₃ injection. The OHM data showed a net conversion of $\eta_{\text{net}} = 98.3\%$ with a standard uncertainty of 0.5% (absolute). The non-SCR contribution assumed is $\eta_{\text{non-SCR}} = 63.7\%$ with a standard uncertainty of 8.1% (absolute). Using these values, Equation (2) may be solved for the SCR contribution to Hg oxidation, yielding a value of $\eta_{\text{SCR}} = 95.4\%$ with a standard uncertainty of 1.7% (absolute). This SCR Hg conversion estimate from the field data will be compared with predictions from Cormetech's proprietary Hg model in a subsequent section.

Combustion Calculations

Combustion calculations were conducted for the proximate and ultimate analysis of three coal grab samples taken during the second campaign on June 1-3, 2004. Based on the variability of the coal data, the calculated average water content at the SCR location was 9.0% with a standard uncertainty of 0.2% absolute. Three moisture values at the SCR inlet measured by OHM during the second campaign had an average of 8.6% and a standard uncertainty of 1.0% absolute. Using the estimated standard uncertainties, the mean OHM water content result is not statistically different than the mean calculated from combustion calculations at a 99% confidence level based on a standard t-test.

The combustion calculations were done using an average coal Cl content of 631 ppmw (weight basis, dry) with a standard uncertainty of 28 ppmw (dry). The resultant calculated HCl concentration at the SCR was 41 ppmvd with a standard uncertainty of 5 ppmvd. This may be compared to the single measurement at the FGD inlet (34 ppmvdc with a standard uncertainty of 0.5 ppmvdc). This measured value may be corrected using the O₂ content at the SCR location if the assumption that there is no loss of HCl between the SCR and FGD is a valid assumption. The calculated corrected value for the SCR location is 33 ppmvd with a standard uncertainty of 0.5 ppmvd under this assumption. However, the assumption is not valid since the corrected HCl level from the FGD measurement (to the SCR location) is statistically different and lower than the mean value estimated from combustion calculations at a 99% confidence level. Partial adsorption or condensation of HCl on fly ash or similar loss mechanisms may account for the lower value estimated at the SCR from downstream measurement at the FGD inlet. Flue gas HCl from the combustion calculations was therefore used in the SCR Hg model runs.

Modeling of SCR Hg oxidation field data during normal SCR operation with NH₃

Cormetech's proprietary model can predict simultaneous NO_x and Hg performance. The model input parameters include SCR operating parameters (temperature, flue gas

composition, NH_3/NO_x molar ratio, and flue gas flowrate), physical and chemical properties of SCR catalyst including deactivation level, and SCR reactor design information. The model output includes NO_x reduction and Hg oxidation performance that may be expressed as either outlet concentrations or as conversions of inlet NO_x and Hg^0 .

This modeling section covers detailed data analysis and modeling runs based on field data with the SCR on-line with NH_3 injection from the second campaign (excluding May 25th when NH_3 was not injected). The observed net Hg conversion is adjusted using the assumed 63.7% non-SCR Hg conversion to arrive at an “observed” SCR Hg conversion. The NH_3/NO_x molar ratio was not directly measured during the field campaign, so the model value for the molar ratio was adjusted until the model-predicted NO_x reduction matched the observed NO_x conversion. The “predicted” Hg conversion for these model input values is then compared to the “observed” SCR Hg conversion.

During the second campaign, the SCR was operated normally at 93.1% NO_x reduction (conversion of NO_x across the SCR for the selective catalytic reduction reaction of NO_x with NH_3 reductant to form N_2 and H_2O). As detailed in the example following Equation (2) above, the SCR contribution to the observed Hg oxidation was estimated to be 95.4% with a standard uncertainty of 1.7% (absolute) after allowance for the assumed 63.7% non-SCR conversion. This 95.4% “observed” SCR Hg conversion and its uncertainty will be compared to the model predictions below.

Model input parameters were taken from average property data. The flue gas HCl concentration was taken from the combustion calculations. The NH_3/NO_x molar ratio was chosen to match the measured NO_x conversion of 93.1%. Model sensitivity runs were also conducted to estimate the standard uncertainty of the model prediction for elemental Hg oxidation.

Resultant model estimates for SCR conversion of elemental Hg were 92.6% with a standard uncertainty of 2.9%. This predicted result may be compared to “observed” SCR Hg conversion of 95.4% with a standard uncertainty of 1.7%. The model prediction and “observed” SCR Hg conversion are not statistically different at an 80% confidence level based on a standard t-test. Thus, Cormetech’s Hg model prediction for SCR Hg oxidation in Mt. Storm Unit 2 is consistent with the field data.

Modeling of SCR Hg oxidation field data during non-routine operation (no NH_3)

As mentioned previously, the model would predict an additional SCR Hg^0 conversion of only 5% without ammonia injection compared to the ammonia injection case for the conditions at Mt. Storm Unit 2. Thus there was adequate SCR catalyst capability (installed volume and activity) to achieve high Hg conversion in either case for the Mt. Storm Unit 2 SCR at the time of the field test. This discussion should not diminish the strong role that ammonia plays in the reaction chemistry, which is predicted from the model. The impact of ammonia on net Hg^0 conversion would be more evident at

conditions with lower HCl concentration, less catalyst capability, or older catalyst age relative to the conditions during the Mt. Storm Unit 2 field study.

Identification of key field measurement and SCR design parameters based on SCR Hg oxidation model runs over field data uncertainty range

For prediction of simultaneous NO_x and Hg performance, Cormetech's SCR Hg oxidation model requires the following input parameters: reactor design, NO_x and H₂ concentration at the SCR inlet, aged catalyst activity, other inlet flue gas concentrations (including Hg⁰ and Hg⁺²), temperature, and flowrate. When accurate field NO_x performance data is available on an existing unit, the model may alternatively be run to match the observed NO_x reduction performance and predict just the SCR Hg conversion (as was done for the Mt. Storm Unit 2 field data). Aged catalyst activity for NO_x reduction is generally determined by routine pilot testing of SCR samples taken during outages (e.g. after the end of ozone season), or can be predicted from SCR and coal design parameters.

A quantitative model sensitivity analysis was performed for the Mt. Storm Unit 2 data during normal operation with NH₃ injection on June 1-3, 2004. The key field measurement parameters whose standard uncertainty had a major impact on SCR Hg oxidation model predictions included: inlet HCl concentration (or its surrogate, coal Cl content), inlet H₂O concentration, and flue gas flowrate. Estimated field parameters that were not directly measured and whose standard uncertainty had a major impact on SCR Hg oxidation model estimates included: inlet NH₃/NO_x molar ratio and speciated Hg data for the SCR outlet. Speciated Hg measurements were performed at the SCR inlet but not at the SCR outlet. For SCR Hg performance modeling, this situation required estimation of SCR outlet Hg concentration from OHM data downstream of the APH using Equation (2), which increased the standard uncertainty in the estimated SCR contribution to oxidation of elemental Hg. Other field data whose standard uncertainty did not have a major impact on SCR Hg oxidation model estimates included: temperature and SCR inlet concentrations of O₂, Hg, Hg²⁺, and NO_x. The standard uncertainties in the field measurements for these parameters were adequate to avoid significant sensitivity in resultant model estimates of SCR Hg oxidation. Additionally, the standard uncertainty of the aged catalyst activity for NO_x reduction was small for Mt. Storm Unit 2 since pilot testing was done on SCR catalyst samples taken prior to restart of the SCR system for the field test program. The standard uncertainty of this parameter did not have a significant impact on the standard uncertainty of model-predictions for SCR Hg conversion.

Other general SCR considerations and impact on catalyst management

Other key considerations for general purposes include: SCR catalyst performance over its lifetime for NO_x and Hg, availability of (or design for) spare SCR reactor layer(s) for future addition of SCR catalyst, and target/required Hg oxidation levels. SCR catalyst management strategies will need to be adapted to consider NO_x and Hg performance over the catalyst lifetime. Generally, the timing of catalyst additions or replacements may be

dictated by either NO_x or Hg performance requirements, so accurate prediction of SCR Hg oxidation performance decline rates will be important.

Figure 7 provides an example of model sensitivity of predicted SCR outlet percent oxidized mercury, Hg⁺², to (a) gas-phase chloride content and (b) catalyst age for Mt. Storm Unit 2. All of the predictions in Figure 7 are based on the above-design NO_x conversion efficiency of 93.1% observed during the field study. During the field test at Mt. Storm, the gas-phase HCl concentration at the SCR was estimated as 41 ppmvd with a standard uncertainty of 5 ppmvd based on the coal analyses during the field test. For reference, the design coal Cl content corresponds to approximately 75 ppmvd HCl at the SCR. As illustrated in Figure 7, the predicted curve for SCR outlet Hg⁺² percentage plummets dramatically at low gas-phase chloride levels. This effect worsens with catalyst age, as illustrated by model predictions shown as squares in Figure 7 which correspond to the time just prior to the normal future addition of a catalyst layer to maintain design NO_x reduction requirements. This drop-off in SCR outlet Hg⁺² at low HCl levels is ameliorated considerably when the spare layer is then added to the unit during the normal course of SCR catalyst management, as illustrated by model predictions shown as triangles in Figure 7. Thus it is critically important to understand and consider coal Cl content variability, SCR aging effects, and SCR catalyst addition and replacement strategies when the SCR is required to meet both NO_x reduction and Hg oxidation requirements. Cormetech's predictive model for simultaneous DeNO_x and Hg oxidation provides an accurate platform for such predictive requirements, as illustrated by the consistency of the model predictions with the Mt. Storm Hg field data.

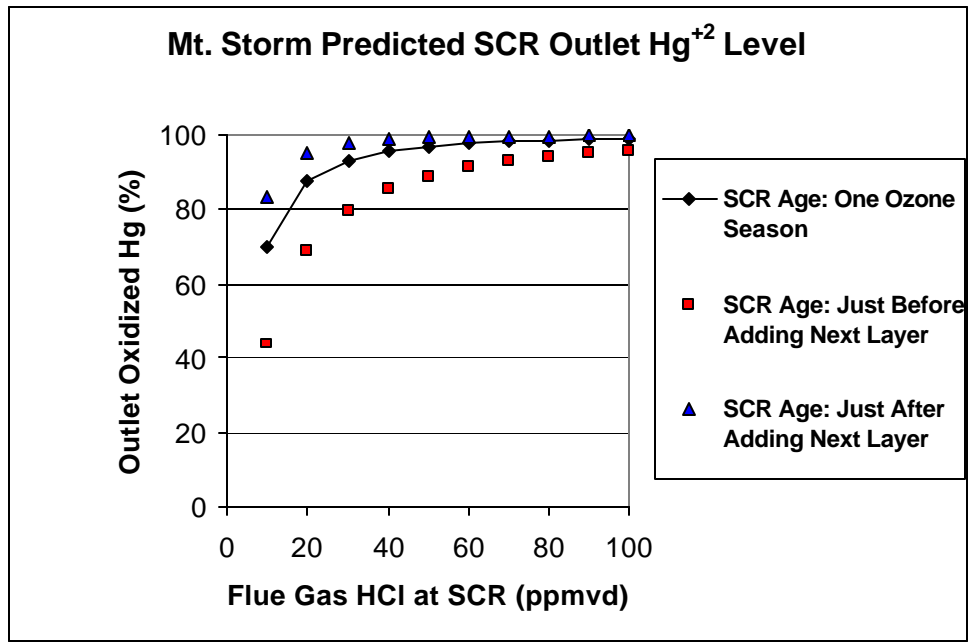


Figure 7- Predicted effect of chloride level based on Cormetech's SCR Hg oxidation model for Mt. Storm Unit 2

CONCLUSIONS

The following conclusions may be made:

- Without the SCR system in service and no injection of NaHS FGD additive, the total mercury removal efficiency across the FGD scrubber was approximately 70%.
- Without the SCR in service and with injection of NaHS, the total mercury removal efficiency through the FGD scrubber increased from to about 78%.
- With the SCR system operating normally, greater than 95% mercury removal efficiency was achieved in the SCR, ESP and wet FGD configuration. There was no incremental improvement from NaHS injection.
- B&W's NaHS injection technology for suppressing re-emission had no effect on SO₂ removal by the wet FGD system, which maintained greater than 95% control of SO₂.
- Cormetech's SCR mercury oxidation model prediction was consistent with the observed conversion of elemental mercury after allowing for 64% downstream non-SCR conversion measured with the SCR in bypass.
- Cormetech's SCR catalyst provided approximately 95% conversion of elemental mercury after one full ozone season of operation at Dominion's Mt. Storm Unit 2 while achieving 93% NO_x reduction efficiency.
- Field studies of SCR Hg oxidation should include accurate values of NO_x conversion, NH₃/NO_x molar ratio, inlet flue gas compositions, temperature, flowrate, and both inlet and outlet speciated Hg concentrations.
- SCR operations strategies to meet Hg regulatory requirements should consider prediction of SCR catalyst performance over time, control of flue gas HCl content (e.g. by coal selection), and catalyst management strategies that address both NO_x reduction and Hg oxidation performance. SCR design strategies should consider the merits of spare layer(s) for improved SCR Hg oxidation performance.

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