

# **Achieving and Maintaining Hg Oxidation Performance through SCR Catalyst Selection and Management**

**Paper # 45**

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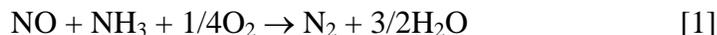
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## **ABSTRACT**

The co-benefit of oxidized Hg capture by desulfurization systems is an effective and economical method to achieve compliance with Utility MACT limits. As is the case for maintaining required DeNOx emission requirements, catalyst additions and replacements (actions) will be managed to achieve and maintain Hg oxidation levels. For DeNOx, catalyst samples are tested annually to determine DeNOx activity, deactivation rate and cause. Data is then used in combination with plant specific considerations to determine the appropriate catalyst action(s) to maintain SCR system performance. Fresh and used catalyst Hg oxidation test results and modeling indicate such annual testing may be used analogously to manage SCR Hg oxidation performance. Also, under more challenging conditions such as low chlorine in flue gas, catalyst actions may include our advanced catalysts which have been designed to significantly improve Hg oxidation. Information including performance and durability testing results are reviewed along with catalyst management case studies.

## INTRODUCTION

The Selective Catalytic Reduction (SCR) of NO<sub>x</sub> using NH<sub>3</sub> as the reductant over V<sub>2</sub>O<sub>5</sub>-(WO<sub>3</sub> or MO<sub>3</sub>)/TiO<sub>2</sub> catalysts is the current state-of-the-art technology for the control of NO<sub>x</sub> emissions from coal-fired utility boilers. SCR has been demonstrated to achieve high NO<sub>x</sub> removal efficiencies of 90% or more. The primary NO<sub>x</sub> reduction reaction proceeds with the following stoichiometry (note that the flue gases from coal-fired boilers typically contain >90% NO):



SCR catalysts are also active for the oxidation of elemental mercury (Hg<sup>0</sup>) present in the flue gas by chlorine as HCl (and/or by bromine as HBr; the reaction is analogous to equation [2]):



The conversion of Hg<sup>0</sup> (water-insoluble) to HgCl<sub>2</sub> or HgBr<sub>2</sub> (water-soluble Hg<sup>2+</sup>) allows for capture of mercury in a downstream flue gas desulfurization system and is expected to be an effective and economical method<sup>1</sup> to achieve compliance with the Mercury & Air Toxics Standard (MATS)(formerly referred to as Utility MACT).

A study<sup>2</sup> conducted by Babcock and Wilcox, Dominion Power, and Cormetech published in 2005 illustrates well the significant positive impact of the SCR system on Hg removal at full-scale. In this study, the amount of Hg removal increased from 70%-78% to >95% with the SCR in-service compared to when it was in by-pass.

This snapshot of Hg removal performance illustrates the potential of co-benefits. However, development of a catalyst management strategy for Hg<sup>0</sup> oxidation is necessary in order to utilize co-benefits as a continuous compliance tool.

An undesirable reaction that occurs over SCR catalysts is the oxidation of SO<sub>2</sub> to SO<sub>3</sub>:



Thus, an optimal SCR catalyst design for a given unit will maximize the rates of reactions [1 – 2], while minimizing the rate of reaction [3].

Routinely, SCR catalyst is formulated given a maximum allowed SO<sub>2</sub> oxidation rate to minimize the negative effects of high SO<sub>3</sub> such as air pre-heater plugging or opacity concerns, while meeting the DeNO<sub>x</sub> and NH<sub>3</sub> slip requirements; i.e. the amount that the catalyst can be formulated for DeNO<sub>x</sub> activity is typically limited by this maximum SO<sub>2</sub> oxidation. For example, the vanadium content, which benefits the DeNO<sub>x</sub> reaction, is limited in the catalyst since it also increases the SO<sub>2</sub> oxidation rate.

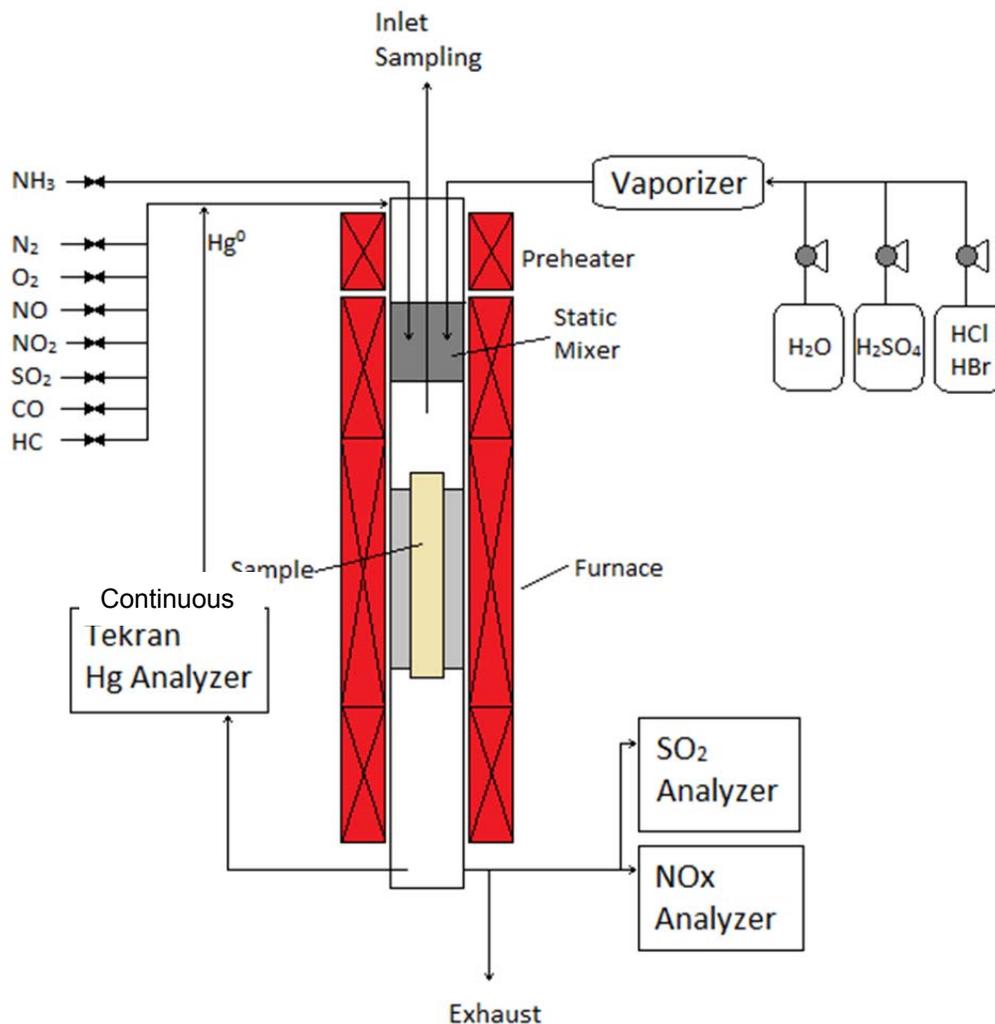
New catalysts and technologies, such as Cormetech's NExtGen COMET™, greatly improve this trade-off between DeNO<sub>x</sub> and SO<sub>2</sub> oxidation and moreover, can greatly increase the Hg<sup>0</sup> oxidation activity.

Through presentation of an example dataset, we show that the Hg<sup>0</sup> oxidation reaction is more complex than the DeNO<sub>x</sub> reaction. The data set illustrates some of the key tendencies resulting from changes in system parameters, such as flue gas conditions and catalyst selection and age, in order to discuss catalyst management for Hg<sup>0</sup> oxidation compared to DeNO<sub>x</sub>. Due to the number of factors and interactions between them, presentation of the comprehensive dataset used to predict catalyst performance is beyond the scope of this paper.

## EXPERIMENTAL

Two reactor systems are used by Cormetech for measuring the  $\text{Hg}^0$  oxidation performance of catalyst samples (both systems are also capable of DeNO<sub>x</sub> and SO<sub>2</sub> oxidation measurements): a micro-scale reactor located at Cormetech and a bench scale reactor located at Mitsubishi Heavy Industries' Hiroshima R&D Center (MHI).

The micro-reactor at Cormetech is used mainly for parametric studies of both fresh and deactivated catalyst. The reactor is a fully automated and continuous system capable of injecting a wide variety of gaseous and aqueous species and measuring DeNO<sub>x</sub>, SO<sub>2</sub> oxidation, and  $\text{Hg}^0$  oxidation. A schematic of the Cormetech system is shown below in Figure 1.



**Figure 1.** System diagram of the Cormetech micro-reactor. The reactor is capable of automated DeNO<sub>x</sub>, SO<sub>2</sub> oxidation, and  $\text{Hg}^0$  oxidation testing over a single layer with complex synthetic flue gas.

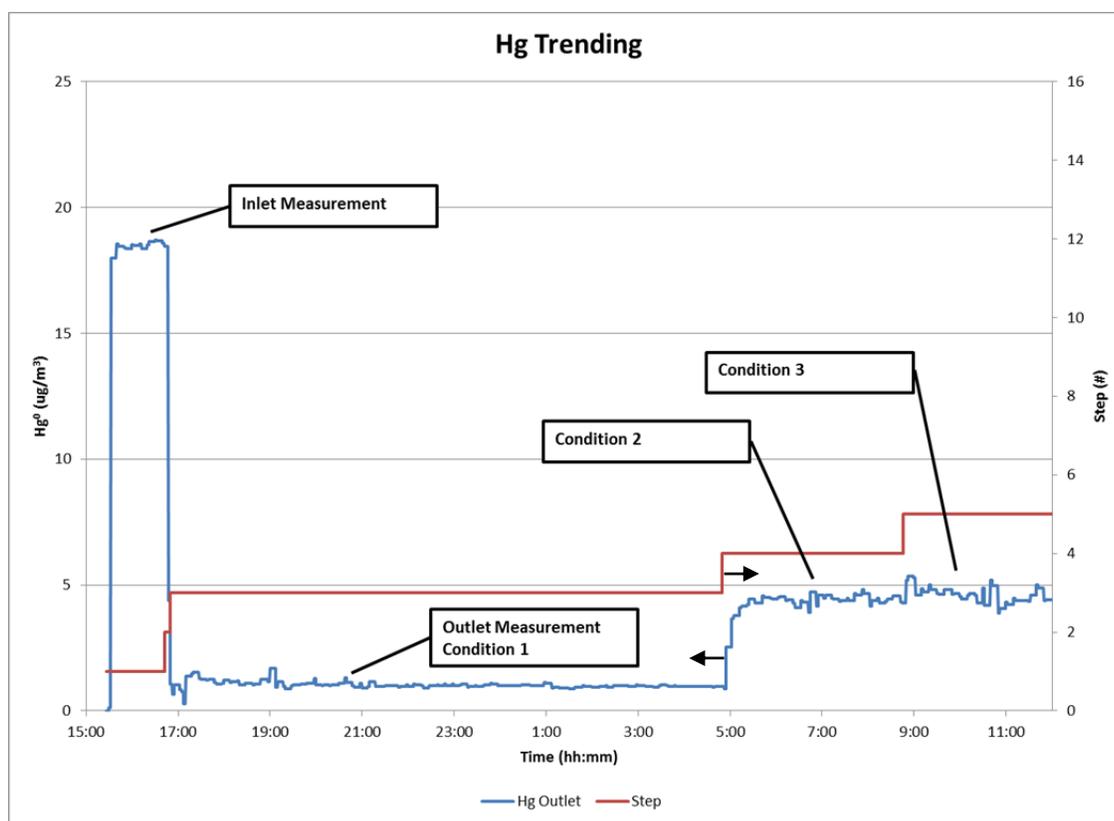
$N_2$ ,  $O_2$ ,  $NO$ ,  $NO_2$ ,  $SO_2$ ,  $NH_3$ ,  $CO$ , hydrocarbons, and  $Hg^0$  are injected as gases, and  $H_2O$ ,  $H_2SO_4$ ,  $HCl$ ,  $HBr$ , and  $Hg^{2+}$  are injected as vaporized liquids.  $Hg^0$  and  $Hg^{2+}$  concentrations are measured by a continuous Hg analyzer, which also serves as the  $Hg^0$  source.  $NO_x$  concentration is measured using a chemiluminescence analyzer,  $O_2$  is analyzed by a paramagnetic analyzer, and  $SO_2$  is measured by a UV-vis analyzer. A picture of the Cormetech reactor system is shown below in Figure 2.



**Figure 2.** Picture of the Cormetech mercury oxidation micro-reactor system. The reactor is enclosed in a floor to ceiling fume hood.

The integrity of the Cormetech micro-reactor is checked periodically to ensure that the empty reactor system does not contribute appreciably to the measured  $\text{Hg}^0$  oxidation performance. Inert materials are used in the reactor construction (it is predominantly made of quartz).

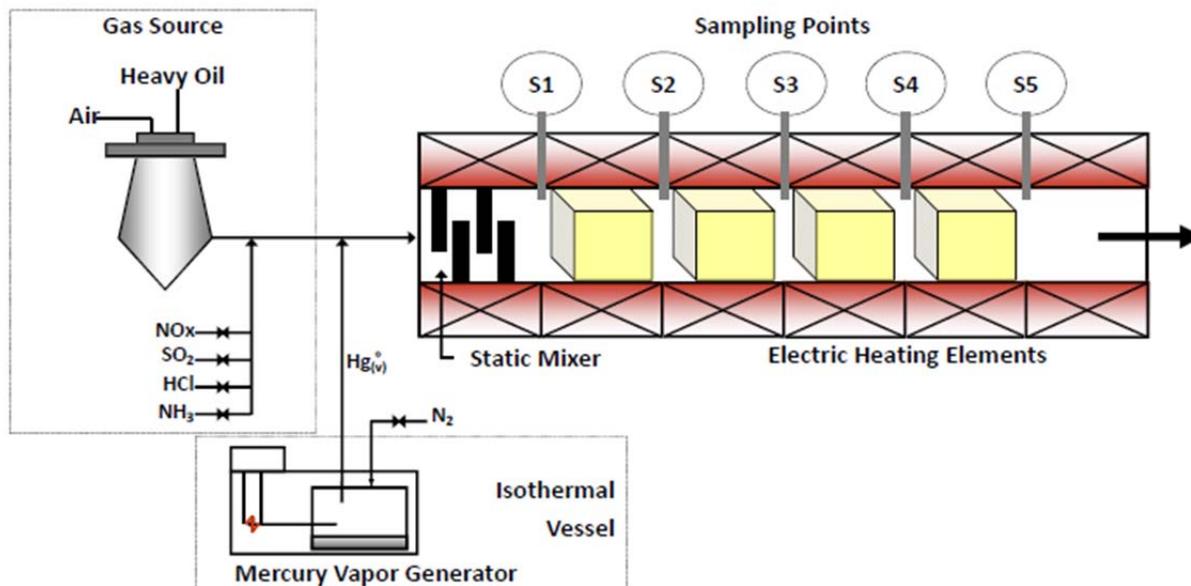
The micro-reactor uses sophisticated automated controls for controlling the temperature, gas feed, and the sampling and analyzer system. It follows a predefined testing sequence, and uses stability criteria to make independent decisions when to progress to next step in the sequence. The automation enables the reactor to quickly test a large number of parameters on an automated basis, which is important because of the large number of factors that affect  $\text{Hg}^0$  oxidation. Among the factors that affect  $\text{Hg}^0$  oxidation are temperature, AV, and  $\text{Hg}^0$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ , CO, HCl, and HBr concentrations. An example of a continuous mercury test is shown below in Figure 3; note the stability of the data.



**Figure 3.**  $\text{Hg}^0$  trend of an example experiment. Condition 1 is  $T = 400\text{ }^\circ\text{C}$ ,  $\text{SO}_2 = 1000\text{ ppm}$ ,  $\text{NO} = 350\text{ ppm}$ ,  $\text{NH}_3 = 0\text{ ppm}$ ,  $\text{HCl} = 50\text{ ppm}$ ,  $\text{SO}_3 = 10\text{ ppm}$ ,  $\text{H}_2\text{O} = 11\%$ , and  $\text{O}_2 = 4\%$ . Condition 2 changes from Condition 1 to  $\text{NH}_3 = 315\text{ ppm}$ . Condition 3 changes from Condition 2 to  $\text{SO}_2 = 2500\text{ ppm}$ .

The bench reactor at MHI is used mainly for total system testing of both fresh and deactivated catalyst. The reactor is capable of testing up to four layers of catalyst and  $\text{DeNO}_x$ ,  $\text{SO}_2$  oxidation, and  $\text{Hg}^0$  oxidation are measured at each port. A schematic of the

system is shown below in Figure 4.  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{HCl}$ , and  $\text{NH}_3$  are injected as gases, while  $\text{Hg}^0$  is injected from a vapor generator.  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  concentrations are measured by the Ontario Hydro Method.  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HCl}$ , and  $\text{NH}_3$  are measured by wet chemical analysis.  $\text{NO}_x$  concentration is measured using a chemiluminescence analyzer, while  $\text{O}_2$  is analyzed by a paramagnetic analyzer.



**Figure 4.** System diagram of the MHI bench reactor. The reactor is capable of measuring DeNO<sub>x</sub>, SO<sub>2</sub> Oxidation, and Mercury Oxidation for each of up to four layers.

## RESULTS

The Hg<sup>0</sup> oxidation reaction (equation [2]) differs significantly from the DeNO<sub>x</sub> reaction (equation [1]) with respect to the number of factors that influence its reaction kinetics and ultimately the measured catalyst performance. This section will first focus on the effect of reaction conditions (i.e., temperature and gas composition) on the Hg<sup>0</sup> oxidation reaction, to illustrate the key differences with the DeNO<sub>x</sub> reaction, and reveal the considerations that need to be accounted for when predicting the Hg<sup>0</sup> oxidation performance of a catalyst layer or full reactor system. Next, example data for field deactivated catalyst samples will be reviewed, which will illustrate that deactivation rates for Hg oxidation are correlated to those for DeNO<sub>x</sub>, for a given set of conditions. Finally, a case study will be presented that will show the impact that catalyst type can have on the Hg<sup>0</sup> oxidation performance for an SCR unit on a challenging PRB-firing coal application.

### Impact of Reaction Conditions on Hg<sup>0</sup> Oxidation

All of the fresh catalyst data presented in this section were obtained for a single catalyst sample using Cormetech's Hg oxidation micro-reactor, in order to illustrate the main factors impacting Hg<sup>0</sup> oxidation. It is important to note that these factors can have strong interactions, and they can vary with catalyst type, so the examples given in this section provide a snapshot of the effects. For the lab testing (i.e., for the fresh catalyst in this section, and for the deactivated and case study testing in the following sections), the inlet Hg injected into the micro-reactor was 100% Hg<sup>0</sup>. Thus, the % Hg<sup>0</sup> oxidation across the SCR catalyst sample was calculated using the following equation:

$$\% \text{ Hg}^0 \text{ oxidation} = (\text{Hg}_{\text{IN}}^0 - \text{Hg}_{\text{Out}}^0) / \text{Hg}_{\text{IN}}^0 \quad [4]$$

Although the reaction kinetics for Hg<sup>0</sup> are not well-described by a simple first order kinetic rate law due to the complex dependencies among the various factors (i.e., temperature, gas composition, and catalyst type), it can be convenient to calculate a first order rate constant ( $K_{\text{HgOx}}$ , equation [5]) in order to gauge the relative impact of changing these factors on the catalyst potential for Hg<sup>0</sup> oxidation (note: AV = area velocity = total gas flow / total geometric catalyst surface area = Nm<sup>3</sup>/m<sup>2</sup>h).

$$K_{\text{HgOx}} = -AV * \ln (1 - \% \text{ Hg}^0 \text{ oxidation}) \quad [5]$$

This equation is similar to the DeNO<sub>x</sub> K equation used by the industry for catalyst management, valid for a MR = 1 condition<sup>3</sup>:

$$K_{\text{DeNOx}} = -AV * \ln (1 - \% \text{ DeNOx}) \quad [6]$$

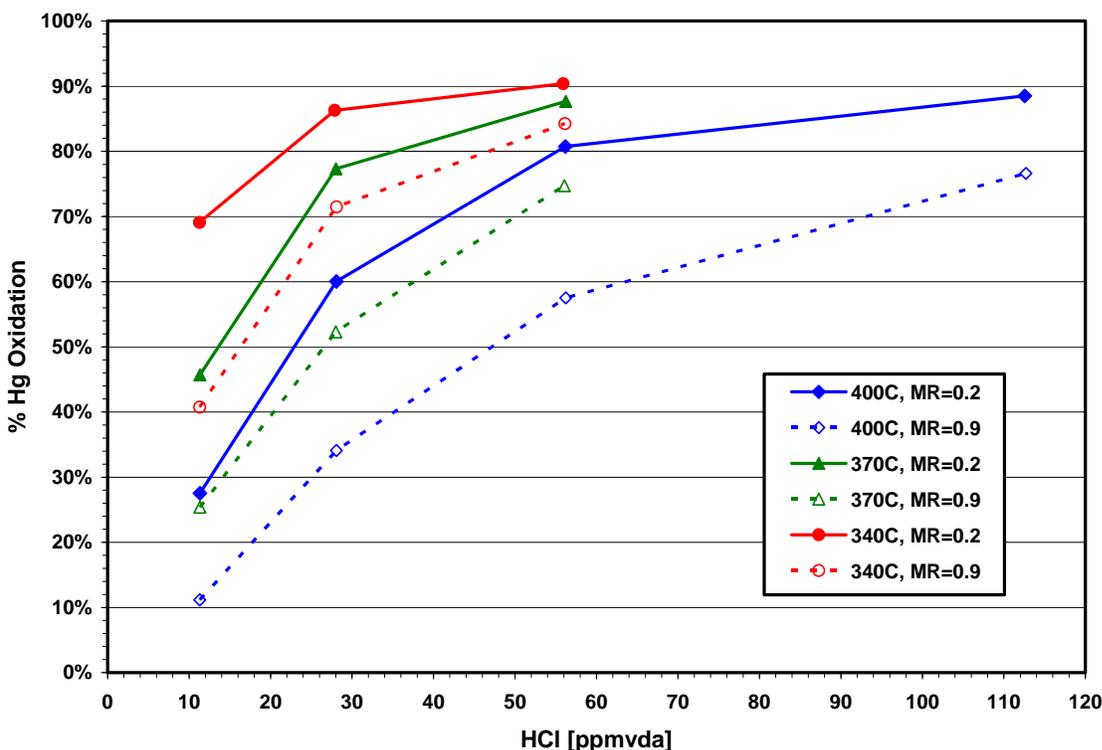
To assess the impact of NH<sub>3</sub> on Hg<sup>0</sup> oxidation, two MR (molar ratio = NH<sub>3</sub>/NO<sub>x</sub>) levels were used: 0.2 and 0.9. The MR = 0.9 condition is consistent with a layer 1 position in

the SCR where the catalyst inlet experiences the full NH<sub>3</sub> injection rate. The MR = 0.2 condition reflects a downstream layer position, where the inlet to the layer does not see the full injection NH<sub>3</sub> injection rate due to NO<sub>x</sub> reduction and NH<sub>3</sub> consumption in the upstream layers. It will be shown that the Hg<sup>0</sup> oxidation potential of the catalyst can be strongly influenced by the NH<sub>3</sub> concentration.

In Figure 5, the following observations are apparent regarding the impact of HCl, temperature and NH<sub>3</sub> on Hg<sup>0</sup> oxidation:

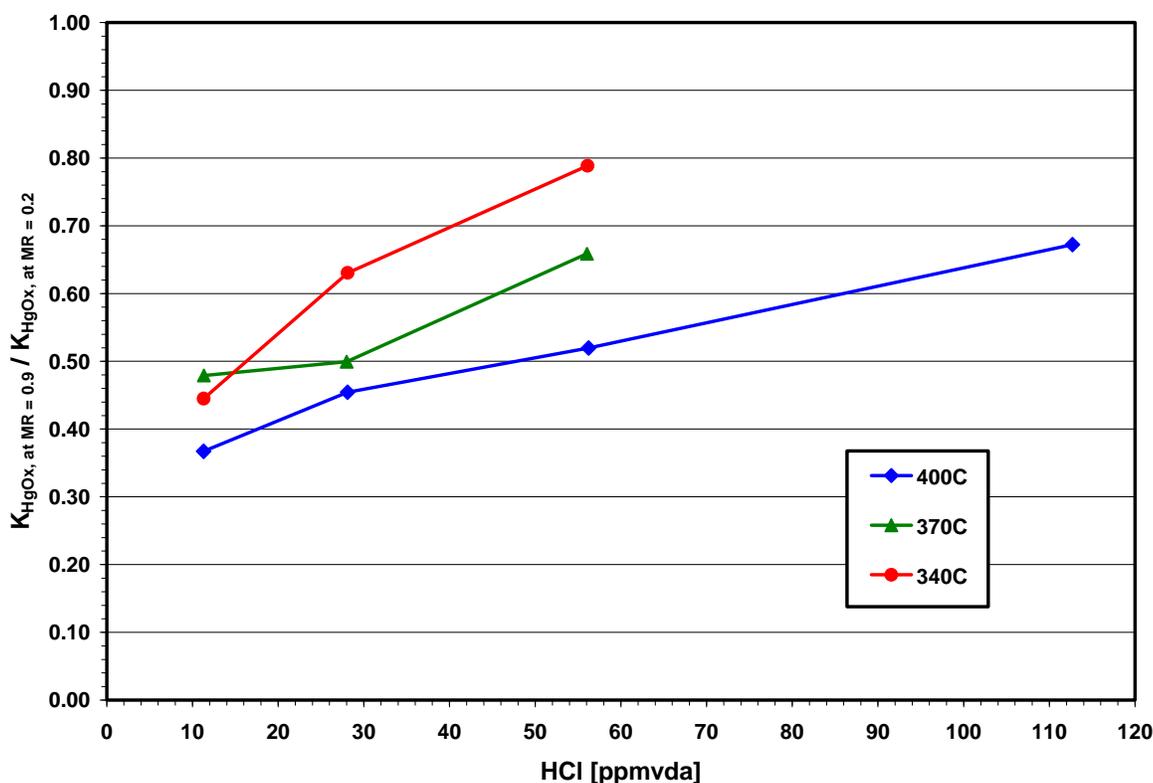
- HCl concentration has a significant positive effect on Hg<sup>0</sup> oxidation (in contrast to the DeNO<sub>x</sub> reaction, which is unaffected by HCl in the typical coal flue gas range<sup>4</sup>).
- Increasing temperature has a negative effect on Hg<sup>0</sup> oxidation (it has a positive effect on the DeNO<sub>x</sub> reaction). The negative impact of temperature on Hg<sup>0</sup> oxidation is more pronounced at low HCl concentration.
- NH<sub>3</sub> has a strong inhibitory effect on Hg<sup>0</sup> oxidation, the extent to which is influenced by the HCl concentration and temperature (see Figure 6 for further analysis). The DeNO<sub>x</sub> reaction is of course dependent on NH<sub>3</sub> to proceed.

It should be noted that these reaction conditions effects have a strong interaction with catalyst type; the data shown here provide a snapshot of the typically observed effects.



**Figure 5.** Impact of HCl concentration on Hg oxidation performance. Micro-reactor test conditions: Temperature = 340 – 400°C, MR = NH<sub>3</sub>/NO<sub>x</sub> = 0.2 – 0.9, H<sub>2</sub>O = 11%, O<sub>2</sub> = 3.5%, NO<sub>x</sub> = 350 ppmvda, SO<sub>2</sub> = 1000 ppmvda, SO<sub>3</sub> = 10 ppmvda, CO = 100 ppmvda, HCl = 11 – 112 ppmvda, inlet Hg<sup>0</sup> = 20 µg/Nm<sup>3</sup>.

As is generally known to the industry<sup>3</sup>, the effect of NH<sub>3</sub> on the DeNO<sub>x</sub> kinetics, for a coal flue gas condition, is close to zero order, and as a result, MR = 1 single layer tests with the assumption that the catalyst potential of individual layers are additive regardless of layer position provides a reasonable basis for catalyst management. A similar approach to catalyst management for Hg<sup>0</sup> oxidation will not accurately work because of the strong inhibitory impact of NH<sub>3</sub>, which makes the catalyst potential a strong function of layer position and requires a detailed understanding of the NH<sub>3</sub> profile along the length of the SCR catalyst layers. Figure 6 reanalyzes the Figure 5 data as a ratio of the first-order Hg oxidation rate constants to convey the magnitude of the NH<sub>3</sub> inhibition of catalyst potential. The negative impact of NH<sub>3</sub> on the first-order rate constant is quite large (it can exceed a 60% decrease for this data set) and is a strong function of HCl and temperature: the inhibition decreases as HCl is increased and temperature is lowered, highlighting strong interaction effects between these factors.



**Figure 6.** Impact of NH<sub>3</sub> on Hg oxidation performance. Micro-reactor test conditions: Temperature = 340 – 400°C, MR = NH<sub>3</sub>/NO<sub>x</sub> = 0.2 – 0.9, H<sub>2</sub>O = 11%, O<sub>2</sub> = 3.5%, NO<sub>x</sub> = 350 ppmvda, SO<sub>2</sub> = 1000 ppmvda, SO<sub>3</sub> = 10 ppmvda, CO = 100 ppmvda, HCl = 11 – 112 ppmvda, inlet Hg<sup>0</sup> = 20 µg/Nm<sup>3</sup>.

Figure 7A shows how area velocity (AV) can influence Hg<sup>0</sup> oxidation performance. Decreasing the AV from a single catalyst layer level (normalized AV = 1.0) to a two catalyst layer level (normalized AV = 0.50) increases the % Hg<sup>0</sup> oxidation across the catalyst, for both the low HCl (11 ppm) and higher HCl (56 ppm) conditions. The positive impact of decreasing AV is greater for the high MR case (MR = 0.90) than for the low MR case (MR = 0.20) due to the increased NH<sub>3</sub> consumption that will occur at lower AV (i.e., higher DeNO<sub>x</sub>).

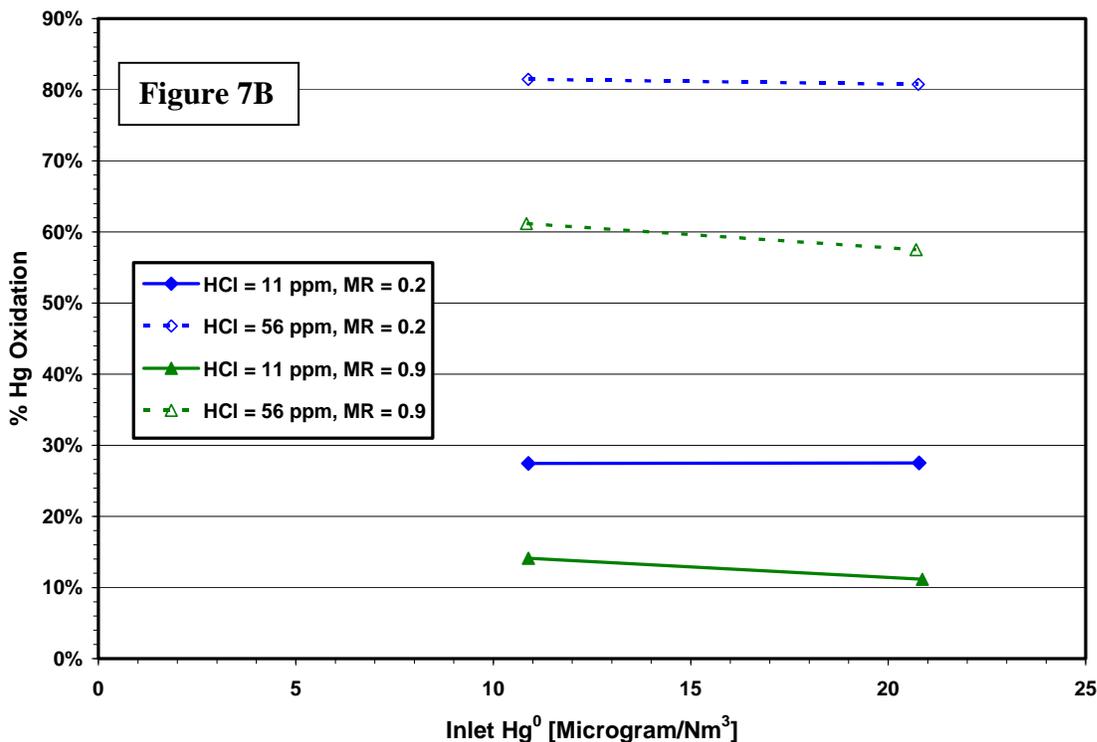
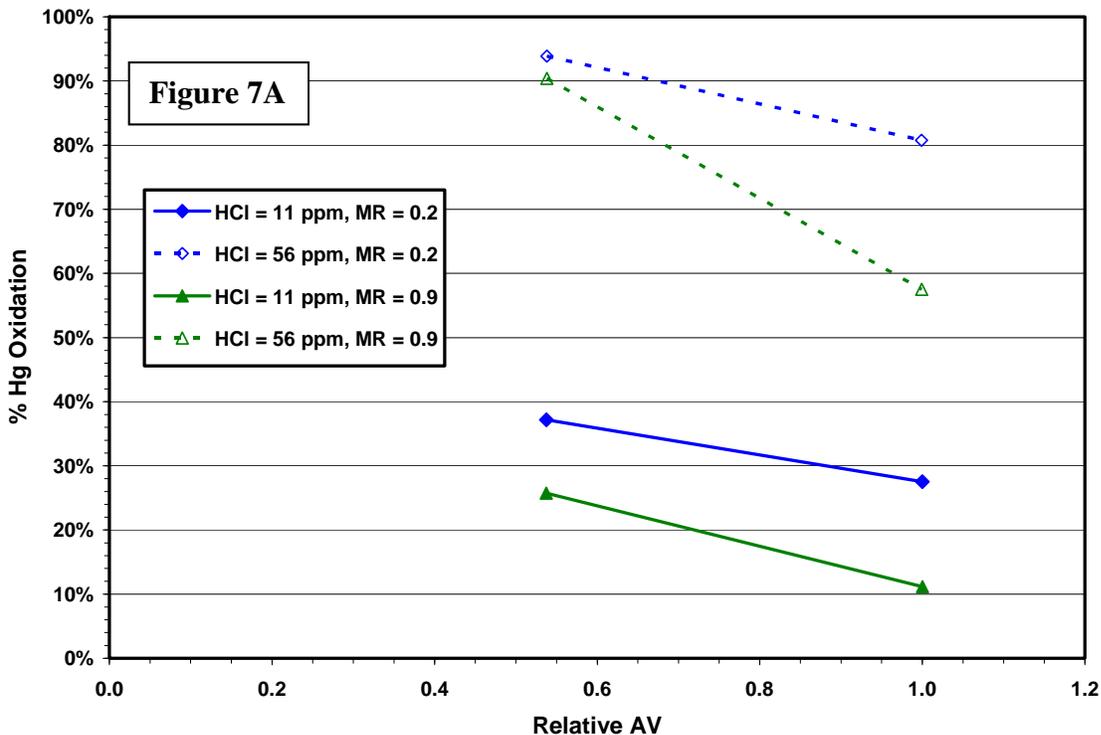
The catalyst inlet Hg<sup>0</sup> concentration does not have a significant impact on Hg<sup>0</sup> oxidation (see Figure 7B). Thus, the % Hg<sup>0</sup> oxidation achieved across an SCR catalyst layer or system is largely independent of the inlet Hg<sup>0</sup> concentration.

Figures 8 – 10, which illustrate the impact of CO, SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O on Hg<sup>0</sup> oxidation, will only include data for the MR = 0.20 condition (layer 2 or layer 3 inlet), in order to reveal the impact of these factors under low NH<sub>3</sub> conditions.

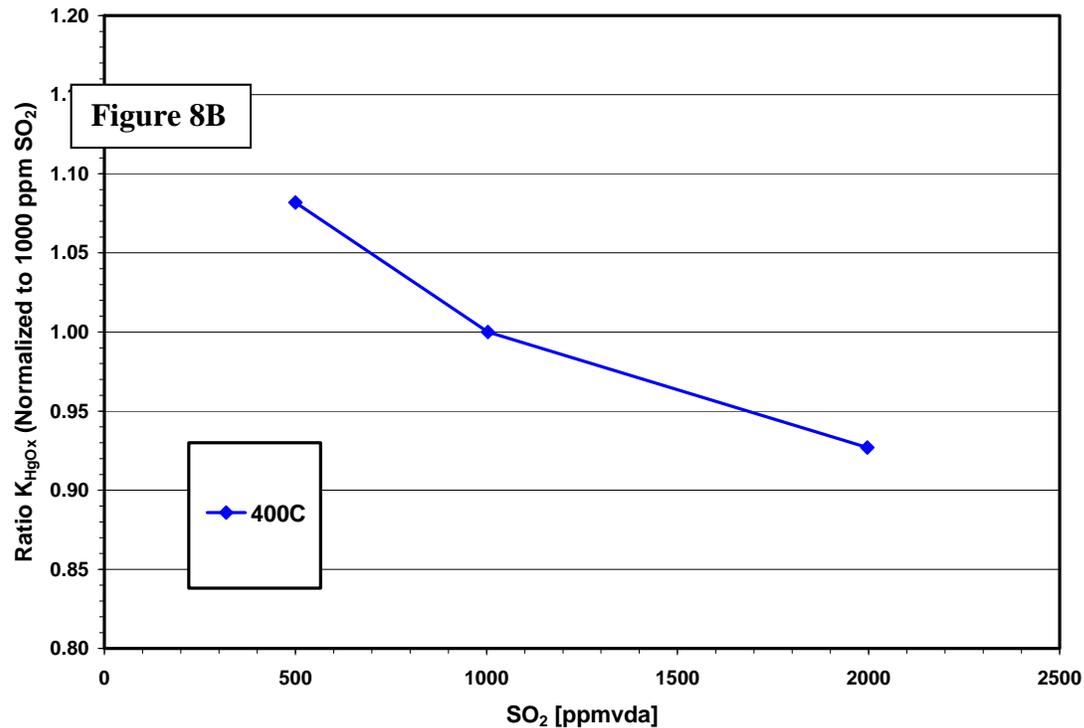
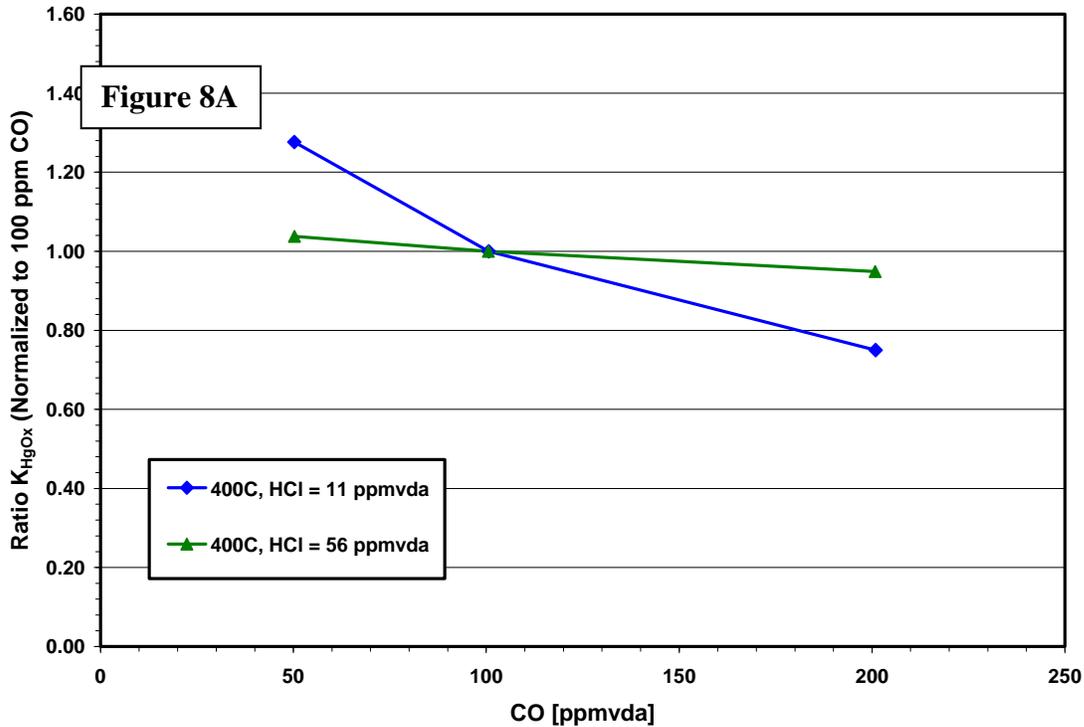
The flue gas CO (Figure 8A) and SO<sub>2</sub> concentrations (Figure 8B) both have a negative impact on Hg<sup>0</sup> oxidation, but the concentrations of these gases are nearly constant across the catalyst layers and only need to be accounted for on the basis of their inlet values. The inhibitory effect of CO is much stronger than that of SO<sub>2</sub>; the negative impact again reduces at higher HCl concentration, as it did for NH<sub>3</sub>. These data, as well as the data in Figures 5 and 6, reveal the additional factors that influence Hg<sup>0</sup> oxidation kinetics as compared to the DeNO<sub>x</sub> reaction. For comparative purposes, the DeNO<sub>x</sub> kinetics are unaffected by CO in this concentration range, while they are mildly influenced by the SO<sub>2</sub>/SO<sub>3</sub> content of the flue gas, as sulfur gases serve to increase the acidity of the catalyst and promote the DeNO<sub>x</sub> reaction.

The effects of O<sub>2</sub> and H<sub>2</sub>O concentrations on Hg<sup>0</sup> oxidation performance are shown in Figures 9A and 9B, respectively. O<sub>2</sub> has a strong positive impact on the kinetics, while H<sub>2</sub>O has a strong negative impact. The magnitude of these impacts is much greater than that observed for the DeNO<sub>x</sub> reaction, which are less than 5% on a K basis in this range.

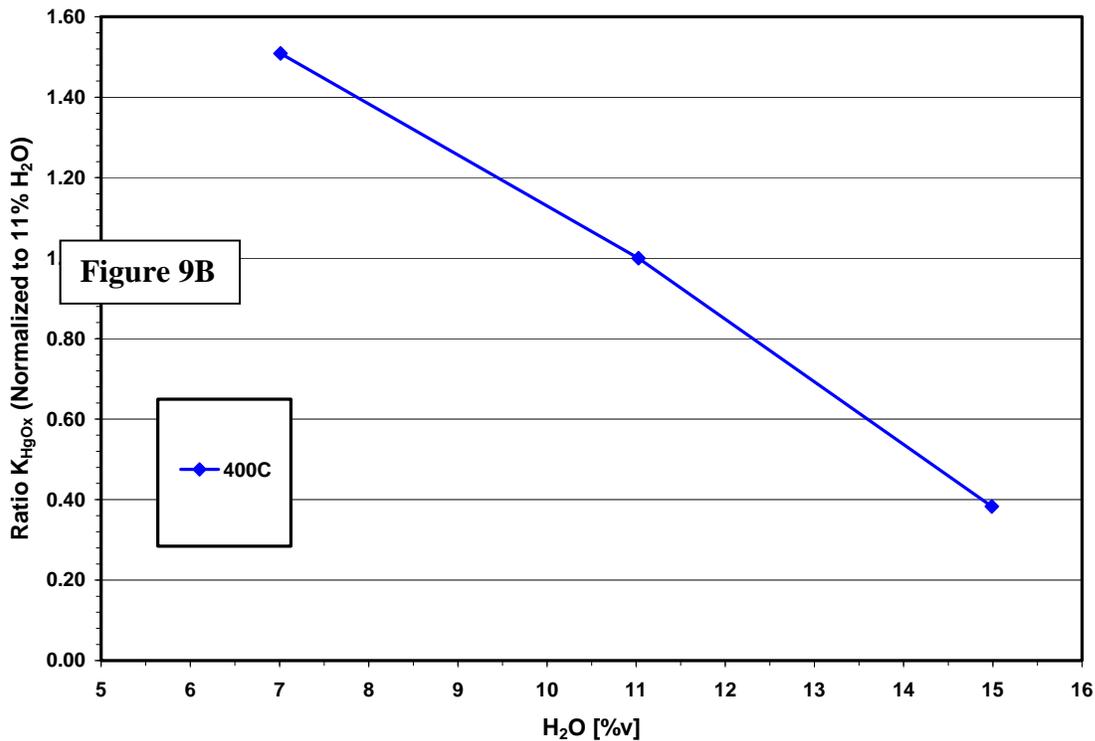
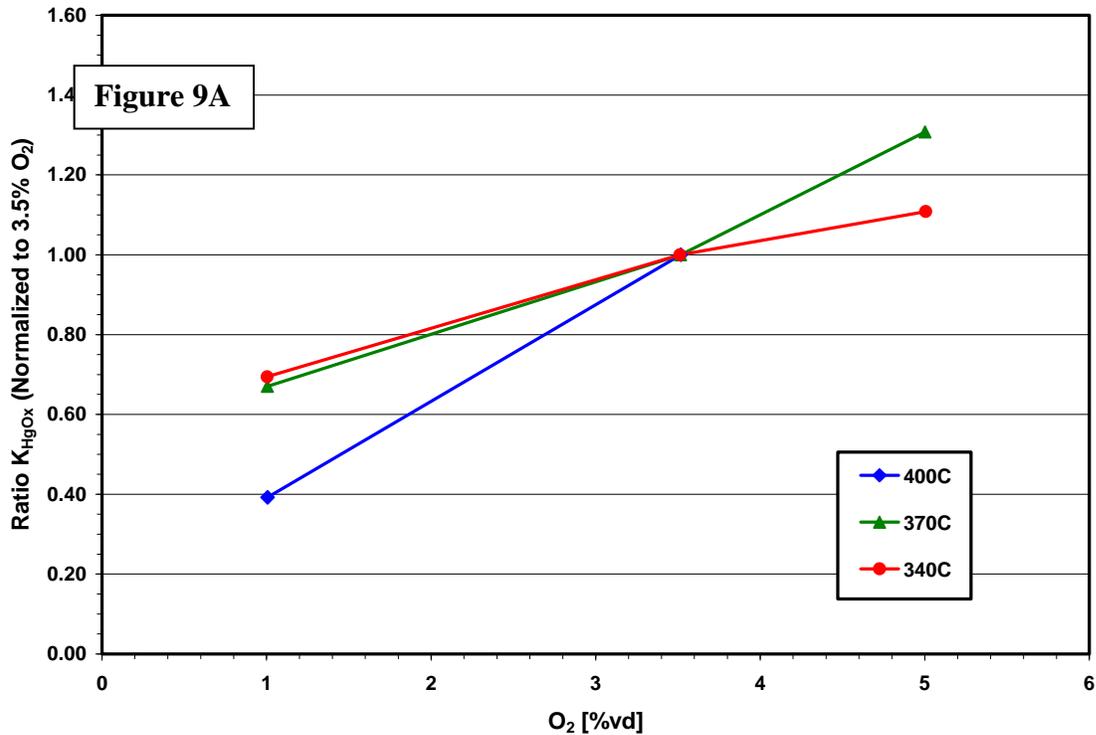
HBr addition to the flue gas, for those units that have that capability, has a beneficial impact on Hg<sup>0</sup> oxidation (Figure 10A). For a case where Hg<sup>0</sup> oxidation is quite low (400°C, HCl = 5 ppm, MR = 0.2 – 0.9), a small addition of HBr at ~ 1 ppm level has a profound impact, raising the performance from <10% to 90%. Note that similar to HCl, the extent of NH<sub>3</sub> suppression of rate reduces significantly with the addition of HBr. At ~ 2 ppm HBr, Hg<sup>0</sup> oxidation was almost unaffected by the addition of NH<sub>3</sub> up to MR = 0.90 (Figure 10B).



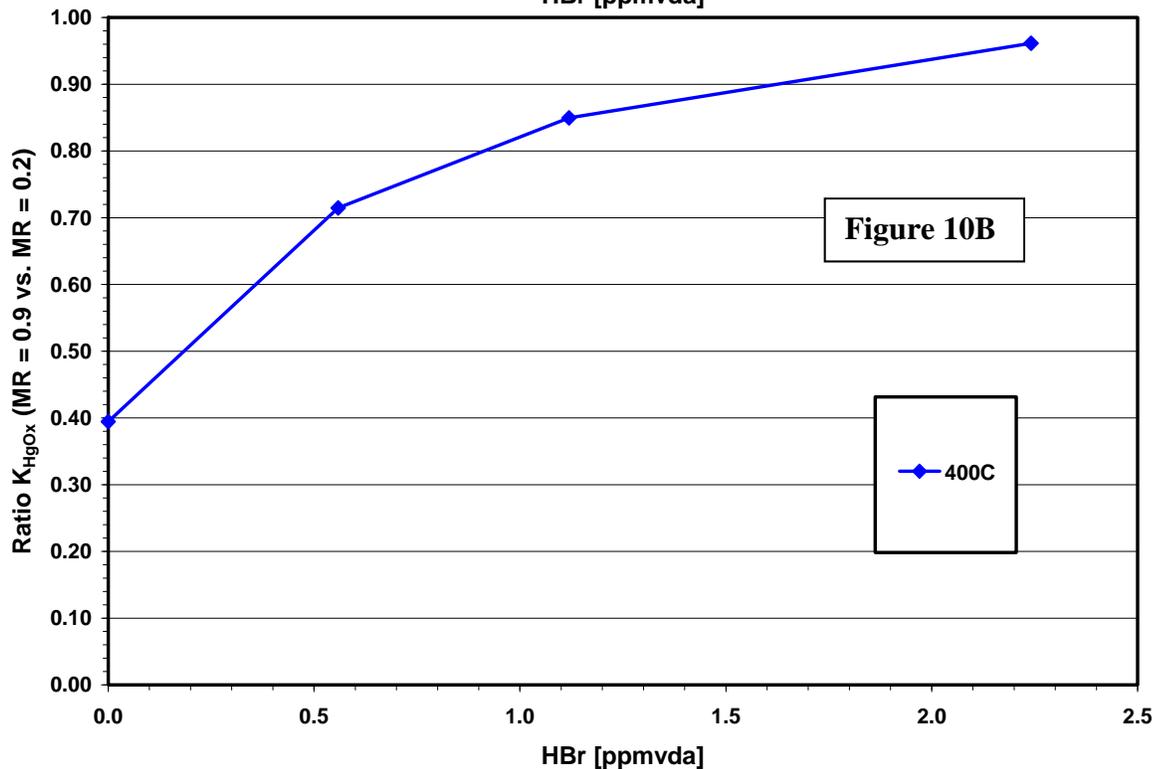
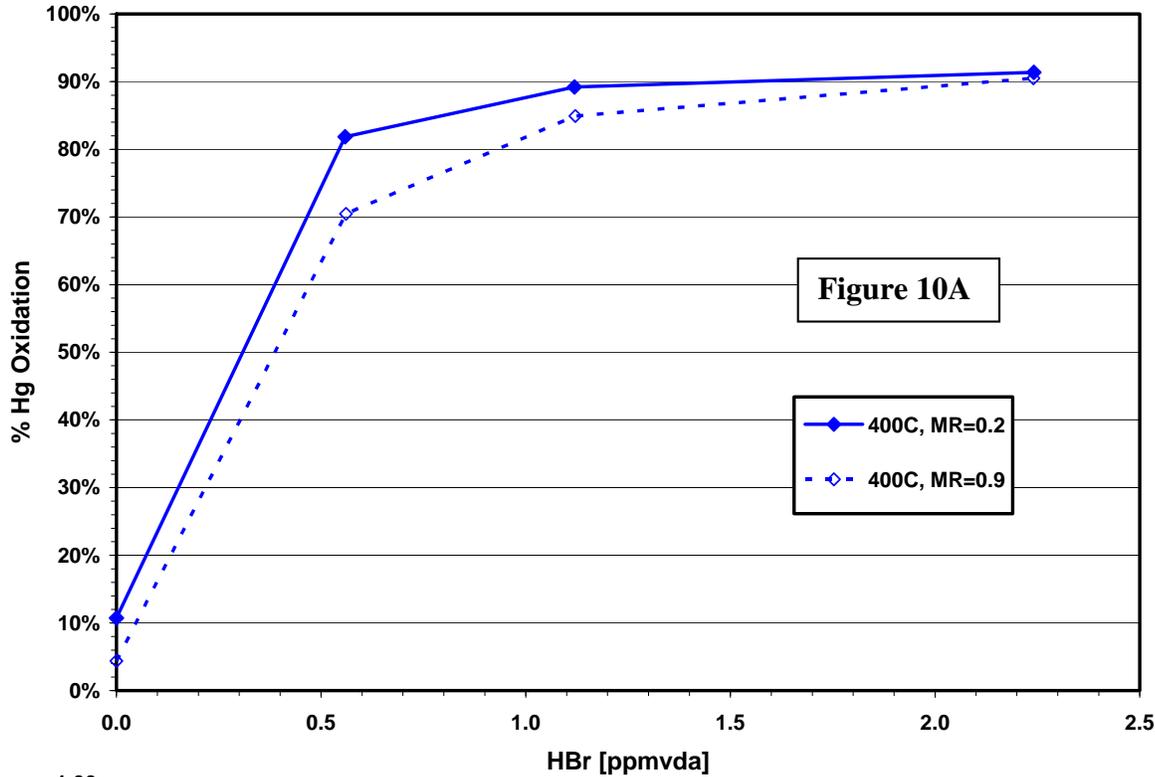
**Figure 7.** Impact of AV (Figure 7A) and total inlet Hg<sup>0</sup> (Figure 7B) on Hg<sup>0</sup> oxidation performance. Micro-reactor test conditions: Temperature = 400°C, MR = NH<sub>3</sub>/NO<sub>x</sub> = 0.2 – 0.9, H<sub>2</sub>O = 11%, O<sub>2</sub> = 3.5%, NO<sub>x</sub> = 350 ppmvda, SO<sub>2</sub> = 1000 ppmvda, SO<sub>3</sub> = 10 ppmvda, CO = 100 ppmvda, HCl = 11 – 56 ppmvda, inlet Hg<sup>0</sup> = 20 µg/Nm<sup>3</sup> (Figure 7A).



**Figure 8.** Impact of CO (Figure 8A) and SO<sub>2</sub> (Figure 8B) on Hg<sup>0</sup> oxidation performance. Micro-reactor test conditions: Temperature = 400°C, MR = NH<sub>3</sub>/NO<sub>x</sub> = 0.2, H<sub>2</sub>O = 11%, O<sub>2</sub> = 3.5%, NO<sub>x</sub> = 350 ppmvda, SO<sub>2</sub> = 1000 ppmvda, SO<sub>3</sub> = 10 ppmvda, HCl = 11 – 56 ppmvda (Figure 8A) and 11 ppmvda (Figure 8B), inlet Hg<sup>0</sup> = 20 µg/Nm<sup>3</sup>. For the SO<sub>2</sub> variation, the SO<sub>2</sub>/SO<sub>3</sub> ratio was kept constant at 100:1.



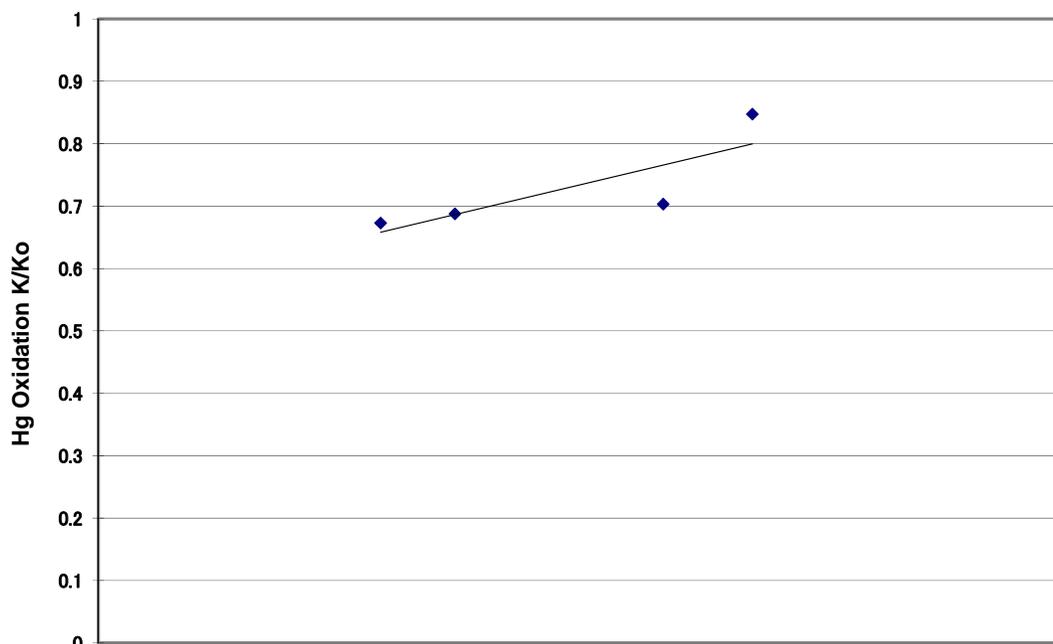
**Figure 9.** Impact of O<sub>2</sub> (Figure 9A) and H<sub>2</sub>O (Figure 9B) on Hg<sup>0</sup> oxidation performance. Micro-reactor test conditions: Temperature = 400°C, MR = NH<sub>3</sub>/NO<sub>x</sub> = 0.2, H<sub>2</sub>O = 11%, O<sub>2</sub> = 3.5%, NO<sub>x</sub> = 350 ppmvda, SO<sub>2</sub> = 1000 ppmvda, SO<sub>3</sub> = 10 ppmvda, HCl = 11 ppmvda, inlet Hg<sup>0</sup> = 20 µg/Nm<sup>3</sup>.



**Figure 10.** Impact of HBr addition on  $Hg^0$  oxidation performance (Figure 10A). Impact of HBr on  $NH_3$  suppression (Figure 10B). Micro-reactor test conditions: Temperature = 400°C, MR =  $NH_3/NO_x = 0.2$ ,  $H_2O = 11\%$ ,  $O_2 = 3.5\%$ ,  $NO_x = 350$  ppmvda,  $SO_2 = 1000$  ppmvda,  $SO_3 = 10$  ppmvda,  $HCl = 5$  ppmvda, inlet  $Hg^0 = 20 \mu g/Nm^3$ .

## Deactivation

The tendency of  $\text{Hg}^0$  oxidation deactivation correlates with DeNO<sub>x</sub> deactivation. However, using the simplified  $K_{\text{HgOx}}$ , the correlation changes with layer position due to the  $\text{NH}_3$  impacts described above. Figure 11 shows an example correlation between DeNO<sub>x</sub> K/Ko and  $\text{Hg}^0$  oxidation K/Ko at one set of conditions obtained for three coal-fired units with up to 20,000 hours exposure on the catalyst samples. The performance data were measured using the MHI bench reactor and represent the average of all catalyst layers. (Note that the deactivation behavior of the individual layers using simplified  $K_{\text{HgOx}}$  is different than that for the cumulative system. This is not surprising, given the deviation of the reaction from a simple first order reaction as was described above. and in particular the fact that  $\text{NH}_3$  has an inhibitive effect on the  $\text{Hg}^0$  oxidation rate, and the  $\text{NH}_3$  profile changes with time as the catalyst layers deactivate.)



**Figure 11.** Relationship between K/Ko for the  $\text{Hg}^0$  oxidation and the DeNO<sub>x</sub> reactions. Bench reactor test conditions: Temperature = 350°C, MR =  $\text{NH}_3/\text{NO}_x = 0.9$ , HCl = 50 ppmvda

## Case Study: Impact of Catalyst Type on $\text{Hg}^0$ Oxidation Performance for PRB-Firing Application

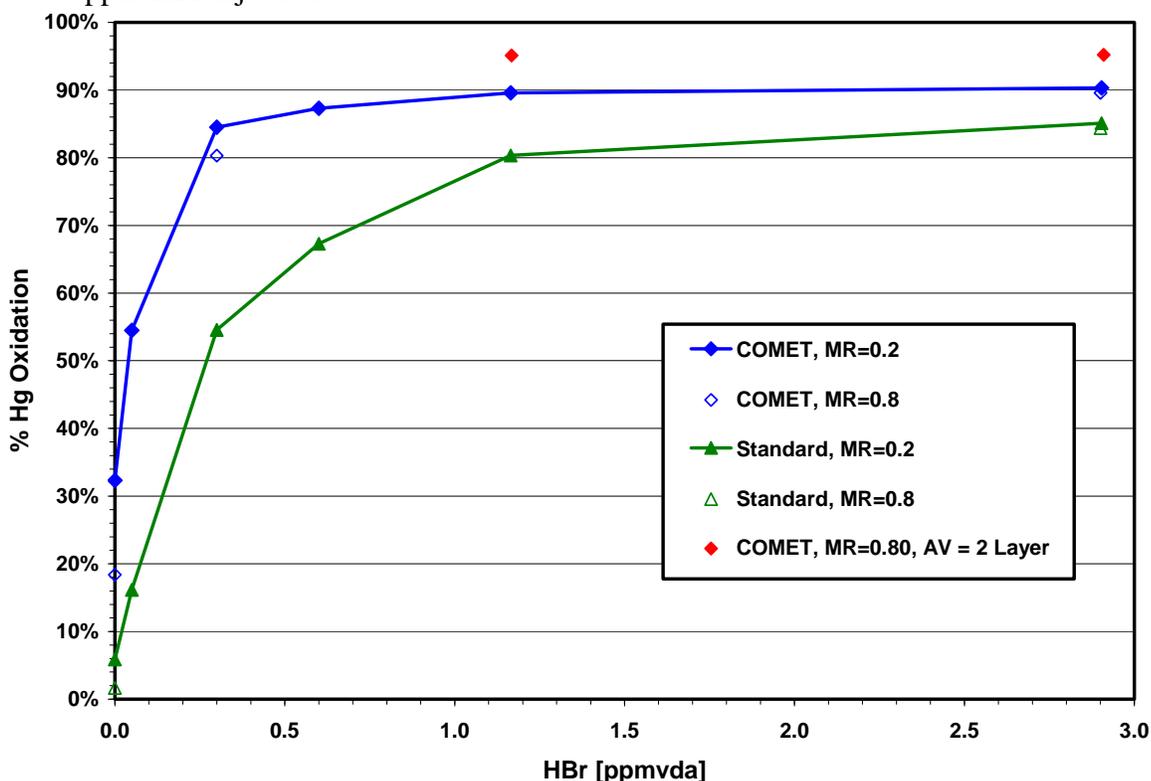
The chlorine content of PRB coals is typically quite low, generating <10 ppm of HCl in the flue gas, while the moisture content of coal is fairly high, leading to flue gas  $\text{H}_2\text{O}$  content in the 11 – 14% range. In addition, the SCR temperature for PRB-firing units tends to be on the higher end (370 – 410°C). The combination of these factors can lead to low  $\text{Hg}^0$  oxidation performance over

the SCR catalyst. Fortunately, selection of a catalyst type optimized for Hg oxidation can yield a significant performance improvement under these conditions.

Figure 12 presents a comparison of COMET™ vs. Standard SCR catalyst for a particularly challenging PRB case (the reaction conditions are listed in the Figure caption; note that both the DeNOx potential and the SO<sub>2</sub> oxidation are the same for both catalysts under these conditions). Except where noted, the performance shown is that for a single layer.

The following observations can be made in Figure 12:

- Single layer performance without HBr injection is much higher for COMET than for Standard catalyst (COMET™ Hg<sup>0</sup> oxidation is ~32% at MR = 0.2 and ~18% at MR = 0.8 vs. Standard at <8%).
- HBr injection has a strong positive impact for both catalysts; however, the effect of HBr saturates at a much lower HBr injection amount for COMET™ than for Standard catalyst, requiring less Br injection to achieve optimal performance. Note that at 0.3 ppm HBr injection, COMET™ is already at ~85% Hg<sup>0</sup> oxidation, while Standard catalyst is at ~54%.
- At MR = 0.80, and a 2-layer AV, COMET™ is able to achieve 95% Hg<sup>0</sup> oxidation, even at ~1 ppm HBr injection.



**Figure 12.** Hg<sup>0</sup> oxidation performance of COMET™ catalyst vs. Standard catalyst. Temperature = 404°C, MR = NH<sub>3</sub>/NO<sub>x</sub> = 0.2 – 0.8, H<sub>2</sub>O = 14%, O<sub>2</sub> = 3.5%, NO<sub>x</sub> = 110 ppmvda, SO<sub>2</sub> = 350 ppmvda, SO<sub>3</sub> = 3 ppmvda, HCl = 8 ppmvda, inlet Hg<sup>0</sup> = 10 µg/Nm<sup>3</sup>.

## DISCUSSION

The results of our tests for fresh and field-deactivated catalyst samples indicate that SCR reactor catalyst management for maintaining  $\text{Hg}^0$  oxidation and that for maintaining DeNO<sub>x</sub> at desired levels can use analogous approaches, with a few significant differences, in particular, the impact that  $\text{NH}_3$  has on suppressing the rate of  $\text{Hg}^0$  oxidation.

With the testing and modeling of the impact of static parameters, such as temperature, exhaust flow, and the concentrations of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_x$ , and in addition for  $\text{Hg}^0$  oxidation,  $\text{Hg}_{\text{total}}$ , HCl, HBr, and CO, one can set a design condition or a set of design conditions for the evaluation of catalyst performance. At a given boiler operating condition, these factors are static in that their values do not change significantly from the inlet to the outlet of the SCR reactor.

For DeNO<sub>x</sub>, the design condition (i.e., the catalyst volume-controlling case) is typically the full load operating condition, since this is the highest flue gas flow condition. Although temperature decreases as load decreases, and DeNO<sub>x</sub> catalytic activity is negatively impacted by a decrease in temperature, the corresponding decrease in flow that must be treated typically more than compensates for the decrease in activity. For the  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_x$  concentrations, the DeNO<sub>x</sub> reaction is not that sensitive to the typical range observed for these parameters; thus, the design condition can be set at their average or typical values at full load.

For  $\text{Hg}^0$  oxidation, the design condition is also expected to be the full load operating condition, since at lower loads, the decrease in both flow and temperature (Figures 7A and 5) has a positive impact on  $\text{Hg}^0$  oxidation rate. The range of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_x$ , and CO at full load must also be considered in order to select an appropriate design condition, especially given the significant impact of  $\text{O}_2$  and  $\text{H}_2\text{O}$ , and CO content on  $\text{Hg}^0$  oxidation. In addition, chlorine concentrations vary widely depending on the coal composition (Figure 13). Since the HCl concentration has a very significant impact on  $\text{Hg}^0$  oxidation, selection of the design conditions or multiple design conditions must be set considering the range of HCl. Also, of course, the range of Hg concentrations in the coal must be considered in order to determine the amount of oxidation and removal required (Figure 13). Once these parameters are established for a given SCR unit, one can then set the inlet design conditions for dynamic parameters such as  $\text{NO}_x$ ,  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and  $\text{NH}_3$  (based on DeNO<sub>x</sub> requirements). These parameters are dynamic in that, at any given boiler operating condition, their values change significantly from the inlet to the outlet of the reactor and change over time due to deactivation of the catalyst.

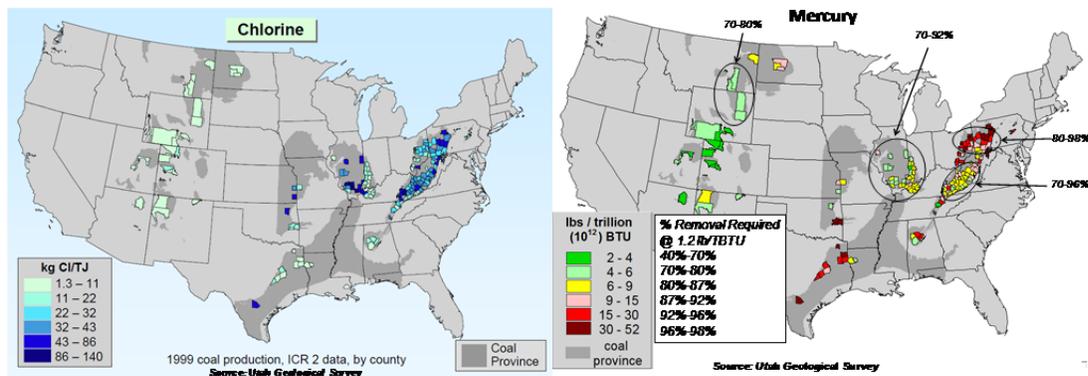


Figure 13. Variation in chlorine and mercury contents in US coals<sup>5</sup>.

Once the static and inlet design conditions are set, one can first use the same kinetic model routinely used for DeNO<sub>x</sub> performance to predict the change in NO<sub>x</sub> and NH<sub>3</sub> over the length of the catalyst, given the catalyst type and formulation. Although not shown in the results above, years of SCR experience have shown that the DeNO<sub>x</sub> reaction is not influenced by the Hg<sup>0</sup> oxidation reaction. Therefore, the modeling of the change in NO<sub>x</sub> and NH<sub>3</sub> across the catalyst can be decoupled from the Hg<sup>0</sup> oxidation reaction. And by utilizing established deactivation models for the DeNO<sub>x</sub> reaction, the changes in the NO<sub>x</sub> and NH<sub>3</sub> profile from inlet to outlet of the reactor over time can be predicted.

With the NH<sub>3</sub> profile from catalyst inlet to outlet over time prediction, we can then use a Hg<sup>0</sup> oxidation prediction model derived from parametric tests (like those shown in the Results section) to predict the Hg<sup>0</sup> oxidation across each catalyst layer and thus predict the outlet Hg<sup>0</sup> and Hg<sup>2+</sup> concentrations over time. This procedure forms the basis for a catalyst management strategy for Hg<sup>0</sup> oxidation.

For an existing SCR unit, as is done today for the DeNO<sub>x</sub> reaction through periodic sample testing, the performance of the existing catalyst can be baseline tested, either one layer at a time with a micro reactor for instance like that shown in Figure 1, given the design conditions and expected inlet conditions to each layer; or through a multi-layer reactor test like that shown in Figure 4. This information can then be used to predict the need for a layer action (addition or replacement) and select the appropriate type of catalyst given SO<sub>2</sub> oxidation constraints, DeNO<sub>x</sub> and slip limits, and the desired Hg<sup>0</sup> and Hg<sup>2+</sup> concentrations at the outlet of the reactor over time after the action. It is also highly recommended to baseline the field performance of the existing unit, at least through stack Hg CEMS measurements, so that the expected impact of the layer action on emissions can be predicted. Of course, stack Hg CEMS measurements taken after the layer action to check the prediction is recommended.

Although analogous in the general approach of selecting design condition(s) and baseline testing to assess need for catalyst actions, catalyst management for Hg<sup>0</sup> oxidation includes additional complexities, especially the impact of additional factors and the change in potential between layers due to a changing NH<sub>3</sub> profile over the layers and over time. These complexities may be overcome through development of Hg<sup>0</sup> oxidation performance models derived from extensive

parametric studies using automated reactors as exemplified in the Results. Also, a new dimension is added to catalyst selection, in that given the same SO<sub>2</sub> oxidation constraint, different catalyst types designed for Hg<sup>0</sup> oxidation, like COMET™, may be selected to greatly increase Hg<sup>0</sup> oxidation.

## SUMMARY AND RECOMMENDATIONS

The Hg<sup>0</sup> oxidation reaction is a more complex reaction than the DeNO<sub>x</sub> reaction. For the purposes of catalyst management, it does not afford itself to a simple model like that for DeNO<sub>x</sub>, based on performance tested under the same conditions for each layer; i.e., a MR=1 K test, where the sum of the resulting catalyst potentials for each layer may be used to predict concentrations of NO<sub>x</sub> and NH<sub>3</sub> at the outlet of the SCR reactor.

Also, whereas the DeNO<sub>x</sub> reaction can be characterized by a simple K rate constant, and where K is mainly dependent on catalyst composition (given SO<sub>2</sub> oxidation constraints), temperature, and AV, with minor influences of O<sub>2</sub>, H<sub>2</sub>O, SO<sub>x</sub>, and NH<sub>3</sub>; the Hg<sup>0</sup> oxidation reaction cannot be characterized by a simple K rate constant and is greatly influenced by O<sub>2</sub>, H<sub>2</sub>O, and NH<sub>3</sub> and, in addition, by HCl, HBr, and CO. Moreover, given the same SO<sub>2</sub> oxidation constraint, catalyst type (i.e. COMET™ vs. Standard) can have a very significant impact on Hg<sup>0</sup> oxidation performance.

Therefore, new models are required to account for the complexities of the Hg<sup>0</sup> oxidation reaction that move beyond the use of simple K rate constant for performance prediction. Development of such a model requires a large data density due to the greater number of factors involved compared to the DeNO<sub>x</sub> reaction. An automated reactor like that described in the Experimental section is ideal for accommodating such requirements. This new model for Hg<sup>0</sup> oxidation can then be combined with existing DeNO<sub>x</sub> performance models to develop predictions and catalyst management strategies for Hg<sup>0</sup> oxidation.

Given the need to comply with the Mercury Air Toxics Rule by 2015/2016, and given the learning curve expected with a new catalyst management strategy for Hg<sup>0</sup> oxidation, we recommend that SCR owners start evaluating and testing their strategies today.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the contributions of the following people to the overall success of the project: Travis Jones, Austin Munnell, Gavin MacInnes, Mike Close, Raymond Oh, James Altizer, Jeff Walker, Christian Trefzger, and Kozo Iida.

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