SCR Catalyst Selection and Management for Improved Hg Oxidation Performance

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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 MATS, either solely, or in combination with other technologies. Catalyst selection and management for Hg emission control is analogous to that for DeNOx except for some key differences due to the nature and complexity of the Hg0 oxidation reaction kinetics. Cormetech's unique capability of testing catalysts has been used to measure the influence of temperature, flue gas composition, catalyst type and catalyst age on Hg oxidation activity, facilitating the development of predictive models and advanced catalysts with significantly improved Hg oxidation performance that maintain high DeNOx activity and equivalent SO2 oxidation performance. These tools form the basis of Cormetech's COMET™ technology that can be applied to characterize and optimize the role of the SCR system in Hg compliance strategies. Case studies are presented which demonstrate the application of this technology toward developing catalyst management strategies.

INTRODUCTION

The United States Environmental Protection Agency (USEPA) under the authority of the Clean Air Act (CAA) established National Emission Standards for Hazardous Air Pollutants (NESHAP) for coal and oil fired Electric Utility Steam Generating Units (EGUs) effective April 2012 with compliance required by 2015 or 2016 with a qualified extension. The rule, referred to as the Mercury and Air Toxics Standards (MATS)[1], was upheld in April 2014 by the U.S. Court of Appeals for the District of Columbia Circuit. Although the rule encompasses smaller non-utility units and other non-mercury pollutants as well, the focus of this discussion will be on the coal-fired EGU segment and specifically mercury as the pollutant. While the rule is the first of its kind related to controlling mercury emissions and is currently applicable only in the United States (US), the infrastructure for the technology discussed is widely utilized in the worldwide EGU market and thus applicability can be widely considered.

At the core of this discussion is the utilization of existing equipment infrastructure, namely selective catalytic reduction (SCR) and flue gas desulfurization (FGD) systems alone, or in combination with advanced catalyst technology and/or other technologies such as fuel additives, activated carbon injection, boiler optimization, etc., to assure compliance with the established emission limits at the lowest cost. This "co-benefit" use of the existing equipment based on oxidation of mercury in the SCR and downstream equipment and subsequent collection in the FGD, provides the foundation for an optimized approach for obtaining and maintaining compliance. Specific advancements in FGD technology including additives are available to prevent re-emission of the captured oxidized mercury. In addition, other technologies that can be used to supplement mercury capture such as activated carbon injection (ACI) are available. However, the emphasis herein is on Cormetech's Oxidized Mercury Emissions Technology (COMET™) which consists of both an engineering technology and catalyst product. The tool is used to establish goals, characterize catalyst features, model reactor performance, and ultimately design and provide a catalyst management plan and product, as needed, to obtain the necessary levels of mercury oxidation through the SCR.

The Selective Catalytic Reduction (SCR) of NOx using NH_3 as the reductant over V_2O_5-(WO_3 or MO_3)/TiO_2 catalysts is the current state-of-the-art technology for the control of NO_x emissions from coal-fired utility boilers. SCR has been demonstrated to achieve high NO_x removal efficiencies of 90% or more. The primary NO_x reduction reaction proceeds with the following stoichiometry (note that the flue gases from coal-fired boilers typically contain >90% NO):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad [1]$$

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \qquad [2]$$
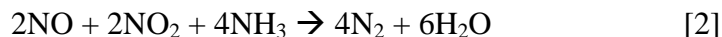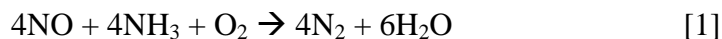
SCR catalysts are also active for the oxidation of elemental mercury (Hg^0) present in the flue gas by chlorine as HCl (and/or by bromine as HBr; the reaction is analogous to equation [3]):

$$2Hg^0 + 4HCl + O_2 \rightarrow 2HgCl_2 + 2H_2O \qquad [3]$$

The conversion of Hg^0 (water-insoluble) to $HgCl_2$ or $HgBr_2$ (water-soluble Hg^{2+}) allows for capture of mercury in a downstream flue gas desulfurization system and is expected to be an effective and economical method[2] to achieve compliance with the Mercury & Air Toxics Standard (MATS) (formerly referred to as Utility MACT).

A study[3] 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^0 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_2 to SO_3:

$$SO_2 + 1/2O_2 \rightarrow SO_3 \qquad\qquad\qquad [4]$$

Thus, an optimal SCR catalyst design for a given unit will maximize the rates of reactions [1 – 3], while minimizing the rate of reaction [4].

Routinely, SCR catalyst is formulated given a maximum allowed SO_2 oxidation rate to minimize the negative effects of high SO_3 such as air pre-heater plugging or opacity concerns, while meeting the DeNOx and NH_3 slip requirements; i.e. the amount that the catalyst can be formulated for DeNOx activity is typically limited by this maximum SO_2 oxidation. For example, the vanadium content, which benefits the DeNOx reaction, is limited in the catalyst since it also increases the SO2 oxidation rate. New catalysts and technologies, such as Cormetech's COMET™, greatly improve this trade-off between DeNOx and SO_2 oxidation and moreover, can greatly increase the Hg^0 oxidation activity.

For DeNOx, the SCR design requirements (or performance threshold) are clearly understood since only the SCR impacts the DeNOx capability of the Air Quality Control System (AQCS). For Hg^0 oxidation, the SCR design requirements are less clear since the total Hg removal performance of the AQCS is dependent on the impacts of downstream equipment as well as the SCR. Therefore, the contribution of downstream equipment to Hg^0 oxidation, capture & re-emission must be understood in order to define the Hg^0 oxidation requirements for the SCR.

Through presentation of an example dataset, we show that the Hg^0 oxidation reaction is more complex than the DeNOx reaction. The data set illustrates some of the key tendencies resulting from changes in system parameters, such as flue gas conditions, catalyst selection and age, in order to discuss catalyst management for Hg^0 oxidation compared to DeNOx. Although analogous in the general approach of selecting design condition(s) and baseline testing to assess need for catalyst actions, catalyst management for Hg^0 oxidation includes additional complexities, especially the impact of additional factors and the change in potential between layers due to a changing NH_3 profile over the layers and over time. Through extensive parametric studies, Hg^0 oxidation performance models have been derived to predict Hg^0 oxidation performance. This is an important tool for evaluation of different options to achieve defined Hg^0 oxidation performance goals of the SCR. Also, a new dimension is added to catalyst selection, in that different catalyst types designed for Hg^0 oxidation, like COMET™, may be selected to greatly increase Hg^0 oxidation while still maintaining appropriate DeNOx and SO_2 oxidation features. Several case studies are presented which show how the integrated combination of advanced Hg oxidation catalyst products, predictive Hg oxidation models and laboratory testing can be used to develop catalyst management and operational strategies to achieve MATS compliance.

EXPERIMENTAL

Three reactor systems are used by Cormetech for measuring the Hg^0 oxidation performance of catalyst samples (all three systems are also capable of DeNOx and SO_2 oxidation measurements): a micro-scale reactor located at Cormetech, a semi-bench scale reactor located at

Mitsubishi Heavy Industries' Hiroshima R&D Center (MHI), and a full-bench scale reactor located at Cormetech.

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 DeNOx, SO_2 oxidation, and Hg^0 oxidation. A schematic of the Cormetech system is shown below in Figure 1.

Figure 1. System Diagram of the Cormetech Micro-Reactor
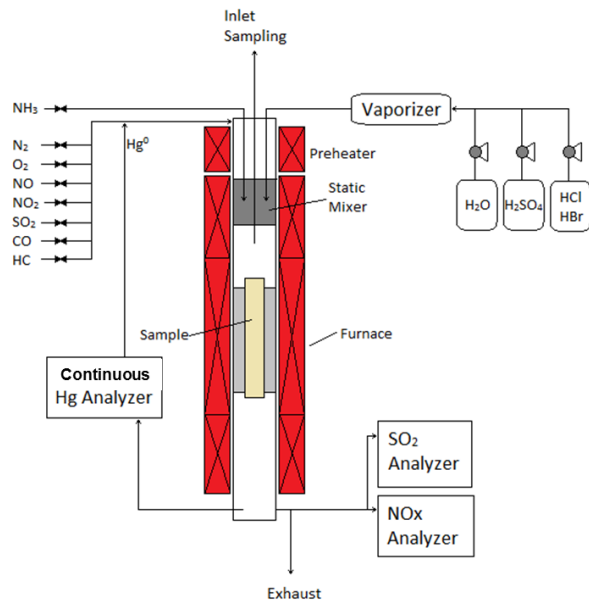
N_2, O_2, NO, NO_2, SO_2, NH_3, CO, hydrocarbons, and Hg^0 are injected as gases, and H_2O, H_2SO_4, HCl, HBr, and Hg^{2+} are injected as vaporized liquids. Hg^0 and Hg^{2+} concentrations are measured by a continuous Hg analyzer, which also serves as the Hg^0 source. NO_x concentration is measured using a chemiluminescence analyzer, O_2 is analyzed by a paramagnetic analyzer, and SO_2 is measured by a UV-vis analyzer.

The integrity of the Cormetech micro-reactor is checked periodically to ensure that the empty reactor system does not contribute appreciably to the measured Hg^0 oxidation performance. Inert materials are used in the reactor construction.

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 Hg^0 oxidation. Among the factors that affect Hg^0 oxidation are temperature, AV, and Hg^0, NH_3, SO_2, CO, HCl, and HBr concentrations.

The semi-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 (~1/4 cross-

section). DeNOx, SO_2 oxidation, and Hg^0 oxidation are measured at each port. A schematic of the system is shown below in Figure 2. NO_x, SO_2, HCl, and NH_3 are injected as gases, while Hg^0 is injected from a vapor generator. Hg^0 and Hg^{2+} concentrations are measured by the Ontario Hydro Method. SO_2, SO_3, HCl, and NH_3 are measured by wet chemical analysis. NO_x concentration is measured using a chemiluminescence analyzer, while O_2 is analyzed by a paramagnetic analyzer.

**Figure 2. System Diagram of the MHI Semi-Bench Reactor**
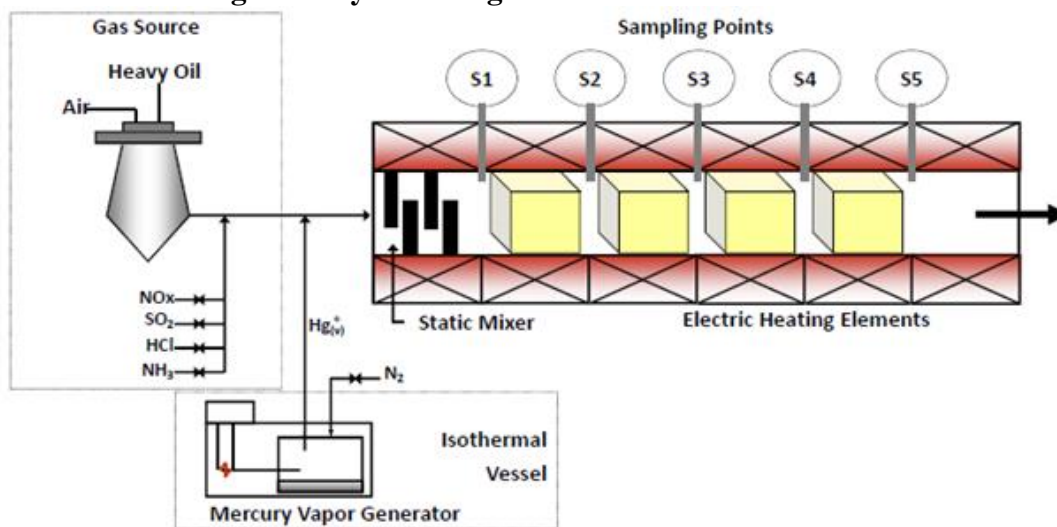
In addition to the two reactors described, a third reactor (Figure 3) capable of Hg oxidation testing has been brought on-line and validated early this year in Cormetech's Durham, NC laboratory. A schematic of the Cormetech full-bench scale system is shown in Figure 3. The reactor is capable of testing up to 4 full-length layers of catalyst with full cross-section. DeNOx, SO2 oxidation and Hg^0 oxidation can be measured across each layer. This reactor is being used for single layer and multi-layer system testing of full size fresh catalyst and field samples for field audit testing, product quality assurance testing, and catalyst development.

For the full-bench reactor, NO_x is generated by combustion of NH_3 within the natural gas burner system. NH_3, SO_2, CO, SO_3, HCl, HBr and Hg^0 are injected into the flue gas stream and mixed well before entering the reactor. Water is set to the desired level by precisely controlled condensation of water from the flue gas followed by re-heating. Hg^0 and Hg^{2+} concentrations are measured before and after each catalyst layer, for example with speciated sorbent traps. HCl, HBr, and NH_3 are measured by wet chemical analysis. 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. Water is measured by FTIR which also gives secondary measurement of HCl, NO_x, NH_3, SO_2 and CO.

Each of the three different reactors described above, operating from micro to semi-bench to full-bench scale, have demonstrated the ability to generate high quality Hg oxidation measurements that have been applied to catalyst development, design and management. However, each scale of testing apparatus has its own advantages and limitations that must be clearly understood in order

to correctly apply the testing data to catalyst designs and development of catalyst management plans.

Figure 3. System Diagram of the Cormetech Full-Bench Reactor
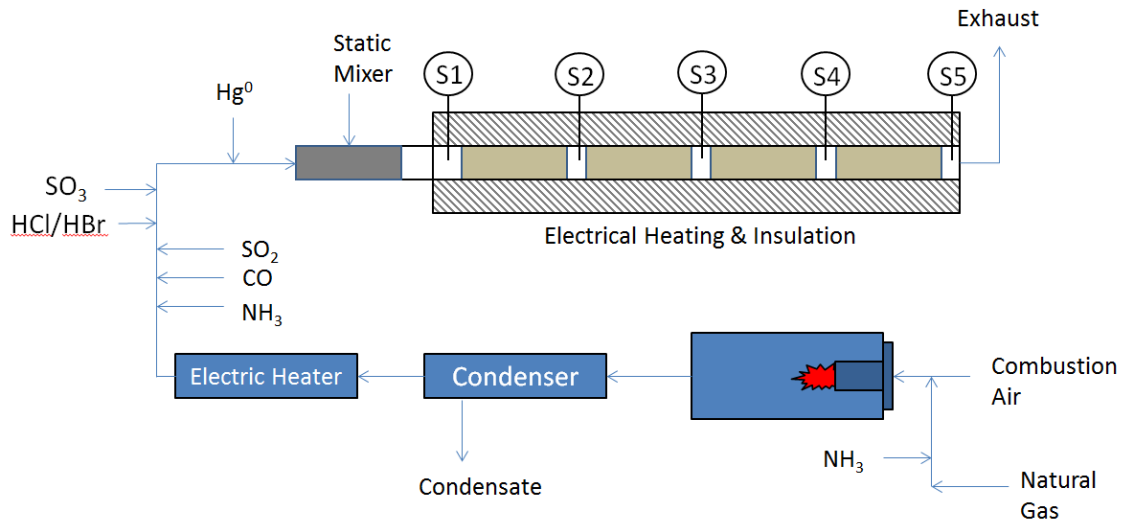
The micro scale reactor is well suited for catalyst development and studies of reaction mechanisms due to the small sample required (typically ~15mm x 15mm x 100mm). However, when using such a small sample size care must be taken when utilizing micro scale data for product quality assurance or field audit sample testing due to potential variability in chemical or physical properties within full size catalyst elements. Depending on the nature of the test, several micro scale tests may be required to fully characterize the performance of the layer. This is especially true for field audit samples where catalyst poisons are not uniformly distributed throughout the length of the full size element.

On the micro scale it is easier to generate the relatively small amount synthetic flue gas required. The required capacity of the Hg source is also small and well within the range of commercially available instrument calibration sources. The micro scale also allows for reactor fabrication using highly inert materials such as quarts to minimize any potential bias from oxidation by the surfaces of the reactor. However, extreme care must be taken to ensure that reactive surfaces are minimized on the micro scale since the ratio of exposed reactor surface to flue gas flow is much higher than on larger scale reactors. Also, periodic empty reactor testing must be done to ensure that surfaces remain inert over time with repeated used.

One of the key advantages of the full bench scale reactor is the ability to test multiple layers of full size elements. When evaluation of total system performance is desired the full bench reactor is ideal since the performance of the system and each individual layer can be measured in a single test or small number of tests. In contrast, to simulate system performance the micro reactor would have to run multiple step-wise tests for each individual layer using the results from the upper layers to set the test conditions for lower layers. This is required to take into account the impact of NH_3 levels changing from layer to layer on the Hg oxidation rate which will be discussed further below.

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Also, because the full-bench reactor tests the full cross-section and length of the catalyst it is ideal for field sample audit testing where there is variability in catalyst poisons throughout the full size element. Variation in chemical or physical properties within fresh catalyst elements can also be accounted for on the full-bench scale. Features like edge hardening are also accounted for on the full scale and must be considered when comparing with micro test data.

Because of the much larger scale, the full-bench requires a high capacity flue gas source as well as a Hg^0 source with high capacity that is well beyond commercially available sources. Steel construction of the full bench reactor is not as inert as the construction of the micro reactor, however, due to the much lower ratio of exposed reactor surface area to flue gas flow this impact is generally not any more significant than on the micro scale. The empty reactor oxidation rate is measured periodically to ensure that the level is low enough as not to introduce any significant bias in the oxidation measurements.

RESULTS AND DISCUSSION

The Hg^0 oxidation reaction (equation [3]) differs significantly from the DeNOx reaction (equations [1], [2]) with respect to the number of factors that influence its reaction kinetics and ultimately the measured catalyst performance. This section will first discuss the effect of reaction conditions (i.e., temperature and gas composition) on the Hg^0 oxidation reaction, to illustrate the key differences with the DeNOx reaction, and reveal the considerations that need to be accounted for when predicting the Hg^0 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^0 oxidation are correlated to those for DeNOx, for a given set of conditions. Finally, two case studies will be presented. The first case study shows the impact of catalyst type on the Hg^0 oxidation performance for an SCR unit on a challenging PRB-firing coal application. The second case study will show how COMET™ lab testing and modeling capabilities can be used to characterize system performance and evaluate options for catalyst management actions.

Impact of Reaction Conditions on Hg^0 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^0 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^0. Thus, the % Hg^0 oxidation across the SCR catalyst sample was calculated using the following equation:

$$\% \ Hg^0 \ \text{oxidation} = 100 \ x \ (Hg^0_{IN} - Hg^0_{Out})/ \ Hg^0_{IN} \qquad [5]$$

Although the reaction kinetics for Hg^0 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_{HgOx}, equation [6]) in order to gage the relative impact of changing these factors on the catalyst potential for Hg^0 oxidation (note: AV = area velocity = total gas flow / total geometric catalyst surface area = $Nm^3/m^2 \cdot h$).

$$K_{HgOx} = -AV * \ln (1 - \% \ Hg^0 \ oxidation/100\%) \qquad [6]$$

This equation is similar to the DeNOx K equation used by the industry for catalyst management, valid for a MR = 1 condition[4]:

$$K_{DeNOx} = -AV * \ln (1 - \% \ DeNOx/100\%) \qquad [7]$$

To assess the impact of NH_3 on Hg^0 oxidation, two MR (molar ratio = NH_3/NO_x) 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_3 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_3 injection rate due to NO_x reduction and NH_3 consumption in the upstream layers. It will be shown that the Hg^0 oxidation potential of the catalyst can be strongly influenced by the NH_3 concentration.

In Figure 4, the following observations are apparent regarding the impact of HCl, temperature and NH_3 on Hg^0 oxidation:
- HCl concentration has a significant positive effect on Hg^0 oxidation (in contrast to the DeNOx reaction, which is unaffected by HCl in the typical coal flue gas range[5]).
- Increasing temperature has a negative effect on Hg^0 oxidation (it has a positive effect on the DeNOx reaction). The negative impact of temperature on Hg^0 oxidation is more pronounced at low HCl concentration.
- NH_3 has a strong inhibitory effect on Hg^0 oxidation, the extent to which is influenced by the HCl concentration and temperature (see reference 6 for further analysis). The DeNOx reaction is of course dependent on NH_3 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.

As is generally known to the industry[4], the effect of NH_3 on the DeNOx 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^0 oxidation will not accurately work because of the strong inhibitory impact of NH_3, which makes the catalyst potential a strong function of layer position and requires a detailed understanding of the NH_3 profile along the length of the SCR catalyst layers. The negative impact of NH_3 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.[6]

Figure 4. Impact of HCl concentration on Hg oxidation performance.
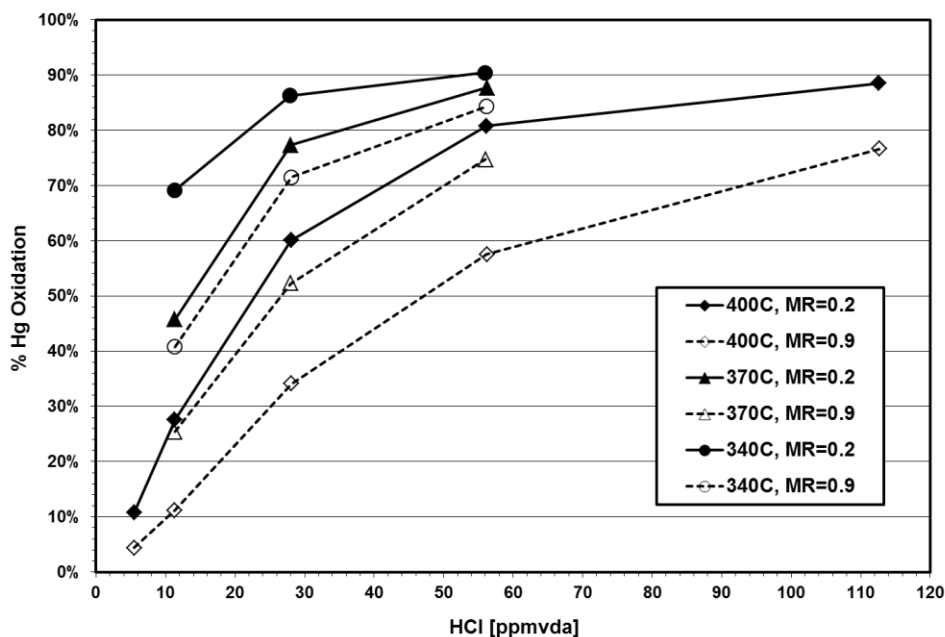
Micro-reactor test conditions: Temperature = 340 – 400°C, MR = NH_3/NO_x = 0.2 – 0.9, H_2O = 11%, O_2 = 3.5%, NO_x = 350 ppmvda, SO_2 = 1000 ppmvda, SO_3 = 10 ppmvda, CO = 100 ppmvda, HCl = 11 – 112 ppmvda, inlet Hg^0 = 20 μg/Nm^3.

The impact of additional flue gas constituents on Hg^0 oxidation have been reported previously[6] and reveal the additional factors that influence Hg^0 oxidation kinetics as compared to the DeNOx reaction.

The catalyst inlet Hg^0 concentration does not have a significant impact on Hg^0 oxidation. Thus, the % Hg^0 oxidation achieved across an SCR catalyst layer or system is largely independent of the inlet Hg^0 concentration.

The flue gas CO and SO_2 concentrations both have a negative impact on Hg^0 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_2; the negative impact again reduces at higher HCl concentration, as it does for NH_3. For comparative purposes, the DeNOx kinetics are unaffected by CO in this concentration range, while they are mildly influenced by the SO_2/SO_3 content of the flue gas, as sulfur gases serve to increase the acidity of the catalyst and promote the DeNOx reaction.

In addition, O_2 has a strong positive impact on the kinetics, while H_2O has a strong negative impact. The magnitude of these impacts is much greater than that observed for the DeNOx 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^0 oxidation. For a case where Hg^0 oxidation is quite low, a small addition of HBr at ~ 1 ppm level can result in a profound increase in the Hg^0 oxidation performance independent of other non-SCR catalyst interactions. Note that similar to HCl, the extent of NH_3 suppression of rate reduces significantly with the addition of HBr. As shown previously[6], at ~ 2 ppm HBr, Hg^0 oxidation was almost unaffected by the addition of NH_3 up to MR = 0.90.

Deactivation

The tendency of Hg^0 oxidation deactivation generally correlates with DeNOx deactivation. However, using the simplified K_{HgOx}, the correlation changes with layer position due to the NH_3 impacts described above. Figure 5 shows examples of the correlation between DeNOx K/Ko and Hg^0 oxidation K/Ko for four different catalysts. The data for Catalyst A represent a single operating condition, whereas the data for Catalyst B, C, D and E were measured at multiple operating conditions (i.e., varying temperature, ammonia, and halide concentration). Figure 5 shows that although there is a general correlation between DeNOx deactivation and Hg^0 oxidation deactivation, the two are not equivalent and can deviate significantly from each other depending on operating conditions, as is demonstrated by the variability of the data for Catalyst B, C, D and E relative to the parity line. Figures 6 and 7 show the source of this variability in more detail, looking at the impact of NH_3 and HCl on the correlation between DeNOx K/Ko and Hg^0 oxidation K/Ko. Figure 6 presents data for a high SO_2 conversion limit catalyst formulation from a PRB fired unit and Figure 7 presents data for a lower SO_2 conversion limit catalyst formulation from a bituminous fired unit. In general, Hg^0 oxidation deactivates due to the impacts of accumulated poisons as well as due to the impact of a shifting NH_3 profile through the layer as the DeNOx activity decreases.

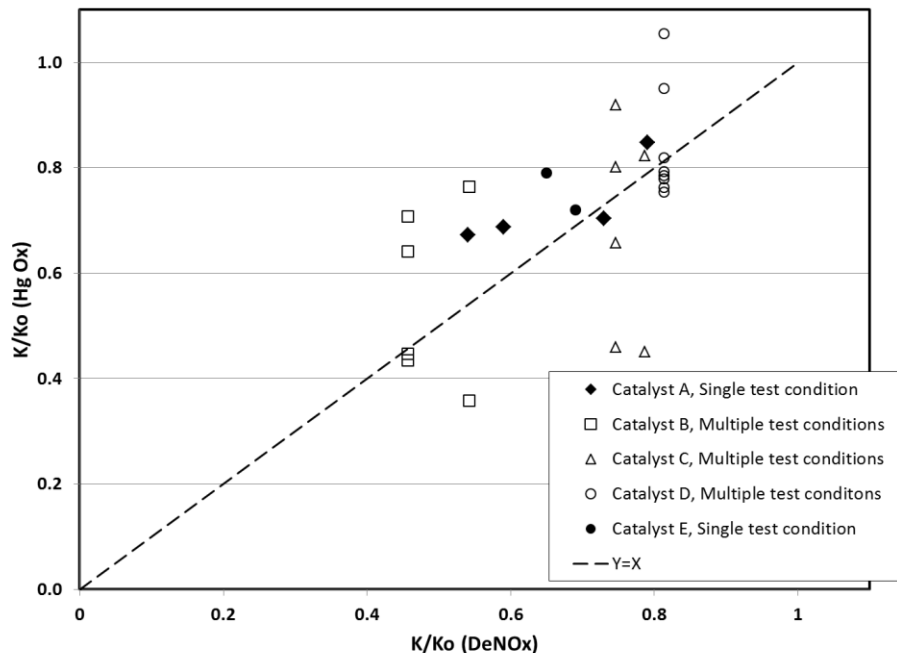**Figure 5. Relationship between K/Ko for the Hg^0 oxidation and the DeNOx reactions.**

Figure 6. K/Ko for DeNOx and Hg^0 oxidation versus catalyst age - high SO$_2$ conversion limit formulation from a PRB fired unit.
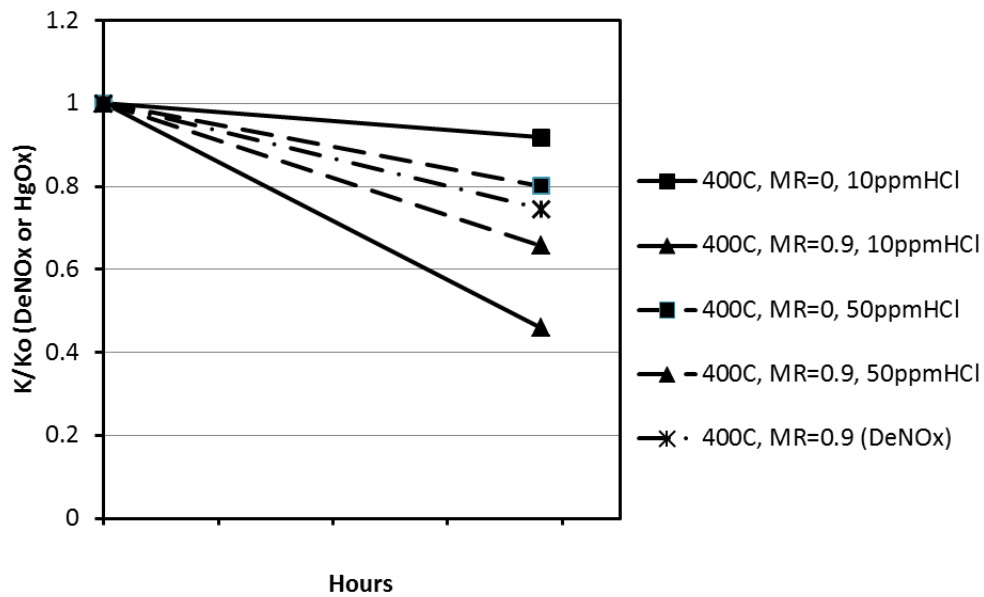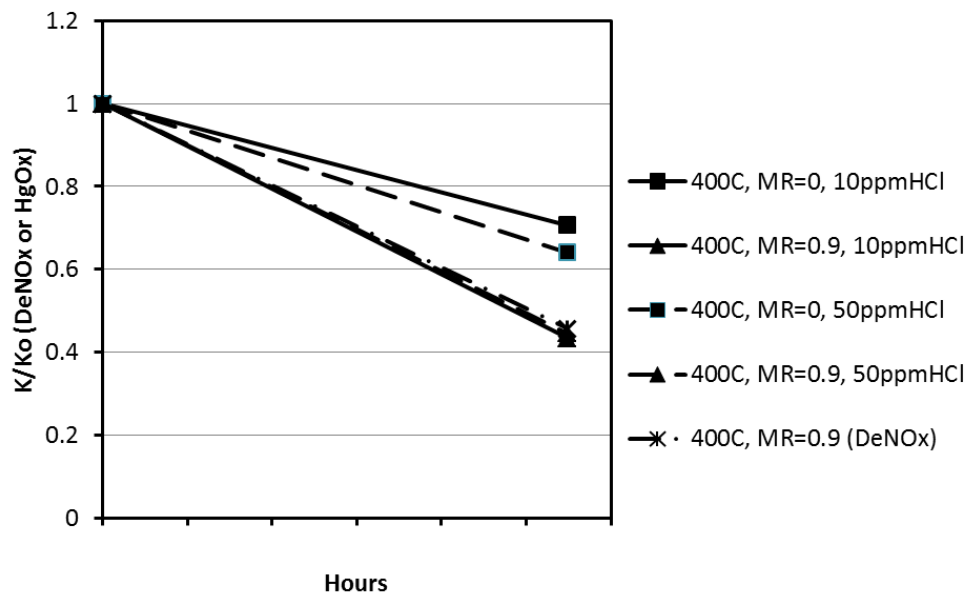

Figure 7. K/Ko for DeNOx and Hg^0 oxidation versus catalyst age - lower SO$_2$ conversion limit formulation from a bituminous fired unit.

For both DeNOx and Hg^0 oxidation, activity is lost as poisons are accumulated resulting in active site blocking, pore plugging, etc. These impacts are seen in Figures 6 and 7 where K/Ko for Hg^0 oxidation is measured with no NH_3 present (MR=0). For the two cases shown, at MR=0 the Hg^0 oxidation tends to deactivate less than DeNOx. This is due to differences in the reaction kinetics, and possible differences in the deactivation mechanisms and the nature of active sites for Hg^0 oxidation versus DeNOx. It is important to note that catalyst type and formulation will have an impact on how Hg^0 oxidation K/Ko correlates with DeNOx K/Ko at MR=0 and therefore results cannot be applied without a keen understanding of the interactions.

As mentioned above, since the K_{HgOx} assumes a simplified first order behavior, it is very dependent on the NH_3 level. As the DeNOx activity decreases within a layer, the NH_3 profile in the log shifts to higher NH_3 levels. Also, for a multi-layer system, all layers after the first will see an additional NH_3 increase due to deactivation from each of the preceding layers. This impact can be seen in Figures 6 and 7, comparing K/Ko at MR=0.9 versus MR=0.

While the use of DeNOx K/Ko as a surrogate for Hg^0 oxidation K/Ko could greatly simplify the testing required for catalyst management, the data presented shows that in some cases this could lead to an over-estimate of Hg^0 oxidation deactivation in some cases and lead to an under-estimate in other cases. The level of error introduced in this approximation will also be highly condition and catalyst dependent. In general terms, higher HCl will tend to minimize the negative impacts of NH_3, and therefore reduce the impact of changes in the NH_3 profile through the catalyst. Also, for the lower catalyst layers the NH_3 levels tend to be relatively low and therefore DeNOx deactivation may not significantly impact Hg^0 oxidation performance. Therefore applicability of this approach must be determined on a case by case basis.

Case Study: Impact of Catalyst Type on 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 H_2O 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 Hg^0 oxidation performance over the SCR catalyst. Fortunately, selection of a catalyst type optimized for Hg^0 oxidation can yield a significant performance improvement under these conditions.

Figure 8 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_2 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 8:
- Single layer performance without HBr injection is much higher for COMET™ than for Standard catalyst (COMET™ Hg^0 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^0 oxidation, while Standard catalyst is at ~54%.
- At MR = 0.80, and a 2-layer AV, COMET™ is able to achieve 95% Hg^0 oxidation, even at ~1 ppm HBr injection.

Figure 8. Hg^0 oxidation performance of COMET™ catalyst vs. Standard catalyst.
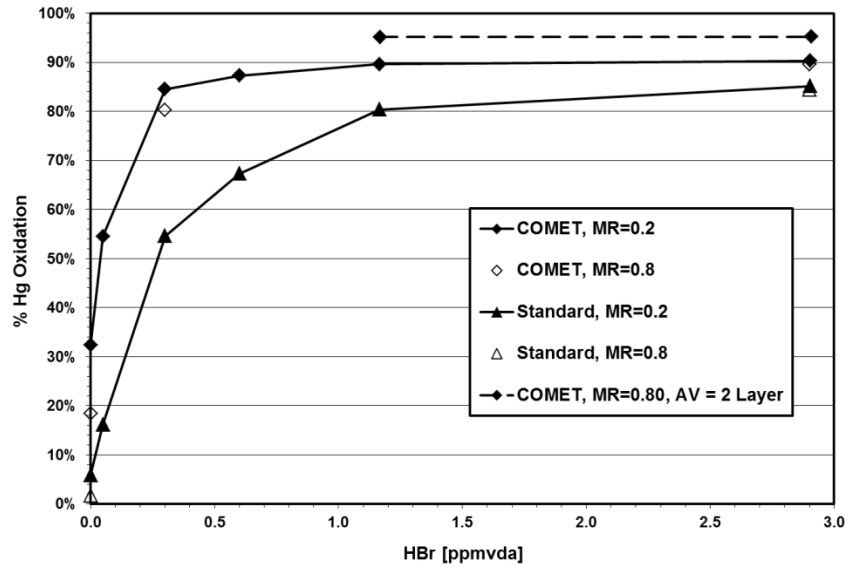
Temperature = 404^oC, MR = NH_3/NO_x = 0.2 – 0.8, H_2O = 14%, O_2 = 3.5%, NO_x = 110 ppmvda, SO_2 = 350 ppmvda, SO_3 = 3 ppmvda, HCl = 8 ppmvda, inlet Hg^0 = 10 $\mu g/Nm^3$.

## Case Study: Catalyst Management for DeNOx and Hg Oxidation

The results of our tests for fresh and field-deactivated catalyst samples indicate that SCR reactor catalyst management for maintaining Hg^0 oxidation and that for maintaining DeNOx at desired levels can use analogous approaches, with a few significant differences, in particular, the impact that NH_3 has on suppressing the rate of Hg^0 oxidation.

In the following case study we will look at how catalyst management decisions can be impacted by new considerations of Hg oxidation requirements. In the following figures we present a hypothetical case of a (2+1) SCR which requires 85% DeNOx efficiency with a maximum slip of 2ppm. At 70,000 hrs of operation the unit requires a catalyst action based on DeNOx performance. We will look at several scenarios that show how Hg oxidation requirements can impact catalyst management decisions and some potential catalyst actions to meet DeNOx and Hg oxidation requirements.

Figure 9 shows the baseline catalyst management plan for this unit based only on DeNOx performance requirements. The unit starts operation with two fresh layers of catalyst, then at 28,000 hrs a third layer is added. At 70,000 hrs a catalyst action is needed due to slip increasing

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to the limit of 2ppm.   Another layer replacement would be done at about 96,000 hrs based on the expected deactivation rate.

Figure 9. Baseline catalyst management plan – based on DeNOx performance only.
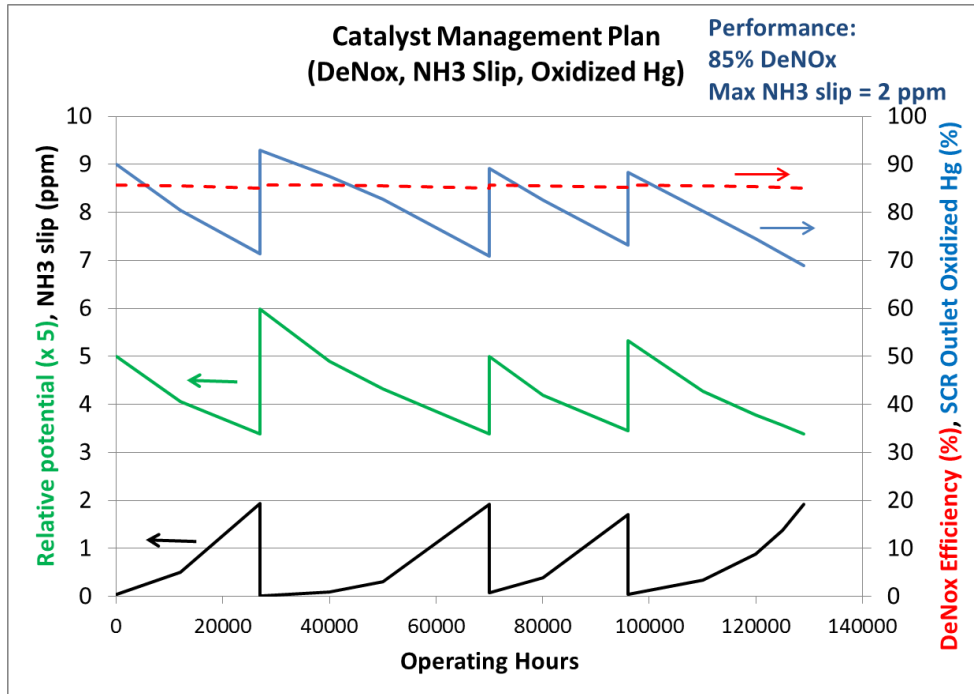
When Hg oxidation requirements are added to the SCR DeNOx requirements, one or the other becomes the controlling requirement and will depend on the relative catalyst potential and performance requirements for each of the reactions. We can see in the baseline case, if the required SCR outlet oxidized Hg is only 70% at end of life, then the DeNOx reaction is still the controlling reaction and Hg oxidation requirements can be met with the historical catalyst management plan.

In Figure 10 a scenario is shown where the required end of life oxidized Hg at the SCR outlet is increased to 80%. In this scenario, the baseline catalyst management plan is not adequate. One option may be to inject halogens in order to boost the Hg oxidation performance of the SCR.

If the required end of life oxidized Hg is increased further to 90%, then the halogen injection level shown in Figure 10 is not adequate and another option would be to initially change 2 layers to maximum lengths of COMET™ advanced Hg oxidation catalyst and then repeat for the replacement of the third layer (Figure 11). You can see that in this case of high Hg oxidation requirement, DeNOx is no longer a controlling factor and Hg oxidation performance drives the catalyst management planning.

Figure 10. Use of Halogen Injection to Meet 80% Oxidized Hg Requirement.
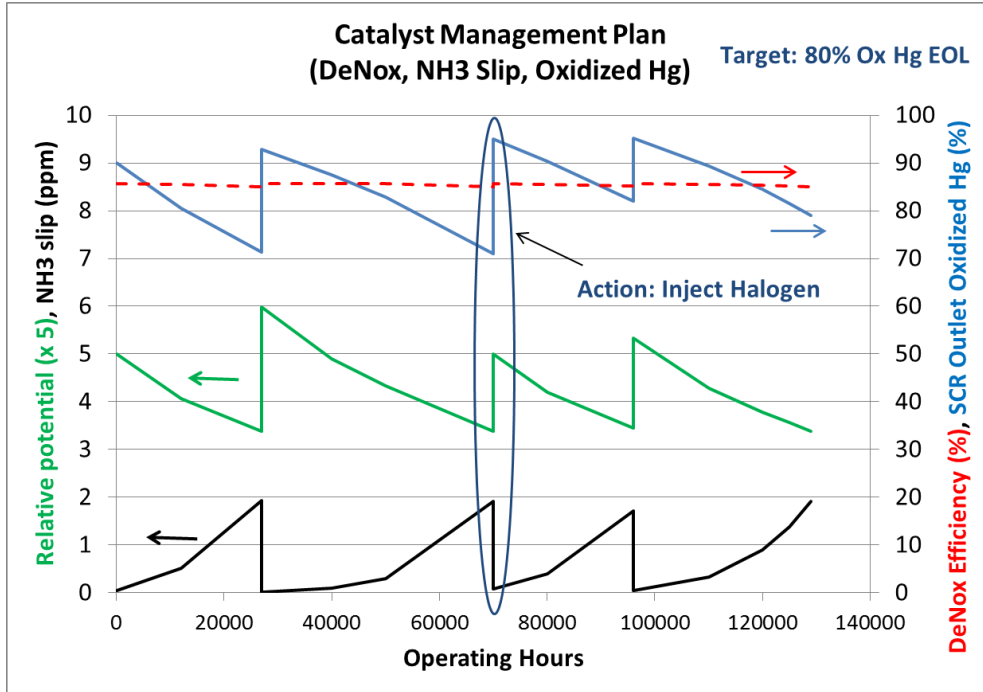

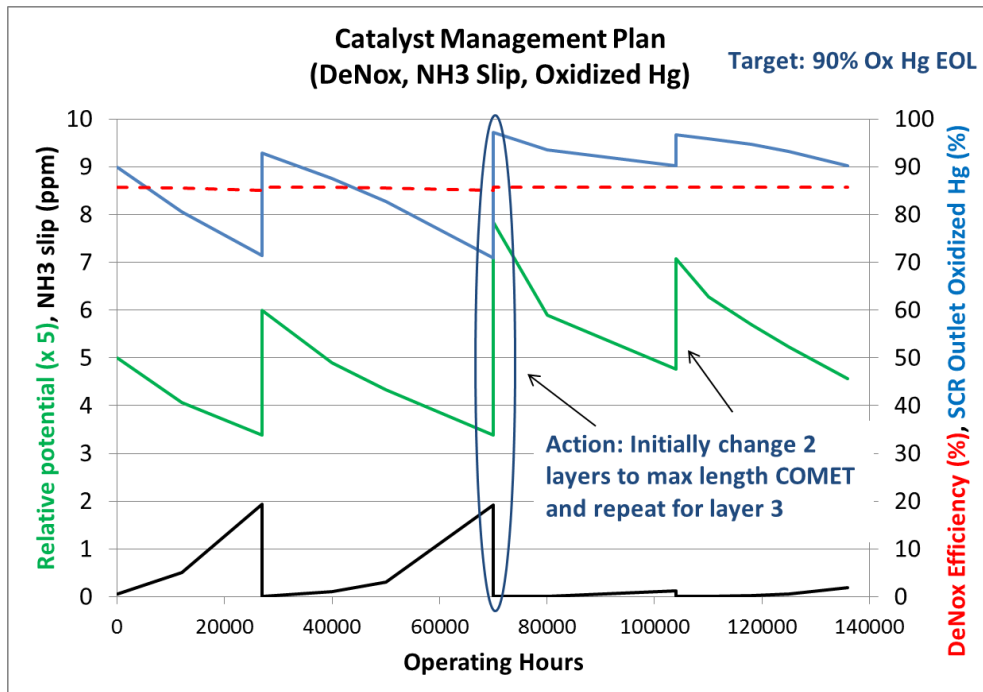**Figure 11. COMET™ Catalyst Employed to Meet 90% Oxidized Hg Requirement.**

Figure 12 shows a final scenario in which the COMET™ advanced Hg oxidation catalyst is being utilized in conjunction with halogen injection. In this case the 90% oxidized Hg requirement can be met and a catalyst action is significantly deferred which can provide flexibility needed for outage planning.

Figure 12. COMET™ Catalyst and Halide Injection to Meet 90% Oxidized Hg Requirement.
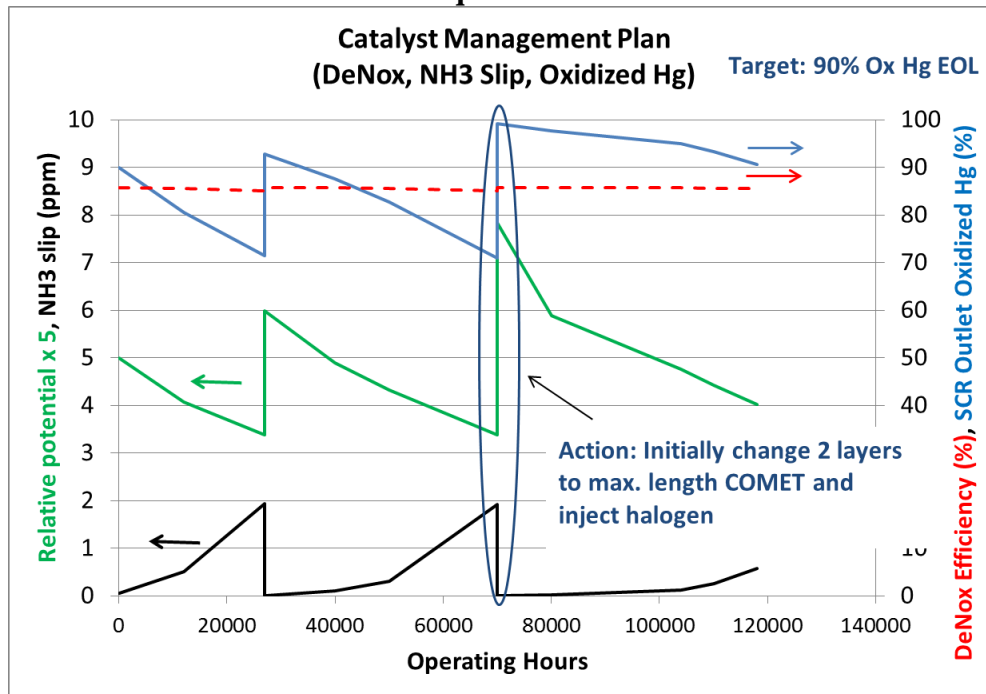
These scenarios demonstrate how catalyst management for DeNOx and Hg oxidation performance are significantly influenced by the amount of Hg oxidation required from the SCR. Also, due to the inhibition of Hg oxidation by ammonia, the operating DeNOx levels will significantly impact the Hg oxidation potential of the SCR and must be taken into account especially if DeNOx requirements for the unit are expected to increase in the future.

Case Study: System characterization, modeling and analysis of management actions

The results of parametric testing of fresh and field deactivated catalysts over a wide range of operating conditions has allowed for the development of Hg^0 oxidation modeling and prediction capabilities. Both laboratory testing and modeling evaluations can be used in an integrated approach along with any available field data to characterize current system performance and evaluate potential catalyst actions.

The following discussion presents a case study in which this integrated approach was used to characterize an existing 4-layer SCR system with multiple catalyst types, ages and formulations.

Also, several catalyst actions were evaluated to determine the overall impact to Hg^0 oxidation through the SCR.

Table 1 shows the composition of the SCR reactor under study and two options that were being considered for catalyst replacement. The existing system (baseline) had honeycomb catalyst from two different manufacturers with two different formulations as well as plate catalyst from a third manufacturer. The plant planned to replace the deactivated first layer with fresh plate catalyst that had already been purchased and was in storage. The two options being considered by the plant were (1) to replace the fourth layer with regenerated catalyst taken from the first layer or (2) to replace the forth layer with fresh COMET™ catalyst.

Table 1. SCR Composition and Options for Catalyst Actions

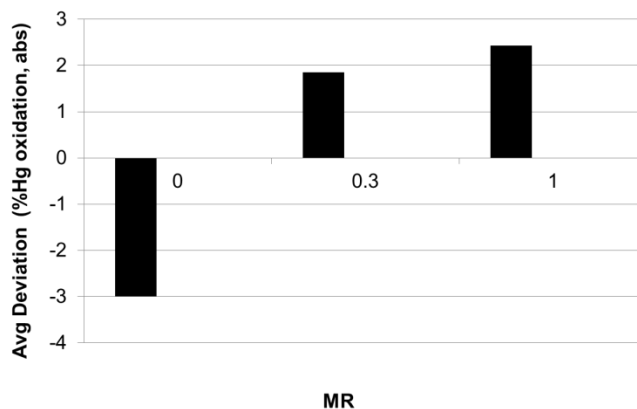|	**Baseline**	**Option 1**	**Option 2**
Layer 1	Aged Honeycomb A	Plate (new)	Plate (new)
Layer 2	Aged Honeycomb B	Aged Honeycomb B	Aged Honeycomb B
Layer 3	Aged Honeycomb B	Aged Honeycomb B	Aged Honeycomb B
Layer 4	Aged Plate	Honeycomb A (regen)	COMET™ (new)
%Hg Oxidation[a]	40	55	70

[a]Model predicted Hg^0 oxidation rate for the 4-layer system

In order to characterize the existing system, field samples of each catalyst type were tested in the laboratory. Samples of the fresh plate catalyst, regenerated first layer catalyst, and fresh COMET™ catalyst were also tested. Each sample was tested in the micro-reactor described above at three molar ratios (0, 0.3, 1) to measure the influence of NH_3 on the Hg^0 oxidation rate. Each condition was repeated 3 times. DeNOx and SO_2 oxidation performance were also measured for several samples. In all, over 60 different laboratory tests were completed on 7 different samples. The automated testing capability of the micro-reactor allowed this large testing matrix to be completed quickly and efficiently.

The laboratory data were then compared to the Hg^0 oxidation model predictions to validate the capability of the model to predict the Hg^0 oxidation performance under these conditions for the given variety of catalyst types, formulations, and levels of deactivation. Figure 13 gives a summary of the overall prediction capability of the model under the given conditions. Across the range of molar ratios, the average deviation between the model and laboratory test data was less than 3% absolute. Therefore, the model was shown to adequately predict the performance of the system under these conditions.

The laboratory and model results were also compared to field data provided by the plant. After an analysis incorporating test methods, catalyst age and operating conditions the results compared well.

Figure 13. Average deviation between model and laboratory data versus MR for this case study.

Once validation of the Hg^0 oxidation model was complete, the model was used to evaluate options for catalyst actions. Table 1 give a summary of the options investigated. The baseline SCR performance under full load conditions was about 40% Hg^0 oxidation. Option 1, which included replacement of layer 1 with fresh plate catalyst and replacement of layer 4 with regenerated catalyst (from layer 1), resulted in a predicted Hg^0 oxidation at beginning of life of about 55%. Option 2, which included replacement of layer 1 with fresh plate catalyst and replacement of layer 4 with fresh COMET™ catalyst, resulted in a predicted Hg^0 oxidation at beginning of life of about 70%.

The overall system performance modeling analysis provided by the COMET™ technology was utilized as a key input in the plants process to decide the best path forward while also considering other key inputs such as, current and future performance requirements, operating conditions, outage planning, and other technology options.

Because of the many changing operational factors that influence overall Hg capture performance, the plant is developing a Hg capture model which incorporates COMET™ SCR performance modeling results along with empirical plant data for Hg capture in downstream equipment. New fuels and fuel blends can have significant impact on SCR Hg oxidation and capture in downstream equipment due to changing levels of Hg, halides, sulfur, ash and moisture. Also, operational flexibility in DeNOx levels or future increases in DeNOx requirements can have significant impacts on Hg capture due to the impact ammonia levels within the SCR. Also, maintenance of the economizer performance and options for de-rating the boiler can be a lever to lower SCR temperatures and improve Hg oxidation performance when needed.

As a key part of the plant Hg capture model, the COMET™ predictive performance model was used to evaluate SCR Hg oxidation performance over a range of three "semi-controllable" process conditions at current and future times: halogen level in the flue gas, flue gas temperature into the SCR, and the level of DeNOx. Figures 14 and 15 show some of the model data generated for different operating conditions.

Figure 14 shows the impacts of halide in the flue gas and NOx reduction target at a fixed (high end of range) flue gas temperature. At a fixed flue gas temperature, the plant can consider changes to the NOx reduction level (within their allowed limits) to minimize the impact of ammonia levels to the Hg oxidation rate of the SCR. With potential for higher NOx reduction requirements in the future, the plant can also use this model to predict the future impacts and mitigation strategies. Also, they can consider different fuel blends to change the level of halogen present in the flue gas while balancing impacts of changing sulfur levels on downstream Hg capture.

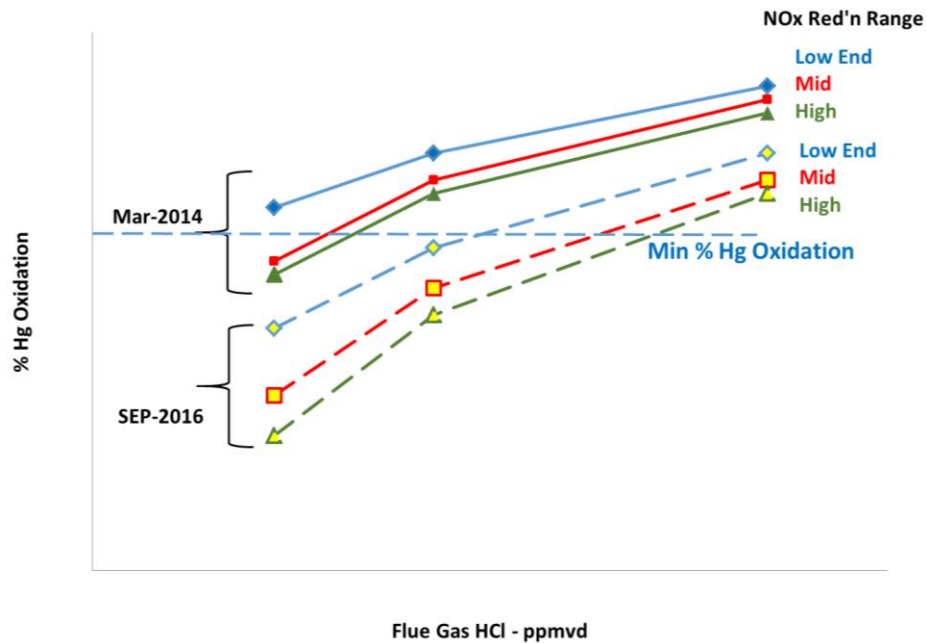**Figure 14. SCR Hg Oxidation at High End Flue Gas Temperature.**

Figure 15 shows the impacts of halide in the flue gas and SCR inlet temperature at a mid-level NOx reduction target. This data helps the plant determine the impacts of possible de-rates of the boiler or increased cleaning of the economizer as a means of lowering SCR temperature and increasing Hg oxidation. Again, fuel blending or halogen addition can be used as another lever for increasing oxidation to help meet the minimum requirement as SCR temperatures increase or as the catalyst ages.

The combination of the COMET™ predictive SCR Hg oxidation model along with an empirical oxidized Hg capture model for downstream equipment provides a valuable tool for understanding how changes to plant operating conditions will impact MATS compliance. These tools are currently being used by the utility to develop catalyst management, fuel management, and operational strategies for the fleet of coal plants in preparation for meeting MATS compliance deadlines in 2015.

Figure 15. SCR Hg Oxidation at Mid-Level %NOx Reduction vs. Flue Gas HCl.
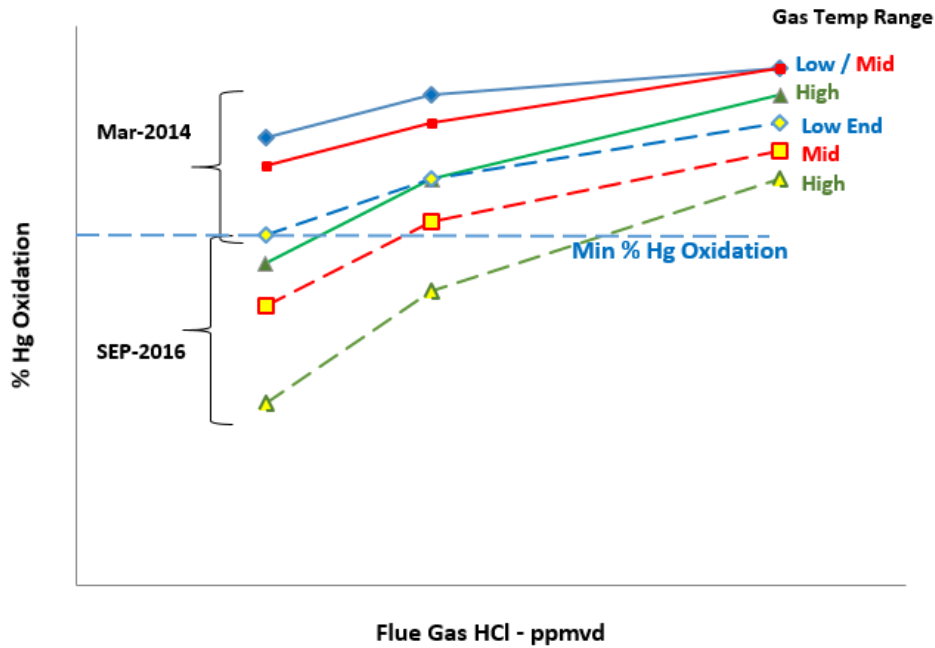

Benefits of an Integrated Approach

Figure 16 reflects the recommended process for integration of modeling, laboratory and field testing to assist in assuring compliance with mercury emissions goals. Prior discussion herein reflects the laboratory testing approach for model development and catalyst management process. Additional considerations include the planning, assessment and utilization of field results.

Ideally, accurate measurements of speciated mercury as well as other influential factors at key locations from the boiler outlet through the stack should be obtained. These locations would include fuel, SCR inlet, SCR outlet/APH inlet, APH outlet/Particulate collection inlet, FGD inlet and stack. This capability would allow specific understanding of the impact of each piece of equipment on mercury (Hg^0, Hg^{+2}, Hg(p)). While we have demonstrated some success with this method as illustrated in Figure 13, in practice the measurement of mercury species in dust laden environment can be very difficult. An alternative approach may also be considered which utilizes a combination of techniques to assess and validate a particular unit's capability to achieve the mercury emission goal. For example, focus on field based measurements for fuel, ash measurements, and FGD Hg retention, while utilizing laboratory evaluation of SCR and APH. This proposed method utilizes the most proven measurement techniques and equipment in each area to reduce uncertainty and thus has the potential to both improve the analysis and decision making process while reducing cost.

Figure 16. Approach to Integrating SCR in Hg emissions compliance
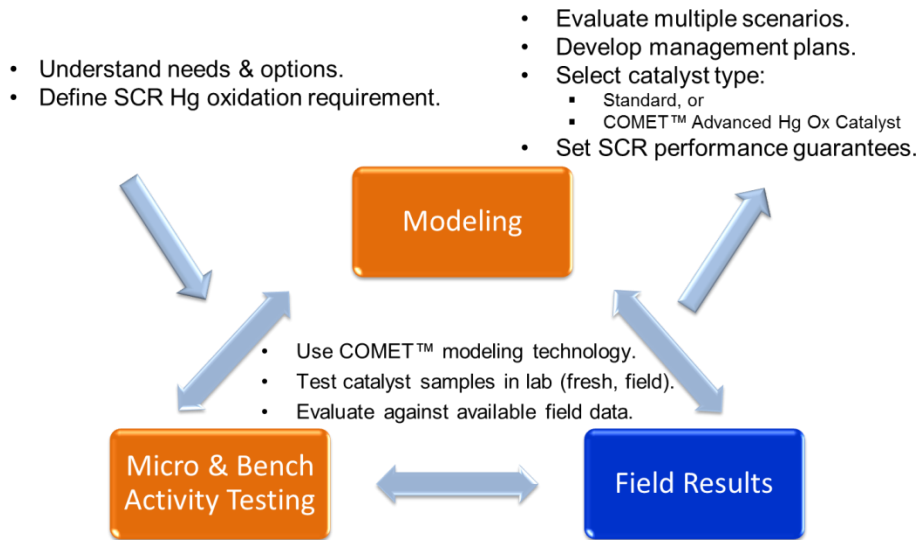
SUMMARY

The Hg^0 oxidation reaction is a more complex reaction than the DeNOx reaction. For the purposes of catalyst management, it does not afford itself to a simple model like that for DeNOx, 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_x and NH_3 at the outlet of the SCR reactor.

Also, whereas the DeNOx reaction can be characterized by a simple K rate constant, and where K is mainly dependent on catalyst composition (given SO_2 oxidation constraints), temperature, and AV, with minor influences of O_2, H_2O, SO_x, and NH_3; the Hg^0 oxidation reaction cannot be characterized by a simple K rate constant and is greatly influenced by O_2, H_2O, and NH_3 and, in addition, by HCl, HBr, and CO. Moreover, given the same SO_2 oxidation constraint, catalyst type (i.e. COMET™ vs. Standard) can have a very significant impact on Hg^0 oxidation performance. Furthermore, while deactivation for DeNOx may correlate to some degree with Hg^0 oxidation deactivation, the impact of NH_3 profile changes over time creates additional complexity in predicting Hg^0 oxidation performance as a function of catalyst life.

Therefore, new models are required to account for the complexities of the Hg^0 oxidation reaction that move beyond the use of simple K_{HgOx} first order 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 DeNOx reaction. An automated reactor like that described in the Experimental section is ideal for accommodating such requirements. Models for Hg^0 oxidation can then be combined with existing DeNOx performance models to develop prediction tools and catalyst management strategies for Hg^0 oxidation. Cormetech's COMET™ technology

combines these characterization and prediction capabilities with advanced Hg^0 oxidation catalyst to provide the tools necessary to optimize the SCR co-benefit as part of a robust mercury compliance strategy.

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KEYWORDS

COMET™, mercury, oxidation, SCR, catalyst, MATS.