

# Addressing the mercury emissions issue

**As the issue of controlling mercury emissions gains prominence globally, Scot Pritchard, Masashi Kiyosawa and Katsumi Nochi explain how an advanced SCR catalyst is capable of achieving 95 per cent oxidized mercury, and thereby enabling it to be readily captured in a downstream FGD process.**

Recent initiatives to reduce global mercury emissions from power plants were addressed by governments participating in the United Nations Environmental Programme (UNEP). Specifically, on 19 January 2013, the UNEP's International Negotiating Committee convened in Switzerland, involving the governments of the US, the European Union, China and India, to draft a legally-binding instrument called the *Minamata Convention on Mercury*, named after the Japanese city where serious damage to people's health occurred because of methyl mercury pollution in the mid-20th century. The instrument, slated to be ratified during the UNEP Diplomatic Conference in Japan in October 2013, calls for the installation of Best Available Technologies for new power plants and legally binding countries to implement plans to cut mercury emissions.

Coal combustion, most notably in utility boilers, has been targeted as a major source of mercury emissions. Mercury levels in coal mined in the US typically range from 0.05–0.2 ppmw. In the high-temperature regions of coal-fired boilers, mercury in coal is volatilized and converted to its elemental metallic form ( $Hg^0$ ). A complex series of reactions occurs as the flue gas is cooled converting  $Hg^0$  to oxidized (ionic) mercury ( $Hg^{2+}$ ) and/or mercury compounds that are solid-phase (particle bound) ( $Hg_p$ ). The partitioning of mercury into its three forms ( $Hg^0$ ,  $Hg^{2+}$  and  $Hg_p$ ) is referred to as mercury speciation, and the degree to which speciation occurs can substantially impact

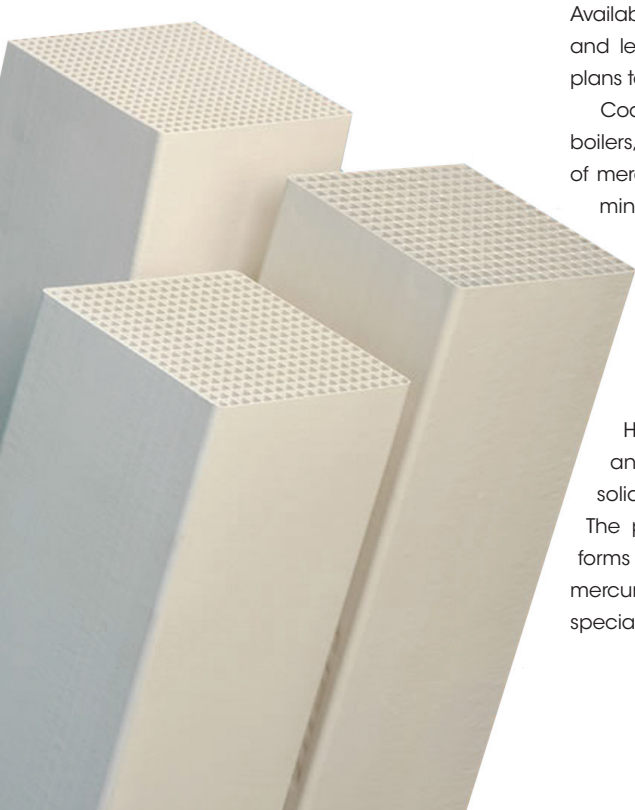
mercury control approaches. Mercuric chloride ( $HgCl_2$  or  $Hg^{+2}$ ) compounds are soluble and can be captured in FGD systems used for sulfur dioxide ( $SO_2$ ) removal.  $Hg_p$  compounds or Hg compounds adsorbed onto the surface of other particles can be captured to varying degrees using particulate matter (PM) control devices, such as fabric filters or electrostatic precipitators. This process may be facilitated by use of additives such as activated carbon. The emissions control device capture points for oxidized and particle-bound mercury are shown schematically in Figure 1.

## The chemistry of mercury oxidation

As noted above and as shown in Figure 1, oxidized and particulate forms of mercury can be effectively captured in new or existing multi-pollutant control processes installed for reducing  $SO_2$  and PM. It is also well known that catalysts used for selective catalytic reduction (SCR) of nitrogen oxides ( $NO_x$ ) compounds can exhibit the co-benefit of promoting mercury oxidation. In addition to reacting with  $NO_x$  compounds to form nitrogen and water, titania-based SCR catalysts containing oxides of vanadium and molybdenum, or tungsten have been shown to be effective in oxidizing elemental mercury to its  $Hg^{2+}$  form.

## Key performance parameters

A number of factors are known to affect the degree of oxidation of elemental mercury. The major ones include, halogen content (e.g. Cl, Br), temperature, reductants (e.g.  $NH_3$  and  $SO_2$ ), catalyst chemistry and catalyst age, as well as flue gas constituents e.g.  $Hg$ ,  $H_2O$ .



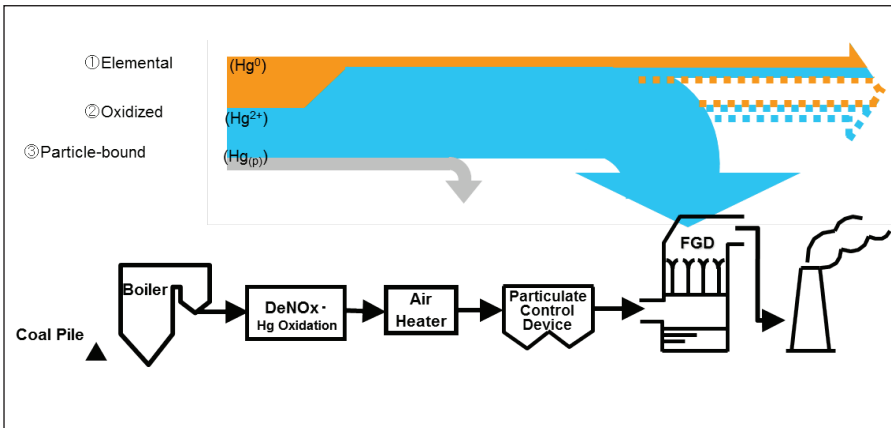


Figure 1: Capture points for the three forms of mercury in flue gas, showing  $Hg_0$  collected in the particulate collection device and  $Hg^{2+}$  captured in the FGD scrubber

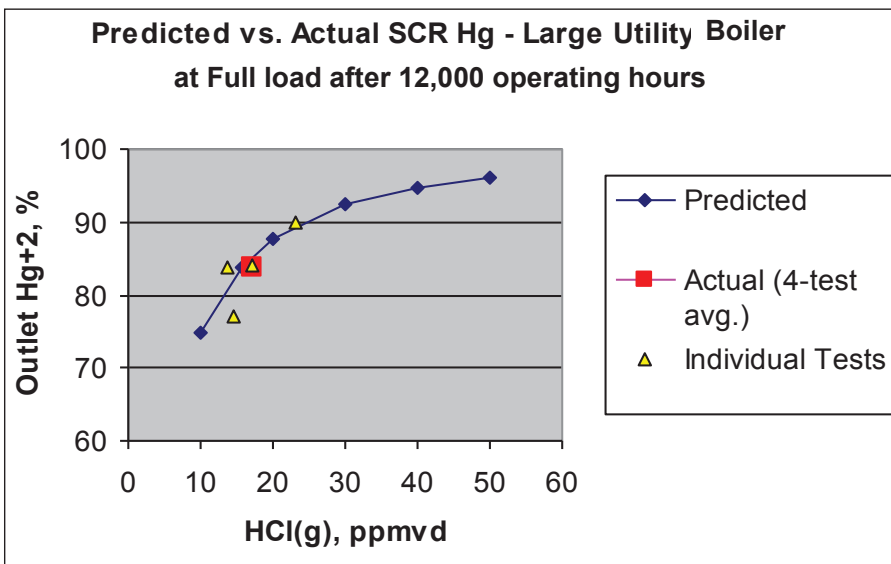


Figure 2: Oxidized mercury levels at varying HCl concentrations

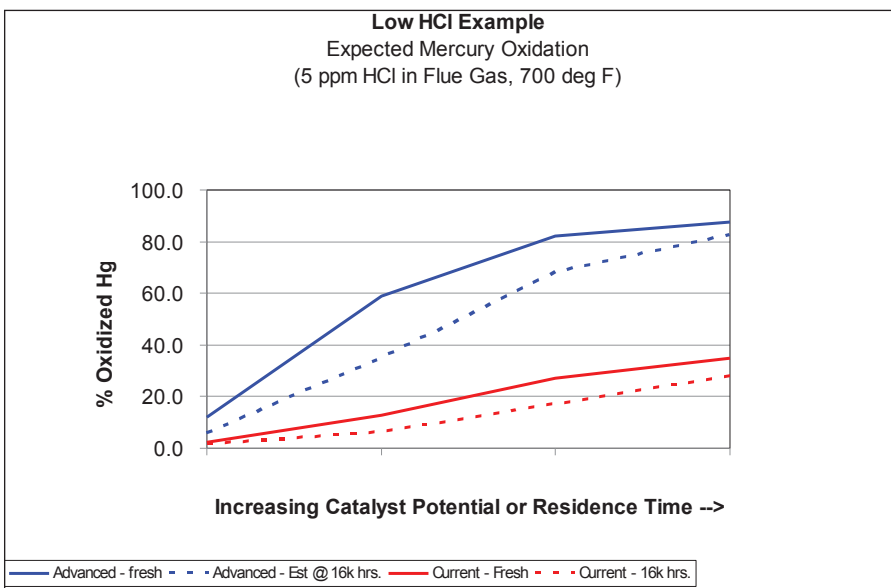


Figure 3: Oxidized mercury levels at varying catalyst potential at 5 ppm HCl

Halogen content in the fuel and flue gas is an important driver for achieving mercury oxidation through the SCR catalyst. Chlorine levels in some bituminous coals exceed 500 ppmw resulting in HCl levels in the flue gas of greater than 35 ppm so helping to drive greater formation of oxidized mercury via the SCR. For sub-bituminous coals typical chlorine levels are <100 ppmw, resulting in HCl levels in the flue gas of <10 ppm. This low level of halogen in the flue gas, however, can limit the SCR performance for oxidizing mercury and this presents one of the challenges to catalyst manufacturers. Methods to enhance performance include improved catalysts that can be used exclusively or in combination with halogen additives.

The temperature of the flue gas is another factor that can significantly impact the oxidation of mercury across the SCR. Thermodynamically, elemental mercury is more likely to be oxidized at lower temperatures so higher temperature applications present more of a challenge. In addition, if  $SO_2$  oxidation is a concern, catalyst chemistry, especially at higher temperatures, must be modified to help reduce such activity. This can adversely impact mercury oxidation performance posing an additional consideration in the development of an advanced catalyst.

Oxidized mercury can also be reduced back to its elemental form if there is an excess amount of reductants, such as ammonia ( $NH_3$ ) and  $SO_2$ . The latter is the most significant reductant to be considered.

Catalyst chemistry is critical to driving mercury oxidation performance; however it must be balanced with the other critical performance needs from the SCR including  $NO_x$  activity and  $SO_2$  oxidation. Understanding the interactive effects of the flue gas conditions and catalyst chemistry is critical to the optimization process. The age of the catalyst also affects the degree of mercury oxidation because the catalyst potential decreases with time. The effects of catalyst aging on mercury oxidation can however be minimized through a combination of proper chemical formulation and catalyst management procedures.

Other flue gas constituents: The relative rate of mercury oxidation is higher in cases where the inlet concentration of  $Hg^0$  is

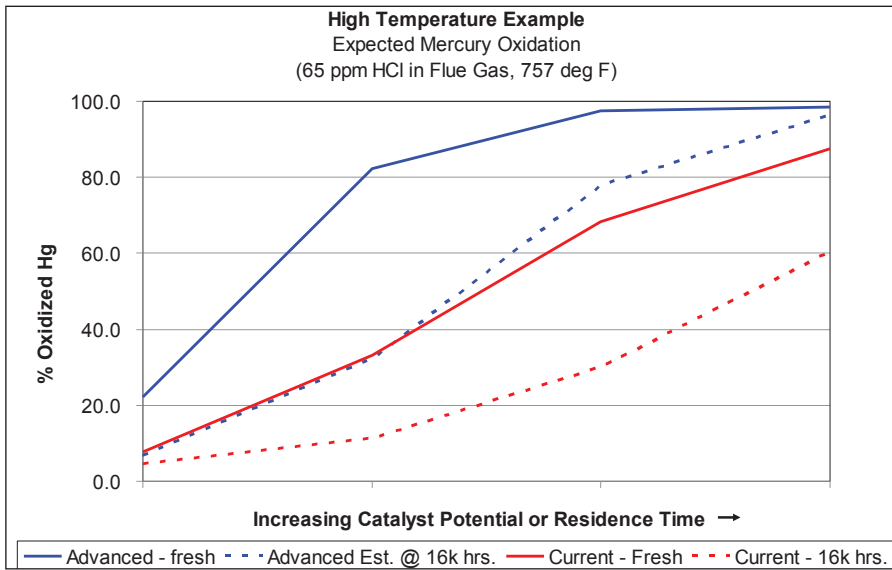


Figure 4: Oxidized mercury levels at varying catalyst potential at 65 ppm HCl

higher. In a study jointly conducted by the US Department of Energy, the Environmental Protection Agency and the Electric Power Research Institute, high levels of mercury oxidation over the SCR were observed at plants firing eastern US bituminous coal where the level of Hg<sub>0</sub> is high. However, oxidation was shown to be insignificant when the inlet mercury was already in the oxidized form.

## Performance modeling

Information gathered through a combination of significant laboratory testing and field data analysis over the last decade has resulted in the development of performance models. These models are a key tool that allows parametric performance assessments to be run to determine the best methods to achieve desired performance levels from the SCR. In order to set the desired performance target from the SCR, a full system evaluation should be considered. Typical questions which make up the model input include:

- What is the overall system goal?
- What are the fuels and fuel blends to be considered?
- What are the operating conditions and other key performance requirements of the SCR e.g. NO<sub>x</sub> reduction, SO<sub>2</sub> conversion, etc.?
- What level of mercury oxidation should be expected through the air preheater?
- Will the dust collection system contribute to mercury reduction performance?

- Will fuel or post-combustion additives be utilized?
- What collection efficiency should be expected from the FGD system, including consideration of re-emission control?

Economic considerations should also be made, including, but not limited to: cost of additives, cost of catalyst, pressure loss, impact on ash sales, boiler corrosion and material handling equipment.

Once requirements are understood, a series of 'what-if' scenarios can be run and supplemented with additional testing as needed. The net result will allow the user to assess the best method(s) to achieve desired performance requirements at the lowest total ownership cost.

## Catalyst advancements

As noted above, there are a number of issues that can affect mercury oxidation. Two of the bigger influences, namely temperature and halogen content, are highlighted below to illustrate the differences between advanced Hg oxidation SCR catalysts versus standard SCR catalyst products. Figure 2 gives an example of actual field performance versus predictive models for aged SCR catalyst at varying levels of HCl in the flue gas. At a temperature of approximately 690°F (366°C), the percentage of oxidized mercury at the SCR outlet measured during actual tests on an aged catalyst ranged from 75–90 per cent over a range in flue gas HCl concentration of 10–25 ppmvd. The predicted levels of

oxidized mercury increased to >95% levels at higher levels of HCl.

MHI and Cormetech have developed an advanced catalyst tailored to oxidize mercury to high levels under challenging conditions involving high temperatures and low HCl concentrations both of which as outlined above negatively impact mercury oxidation across conventional SCR catalysts.

Figure 3 illustrates the performance of the advanced Hg oxidation catalysts versus standard catalyst at extremely low HCl concentrations and moderate flue gas temperatures (5 ppmvd and 700°F). The advanced catalyst, which exhibited high levels of oxidized mercury for both the fresh and aged catalyst, shows a substantial increase over an existing standard catalyst.

In Figure 4, the percentage of oxidized mercury is shown, as expected, to be greater due to the higher HCl concentration despite a higher temperature (65 ppmvd and 757°F).

## Conclusion

It has been demonstrated that mercury reduction technologies that exist today could be used to set future regulations for mercury emission. MHI and Cormetech have jointly leveraged their extensive SCR catalyst formulation expertise to assist in the development of advanced mercury oxidation catalysts with demonstrable benefits over current products.

However, in order to determine the applicability of such products, alone or in combination with other technologies, each plant must review their unique capabilities and challenges to meet the upcoming goals. A holistic approach must be considered to include all components of the existing system from the coal pile through to the stack, with the net goal of reducing the overall cost to achieve anticipated regulatory requirements.

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