

# SCR CATALYST, A LOW COST TECHNOLOGY FOR MERCURY MITIGATION

Authors:

**Takanori Nakamoto**

**Yasuyoshi Kato**

**Yoshinori Nagai**

Babcock-Hitachi, K.K., Kure, Japan

**Kyle Neidig**

Hitachi Power Systems America, Ltd.

645 Martinsville Road

Basking Ridge, NJ 07920

## INTRODUCTION AND REGULATIONS

Utilities and operators of large coal combustion facilities will soon have to comply with mercury emission regulations. MATS (Mercury and Air Toxics Standards) regulation which focuses on mercury and other hazardous pollutants will force these facilities to cut emissions, including mercury, starting in the spring of 2015.

With the downturn in the economy lowering load demand along with a change in the priority of power generator unit dispatch shifting from coal to natural gas, this additional regulation could not come at a worse time for coal fired units. Now, more than ever, Utilities are searching for the most economical path to comply with environmental regulations. Whenever a circumstance of this importance arises, an alternative to expensive new equipment purchase to meet the emission regulation mandates is preferred. Optimizing the use and performance of existing air pollution control equipment to comply with regulations will always be a lower cost option than retrofitting with new air pollution control technologies. Hitachi has designed an SCR (Selective Catalytic Reduction) catalyst that can be used with an existing SCR to optimize the oxidation of mercury as a co-benefit solution for this regulation.

In 2003, in anticipation of the CAMR (Clean Air Mercury Rule) regulation, Hitachi began and has successfully developed a new type of SCR catalyst called TRAC<sup>®</sup>. This new design archives high mercury oxidation and low SO<sub>2</sub> to SO<sub>3</sub> conversion requirements for low chlorine coal-fired power plants. Through extensive research, pilot testing, and field demonstrations in the U.S and in Europe TRAC<sup>®</sup> has been commercially available with full mercury oxidation guarantees since 2007. Hitachi was able to develop a new method of formulation for SCR catalyst in such a way as to maintain high NO<sub>x</sub> reduction, low SO<sub>2</sub> conversion rate and significantly increase the oxidation of mercury from conventional catalyst. The basis for this approach is to oxidize as much elemental mercury as possible to allow the downstream AQCS (Air Quality Control System) equipment to remove the mercury. With 12 commercial applications of TRAC<sup>®</sup> catalyst as of January 2013 and several more planned for installation in 2013 and 2014, several customers have already determined that this product can eliminate or significantly reduce the need for ACI

(Activated Carbon Injection), halogen, or other sorbent injection thereby making the evaluation for TRAC<sup>®</sup> a simple economic winner.

## MERCURY ABATEMENT TECHNOLOGY USING SCR CATALYST

As shown in Figure 1, it is well known that SCR catalyst can oxidize the elemental form of mercury ( $\text{Hg}^0$ ) emitted from coal fired boilers to the oxidized form ( $\text{Hg}^{2+}$ ) in a gaseous state and oxidized mercury is easy to capture in downstream AQCS equipment unlike elemental mercury. Therefore, increasing mercury oxidation rate across SCR catalyst is a key technology for the plants where SCR and flue gas desulfurization (FGD) are equipped to remove  $\text{NO}_x$  and  $\text{SO}_x$  from the flue gas. It is called as “Co-Benefit” technology for mercury control. In this technology, however mercury oxidation catalyst is required to enhance mercury oxidation while keeping low  $\text{SO}_2$  to  $\text{SO}_3$  conversion rate in order to avoid the trouble caused by  $\text{SO}_3$  such as air heater fouling, flue corrosion and visible stack plumes.

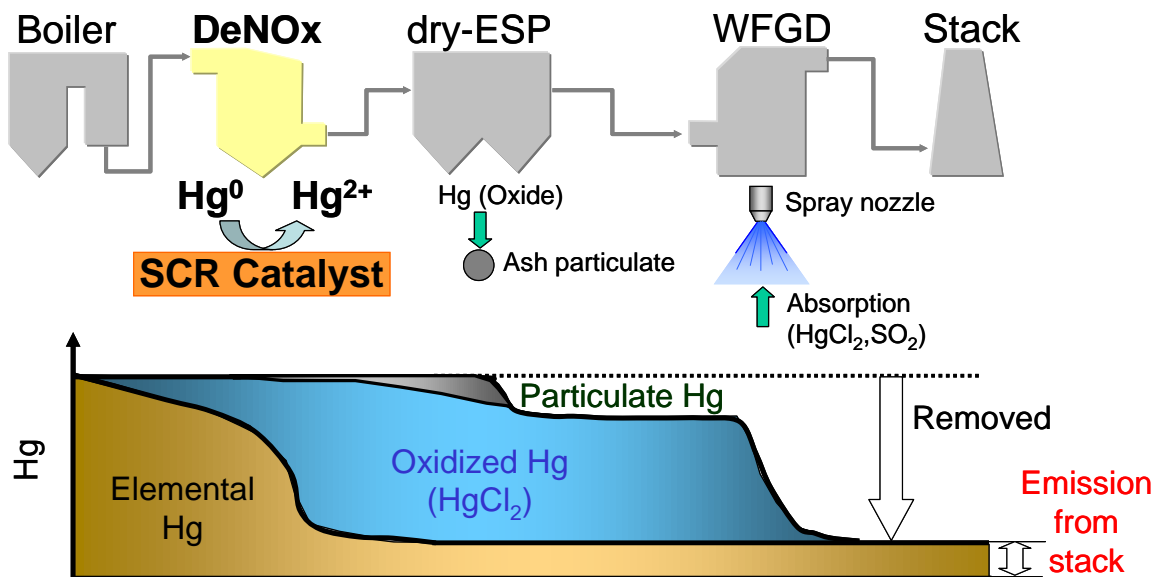



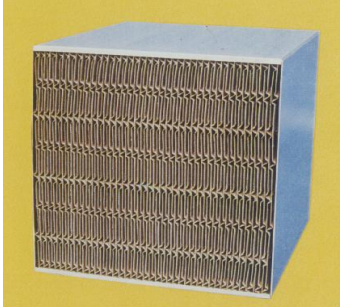


Figure 1 Behavior of Mercury Emitted from Coal Fired Boiler

## HITACHI'S APPROACH TO DEVELOP NEW SCR CATALYST

In this development program, Hitachi conducted several hundred screening tests for mercury oxidation catalyst using laboratory scale and verification test facility (refer to the Figures 2 & 3). Then, Hitachi conducted several pilot and slipstream reactor (SSR) tests to demonstrate the technology (refer to Figure 4) and confirmed reliability in the actual plant conditions.

Standardization of fabrication methods (Figure 5) is the final step in commercialization. This step by step development for technology reliability is the basis of Hitachi policy.

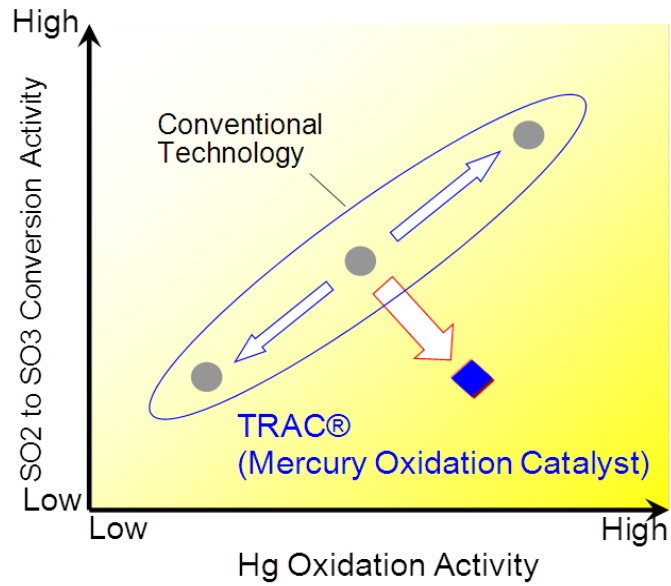
<p><b>2. Laboratory Test Facility</b>          Screening/Deterioration          Daily QC Control          • Study on characteristics of various components          • Production of prototypes          Simulated gas without SO<sub>3</sub></p>	<p><b>3. Verification Test Facility</b>          Performance Test          Coal fired flue gas          • W/ SO<sub>3</sub></p>	<p><b>4. Demonstration Test</b>          • Pilot (SSR) tests          • Durability of sample in actual plan            Coal Fired Flue Gas          • w/SO<sub>3</sub></p>	<p><b>5. Practical Application</b>          • Standardization of design and manufacturing method.</p>
			

Figures 2-5 Hitachi's Approach for Development of New SCR Catalyst

## HITACHI TRAC<sup>®</sup> CATALYST

Figure 6 shows the non-conventional concept of TRAC<sup>®</sup>. Hg oxidation of SCR catalyst increases with an increase in SO<sub>2</sub> to SO<sub>3</sub> conversion for conventional technology, while Hg oxidation of TRAC<sup>®</sup> remains high without an increase in SO<sub>2</sub> to SO<sub>3</sub> conversion. Hitachi then tried to develop new SCR catalyst to meet future mercury control regulation by changing catalyst composition and its manufacturing process, Figure 7 shows the proposed reaction model on mercury oxidation catalyst compared with conventional SCR catalyst. Hitachi Mercury Oxidation catalyst, named TRAC<sup>®</sup> had developed to enhance mercury oxidation activity while keeping SO<sub>2</sub> conversion rate by means of addition of new chemical to activated TiO<sub>2</sub> base oxide and to control SO<sub>2</sub> adsorption to form SO<sub>3</sub>.

Figure 8 shows a comparison of TRAC<sup>®</sup> vs. conventional catalyst, Hg oxidation, SO<sub>2</sub> to SO<sub>3</sub> conversion, and DeNO<sub>x</sub> of TRAC<sup>®</sup>. Also shows that DeNO<sub>x</sub> and SO<sub>2</sub> to SO<sub>3</sub> conversion of TRAC<sup>®</sup> is the same as that of conventional catalysts, while Hg oxidation of TRAC<sup>®</sup> is significantly higher than that of conventional catalysts.



**TRAC® (Triple Action Catalyst) with Higher Hg Oxidation & Lower SO<sub>2</sub> Conversion**

Figure 6 Development Concept of TRAC®

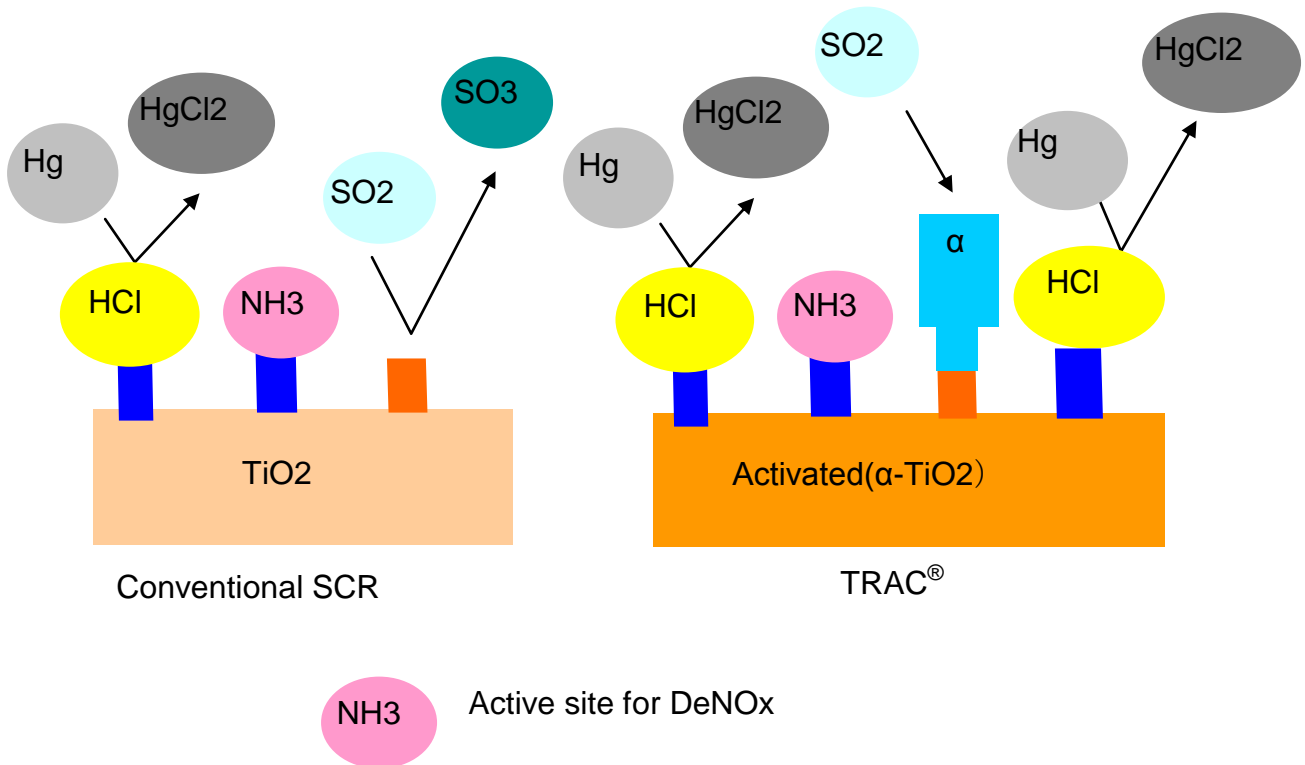


Figure 7 Reaction model on mercury oxidation catalyst compared with conventional catalyst

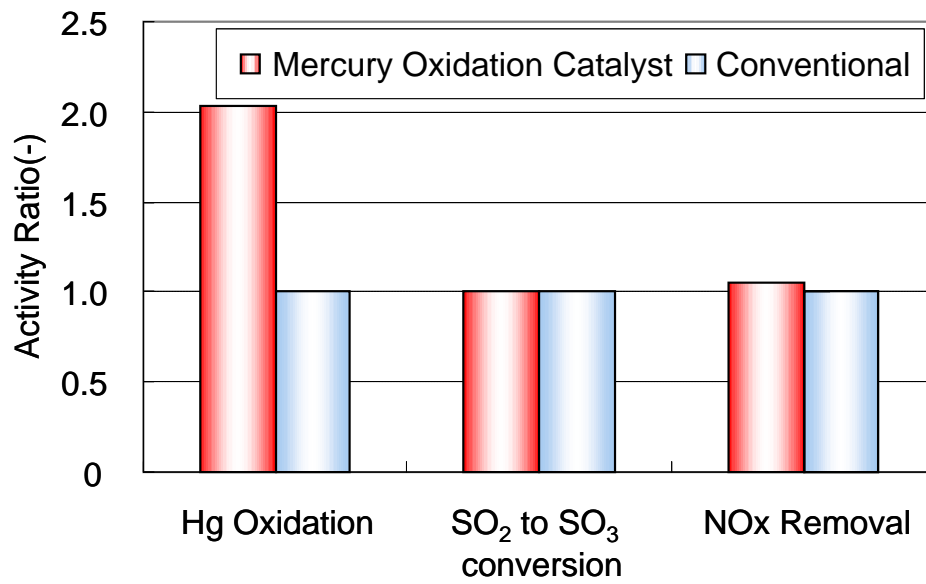


Figure 8 Performance Comparison between TRAC<sup>®</sup> and Conventional catalyst

# TRAC<sup>®</sup> TESTING AND THE FACTORS THAT IMPACT MERCURY OXIDATION PERFORMANCE

## THE EFFECT OF NH<sub>3</sub> INJECTED UPSTREAM OF SCR REACTOR

For mercury oxidation as a co-benefit of conventional SCR catalyst, it is experimentally well known that flue gas and design conditions listed below in Figure 9 will affect the mercury oxidation activity during plant operation. This is especially important for Catalyst Management Plan consideration. Utilities should consider the most effective way to minimize operational cost. Among them for catalyst replacement, the only factor which effect the total plant mercury mitigation efficiency is the concentration of NH<sub>3</sub> that is injected upstream of SCR reactor to reduce NO<sub>x</sub>. That is, the owners need only decide which layer should be replaced based on NO<sub>x</sub> activity.

As explained before, active sites for mercury oxidation reaction seems to be adjacent to or the same as the DeNO<sub>x</sub> site and therefore a large amount of NH<sub>3</sub> injected may affect the mercury oxidation reaction if the catalyst is installed into the upper layer. In this case, the catalyst may work very well as DeNO<sub>x</sub> but not as well as a mercury oxidizer.

To minimize the effect of injected NH<sub>3</sub>, TRAC<sup>®</sup> has been designed to have less effect of NH<sub>3</sub> from the economical point of view, even if TRAC<sup>®</sup> is installed upper layer of SCR reactor (see Figure 10). Hitachi has conducted several types of tests to confirm each factor, with the conditions to achieve more than 90% NO<sub>x</sub> removal under actual plant condition for commercial application.

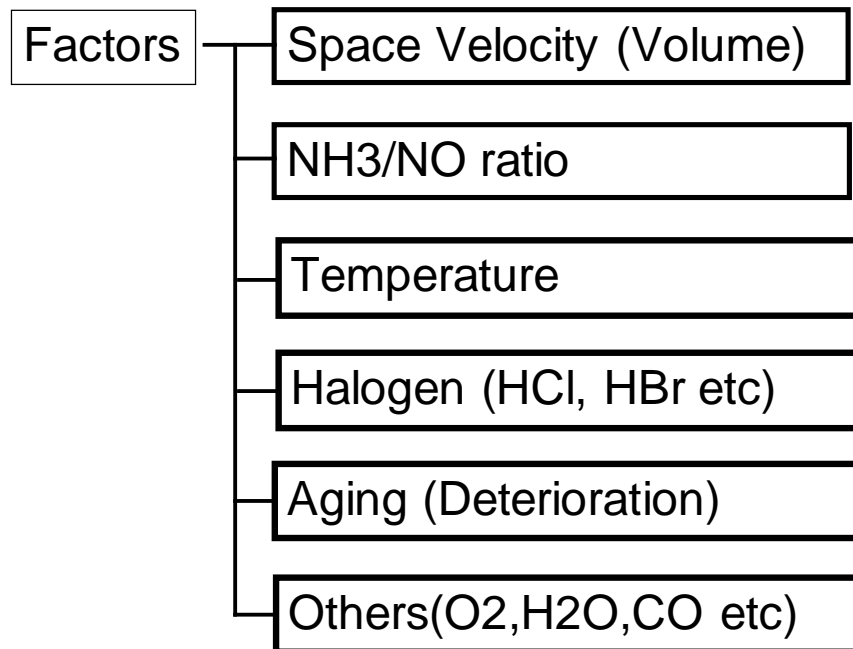


Figure 9 Factors affect on Mercury Oxidation Rate of SCR Catalyst

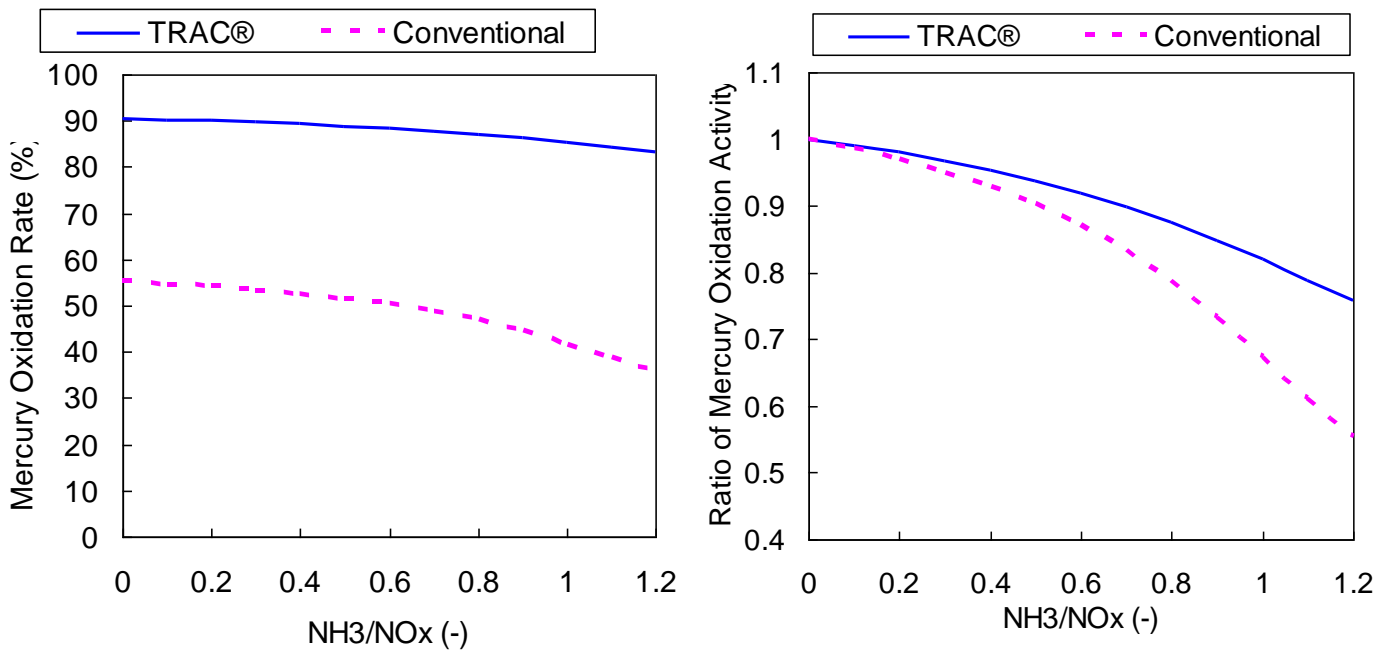
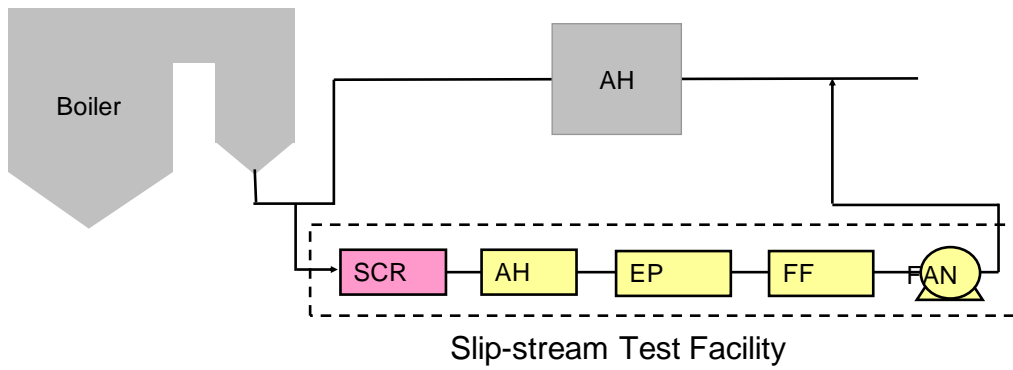


Figure 10 Effect of NH3 Injected upstream of SCR Catalyst

### THE EFFECT OF TEMPERATURE AND HALOGEN ON MERCURY OXIDATION ACTIVITY

A large-scale slipstream test was conducted to see the effect of temperature and halogen at MRC with low sulfur bituminous coal. This plant is equipped with air quality control systems (AQCS) downstream of the SSR as shown in Figure 11. Actual flue gas was extracted from the outlet of a low sulfur coal fired boiler and introduced into SSR-AQCS system by an ID fan, and then returned to actual Air heater (AH) outlet flue. This SSR consists of two (2) layers of full scale catalyst modules. The flue gas velocities and temperatures were fully controlled during testing. The SSR testing was conducted in 2009. Figure 11 also shows mercury oxidation test conditions and outline of SSR respectively. At this test facility, Hitachi was also able to confirm the performance differences between our conventional SCR catalyst and TRAC® under certain flue gas conditions.

Figure 12 shows mercury oxidation activity for both conventional SCR catalyst and TRAC® against halogen (Cl) concentration and flue gas temperature respectively. As can be seen in the left side graph in figure 12, TRAC® has excellent mercury oxidation activity in the test conditions even though mercury oxidation activity for conventional catalyst was decreased with halogen concentration tested. And also the performance of TRAC® was stable even if flue gas temperature is high.



- Fires Low Sulfur Bituminous Coal
- Flue gas was introduced to slip-stream test rig from upstream of AH
- Measured by SCEM

Flue Gas Conditions

Item	Unit	Condition
Gas Flow Rate	lb/hr	50,500
Temperature	F	626-752(698)
NOx	ppm	180-230
Cl	ppm	110-350(130)
NOx Removal	%	90
slip-NH3	ppm	2

Figure 11 Slipstream Reactor (SSR) Test Facility in USA and Flue Gas Condition

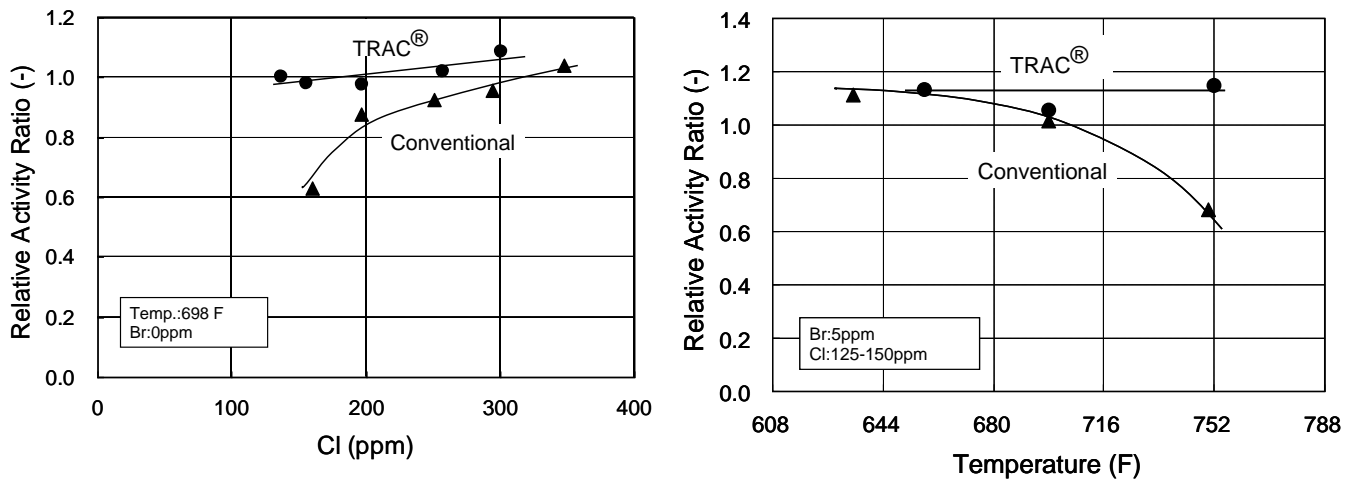


Figure 12 Mercury Oxidation Activity vs. Halogen(HCl) and Temperature



## PERFORMANCE CHANGES WITH OPERATION HOURS

A sample of TRAC<sup>®</sup> catalyst was installed and tested to confirm the durability of Hg oxidation at several power plants. The Hg oxidation rate of the sample catalyst was measured at the laboratory scale facility. The test facility and test conditions are shown in Figure 5. In evaluating the durability of Hg oxidation in TRAC<sup>®</sup>, Hg oxidation ratios were calculated using the following formula:

$$\text{EQ-1: } K = -AV \cdot \ln(1 - X/100)$$

where, K : Hg oxidation (m/h),

AV: Area velocity for Hg oxidation rate measurement (m/h)

X: Hg oxidation rate (%)

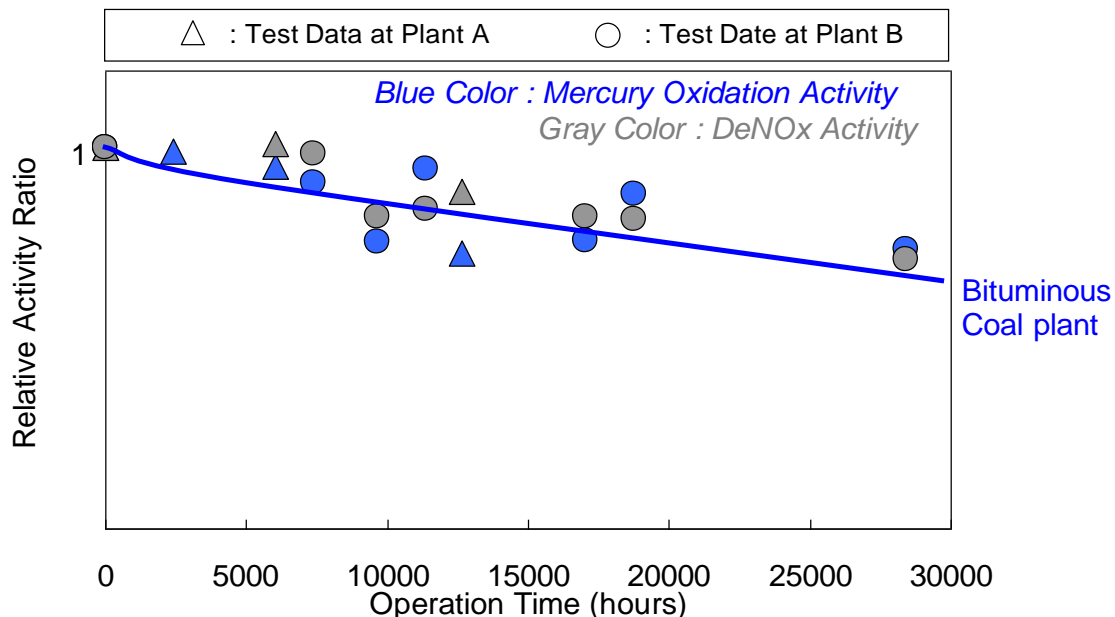
And the Hg oxidation ratio was calculated as follows:

$$\text{EQ-1: } \text{Hg oxidation ratio} = K_t / K_0$$

where, K<sub>t</sub> : Hg oxidation after t hours operation (m/h)

K<sub>0</sub> : Hg oxidation of unused catalyst (m/h)

Figure 13 shows the mercury oxidation activity changes over a total of approx. 28,000-hour operating time for bituminous coal firing plant. Hg oxidation rate for the TRAC<sup>®</sup> catalyst remained high during this three-year test period, even though the results indicate a gradual decrease in mercury oxidation over time. The mercury oxidation deterioration rate of TRAC<sup>®</sup> catalyst was the same as that for DeNO<sub>x</sub>. Robust mercury oxidation performance and superior durability of the TRAC<sup>®</sup> catalyst were observed through the sample catalyst testing.



- Deterioration rate of Hg oxidation was similar as DeNO<sub>x</sub> activity
- TRAC<sup>®</sup> maintained high level of Hg oxidation and DeNO<sub>x</sub> after 28,000 hours

Figure 13 DeNO<sub>x</sub> and Mercury Oxidation Rate Changes with Operation Hours



## TRAC® EXPERIENCES AT US COMMERCIAL PLANT

The following example shows the US experience for applying TRAC® at Plant M, which has four identical 700 MW, 100% PRB coal fired units, with two units being equipped with TRAC® and two with conventional catalyst only. Each of these four units is equipped with a cold-side ESP and wet scrubber.

Table 1 below shows a summary of the catalyst management constituents. Sulfur and chlorine contents listed in the table represent the average values for the entire period of evaluation.

Figure 15 shows the continuous emissions data (MCEM) at the stack vs. operation hours. The data shows a period of low DeNOx operation (75%) at the end of 2010. Starting in 2011 the DeNOx level was raised to the normal 80%. The increase in mercury emissions demonstrates the sensitivity of DeNOx efficiency for this unit. From roughly January 1, 2011, to February 15, 2011, represents the baseline emissions data of about 4.8 lb/TBtu prior to the addition of TRAC® in the fourth layer of the reactor. After the installation of TRAC® in mid-March, the mercury emissions dropped substantially to roughly half that of the prior period of operation without TRAC®. This period of operation showed average emissions of 2.4 lb/Tbtu, which equates to roughly 60% mercury removal. Overall, the data show the clear beneficial co-benefit on emissions as a result of the TRAC® catalyst.

Figure 16 summarizes the Method 30B mercury data for both elemental and oxidized mercury at the three measurement locations. As listed in table 1, Units 1 and 2 were equipped with 1 layer of TRAC® when the Method 30B measurement was done.

Figure 16 shows the percentage of oxidized mercury for each location. As shown in this figure, the proportion of oxidized mercury increased as the flue gas moved downstream, however it is clear that a large amount of elemental mercury was converted to oxidized form across SCR for unit1 and 2 compared with unit 4 which had 4 layers of conventional catalysts.

Table 1 Conditions and Catalyst Management Constituents at Plant M

Facility	Plant M			
Unit	Unit 1	Unit 2	Unit 3	Unit 4
Coal Type	Powder River Basin Coal			
Coal Sulfur	0.40%			
Coal Chlorine	37 ppm			
Nominal Capacity	700 MW	700 MW	700 MW	700 MW
Catalyst	3 Layers Conventional 1 Layer TRAC®	3 Layers Conventional 1 Layer TRAC®	4 Layers Conventional 1 Layer Replaced during Study	4 Layers Conventional

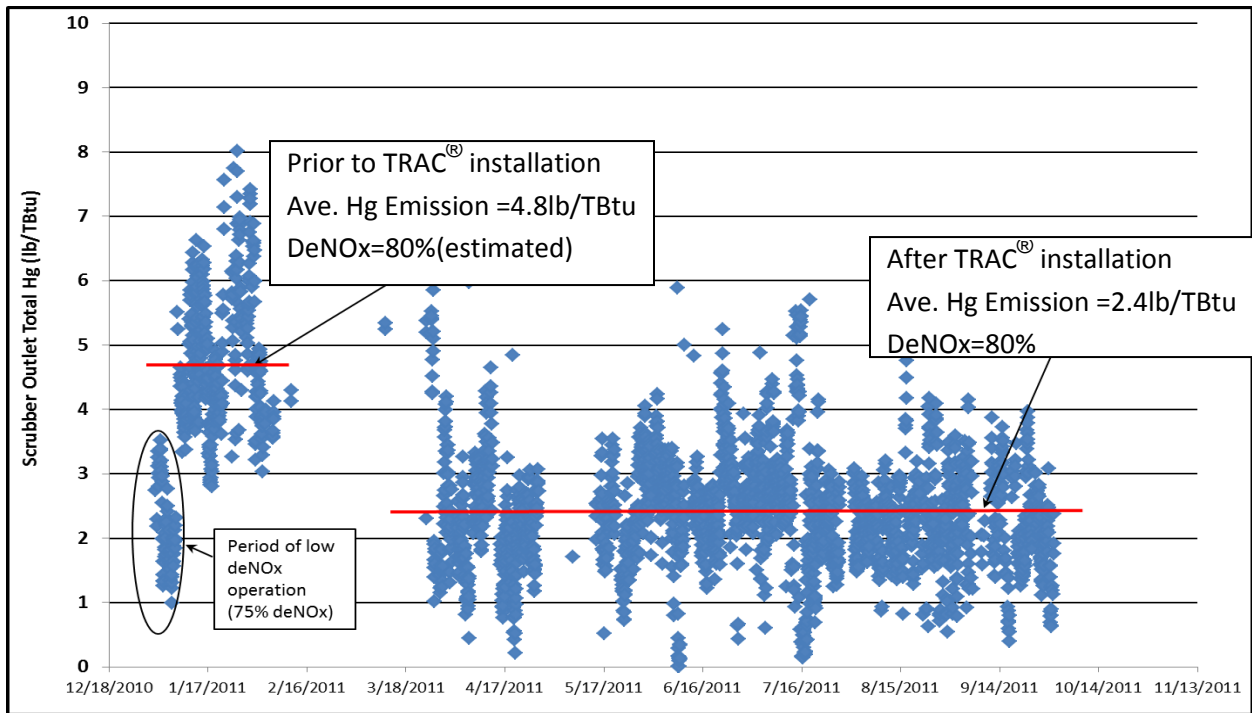


Figure 15 Mercury Continuous Emission Data (MCED) at the Stack

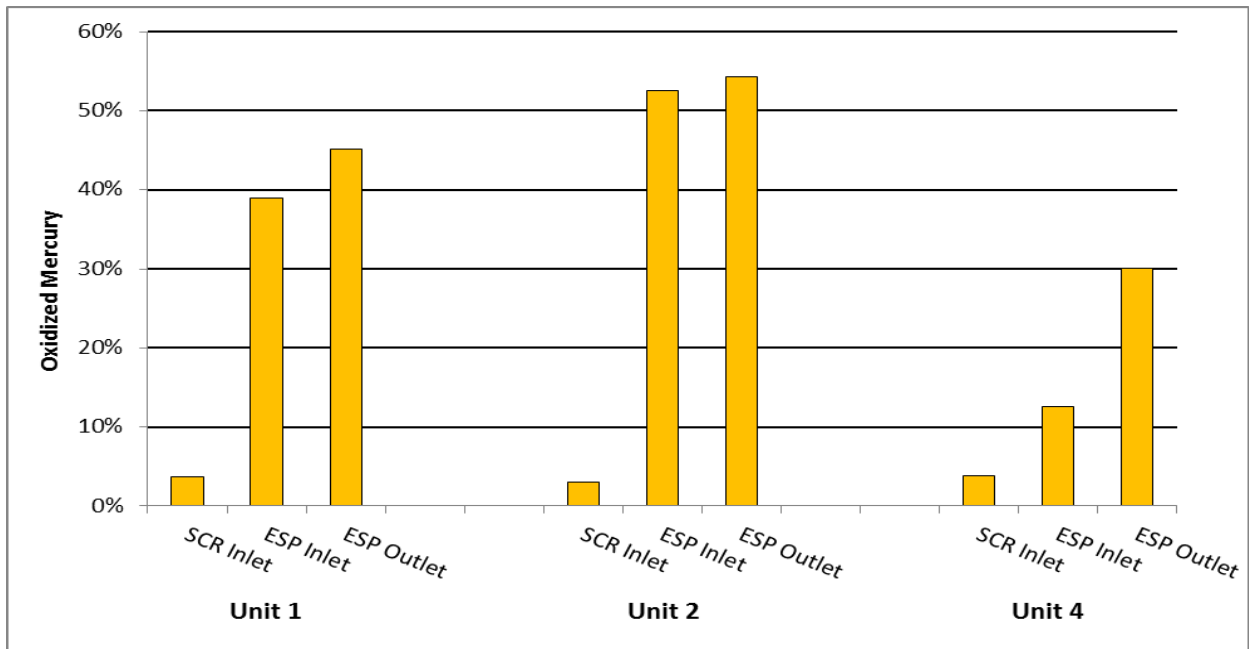
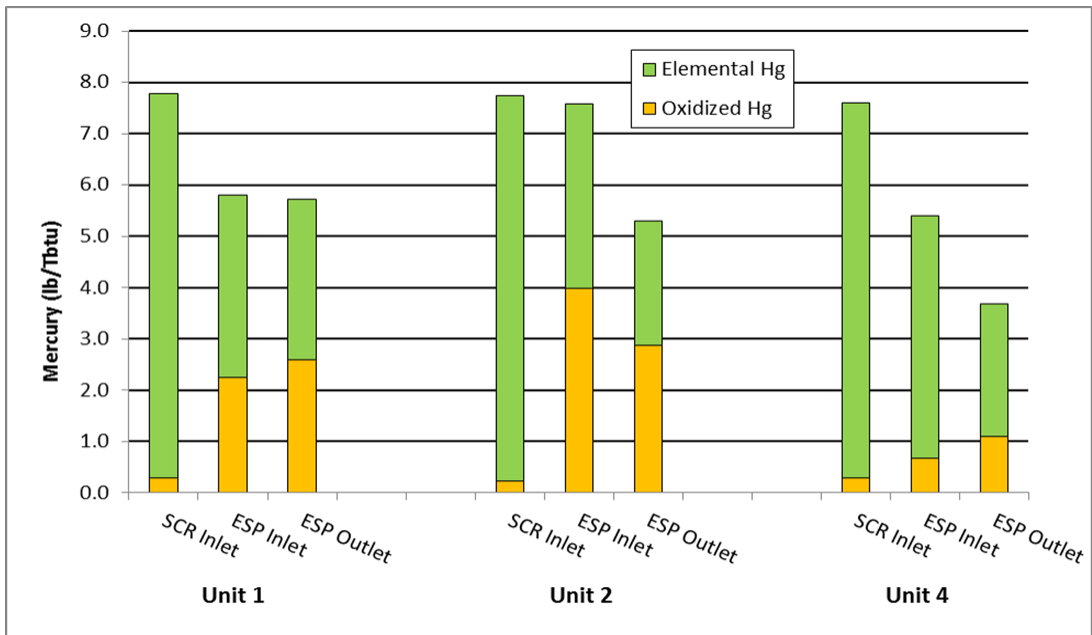


Figure 16 Percentage of Oxidized Mercury at Each Location for Unit1,2 and 4

## CONCLUSION

Hitachi has developed a new commercially available SCR catalyst with advanced mercury oxidation co-benefit that will enhance mercury oxidation for plants firing all coal types. TRAC<sup>®</sup> catalyst has underwent a thorough study and analysis in a controlled lab setting where it significantly outperformed traditional SCR catalyst mercury oxidation performance and proved to be much less sensitive to changes in fuel composition and operation condition changes. These characteristics of TRAC<sup>®</sup> catalyst allow it to achieve higher and more consistent mercury oxidation performance that can be used to comply with mercury emission regulations. Several commercially operating full scale applications have confirmed that the performance benefits of TRAC catalyst are also realized in stack emission measurements. The application of TRAC<sup>®</sup> catalyst on coal fired plants is a low cost, reliable solution for reducing mercury emission.

## REFERENCES

1. Ghorishi, S.B.; Gullett, B.K.; Jozewicz, W. Waste Management Research. 1998, 16:6, 582-593.
2. Evans, A.P.; Holmes, M.J.; Redinger, K.E., Advanced Emissions Control Development Program-Phase II Final Report, U.S. Department of Energy Contract: DE-FC22-94PC94251, April, 1998.
3. Laudal, D.L.; Thompson, J.S.; Pavlish, J.H.; Brickett, L.; Chu, P.; Srivastava, R.K.; Lee, C.W.; Kilgroe, J.D., *Evaluation of Mercury Speciation at Power Plants Using SCR and SCR NOx Control Technologies*, 3<sup>rd</sup> International Air Quality Conference, Arlington, Virginia, September 9-12, 2002.
4. Machalek, T., Ramavajjala, M., Richardson M., Richardson, C.; Dene, C., Goeckner, B., Anderson, H., Morris, E., *Pilot Evaluation of Flue Gas Mercury Reactions across an SCR Unit*, paper presented at the EPRI-DOE-EPA Combined Air Pollution Control Symposium: The Mega Symposium, Washington, DC, May 19-22, 2003.
5. Constance L. Senior, ISSN 1047-3289 J. Air & Waste Manage. Assoc. 56:23-31.
6. Yan Cao, Bobby Chen, Jiang Wu, Hong Cui, John Smith, Chi-Kuan Chen, Paul Chu, and Wei-Ping Pan, Energy & Fuels 2007, 21, 145-156.
7. Favale, A, Morita, I, and Lin, C, *The Mitigation of SO<sub>3</sub> at AEP Gavin Unit 1 Following the SCR Installation*, Electric Power 2006, Atlanta, GA, May 2-4, 2006.
8. Keiichiro Kai, Hirofumi Kikkawa, Yasuyoshi Kato, Yoshinori Nagai, William J Gretta, *SCR Catalyst with High Mercury Oxidation and Low SO<sub>2</sub> to SO<sub>3</sub> Conversion, Power Plant Air Pollutant Control Megasymposium, Baltimore, MD, August 28-31, 2006*
9. Keiichiro Kai, Seiji Ikemoto, Yasuyoshi Kato, Isato Morita, Yu Urabe, Effect of Gas Compositions on Oxidation Efficiency and Speciation of Mercury through SCR Catalyst , VDI Wissensforum , September 29-30, 2010.
10. Yoshinori Nagai, Yasuyoshi Kato, Keiichiro Kai, Hirofumi Kikkawa, Isato Morita, Katsuhiko Yashiro, Commercialization of Mercury Oxidation Catalyst (TRAC<sup>®</sup>) for Coal-Fired Power Plants, The 11<sup>th</sup> China-Japan Symposium on Coal and C1 Chemistry, August 3-7, 2011
11. Anthony Favale, Stephen Guglielmo, and Peter Jin, Hitachi Power Systems America Ltd.; Yoshinori Nagai, Babcock Hitachi, K.K., Japan; and Corey Tyree, Southern Company Research & Environmental Group, An SCR Can Provide Mercury Removal Co-Benefits, Power No.155, Vol.10, October, 2011
12. Anthony Favale, Takanori Nakamoto, Yosuyoshi Kato, Yushinori Nagai, Mercury Mitigation Strategy Through The Co-Benefit of Mercury Oxidation with SCR Catalyst, Power Engineering, January 2013 Edition, Copyright 2013 by PennWell Corporation