Mercury Mitigation Strategy through the Co-Benefit of Mercury Oxidation with SCR Catalyst

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Market and Regulation

Utilities with coal fired power plants will soon have to comply with the new MATS (Mercury and Air Toxics Standards) regulation which focuses on mercury and other hazardous pollutants. With the downturn in the economy lowering load demand along with a flip-flop on priority dispatch of 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 an expensive equipment purchase to meet the new performance mandates is preferred. When an existing device can perform in a co-benefit role[1,2] to resolve the performance mandate, the final decision is stress-free. Propitiously, an SCR Catalyst has been developed and is the solution for this regulation.

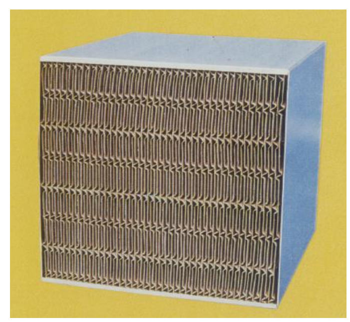
It is well known that SCR catalyst can oxidize the elemental form of mercury (Hg^0) emitted from coal fired boilers to the oxidized form (Hg^{2+}) in a gaseous state and particulate form (Hg(P))[3-5]. However, mercury oxidation rate on the SCR catalyst correlates to the SO_2 oxidation/conversion rate which forms SO_3 that can cause air heater fouling, flue corrosion and visible stack plumes. Several mercury and SO_3 mitigation technologies have become commercially available in recent years[6,7], but these systems can have high initial capital and installation costs along with continuous operational expenses. There are performance limitations and maintenance concerns as well. Hitachi saw this issue developing and started to search for a solution.

In 2003, in anticipation of the CAMR regulation, Hitachi began and has successfully developed a new type of SCR catalyst which called TRAC®. This new design archives high Hg^0 oxidation and low SO_2 oxidation requirements for low chlorine coal-fired power plants. Through extensive research, pilot testing, and field demonstrations in the U.S and in Europe TRAC® 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 NOx reduction high, lower SO_2 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 equipment to remove the mercury. Several

customers have determined that this product can eliminate or significantly reduce the need for ACI, or halogen injection thereby making the evaluation for TRAC® a simple economic calculation. The cost differential more than compensates for the justification of TRAC®.

HITACHI’S Approach to Develop New SCR Catalyst

Hitachi started the study for the mercury mitigation technology was not only for new SCR catalyst but also focused on the whole AQCS. 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 1 & 2). Then, Hitachi conducted several pilot and slipstream reactor (SSR) tests to demonstrate the technology (refer to Figure 3) and confirmed reliability in the actual plant conditions. Standardization of fabrication methods (Figure 4) is the final step in commercialization. This step by step development for technology reliability is the basis of Hitachi policy. As for mercury oxidation catalyst, Figure 5 shows schematic flow of laboratory scale test facility and the standard conditions for screening of new catalysts.

1. Laboratory Test Facility Screening/Deterioration Daily QC Control ・Study on characteristics of various components ・Production of prototypes Simulated gas without SO_3	**2. Verification Test Facility** Performance Test Coal fired flue gas ・W/ SO_3	**3. Demonstration Test** ・Pilot (SSR) tests ・Durability of sample in actual plan Coal Fired Flue Gas ・w/SO3	**4. Practical Application** ・Standardization of design and manufacturing method.
			

Figures 1-4 Hitachi’s Approach for Development of New SCR Catalyst

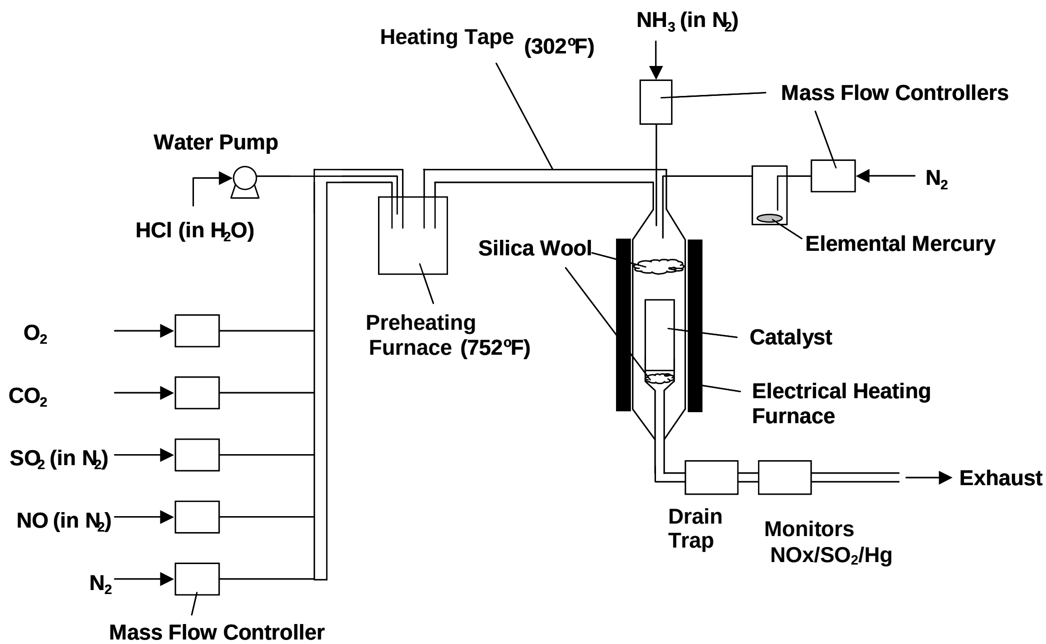


Figure 5 Mercury Test Facility

TRAC®

Figure 6 shows the non-conventional concept of TRAC®. Hg oxidation of SCR catalyst increases with an increase in SO_2 to SO_3 conversion for conventional technology, while Hg oxidation of TRAC® remains high without an increase in SO_2 to SO_3 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® had developed to enhance mercury oxidation activity while keeping SO_2 conversion rate by means of addition of new chemical to activated TiO_2 base oxide and to control SO_2 adsorption to form SO_3[8].

Figure 8 shows a comparison of TRAC® vs. conventional catalyst, Hg oxidation, SO_2 to SO_3 conversion, and DeNOx of TRAC®. Also shows that DeNOx and SO_2 to SO_3 conversion of TRAC® is the same as that of conventional catalysts, while Hg oxidation of TRAC® is extremely higher than that of conventional catalysts.

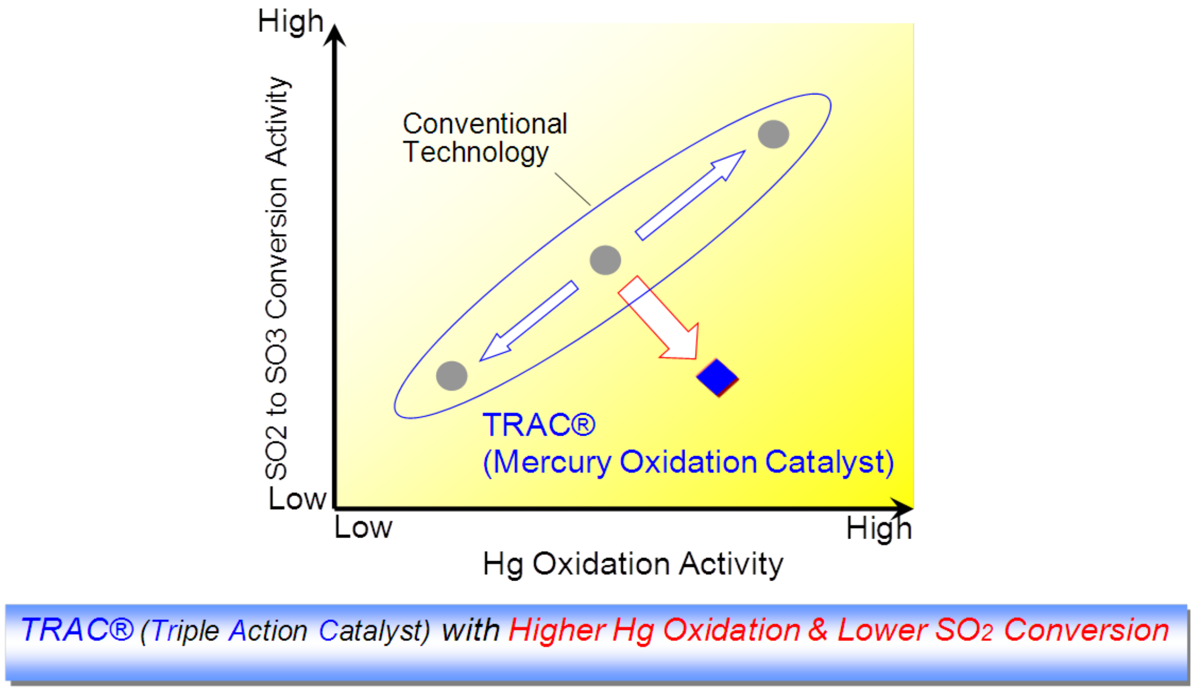


Figure 6 Development Concept of TRAC®

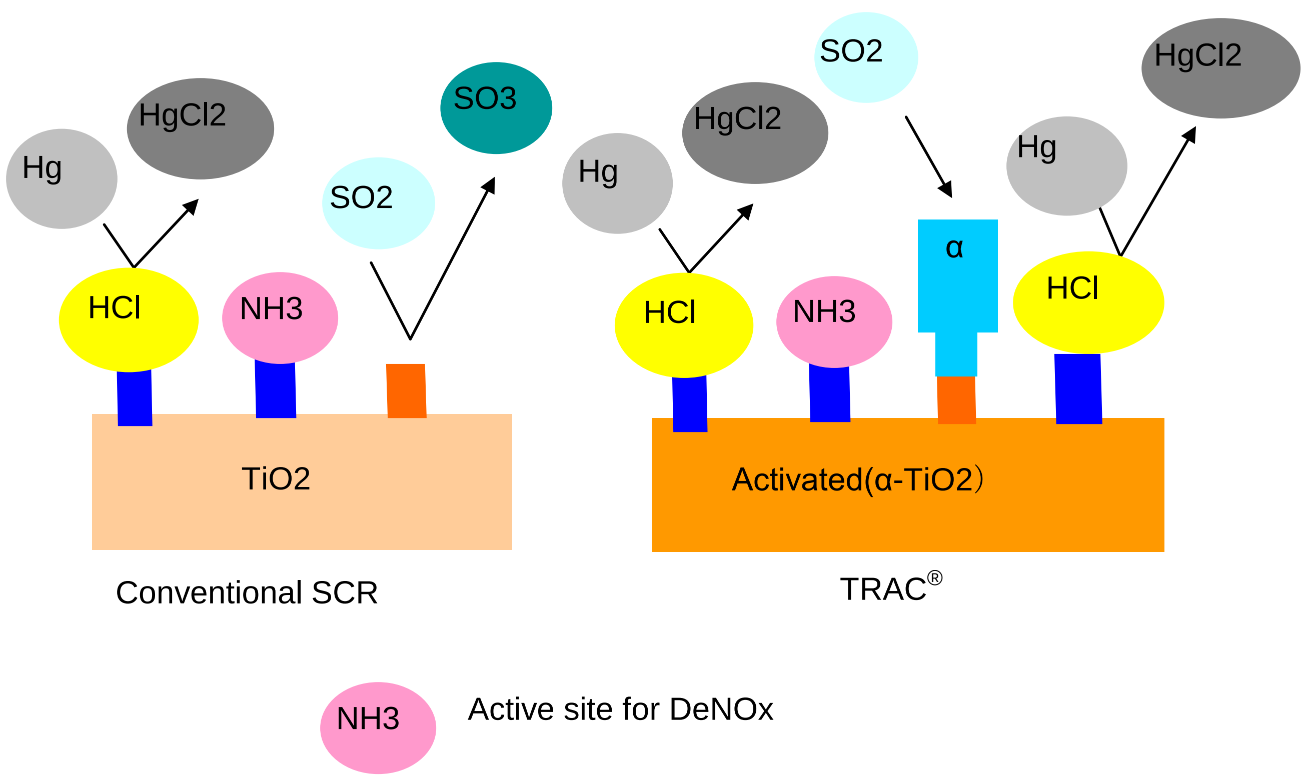


Figure 7 Proposed Reaction Model for TRAC®

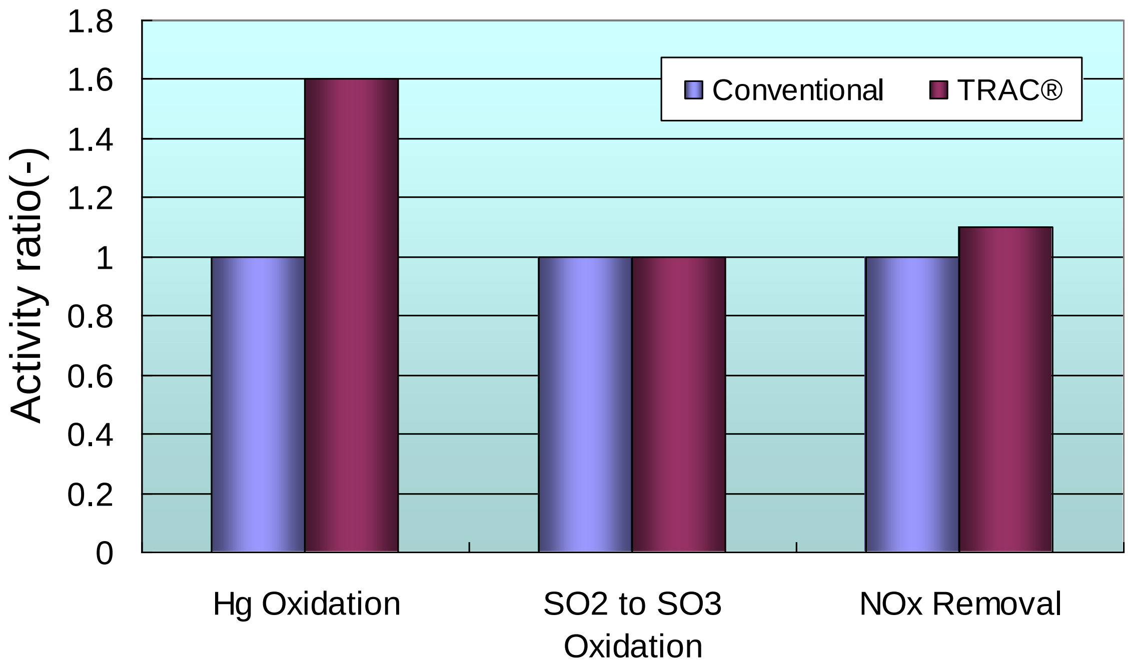


Figure 8 Performance Comparison between TRAC® and Conventional catalyst

The Effect of NH3 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[9,10]. This is especially important for Catalyst Management Plan consideration. Utilities should consider the most effective way to minimize operational cost[11]. Among them for catalyst replacement, the only factor which effect the total plant mercury mitigation efficiency is the concentration of NH_3 that is injected upstream of SCR reactor to reduce NOx. That is, the owners need only decide which layer should be replaced based on NOx activity.

As explained before, active sites for mercury oxidation reaction seems to be adjacent to or the same as the DeNOx site and therefore a large amount of NH_3 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 DeNOx but not as well as a mercury oxidizer.
To minimize the effect of injected NH_3, TRAC® has been designed to have less effect of NH_3 from the economical point of view, even if TRAC® 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% NOx removal under actual plant condition for commercial application.

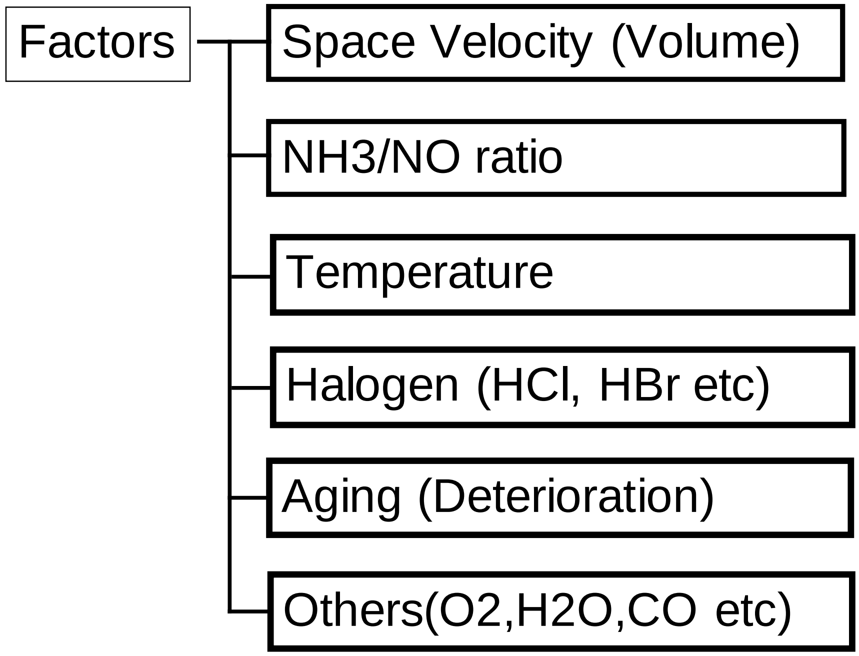


Figure 9 Factors affect on Mercury Oxidation Rate of SCR Catalyst

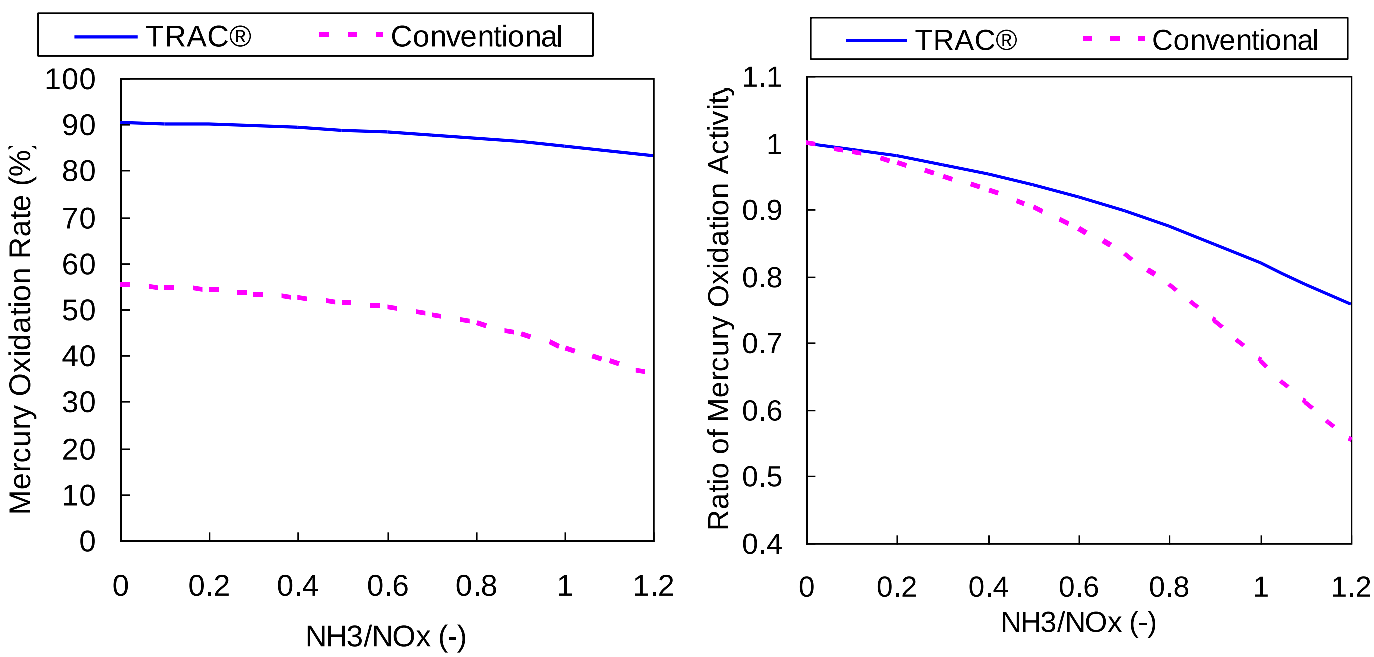
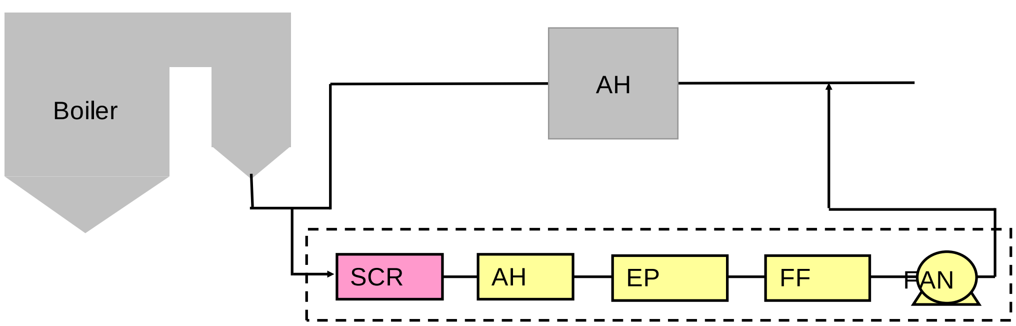


Figure 10 Effect of NH3 Injected upstream of SCR Catalyst

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.



Slip-stream Test Facility

- 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

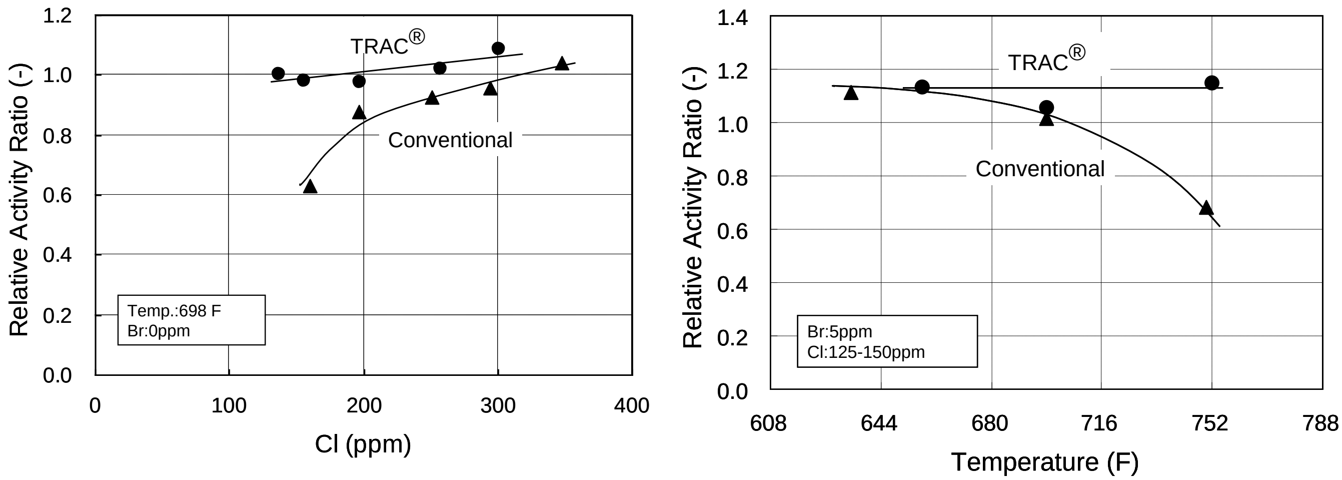


Figure 12 Mercury Oxidation Activity vs. Halogen(HCl) and Temperature

Performance Changes with Operation Hours

A sample of TRAC® 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®, Hg oxidation ratios were calculated using the following formula:

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:

EQ-1: Hg oxidation ratio = K_t / K_0

where, K_t : Hg oxidation after t hours operation (m/h)
K_0 : 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® 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® catalyst was the same as that for DeNOx. Robust mercury oxidation performance and superior durability of the TRAC® catalyst were observed through the sample catalyst testing.

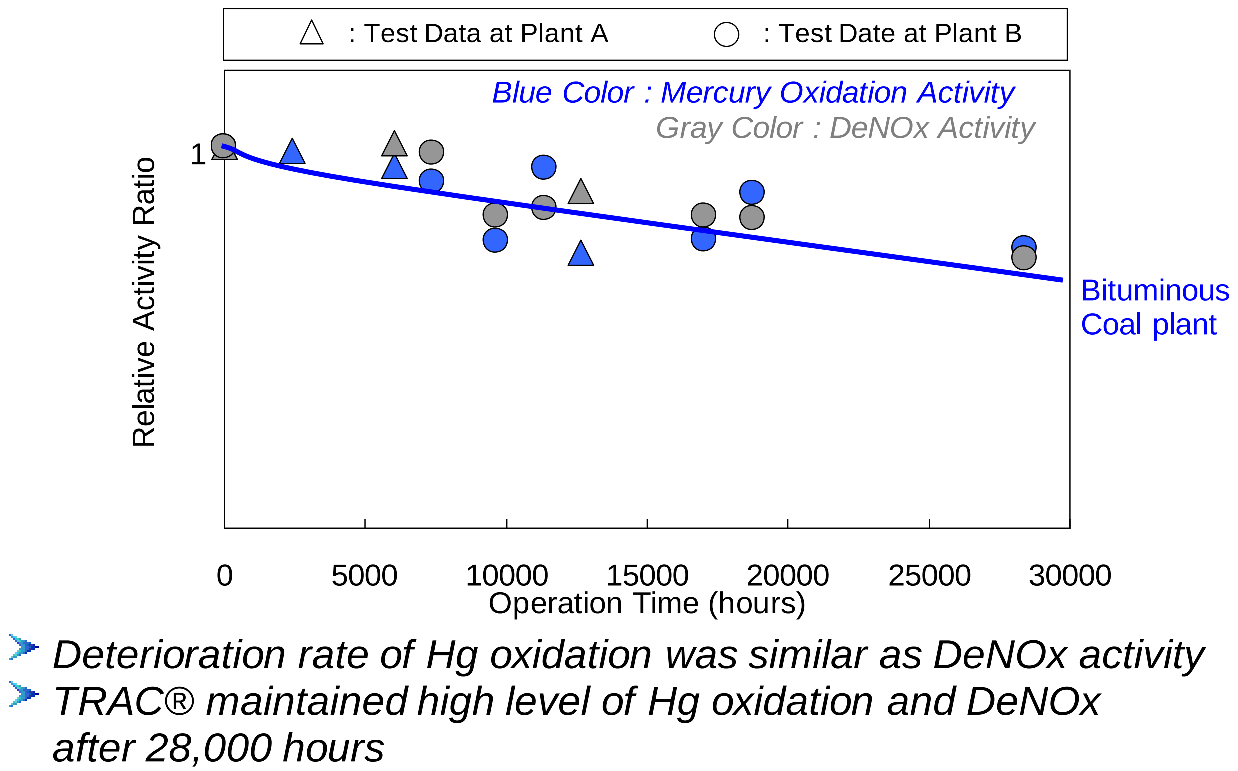


Figure 13 DeNOx and Mercury Oxidation Rate Changes with Operation Hours

TRAC® Experiences at European Commercial Plant

Three tests for Hg oxidation of TRAC® in Plant C in Europe were conducted between 2010 and 2011. The original first three layers were honeycomb catalyst. TRAC® was installed in the 4th layer. After two years of operation Hg concentrations were measured at the SCR inlet and outlet and at the TRAC® inlet. Figure 14 shows the ratio of Hg^{2+} in Plant C. The ratio was up approximately 20 to 30% between the TRAC® inlet and outlet in these tests although the ratio for 3 layers of honeycomb catalyst was just 30-40%.

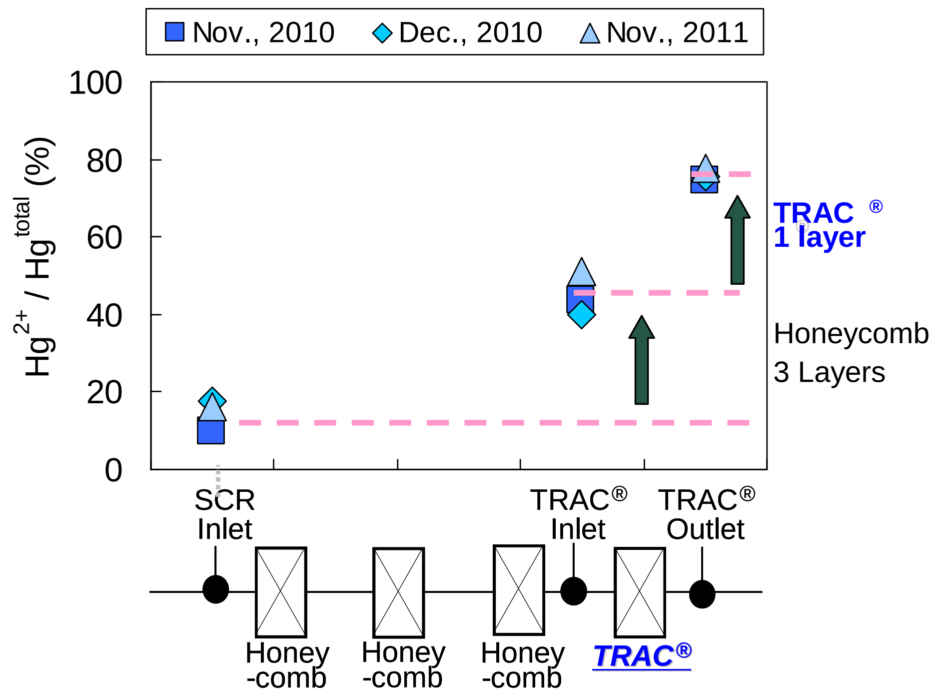


Figure 14 Hg^{2+} Ratio at each test ports across SCR Reactor and Mercury Oxidation Activity

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

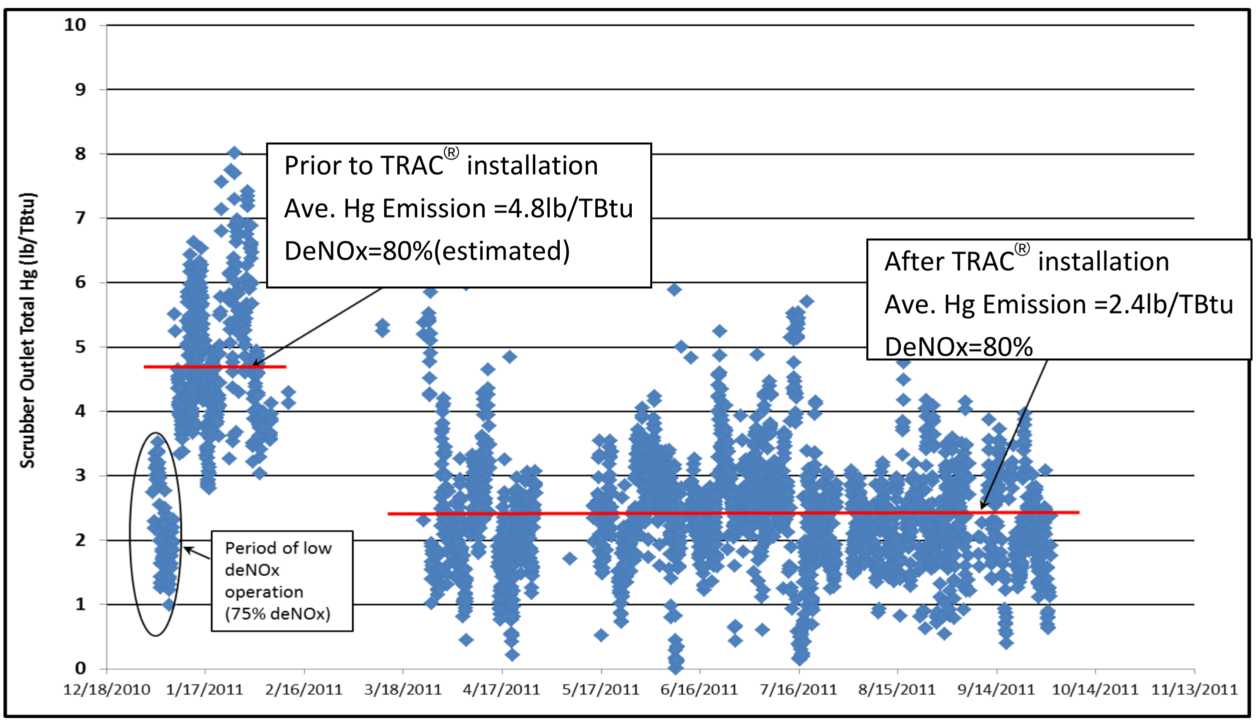
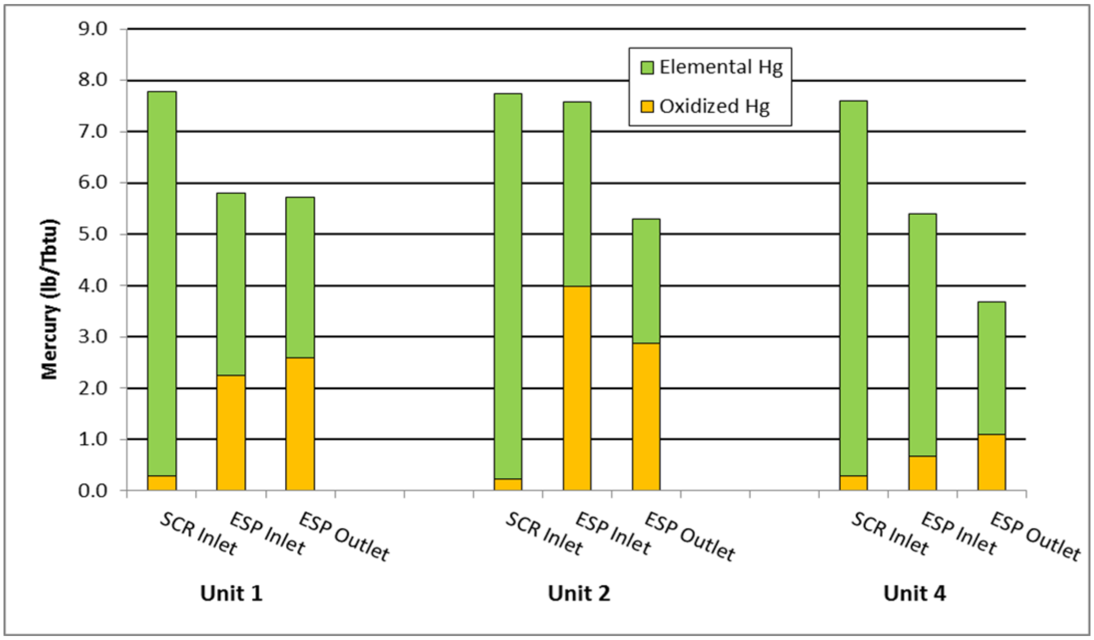


Figure 15 Mercury Continuous Emission Data (MCED) at the Stack



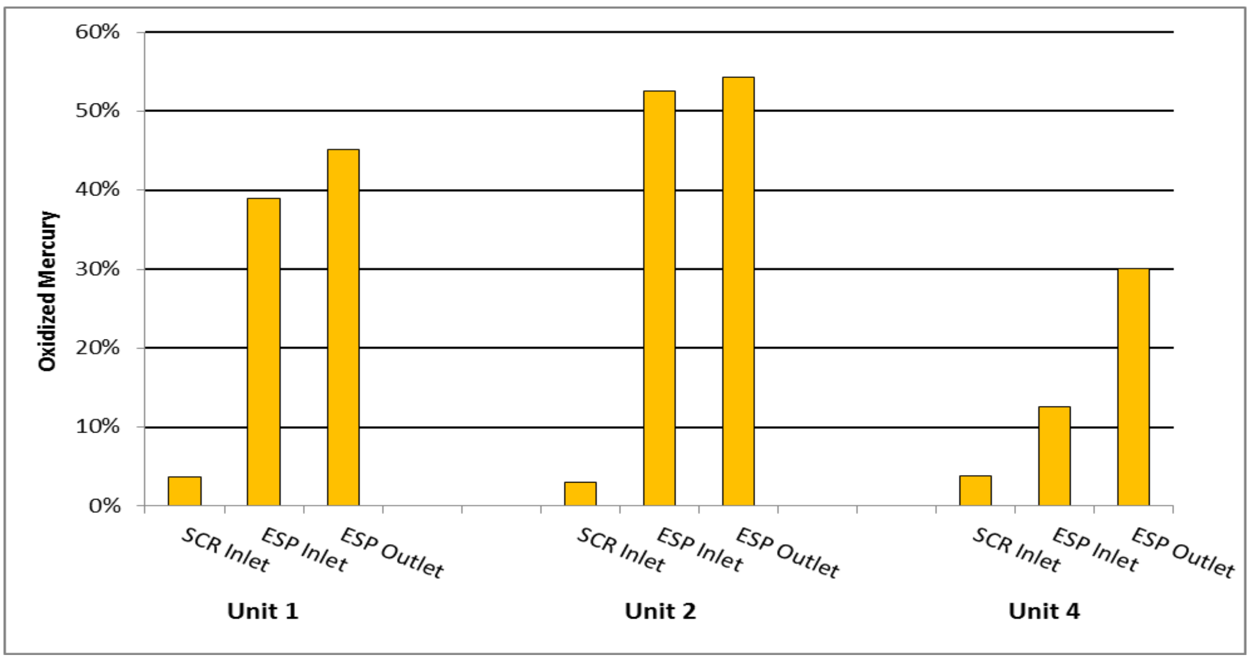


Figure 16 Percentage of Oxidized Mercury at Each Location for Unit1,2 and 4

CONCLUSION

Hitachi has developed a new commercially available SCR catalyst with a co-benefit that can enhance mercury oxidation for coal firing power plant and be applicable to any kinds of coal firing plants. After the durability demonstrations, TRAC® has been applied to commercial SCR plants not only in the US but also in Europe for an economical and reliable solution for reducing mercury emission from coal firing power plant.

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