

# **Using Your SCR as Part of Your Mercury Mitigation Strategy by Co-Benefits**

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## **Introduction**

In March 2005, the U.S. Environmental Protection Agency (EPA) announced two final rules for air pollution that apply to coal-fired power plants: the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR). CAIR is intended for the reduction of nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) emissions that contribute to high levels of ambient O<sub>3</sub> and PM<sub>2.5</sub>. CAMR separately addresses the reduction of mercury (Hg) emissions from U.S. power plants. Although CAMR was eventually vacated, mercury reductions in many cases were continually initiated on a state by state basis. These rules have since been replaced by new regulations, such as the Utility MACT Rule proposed in March 2011 which will become final in November 2011, focusing on 68(?) hazardous pollutants (HAPS). Mercury (Hg) in particular is a major focus of the new regulations, creating new challenge for mercury (Hg) emission control for Utility Power Station Owners. The drafted Utility MACT Rule further necessitates that mercury emissions must meet 11 lb/TBtu for coal <8300 btu/lb and 1 lb/TBtu for coals ≥ 8300 btu/lb on existing units and 0.040 lb/GWhr for coal <8300 btu/lb and 0.00001 lb/GWhr for coal ≥ 8300 btu/lb for any new units.

To meet these new challenges of mercury removal from coal firing plants, it is required for plant owners to select the most cost effective and reliable methods to achieve this goal. A number of technologies have been demonstrated to reduce mercury emissions such as activated carbon injection (ACI) and halogen injection to control the speciation of Hg. However, these systems potentially create other issues to the operating system such as additional cost of installing and operating the equipment, as well as the time and cost to maintain this equipment. In some cases, such as for ACI it also has other negative impacts such as not being able to sell the units fly ash due to the increase in carbon in the ash. Therefore, sometimes the easiest and most cost effective solutions are to take advantage of the co-benefit you get with existing back end equipment.

It is well known that increasing the proportion of oxidized mercury (Hg<sup>2+</sup>) existing in the form of water-soluble mercuric chloride (HgCl<sub>2</sub>), allows for high Hg emission reduction because HgCl<sub>2</sub> can be removed in downstream equipment such as Particulate Control Equipment and FGD systems. Therefore, to increase proportion of Hg<sup>2+</sup> upstream of a wet FGD system will facilitate higher overall mercury removal for the plant. Selective catalytic reduction (SCR)

catalyst has demonstrated the ability to increase  $\text{Hg}^{2+}$  by converting elemental mercury ( $\text{Hg}^0$ ) to  $\text{Hg}^{2+}$  in coal combustion flue gases.

In general, SCR catalyst can oxidize elemental form ( $\text{Hg}^0$ ) to oxidized form ( $\text{Hg}^{2+}$ ) in gaseous form and particulate form ( $\text{Hg(P)}$ ), however, mercury oxidation rate on the SCR catalyst correlates to the  $\text{SO}_2$  oxidation/conversion rate which forms  $\text{SO}_3$  that can cause air heater fouling, flue corrosion and visible stack plumes. Several downstream  $\text{SO}_3$  mitigation technologies have become commercially available in recent years, but these systems can have high initial and operating costs, performance limitations and maintenance concerns. Therefore an SCR catalyst with high  $\text{Hg}^0$  oxidation activity and low  $\text{SO}_2$  to  $\text{SO}_3$  conversion rate is optimal, especially for high sulfur coal firing plants in the U.S. for the most economical solution.

The effect of SCR catalyst on  $\text{Hg}^0$  oxidation appears to be dependent on coal type. Power plants burning high chlorine (Cl) coals, such as U.S. eastern bituminous coals, tend to show relatively high  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  conversion across the SCR.

Although power plants burning low chlorine (Cl) coals, such as PRB coals in the U.S., tend to show limited or no  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  conversion across SCR catalyst. In such application, it would be beneficial to us an enhanced mercury oxidation catalyst to achieve higher mercury removal across the plants air quality control systems (AQCS).

Through extensive research and development, pilot testing, and field demonstration, Hitachi has successfully developed a new type of SCR catalyst, TRAC<sup>TM</sup>, which satisfies the high  $\text{Hg}^0$  oxidation and low  $\text{SO}_2$  oxidation requirements for low chlorine coal-fired power plants. TRAC<sup>®</sup> has been tested and demonstrated in the several slipstream pilot facilities in the U.S successfully. TRAC<sup>®</sup> has been commercially available with full mercury oxidation guarantees since its first installation in a 640MW PRB firing U.S. plant in 2008.

Since 2008 BHK has supplied TRAC<sup>®</sup> catalyst with high mercury oxidation activity to several utilities world wide including to Plant Miller Units 1 & 2 and Plant Barry Unit 5 within the Southern Company fleet of SCRs.

## Development of Enhanced Mercury Oxidation (TRAC) Catalyst

shown in Figure 1 because both  $\text{Hg}^0$  oxidation and the  $\text{SO}_2$  oxidation activities are promoted by Hitachi has been continuously improving the catalyst performance while lowering  $\text{SO}_2$  to  $\text{SO}_3$  conversion since SCR was first applied in U.S. power plants firing bituminous coals. However, lowering  $\text{SO}_2$  to  $\text{SO}_3$  conversion has also resulted in decreasing Hg oxidation because there is a correlation between Hg oxidation activity and  $\text{SO}_2$  oxidation activity. With conventional catalysts, by adding active catalyst components to increase  $\text{Hg}^0$  oxidation activity, the  $\text{SO}_2$  to  $\text{SO}_3$  conversion activity will also increase as the same active sites in the catalyst components.

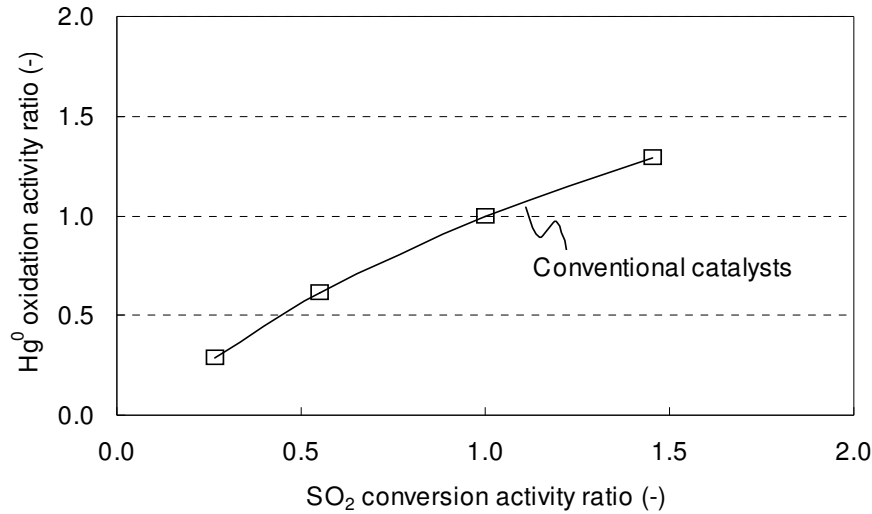


Figure 1. Relationship between  $\text{SO}_2$  conversion and  $\text{Hg}^0$  oxidation across conventional catalyst.

The fundamental reaction mechanisms of Hg oxidation and  $\text{SO}_2$  to  $\text{SO}_3$  conversion across SCR catalysts were investigated in Hitachi laboratory to ascertain the most appropriate catalyst composition and manufacturing methods for the new catalyst.

Figure 2 shows the test results for  $\text{Hg}^0$  oxidation of the TRAC catalyst and conventional catalyst at the pilot-scale test facility. It is observed that the  $\text{Hg}^0$  oxidation activity of TRAC<sup>TM</sup> catalyst was 1.4 – 1.7 times higher than that of the conventional catalyst while improving  $\text{NO}_x$  removal activity and maintaining the same  $\text{SO}_2$  to  $\text{SO}_3$  conversion activity.

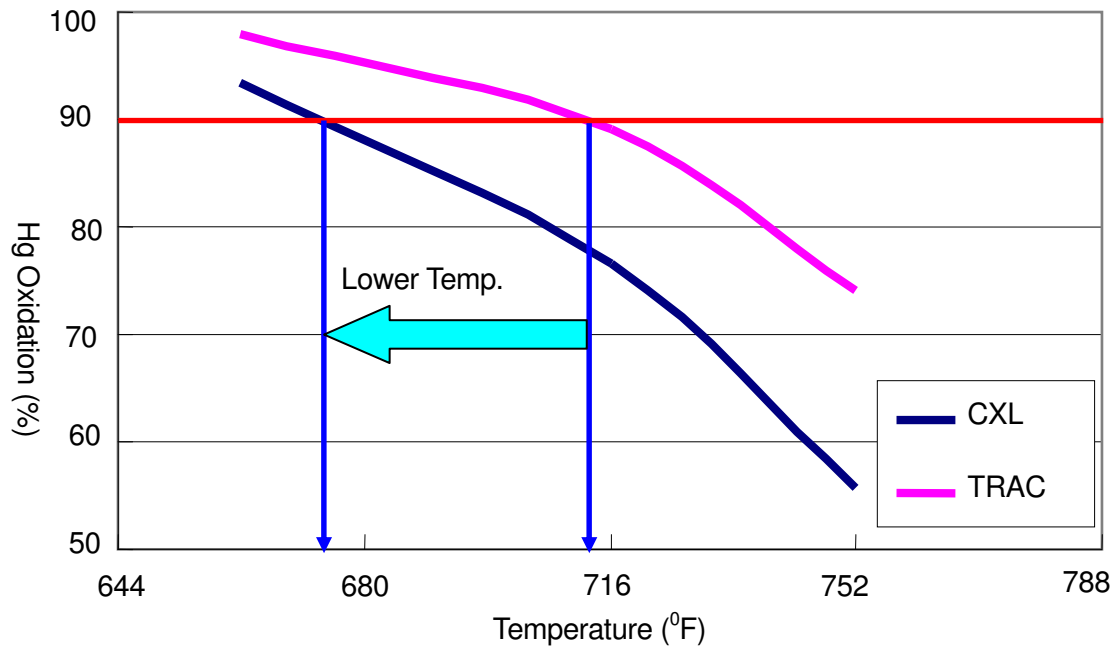


Fig. 2. Hg0 oxidation of TRAC catalyst at Pilot-scale test facility

## **Slipstream Reactor (SSR) Testing at a Power Plant Burning PRB**

In order to ascertain the performance of the TRAC catalyst in an actual operating unit, SSR testing was conducted at a northern U.S. power plant with a 640 MW wall-fired boiler and burning 100% PRB fuel, which had a SCR system installed in 2003. Following the SCR, the flue gases pass through an air heater, an electrostatic precipitator (ESP), and then a wet flue gas desulfurization (WFGD) system (Figure 3).

The SSR with four layers of TRAC catalyst is installed next to the existing SCR reactor. The TRAC catalyst is specifically designed for sub-bituminous fuels containing very low amounts of chlorine. A schematic diagram of the SSR testing is shown in Figure 3. In order to represent actual SCR operating conditions, the inlet duct of the SSR is connected directly to the inlet of the full-scale SCR, just above the first layer of catalyst. This gas contains an adequate amount of ammonia for the DeNOx process. Actual flue gas was extracted from the commercial SCR inlet flue and introduced into SSR by ID fan, and then returned to commercial SCR outlet duct. Flue gas velocity and temperature were fully controlled by a control panel of SSR during testing. No halogen injection was performed during the testing.

In addition to mercury oxidation, inlet and outlet NOx and ammonia slip are measured simultaneously in order to ascertain the interaction between mercury oxidation and DeNOx at various conditions and time intervals. Each layer of SSR catalyst is equipped with air sootblowers, which are operated automatically or at user-specified intervals. The SSR is also equipped with electrical heaters to keep the same temperature across all catalyst layers. An induced draft fan and gas flow control damper is provided at the SSR outlet in order to allow for adjustment of the amount of gas flow through the SSR. Instrumentation is provided in the SSR at various locations to measure temperature, catalyst pressure drop and total gas flow. A local control panel is used to provide user interface at the SSR and a PLC is included with for communication with the plant DCS. All of this data is acquired and stored on an hourly basis for future trending and analysis.

To address the primary objective of this test program, mercury sampling was periodically conducted at test ports throughout the test program. The SSR is equipped with test ports at the inlet, outlet and an intermediate point for performing measurements using the Ontario Hydro Method (OHM). Along with mercury speciation, other measurements simultaneously made include HCl concentration at the SSR inlet, ammonia and NOx concentration at the SCR inlet and outlet and total gas flow. The mercury sampling activities in this test program were divided into five major events: January, April, July, and December 2006, and April 2007. Figure 6 summarizes Hg speciation profiles at each sampling point across SSR.

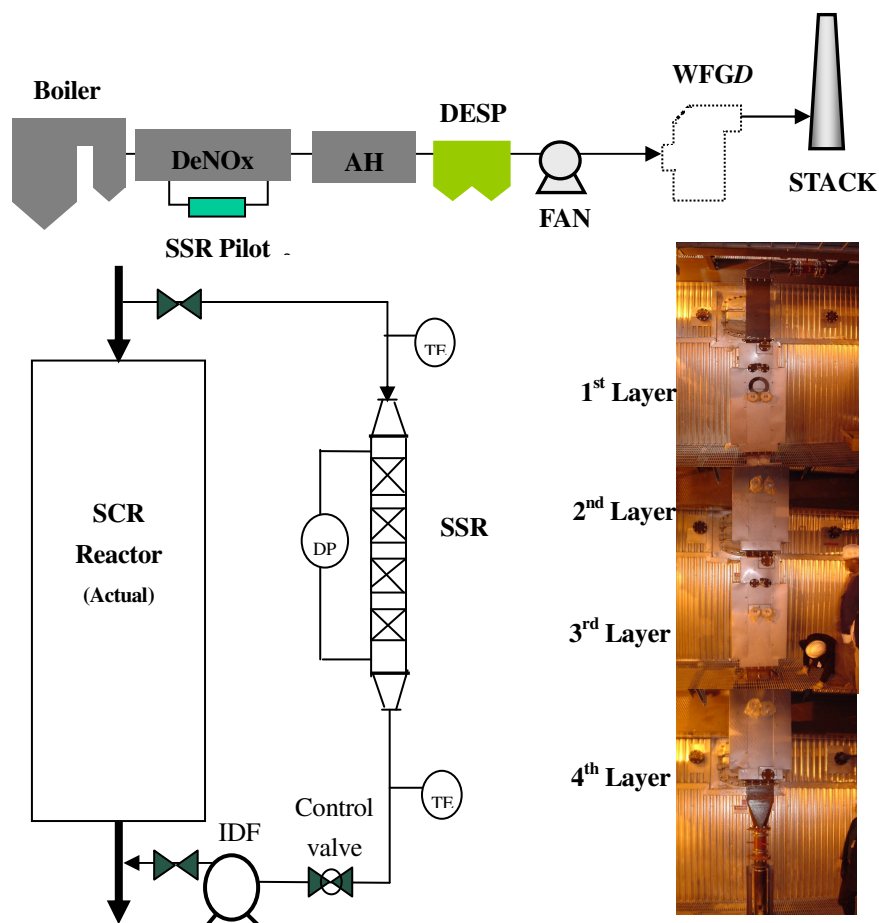


Fig. 3. Schematic of SSR testing configuration at a Power Plant in Northern US.

Table 1 shows the general plant information for this SSR test. Tables 2 and 3 show the representative coal and flue gas data from this testing, respectively. Based on initial measurements at about 1,000 hours of operation, HCl concentration in the flue gas was very low (1 - 4 ppm) due to low chlorine content (33 mg/kg) in the PRB coal, which is a good representation case for mercury oxidation for low chlorine coal-fired power plant.

**Table 1. General Plant Information for SSR.**

Plant Location	Northern US
Unit Capacity	640MW at 100% load
Fuel	PRB Coal
NH <sub>3</sub> Injection	Yes by utilizing commercial SCR inlet flue after NH <sub>3</sub> injection
NH <sub>3</sub> /NO <sub>x</sub> mole ratio	Same as commercial SCR
Catalyst	TRAC <sup>TM</sup> (Designed to achieve 90% NO <sub>x</sub> removal)
SSR Testing Period	December 2005 to April 2007

**Table 2. Representative Coal Analysis Data for Testing Plant.**

Heating Value	8280 Btu/lb, as received
Moisture	30 %, as received
Ash	5.2 %, as received
Sulfur	0.3 %, as received
Chlorine	33 mg/kg
Hg	0.1 mg/kg

**Table 3. Representative Flue Gas Data for SSR Testing.**

Inlet NO <sub>x</sub>	260 – 300 ppm
O <sub>2</sub>	2.9 % (Dry)
CO <sub>2</sub>	15 % (Dry)
H <sub>2</sub> O	12.6 %
HCl	1 - 4 ppm

In order to obtain catalyst durability information under the actual flue gas condition, the SSR was operated for more than one year, from December 2005 to April 2007. During the test period, Hg speciation profiles at SSR inlet, middle, and outlet were measured by the Ontario Hydro Method (OHM) for five times: January, April, July, and December 2006 and April 2007. Figure 4 summarizes Hg speciation profiles at each sampling point across SSR.

The SSR demonstration test for the PRB firing plant showed very good mercury oxidation. As shown in Figure 4, it was observed that significant amount of Hg<sup>0</sup> was oxidized to Hg<sup>2+</sup> across the catalyst in the SSR for all sampling events even with very low Hg<sup>0</sup> content level at the inlet of SSR. Hg oxidation capability of the TRAC<sup>TM</sup> catalyst remained robust after one-year operation. Durability of TRAC<sup>TM</sup> catalyst was confirmed. More than 80% mercury oxidation was obtained across the catalyst in the SSR after 8,000 hours, although HCl concentration in flue gas for PRB firing was very low.

One of the major objectives of this SSR testing is to quantify the mercury oxidation rate over a long period of time. Hg oxidation rate was calculated using the formula below.

$$\text{Hg Oxidation rate (\%)} = \{(\text{Inlet Hg}^0 - \text{Outlet Hg}^0) / \text{Inlet Hg}^0\} \times 100$$

Figure 5 shows the mercury oxidation rate during total of 8,000-hour operating time. HCl concentration at the inlet of SSR was deviated at each test run within the range shown in Table 3. Hg oxidation rate for the TRAC<sup>TM</sup> catalyst remained high during one-year test period under low chlorine level condition, even though the results indicate a gradual decrease in mercury oxidation over time. The mercury oxidation deterioration rate of TRAC<sup>TM</sup> catalyst was the same as that for DeNO<sub>x</sub>. Robust mercury oxidation performance and superior durability of the TRAC<sup>TM</sup> catalyst were observed and confirmed through the SSR testing. Therefore, full-scale commercial application of the TRAC<sup>TM</sup> catalyst becomes the next logic step.

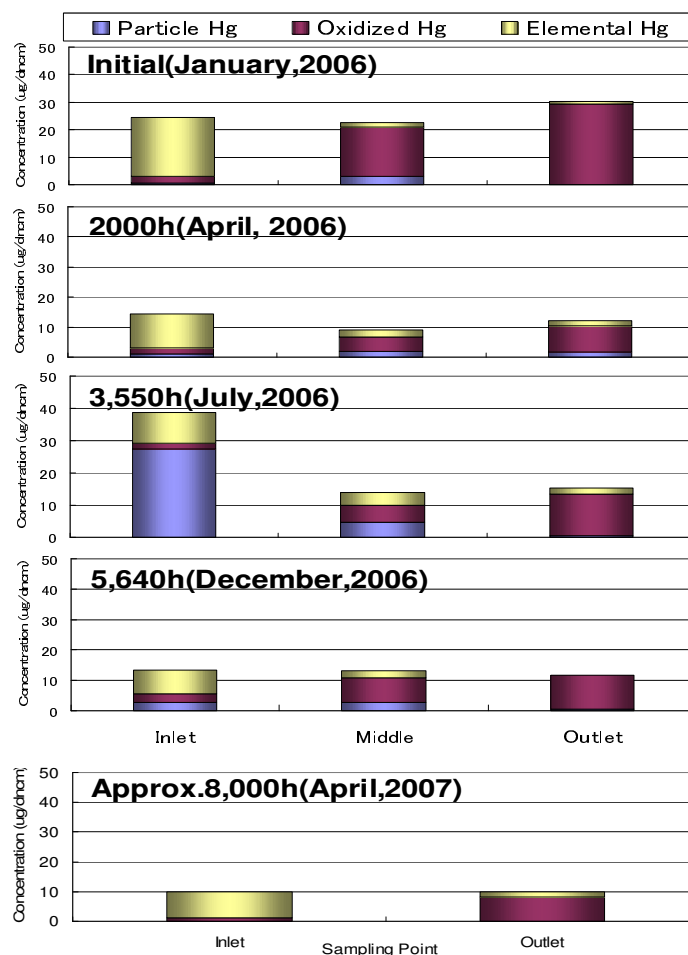


Fig. 4. Hg Speciation Measurement Results at SSR.

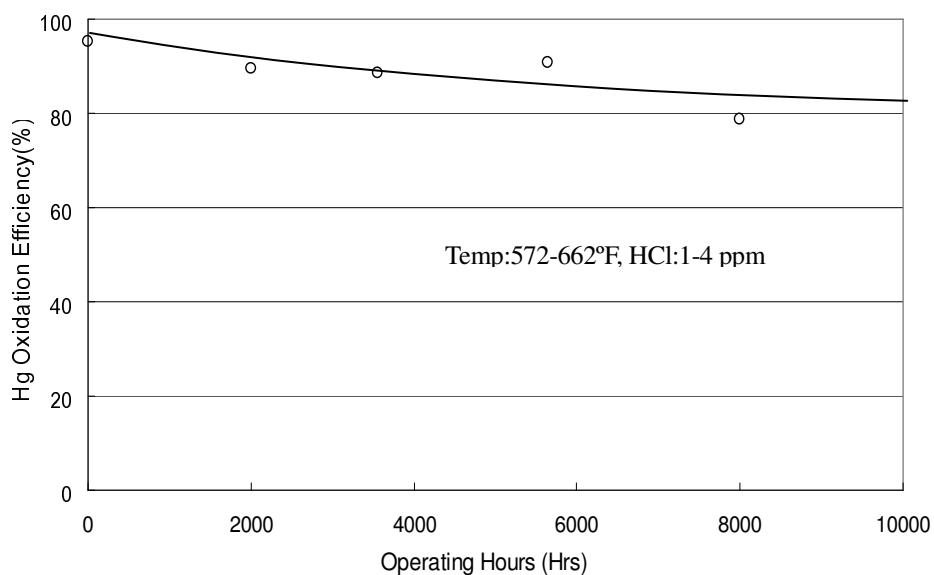


Fig. 5. Mercury oxidation efficiency with operating hours at SSR.



## Large-Scale Pilot Test (MRC) at a Power Plant Burning Bituminous

Hitachi conducted a pilot testing at a low sulfur bituminous coal firing plant at a Southern U.S. power plant. This plant is equipped with air quality control systems (AQCS) downstream of the SSR as shown in Figure 6. Actual flue gas was extracted from the outlet of an actual low sulfur coal fired boiler and introduced into SSR-AQCS system by an ID fan, and then returned to actual Air heater (AH) outlet duct. 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 7 show 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<sup>®</sup> under certain flue gas conditions.

- Fires Low Sulfur Bituminous Coal (75MW)
- Flue gas was introduced to slip-stream test rig from upstream of AH
- Measured by SCEM

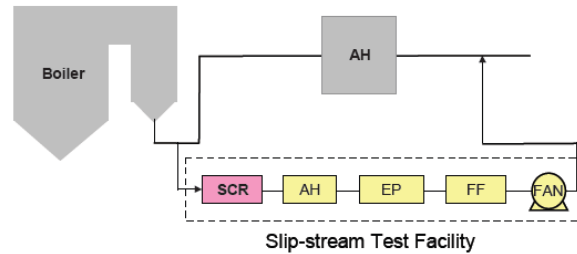
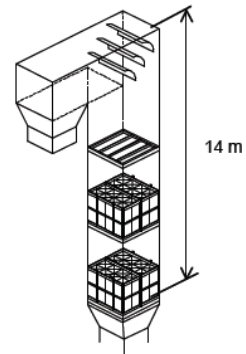


Figure 6 Pilot test facility in the US

Flue Gas Conditions

Item	Unit	Condition
Gas Flow Rate	m <sup>3</sup> N/h	10,705-17,842(10,705)
Temperature	C	330-400(370)
NO <sub>x</sub>	ppm	180-230
Cl	ppm	110-350(130)
Br	ppm	0-50(0)
NO <sub>x</sub> Removal	%	90
slip-NH <sub>3</sub>	ppm	2

( ) : Standard Condition



- Two-Layers of catalyst installed for the test
- Catalyst Volume: 6.7m<sup>3</sup>

Figure 7. Condition for SSR testing and Structure of Pilot Test

Figures 8 and 9 show mercury oxidation activity for both conventional SCR catalyst and TRAC<sup>®</sup> against halogen (Cl) concentration and flue gas temperature respectively.

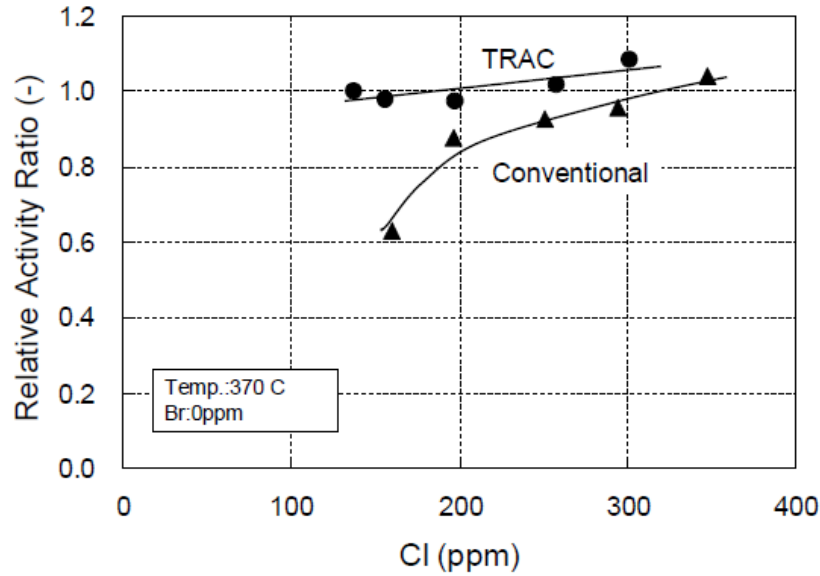


Figure 8 Mercury oxidation activity of the catalyst vs. halogen (Cl) concentration

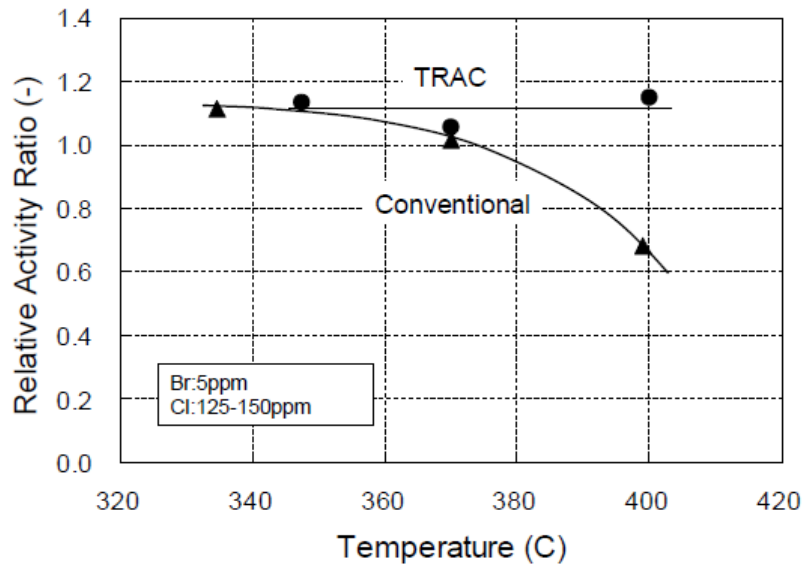


Figure 9 Mercury oxidation activity of the catalyst vs. flue gas temperature

As can be seen in both figures, TRAC<sup>®</sup> has excellent mercury oxidation performance at both lower halogen concentration and high flue gas temperature zones compared to conventional catalysts.

## Full-Scale Commercial Applications

### Northern US Power Plant Unit 4

Upon successful completion of SSR testing for TRAC catalyst performance and durability demonstration, one full-layer of TRAC catalysts was applied to the full-scale SCR reactor as a replacement at the same power plant in order to ascertain the performance of the TRAC catalyst in an actual operating unit. Figure 10 shows the general information for the catalyst replacement application. The 1<sup>st</sup> initial layer of existing catalyst was removed and TRAC catalyst was installed in the 4<sup>th</sup> layer. The general plant information is shown in Table 1. Tables 4 and 5 show the detail coal analysis data and flue gas data, respectively.

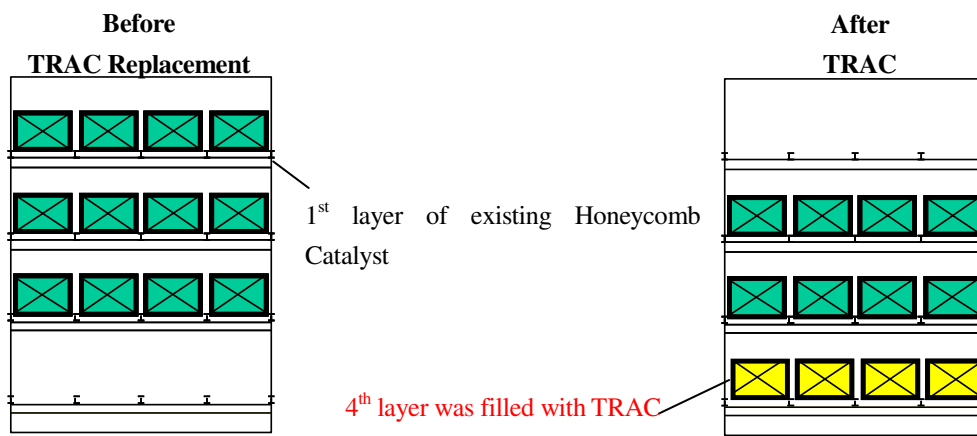


Fig. 10. General information for replacement catalyst with TRAC at a full-scale SCR reactor application

**Table 4. Coal Analysis Data.**

Heating Value	8120 – 8400 (Btu/lb), as received
Moisture	28.7 – 31.0 (%), as received
Ash content	4.9 - 5.7 (%), as received
Volatile matter	17.9 -33.6 (%), as received
Sulfur	0.27 – 0.36 (%), as received
Chlorine	25 – 54 (mg/kg)
Fluorine	33 – 61 (mg/kg)
Bromine	ND
Hg	0.1 (mg/kg)

**Table 5. Flue Gas Data.**

Temperature	384 – 394 ( <sup>o</sup> C)
Moisture	11.0 – 13.8 (%)
O <sub>2</sub>	2.9 - 3.1 (% , Dry)
CO <sub>2</sub>	16.0 – 16.6 (% , Dry)
NO <sub>x</sub>	297 – 336 (ppm)
HCl	0.42 – 0.57 (ppm)
Cl <sub>2</sub>	0.04 – 0.07 (ppm)
HBr	0.01 – 0.13 (ppm)

The TRAC<sup>TM</sup> catalyst was supplied and installed into the reactor and the operation started in June 2008. Hg speciation profiles at WFGD inlet and stack inlet locations were measured by

using plant Hg Continuous Emission Monitor (CEM) system. The effect of TRAC<sup>TM</sup> catalyst on Hg oxidation was determined by comparing the results during two Hg sampling events, April 2008 (before TRAC<sup>TM</sup> replacement) and June 2008 (after TRAC<sup>TM</sup> replacement). For each event, Hg speciation profiles at the WFGD inlet and WFGD outlet (stack inlet) were measured by using the plant Hg Continuous Emission Monitor (CEM) system.

The effect of TRAC<sup>TM</sup> catalyst on Hg speciation was determined by comparing the results obtained during the April 2008 sampling event before TRAC<sup>TM</sup> replacement (existing 3 layers w/o TRAC<sup>TM</sup>) and June 2008 sampling event after TRAC<sup>TM</sup> replacement (existing 2 layers plus one TRAC<sup>TM</sup> layer). Hg speciation profiles at the WFGD inlet and WFGD outlet (stack inlet) for each sampling event are shown in Figure 11. The presence of TRAC<sup>TM</sup> catalyst significantly impacted the Hg speciation profile at the inlet of WFGD system. In the absence of TRAC<sup>TM</sup> catalyst (existing 3 layers w/o TRAC<sup>TM</sup>), the ratio of Hg<sup>2+</sup>/Hg(total) at the inlet of WFGD averaged about 40%. The presence of TRAC<sup>TM</sup> catalyst (existing 2 layers plus one TRAC<sup>TM</sup> layer) increased this ratio to about 70%. Observation showed that the presence of the TRAC<sup>TM</sup> catalyst significantly increased Hg<sup>2+</sup> level at the inlet of WFGD system.

As a result of the increased Hg<sup>2+</sup> at WFGD inlet, total Hg removal across WFGD was increased from 30% (before TRAC<sup>TM</sup> replacement) to 70% (after TRAC<sup>TM</sup> replacement). Results from the full-scale application are in good agreement with SSR testing results and demonstrate that the Hg<sup>0</sup> oxidation activity of the TRAC<sup>TM</sup> catalyst was significantly higher than that of the conventional catalyst with low chlorine coal. Figure 12 presents the Hg CEMS monitoring results before and after TRAC replacement.

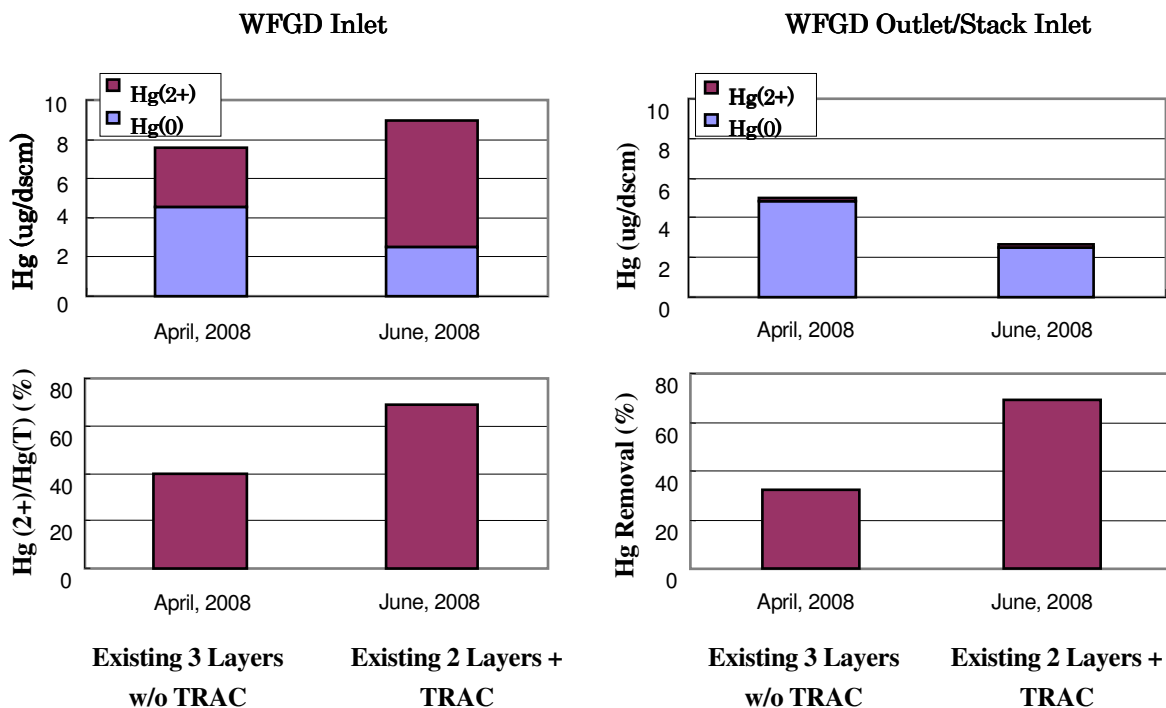


Fig. 11. Effect of TRAC catalyst on Hg oxidation and removal across the WFGD before and after TRAC<sup>TM</sup> replacement.

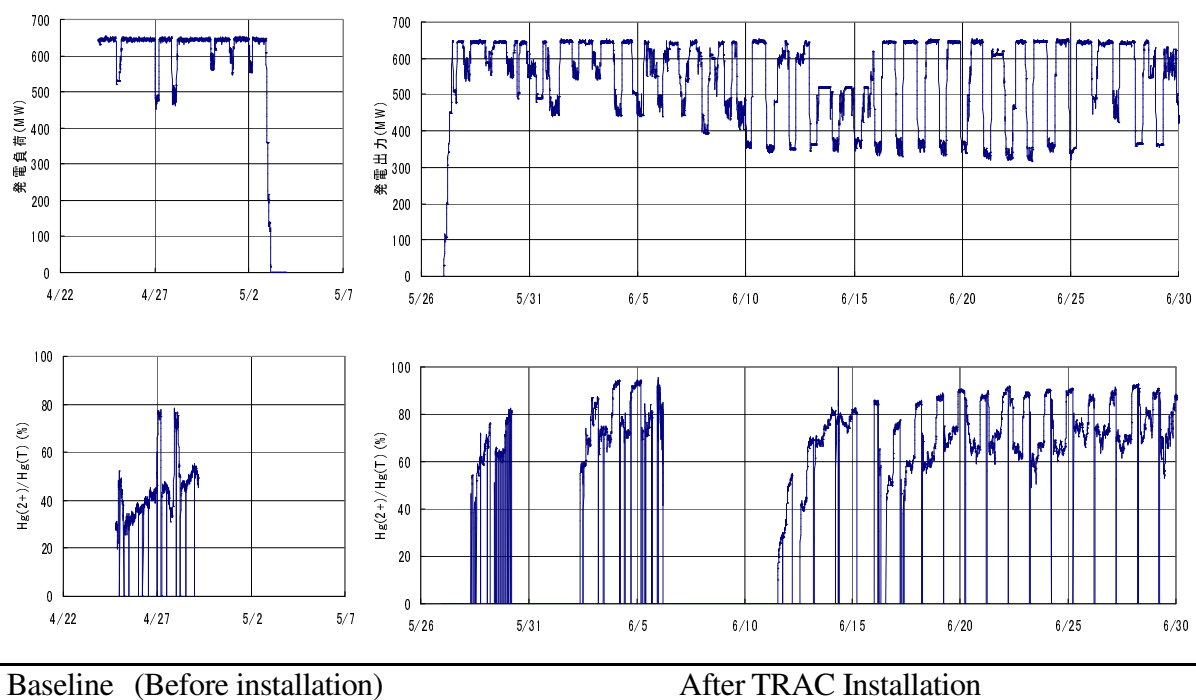


Figure 12. Hg CEMS monitoring results before and after TRAC replacement

**Southern Company Plant Miller 1 & 2 and Barry 5**

## Economic Benefit of TRAC Catalyst

	<b>3 Regular Layers</b>	<b>1 TRAC + 2 Regular Layers</b>	<b>3 TRAC Layers</b>
ACI Injection (lbs/MACF)	2.6	1.8	0
ACI Cost (\$M/yr)	\$2.6/yr	\$1.8/yr	0
Hg Oxidation @ APH Outlet (%)	90%	95	95

Note:

1. Assume \$1/lb for untreated AC

	<b>3 Regular Layers</b>	<b>1 TRAC + 2 Regular Layers</b>	<b>3 TRAC Layers</b>
Oxidized Hg (%) (Without Br Injection)	41%	56%	71%
Br Injecting Concentration (For 90% Hg Oxidation)	25 ppm	4 ppm	3 ppm
Halogen Cost (\$K/yr)	180K	305K	20K

Note:

1. 52% CaBr<sub>2</sub> solution at \$0.9/lb
2. Flue gas Temperature at SCR inlet: 741 Degree F

For PRB application, some halogen injection shall be required to achieve 90% mercury oxidation across the catalyst. TRAC will be effective to reduce operation cost by lowering halogen injection required.

## Summary

Hitachi's commercially available plate-type catalyst, TRAC<sup>®</sup> greatly enhances mercury oxidation for coal firing power plants even for coals with low chlorine content. TRAC<sup>®</sup> catalyst has an Hg<sup>0</sup> oxidation activity that was 1.6 times higher than that of the conventional catalyst, while maintaining the same SO<sub>2</sub> to SO<sub>3</sub> conversion activity. More than 80% mercury oxidation was obtained in the SSR after one-year testing. The results also confirmed that the deactivation rate for mercury oxidation was almost the same as that for DeNO<sub>x</sub> reaction. Results from the full-scale commercial application are in good agreement with SSR results and demonstrate that the Hg<sup>0</sup> oxidation activity of the TRAC<sup>®</sup> catalyst was significantly higher than that of the conventional catalyst for low chlorine coal.

TRAC<sup>®</sup> catalyst can be applied to coal-fired power plants as an integral step to enable cost-effective mercury control strategy.