

MERCURY OXIDATION SCR CATALYST FOR POWER PLANTS FIRING LOW CHLORINE COALS

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ABSTRACT

Mercury exists in three forms in coal combustion flue gases: elemental (Hg^0), oxidized (Hg^{2+}), and particulate ($\text{Hg}(\text{p})$). Hg^{2+} and $\text{Hg}(\text{p})$ are readily removed from flue gases using a typical Air Quality Control System (AQCS) including a wet-FGD. Therefore mercury oxidation is very important to the overall control of mercury emissions from coal-fired power plants. The effect of selective catalytic reduction (SCR) catalyst on mercury oxidation appears to be dependent on coal type, particularly the chlorine (Cl) level. Power plants burning bituminous coals, which generally contain high amounts of Cl, have shown high mercury oxidation across the conventional SCR catalyst. However, for power plants burning low chlorine coals such as PRB, only limited or insignificant mercury oxidation was observed across the conventional SCR catalysts. Therefore, it is essential to develop new SCR catalyst for low chlorine coal-fired boilers to achieve high mercury oxidation and high overall mercury removal.

A new SCR catalyst, TRAC™, has been developed by Hitachi to enhance mercury oxidation for low chlorine coal-fired boilers while maintaining low SO_2 to SO_3 conversion. Hitachi conducted a slip stream reactor (SSR) testing with four layers of TRAC™ catalysts. The SSR was installed next to the existing SCR reactor at a US power plant firing PRB and was operated for more than one year under actual SCR operating conditions to determine long term catalyst performance and durability. It was demonstrated that more than 80% mercury oxidation was obtained in the SSR after one-year testing even as the chlorine concentration in flue gas was extremely low. The results confirmed that the deactivation rate for mercury oxidation was almost the same as that for DeNOx reaction. Robust mercury oxidation performance and superior durability of the TRAC™ catalyst were observed and confirmed through the SSR testing.

After the successful SSR demonstration test, TRAC™ catalyst was installed on the same US power plant in June 2008. With one full layer of TRAC™ catalyst installed in the actual SCR system, the oxidized mercury (Hg^{2+}) was improved to 70% at WFGD inlet from 40% before catalyst replacement. The total Hg removal across WFGD was increased from 30% to 70%. The full-scale test program further demonstrated that the TRAC™ catalyst can significantly enhance mercury oxidation for power plants firing low chlorine coals.

INTRODUCTION

A number of technologies, such as activated carbon injection (ACI) and halogen injection to control the speciation of Hg, have been demonstrated to reduce mercury emissions. It is well known that increasing the proportion of oxidized mercury (Hg^{2+}), which is present in the form of water-soluble mercuric chloride (HgCl_2), allows for high Hg emission reduction because HgCl_2 can be removed in downstream equipment such as ESP and FGD systems^{1,2}. Therefore, increased mercury oxidation upstream of the FGD system will facilitate higher overall mercury removal for power plants. Selective catalytic reduction (SCR) catalyst has been shown to significantly increase mercury oxidation by converting elemental mercury (Hg^0) to Hg^{2+} in coal combustion flue gases³⁻⁵.

However, while oxidizing elemental form (Hg^0) to gaseous form (Hg^{2+}) and particulate form ($\text{Hg}(\text{P})$), conventional SCR catalysts could also increase SO_2 oxidation which forms SO_3 that can cause air heater fouling, flue corrosion, and visible stack plumes. Several downstream SO_3 mitigation technologies have become commercially available in

recent years^{6,7}, but these systems can have both high initial and operating costs and maintenance concerns. Therefore an advanced SCR catalyst, which can achieve high Hg⁰ oxidation activity with low SO₂ to SO₃ conversion, will be the most economical solution for bituminous coal-fired power plants.

In general, the effect of SCR catalyst on Hg⁰ oxidation appears to be dependent on coal type. Power plants burning eastern bituminous coals, which generally contain high amounts of chlorine (Cl), tend to show relatively high Hg⁰ to Hg²⁺ conversion across the SCR catalyst. However, power plants burning low chlorine (Cl) coals, such as Powder River Basin (PRB) coal, tend to show limited or no Hg⁰ to Hg²⁺ conversion across SCR catalyst. Therefore, it is essential to develop new mercury oxidation catalysts to achieve higher mercury oxidation for power plants firing low chlorine coals while maintaining or even improving other parameters such as low SO₂ to SO₃ conversion.

Through extensive research and development, pilot testing, and field demonstration, Hitachi has successfully developed a new type of SCR catalyst, TRACTM, which satisfies the high Hg⁰ oxidation and low SO₂ oxidation requirements for low chlorine coal-fired power plants.

The goal of the testing programs was to evaluate and demonstrate the effect of TRACTM catalyst on the mercury oxidation performance in power plants firing low chlorine coals such as PRB. First, Hitachi conducted a long-term slipstream reactor (SSR) testing to gain a better knowledge of mercury oxidation behavior of the TRACTM catalyst. The SSR was installed next to the existing SCR reactor at a US power plant and was operated for about one year. The main objectives of this SSR testing were to evaluate and determine the long term catalyst performance and durability under actual SCR operating conditions. After the successful SSR demonstration test, one full-layer of the TRACTM catalyst was installed on the same US power plant in June 2008. The objectives was to verify that full-scale mercury oxidation behavior of TRACTM catalyst at an actual SCR system would be in good agreement with the SSR test results and to confirm its enhanced mercury oxidation performance at an actual low chlorine coal-fired power plant.

APPROACH

Laboratory-Scale Testing

Laboratory scale tests were conducted with simulated flue gas for evaluating Hg⁰ and SO₂ oxidation characteristics of SCR catalysts. A schematic diagram of the test apparatus is shown in Figure 1. This apparatus consists of the SCR reactor heated to the typical SCR temperature range (662-752°F), the mercury generation unit, the gas preheating (752 °F) and remixing sections, and the online NO_x and SO₂ analyzers. Flue gas components such as O₂, CO₂, SO₂, NO, and N₂ were supplied to the SCR reactor through a preheating furnace. Moisture and HCl, were also supplied to the preheating furnace as HCl solution using a tube pump. NH₃ was injected directly upstream of the SCR catalysts. Mercury concentration was adjusted by adding a variable volume of mercury-saturated gas to the carrier gas.

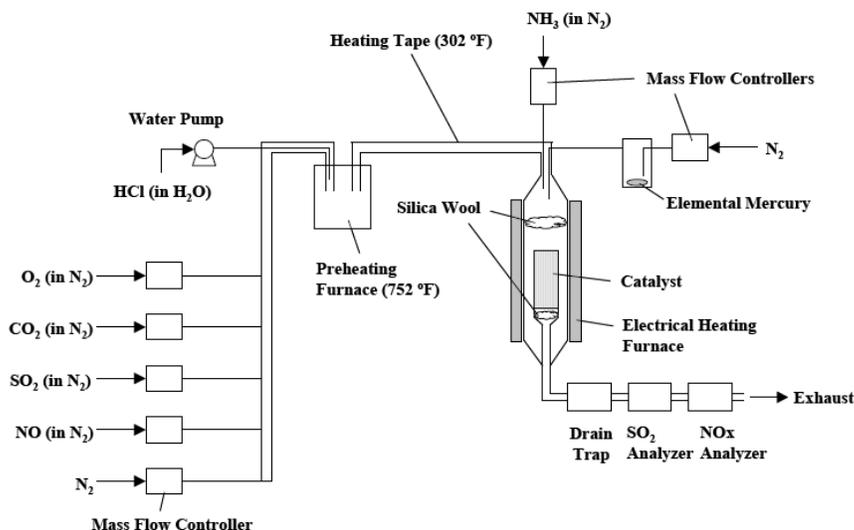


Fig. 1. Schematic of Laboratory-Scale Apparatus to Evaluate SCR Catalysts

Slipstream Reactor (SSR) Testing at the Plant

In 2005, Hitachi and a power company in northern US conducted a slipstream reactor (SSR) testing at one of the PRB fired boilers. The SSR was installed on Unit 2 in order to evaluate TRAC™ catalyst performances including durability with actual operating conditions. Unit 2 is a 640 MW wall-fired boiler, burning 100% PRB fuel, which had a SCR system installed in 2003. Following the SCR, the flue gases pass through an air heater, a electrostatic precipitator (ESP), and then a wet flue gas desulfurization (WFGD) system (Figure 2).

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 2. 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.

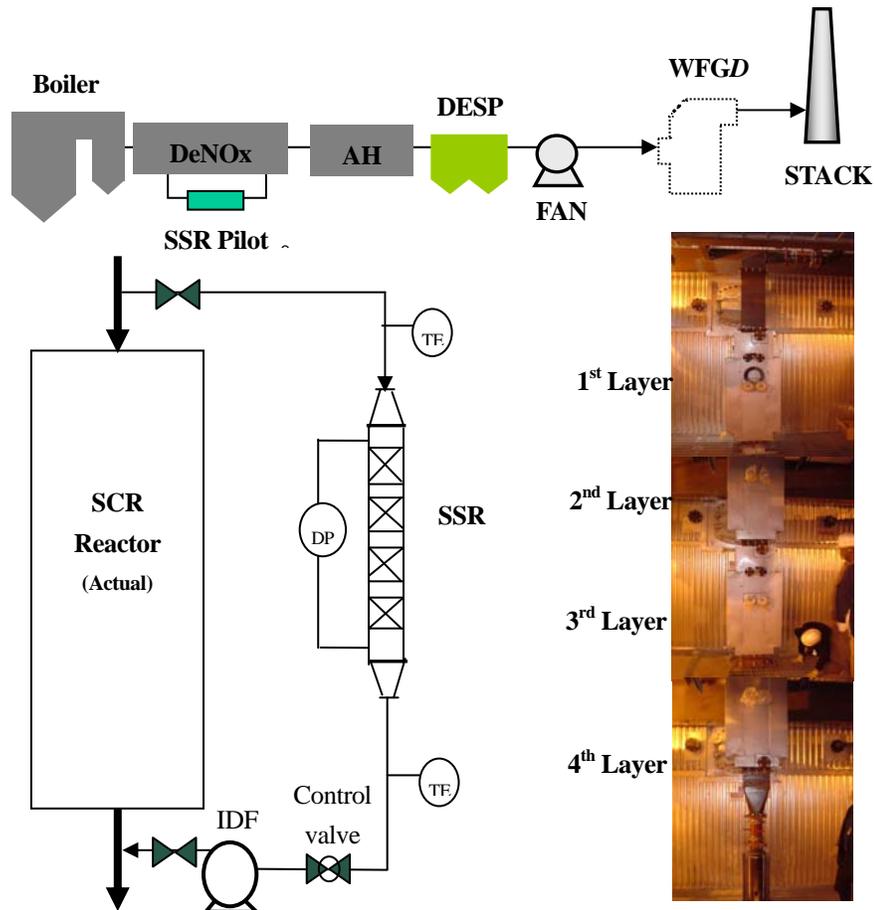


Fig. 2. Schematic of SSR testing configuration at a Power Plant in Northern US.

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.

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 ₃ Injection	Yes by utilizing commercial SCR inlet flue after NH ₃ injection
NH ₃ /NOx mole ratio	Same as commercial SCR
Catalyst	TRAC TM (Designed to achieve 90% NOx 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 NOx	260 – 300 ppm
O ₂	2.9 % (Dry)
CO ₂	15 % (Dry)
H ₂ O	12.6 %
HCl	1 - 4 ppm

Full-Scale Application

Upon successful completion of SSR testing for TRACTM catalyst performance and durability demonstration, one full-layer of TRACTM 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 TRACTM catalyst in an actual operating unit. Figure 3 shows the general information for the catalyst replacement application. Basically, the 1st initial layer of existing catalyst was removed and TRACTM catalyst was installed in the 4th 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.

The TRACTM 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 results were compared with prior test results held on April 2008 before TRACTM catalyst replacement.

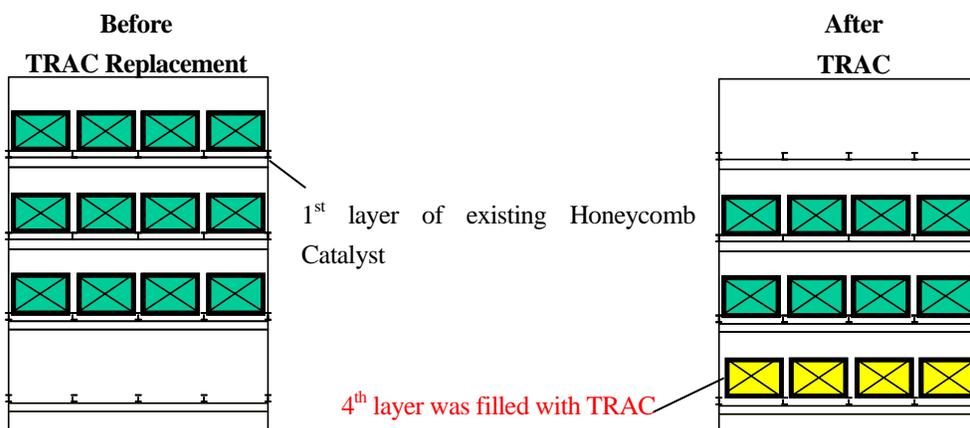


Fig. 3. General information for replacement catalyst with TRAC™ at a full-scale SCR reactor application

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 (°C)
Moisture	11.0 – 13.8 (%)
O ₂	2.9 - 3.1 (%), Dry)
CO ₂	16.0 – 16.6 (%), Dry)
NO _x	297 – 336 (ppm)
HCl	0.42 – 0.57 (ppm)
Cl ₂	0.04 – 0.07 (ppm)
HBr	0.01 – 0.13 (ppm)

RESULTS AND DISCUSSION

Development of TRAC™ Catalyst

Hitachi has been continuously improving the catalyst performance while lowering SO₂ to SO₃ conversion since SCR was first applied in U.S. power plants firing bituminous coals. However, lowering SO₂ to SO₃ conversion has also resulted in decreasing Hg oxidation because there is a correlation between Hg oxidation activity and SO₂ oxidation activity. With conventional catalysts, by adding active catalyst components to increase Hg⁰ oxidation activity, the SO₂ to SO₃ conversion activity will also increase as shown in Figure 4 because both Hg⁰ oxidation and the SO₂ oxidation activities are promoted by the same active sites in the catalyst components.

The fundamental reaction mechanisms of Hg oxidation and SO₂ to SO₃ conversion across SCR catalysts were investigated in a laboratory-scale apparatus at Hitachi to ascertain the most appropriate catalyst composition and manufacturing methods for the new catalyst.

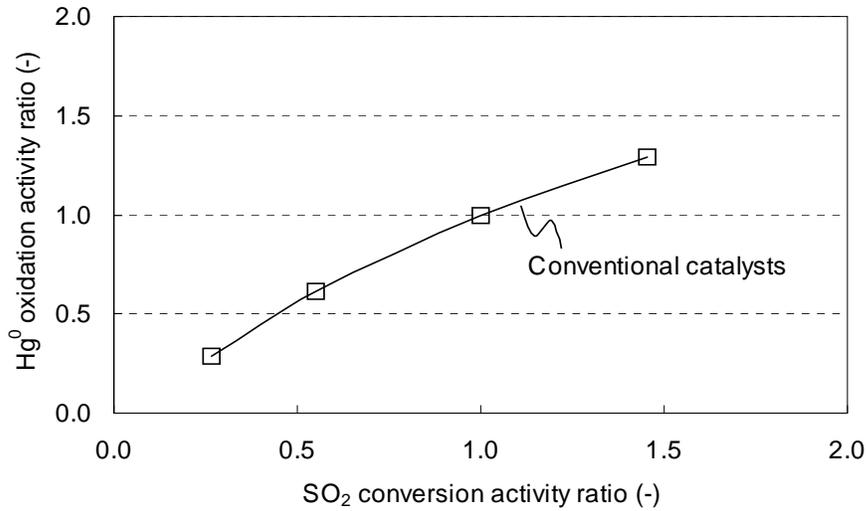


Fig. 4. Relationship between SO₂ conversion and Hg⁰ oxidation across conventional catalyst.

Through extensive research and development, pilot testing, and field demonstration, Hitachi/BHK has developed a new Hg oxidation catalyst, TRACTM (TRiple Action Catalyst)⁸. Figure 5 shows TRACTM catalyst performance in comparison with conventional SCR catalyst. It is observed that the Hg⁰ oxidation activity of TRACTM catalyst was 1.6 times higher than that of the conventional catalyst while improving NO_x removal activity and maintaining the same SO₂ to SO₃ conversion activity.

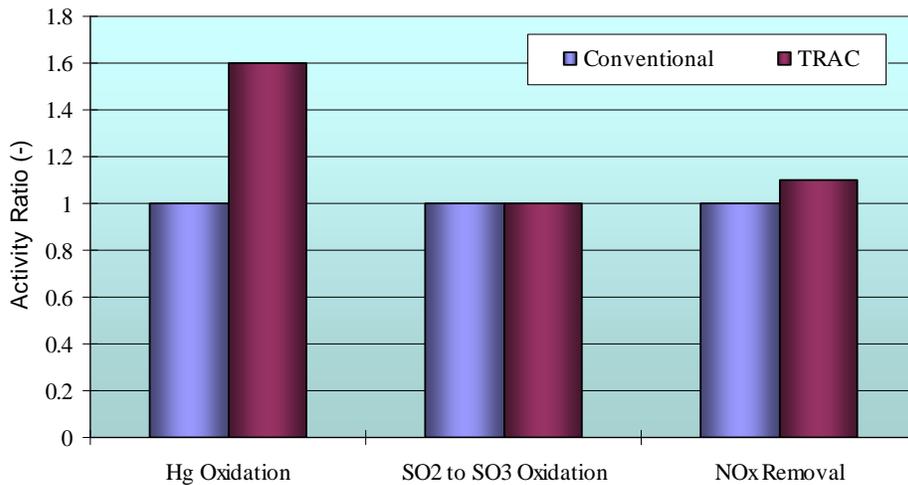


Fig. 5. New mercury oxidation SCR catalyst (TRACTM).

Slipstream Reactor (SSR) Testing at the Plant

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 6 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 6, it was observed that significant amount of Hg^0 was oxidized to Hg^{2+} across the catalyst in the SSR for all sampling events even with very low Hg^0 content level at the inlet of SSR. Hg oxidation capability of the TRACTM catalyst remained robust after one-year operation. Durability of TRACTM 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.

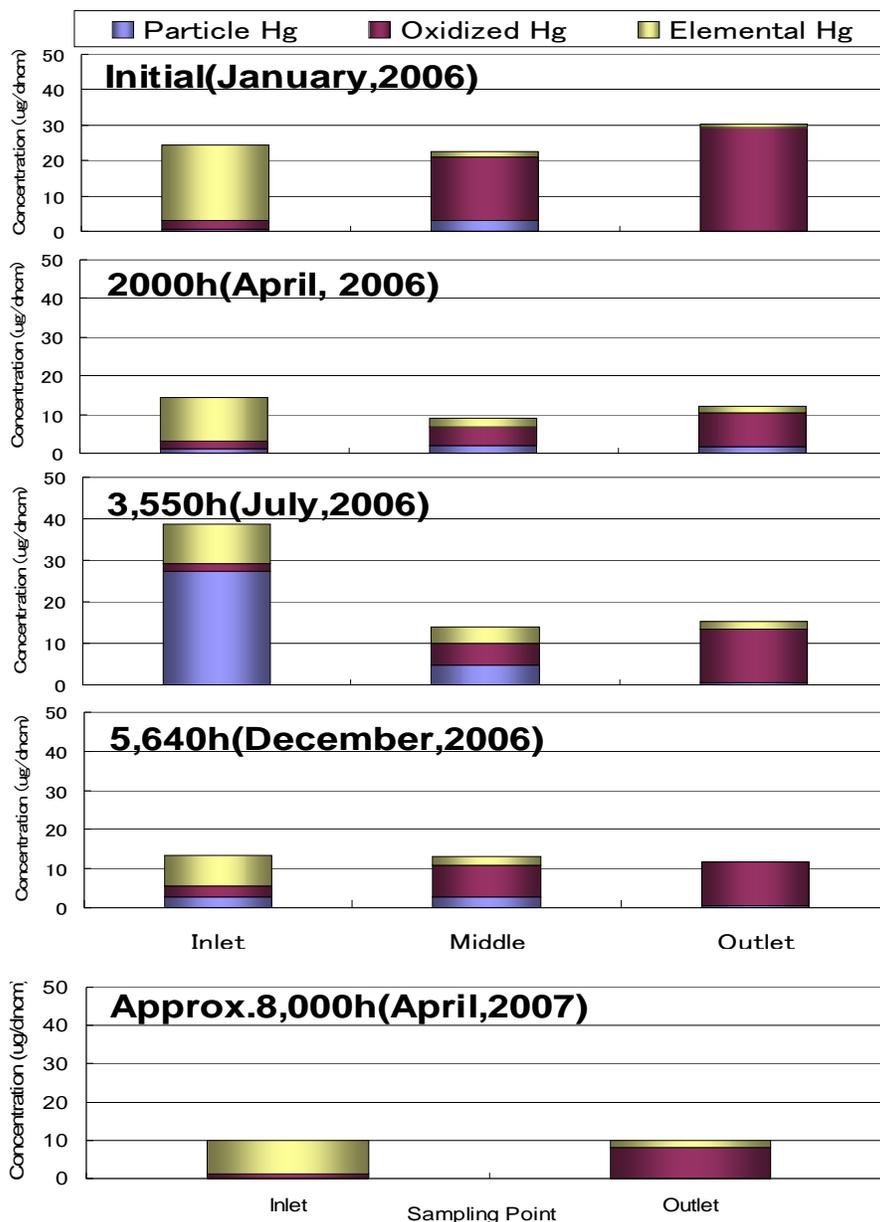


Fig. 6. Hg Speciation Measurement Results at SSR.

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 7 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™ 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™ catalyst was the same as that for DeNOx. Robust mercury oxidation performance and superior durability of the TRAC™ catalyst were observed and confirmed through the SSR testing. Therefore, full-scale commercial application of the TRAC™ catalyst becomes the next logic step.

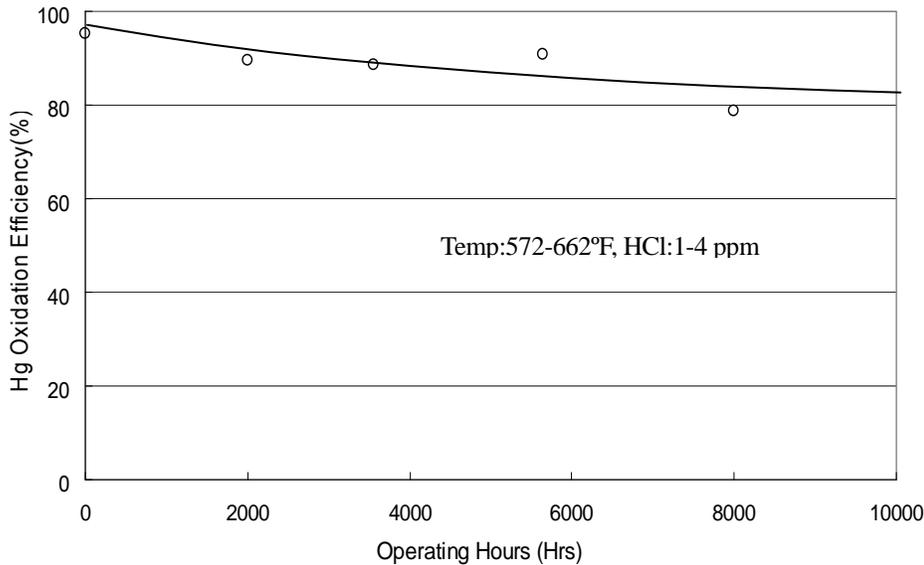


Fig. 7. Mercury oxidation efficiency with operating hours at SSR.

Full-Scale Commercial Application

One layer of the TRAC™ catalyst was applied to the full-scale SCR reactor as a replacement for old catalyst at the plant burning PRB coal (Figure 3) and the operation started in June 2008. The operating conditions of the SCR system are shown in Tables 4 and 5. The effect of TRAC™ catalyst on Hg oxidation was determined by comparing the results during two Hg sampling events, April 2008 (before TRAC™ replacement) and June 2008 (after TRAC™ 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™ catalyst on Hg speciation was determined by comparing the results obtained during the April 2008 sampling event before TRAC™ replacement (existing 3 layers w/o TRAC™) and June 2008 sampling event after TRAC™ replacement (existing 2 layers plus one TRAC™ layer). Hg speciation profiles at the WFGD inlet and WFGD outlet (stack inlet) for each sampling event are shown in Figure 8. The presence of TRAC™ catalyst significantly impacted the Hg speciation profile at the inlet of WFGD system. In the absence of TRAC™ catalyst (existing 3 layers w/o TRAC™), the ratio of Hg²⁺/Hg(total) at the inlet of WFGD averaged about 40%. The presence of TRAC™ catalyst (existing 2 layers plus one TRAC™ layer) increased this ratio to about 70%. Observation showed that the presence of the TRAC™ catalyst significantly increased Hg²⁺ level at the inlet of WFGD system.

As a result of the increased Hg²⁺ at WFGD inlet, total Hg removal across WFGD was increased from 30% (before TRAC™ replacement) to 70% (after TRAC™ replacement). Results from the full-scale application are in good

agreement with SSR testing results and demonstrate that the Hg^0 oxidation activity of the TRACTM catalyst was significantly higher than that of the conventional catalyst with low chlorine coal.

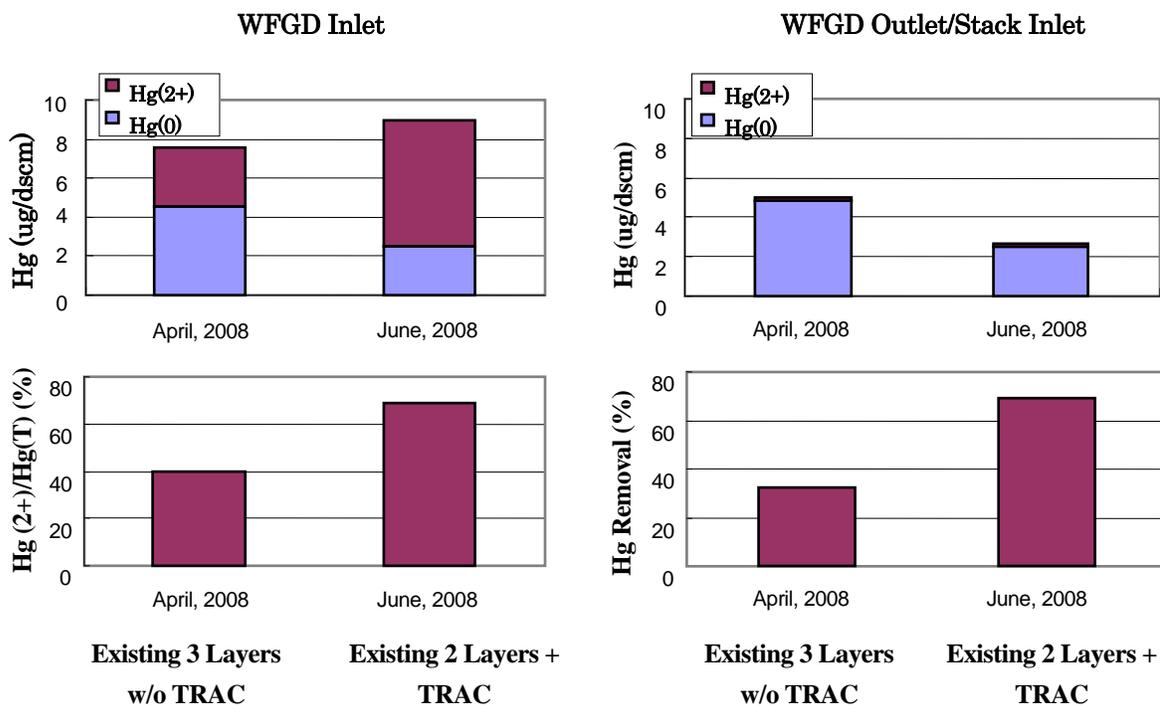


Fig. 8. Effect of TRACTM catalyst on Hg oxidation and removal across the WFGD before and after TRACTM replacement.

CONCLUSIONS

A new plate-type catalyst, TRACTM, was developed by Hitachi to achieve high Hg^0 oxidation for power plants burning coals with low chlorine content. Based on the extensive laboratory-scale testing results, both SSR and full-scale application of TRACTM catalyst were conducted and evaluated at a power plant burning low chlorine coals. The followings can be summarized from the testing programs:

1. TRACTM catalyst has an Hg^0 oxidation activity that was 1.6 times higher than that of the conventional catalyst, while maintaining the same SO_2 to SO_3 conversion activity.
2. 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_x reaction.
3. Results from the full-scale application are in good agreement with SSR results and demonstrate that the Hg^0 oxidation activity of the TRACTM catalyst was significantly higher than that of the conventional catalyst for low chlorine coal.
4. TRACTM catalyst can be applied to low chlorine coal-fired power plants as an integral step to enable cost-effective mercury control.

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 NO_x Control Technologies*, 3rd 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 SO₃ 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 SO₂ to SO₃ Conversion*, Power Plant Air Pollutant Control Megasyposium, Baltimore, MD, August 28-31, 2006