

SCR Catalyst with High Mercury Oxidation and Low SO₂ to SO₃ Conversion

Keiichiro Kai*, Kure Research Laboratory, Babcock-Hitachi K.K.
Hirofumi Kikkawa, Kure Research Laboratory, Babcock-Hitachi K.K.
Yasuyoshi Kato, Kure Research Laboratory, Babcock-Hitachi K.K.
Yoshinori Nagai, Kure Division, Babcock-Hitachi K.K.
William J. Gretta, P.E., Hitachi Power Systems America, Ltd.

ABSTRACT

New selective catalytic reduction (SCR) catalyst has been developed which indicates higher oxidation of elemental mercury (Hg⁰) while keeping very low SO₂ to SO₃ conversion. For conventional SCR catalyst, higher oxidation of Hg⁰ to Hg²⁺, which can be easily removed across a wet-FGD system, has been closely related to higher oxidation of SO₂. Higher SO₂ oxidation in coal-fired applications can cause negative downstream impacts such as air heater fouling, flue corrosion and visible stack plumes. Field-scale test results in an eastern bituminous coal-fired plant¹ using conventional catalyst indicated Hg⁰ oxidation ranging from 78 % to 93 %. However the SO₂ to SO₃ conversion was designed to be less than 1.5 % at SCR design operating conditions. The newly developed SCR catalyst design focuses on the difference in reaction mechanisms of Hg and SO₂. This new catalyst has been tested in a pilot-scale facility at BHK's catalyst development and manufacturing plant in Akitsu, Japan. Test results indicate Hg oxidation over 95 % while maintaining SO₂ to SO₃ conversion below 0.5 %.

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 applies to states in which EPA atmospheric chemistry and transport models have demonstrated that nitrogen oxides (NOx) and sulfur oxides (SOx) emissions contribute to ground level O₃ and PM_{2.5}. EPA has also previously estimated that mercury (Hg) emission from U.S. power plants is 48 tons per year. The CAMR establishes a cap-and-trade program for national emissions of Hg, with national caps set in two phases: 38 tons per year starting in 2010 and 15 tons per year starting in 2018.

Babcock-Hitachi is currently utilizing their in-house Air Quality Control Systems (AQCS), pilot test facility for evaluating technologies that can be applied to the CAIR and CAMR. This facility, located adjacent to BHK's catalyst manufacturing line in Akitsu, Japan, includes air pollution control devices such as selective catalytic reduction (SCR), electrostatic precipitators (ESPs) and wet flue-gas desulphurization (wet-FGD) systems. Utilizing this conventional AQCS equipment for mercury control has significant advantages since many U.S. plants either have this equipment already in place, or will need to install these systems for future CAIR NO_x and SO₂ control requirements. Utilizing the co-benefits of this equipment can result in significant capital and operating cost savings as compared to other mercury control technologies such as activated carbon injection. One of the key components of these conventional systems however is having SCR catalyst that can produce high mercury oxidation, without increased SO₂ oxidation.

SCR technology has become a well-established method for controlling emissions of NO_x from coal-fired power plants. In addition to NO_x control, however, SCR catalyst has been found to affect the mercury speciation; the catalyst can change elemental mercury (Hg⁰) to Hg²⁺ in coal combustion flue gases²⁻⁴. It is well known that increasing the emissions of Hg²⁺, which is present in the form of water-soluble mercuric chloride (HgCl₂), allows for high Hg emission reduction because HgCl₂ can be removed in downstream equipment such as ESP and wet-FGD systems^{5, 6}. Therefore the co-benefit of increased Hg²⁺ through the SCR catalyst is very important to the overall control of mercury emissions from coal-fired power plants.

The effect of SCR catalyst on mercury speciation appears to be dependent on coal type. Power plants burning bituminous coals, which generally contain high amounts of chlorine (Cl) and sulfur (S), have shown high conversion Hg⁰ to Hg²⁺ across the SCR catalyst. In fact, field-scale test results in an eastern bituminous coal-fired plant¹, using a conventional SCR catalyst indicated Hg⁰ oxidation from 78 % to 93 %, however the SO₂ to SO₃ conversion was designed to be less than 1.5 % at SCR operating condition (≥ 90 % NO_x removal). For plants firing bituminous coal, the oxidation of SO₂, which forms SO₃, can accelerate undesirable downstream impacts such as air heater fouling and flue corrosion and can result in visible stack plumes. Several downstream SO₃ mitigation technologies have become commercially available in recent years⁷, but these systems can have both high initial and operating costs, and maintenance concerns. Therefore advanced SCR catalyst, which maintains high Hg⁰ oxidation with low SO₂ to SO₃ conversion, will be the most economical solution for bituminous coal-fired power plants.

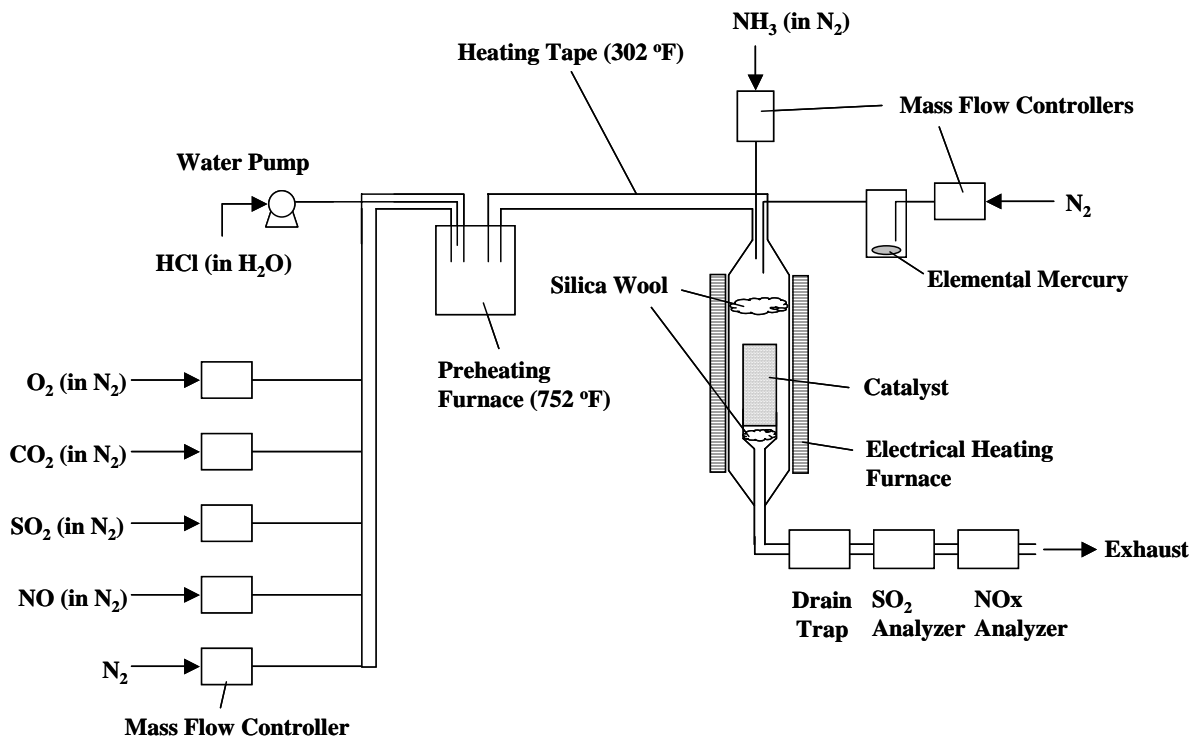
Fundamental studies have been undertaken to better understand the oxidation reaction mechanism of Hg and SO₂, and BHK has subsequently developed a new type of SCR catalyst, which satisfies the high Hg⁰ oxidation and low SO₂ oxidation requirements. The resultant new design indicates Hg⁰ oxidation over 95 % together with SO₂ oxidation below 0.5 %.

EXPERIMENTS

Fundamental Studies

Laboratory scale tests were conducted at simulated flue gas condition for studying Hg^0 and SO_2 oxidation. A schematic diagram of test apparatus is shown in Figure 1. This apparatus consists of the SCR reactor, the mercury generation unit, the preheating and premixing sections of gases, and the online analyzer for NO_x and SO_2 . Flue gas components such as O_2 , CO_2 , SO_2 , NO , and N_2 were supplied to the SCR reactor through a preheating furnace. Moisture together with HCl was also supplied to the preheating furnace using a tube pump as HCl solution. Mercury concentration was adjusted by adding a certain volume of mercury-saturated gas to the carrier gas.

Figure 1: Schematic of SCR Reactor Apparatus



Pilot-scale Tests

Two plate-type catalysts were evaluated in the pilot-scale test facility, equipped with pollution control devices including SCR, DESPs (dry-ESP), wet-FGD, and WESP (wet-ESP) systems. Two types of eastern bituminous coals, which contain high amounts of chlorine (Cl) and sulfur (S), were used in the

tests. A schematic diagram and a photo of the pilot test facility are presented in Figure 2 and Figure 3 respectively.

The combustor is a vertical-type furnace with a burner installed at the top. Coal combustion rate was about 100 kg/h (220 lb/hr). Flue gas temperature at the inlet of the ESP's was controlled to 320 °F by utilizing a gas-gas heater and a gas cooler. Sampling was conducted simultaneously at six points through flue gas stream: at the inlet and outlet of SCR reactor, the inlet and outlet of ESP, the outlet of the wet-FGD, and the stack (i.e. the outlet of WESP). Letters A to F in Figure 2 indicate the sampling points.

Figure 2: Schematic Diagram of the Pilot Test Plant

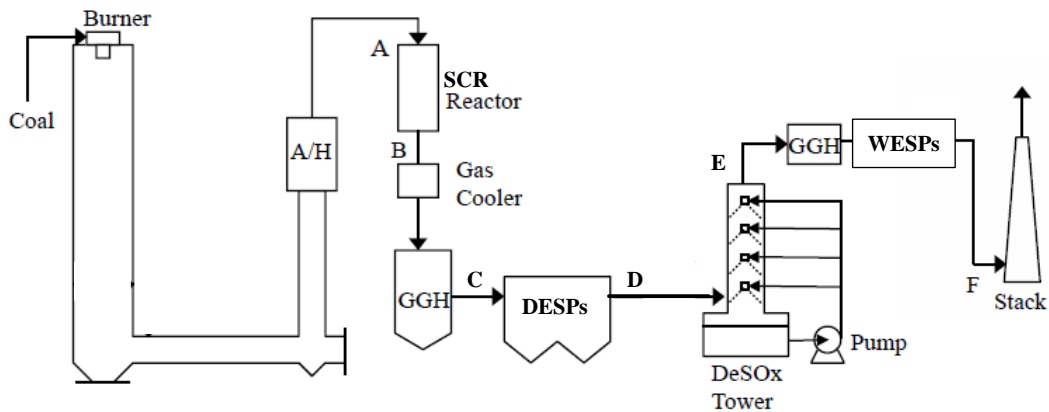
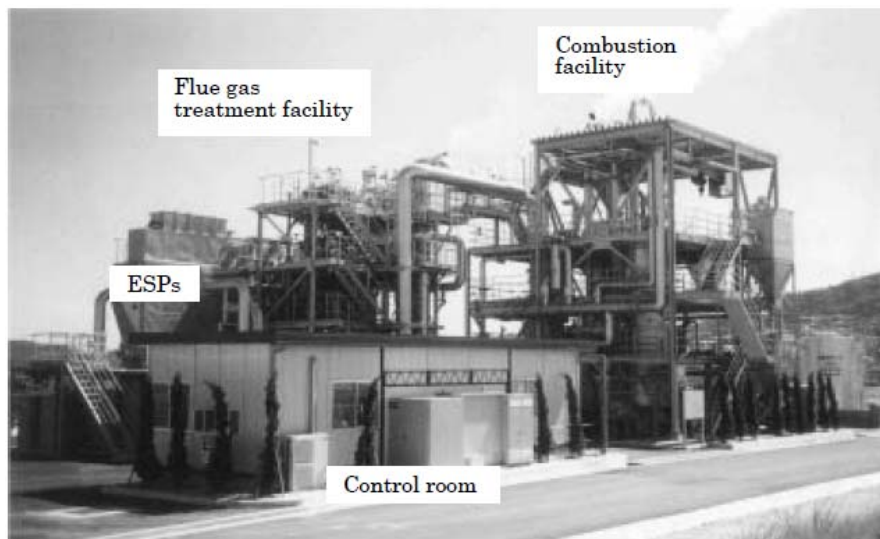


Figure 3: Pilot-scale Test Facility



Sampling and Analysis of Mercury

Figures 4 and 5 show schematics of the mercury sampling trains which were used for the fundamental studies and pilot tests respectively. A filter holder made of glass and Teflon tube was used so that flue gas did not make contact with metallic surfaces. Particle bound mercury and ash particles were collected by the filter, oxidized mercury was collected in an impinger containing a buffer solution (pH=7) and elemental mercury was captured in an impinger containing a $\text{H}_2\text{SO}_4\text{-KMnO}_4$ solution. Samples were recovered and analyzed for mercury using cold-vapor atomic adsorption (Nippon Instruments Corp. MA-1S+ MD-1). Isokinetic sampling rates were utilized based on the range of gas velocity at each point. Sample volumes in the range of 50-100 liters were utilized were considered to be a reliable amount based on the high sensitivity of the atomic absorption analyzer.

The filter with collected fly ash particles was soaked in $\text{H}_2\text{SO}_4\text{-KMnO}_4$ solution and the mercury was completely dissolved in the solution using ultrasonic cleaner. The teflon tube was rinsed with a diluted nitric acid solution and pure water, and then the rinse was added to the buffer solution. The mercury amount in these solutions was determined by the process shown in JIS (Japanese Industrial Standard) K0222. Cold-vapor generation with the addition of stannous chloride solution was used to convert oxidized mercury to its elemental state. The mercury solution was then purged with a carrier gas into the atom absorption cell. Mercury concentrations in solid particles such as coal and fly ash recovered from an ESP and gypsum from a wet-FGD system, were determined by cold-vapor atomic absorption spectroscopy. This method was utilized after the sample was heated and all mercury compounds were decomposed to gaseous elemental mercury.

Figure 4: Mercury Sampling Train for fundamental studies

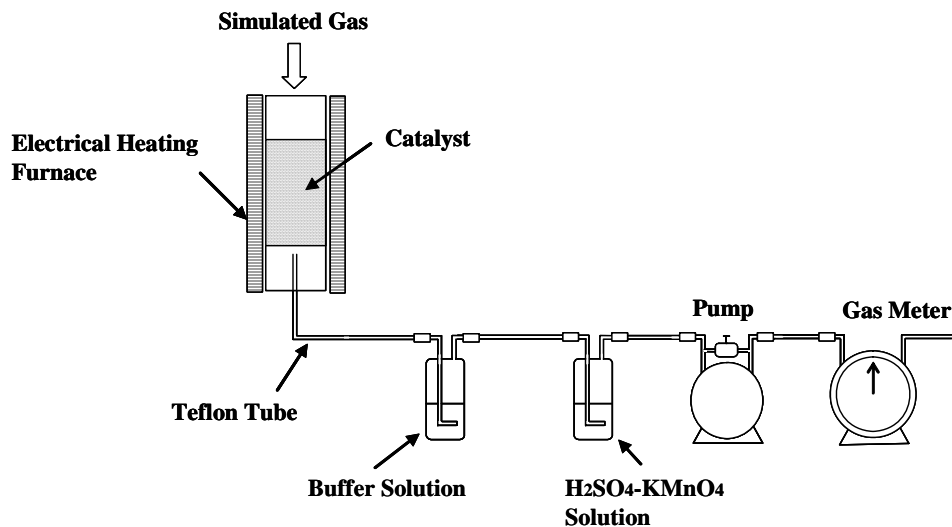
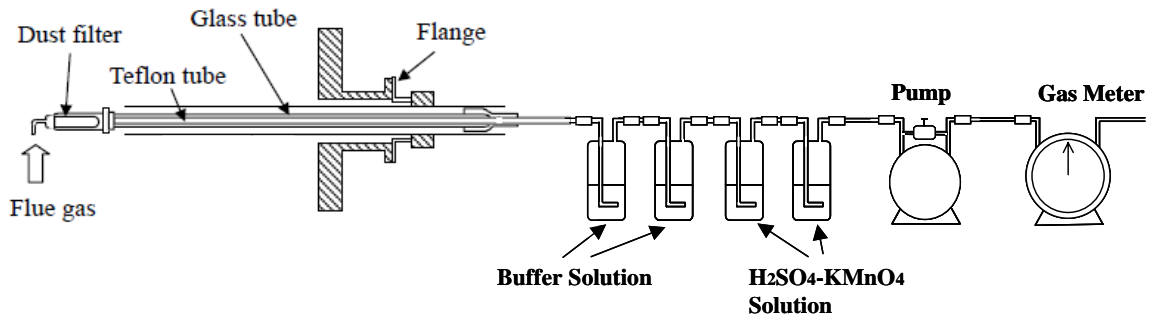


Figure 5: Mercury Sampling Train for pilot tests



RESULTS AND DISCUSSION

Development of Advanced Catalyst

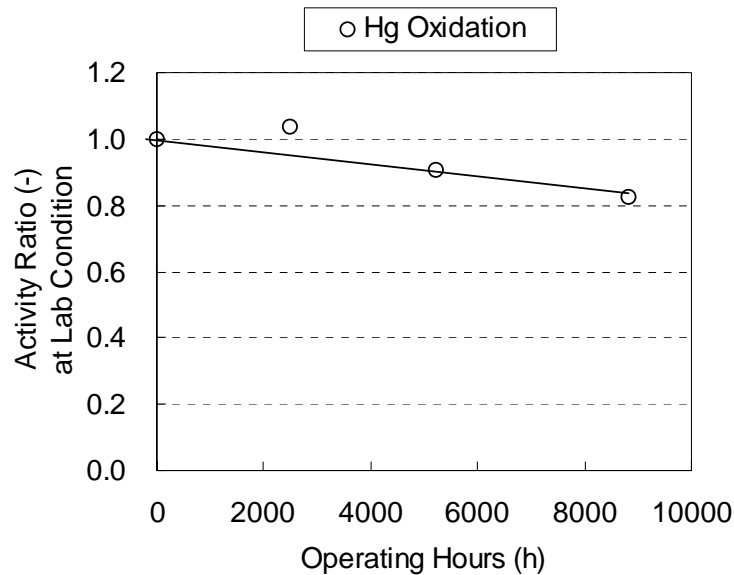
Field-scale test results of conventional catalyst

Table 1 shows the field-scale test results of Hg^0 oxidation for conventional catalyst at a 550 MW bituminous coal-fired power plant at the Louisville Gas and Electric Trimble County Unit 1 plant. In the field-scale tests, high Hg^0 oxidation performance (78 ~ 93 %) was achieved, however, the SO_2 to SO_3 conversion was designed to be less than 1.5 % at the SCR design conditions. The Hg^0 oxidation performance of the tested catalyst has also decreased with operating time in laboratory-scale examination as shown in Figure 6.

Table 1. Performance Test Results of SCR Catalyst in field-scale tests

Items	Condition
Boiler Operation	
Boiler Load (MW)	Approx. 540
ECO Outlet Temperature (°F)	687 ~ 716
Coal Analysis	
Cl (mg/kg)	450 ~ 550
Hg (mg/kg)	0.13 ~ 0.21
Results	
Hg oxidation (%)	78 ~ 93

Figure 6: Change in Hg⁰ Oxidation Activity Ratio of SCR Catalyst



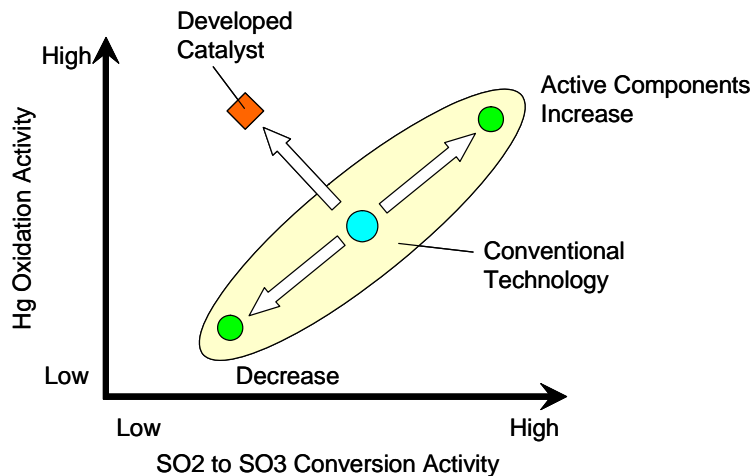
Concept for development of catalyst

Since SCR has been applied in U.S. applications firing bituminous fuels, continuous efforts at BHK have been made to improve the catalyst properties and to lower SO₂ to SO₃ conversion. Through these ongoing efforts, SCR catalyst has been applied for commercial use⁷, and resulting SO₂ conversion rates have decreased to nearly 20 % of original values when SCR was first applied. All of these reductions have taken place with increasing NO_x removal requirements (≥90 %). This low SO₂ conversion however has also resulted in low Hg⁰ oxidation because there is a close correlation between Hg⁰ oxidation activity and SO₂ conversion activity.

Changing the active composition can typically control the catalyst activity of Hg⁰ oxidation and NO_x removal. The SO₂ to SO₃ conversion activity was, however, also dependent on the active composition of the catalyst. Therefore with conventional catalyst technology, the SO₂ to SO₃ conversion activity would increase as shown in Figure 7, by adding the active components to increase Hg⁰ oxidation activity.

The fundamental reaction mechanism of Hg⁰ oxidation and SO₂ to SO₃ conversion were investigated, to ascertain the most appropriate catalyst composition, conformation, and manufacturing methods for the new catalyst based on the characteristics of each reaction mechanism. This ultimate goal is to simultaneously achieve higher Hg⁰ oxidation and lower SO₂ to SO₃ conversion performance.

Figure 7: Concept Image for Development of Advanced Catalyst with High Hg⁰ Oxidation



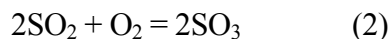
Results of development

As the result of the investigation, it was found that the reaction mechanism of Hg^0 oxidation differed from that of SO_2 to SO_3 conversion. Hg^0 oxidation reaction across SCR catalysts can be expressed by the following reaction:



The reaction of Hg^0 oxidation with hydrogen chloride (HCl) and O_2 can be considered to be a diffusion-controlled reaction in the gas phase because the reaction rate of Hg^0 oxidation is faster than the diffusion velocity of Hg^0 through the catalyst.

On the other hand, the oxidative reaction rate of SO_2 to SO_3 conversion, shown in equation (2), is slower than the diffusion velocity of SO_2 through the catalyst. In other words, the reaction of SO_2 conversion is controlled by the oxidative reaction rate, which has a very close relationship with amounts of active components in the catalyst.



Hence a new-type catalyst with higher Hg^0 oxidation activity and lower SO_2 to SO_3 conversion activity has been developed by modifying the catalyst composition and conformation based on the reaction mechanisms so that the more active components in the catalyst do not work for SO_2 conversion but Hg^0 oxidation.

Figure 8 and Figure 9 show the catalyst activity ratio of conventional catalysts (Catalyst A and B) and the new-type catalyst (Catalyst C) at 716 °F in laboratory-scale tests. As observed in Figure 8, the Hg^0 oxidation activity of Catalyst C was higher than the conventional Catalyst A, while the SO_2 to SO_3 conversion activity was lower. Furthermore, comparing Catalyst C with Catalyst B, the Hg^0 oxidation

activity of Catalyst C was considerably higher in spite of slightly higher SO₂ conversion activity. All of these catalysts also show quite similar NO_x removal efficiency as shown in Figure 9. Thus, Catalyst C provides higher Hg⁰ oxidation and lower SO₂ to SO₃ conversion performance compared with conventional catalyst. This is the result of modifying the catalyst composition to accelerate only the Hg⁰ oxidation rate.

Figure 8: Comparison of Hg Oxidation and SO₂ to SO₃ Conversion Activity of Advanced Catalyst

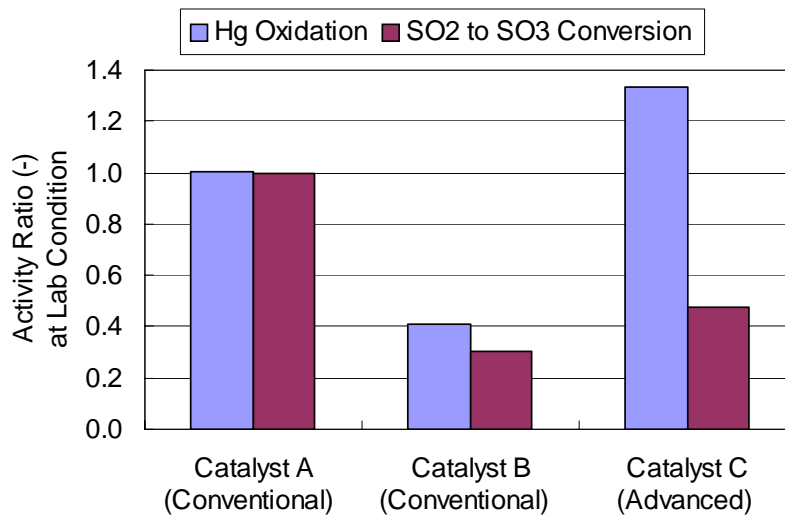
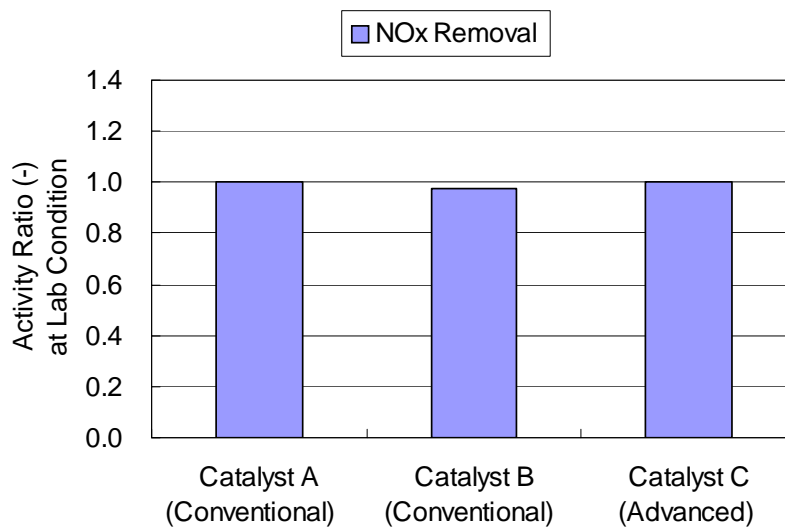


Figure 9: Comparison of NO_x Removal Activity of Advanced Catalyst



Pilot Test Results

Two types of catalysts, Catalyst A and C, were evaluated in the pilot-scale test facility using two types of high-sulfur eastern bituminous coals. The coal analyses and the operating conditions of the pilot tests are shown in Table 2 and Table 3, respectively. As shown in Table 3, all the tests were conducted under the constant condition of 90 % NO_x removal efficiency by controlling NH₃/NO_x to 0.9. In the pilot test facility, the temperature of the flue gas in the SCR reactor was controlled from 662 to 770 °F by injecting water to the coal combustor as needed. The water injection resulted in higher flue gas moisture content in the pilot facility (13-23 %) than what is normally seen in commercial plants (8-10 %). The test results of Hg⁰ oxidation performance shown in Figure 10 were corrected under the condition of appropriate moisture volume, approximately 10 vol%.

Table 2. Coal Analyses for Pilot Test Facility

Coal Type	A	B
Proximate Analysis, wt %		
Moisture	7.16	1.32
Volatiles	40.62	37.11
Fixed Carbon	48.70	55.68
Ash	10.68	7.21
High Heating Value (MJ/kg, dry)	27.88	32.48
Elemental Analysis, dry, wt %		
Ash	10.61	7.13
C	71.32	78.48
H	5.14	5.03
O	8.45	6.41
N	1.58	1.35
S	2.90	1.60
Trace Elements, dry, mg/kg		
Hg	0.10	0.06
Cl	300	650

Table 3. Operating Conditions of the Pilot Testing

Items	Units	Pilot Testing	
Test No	-	RUN 1, 2	RUN 3
Coal Type	-	A	B
Flue Gas Flow (wet)	m ³ N/h	1000	1000
Flue Gas Temp.	°F	662 ~ 770	620 ~ 770
Inlet NOx	ppm	300	300
O ₂	%	5	5
SO ₂	ppm	1800 ~ 2000	800 ~ 1000
HCl	ppm	20 ~ 30	40 ~ 50
Hg	µg/m ³ _N	7 ~ 11	6 ~ 8
NOx Removal Efficiency	%	90	90

Figure 10 and Figure 11 show the test results for Hg⁰ oxidation and SO₂ to SO₃ conversion respectively at the pilot-scale test facility. As shown in Figure 10, the Hg⁰ oxidation performance of the newly developed catalyst (Catalyst C) in the tests of RUN 2 was considerably higher than that of the conventional catalyst (Catalyst A) in the tests of RUN 1. In the tests of RUN 3, the highest Hg⁰ oxidation performance was indicated, which is due to the high Cl content in Coal Type B. As a result, the developed catalyst met the target Hg⁰ oxidation of 95 % at 716 °F. Furthermore, Hg⁰ oxidation of 98 % was also achieved at the temperature of 662 °F. As shown in Figure 11, the SO₂ to SO₃ conversion of Catalyst C was lower than the targeted 0.5 % conversion at the flue gas temperature of approximately below 734 °F, while that of Catalyst A was over 0.5 % at all of the temperatures.

The developed catalyst therefore satisfies both of the requirements of Hg⁰ oxidation and SO₂ to SO₃ conversion performance for high-sulfur bituminous coal-fired power plants.

Figure 10: Hg⁰ oxidation of SCR Catalysts at Pilot-scale test facility

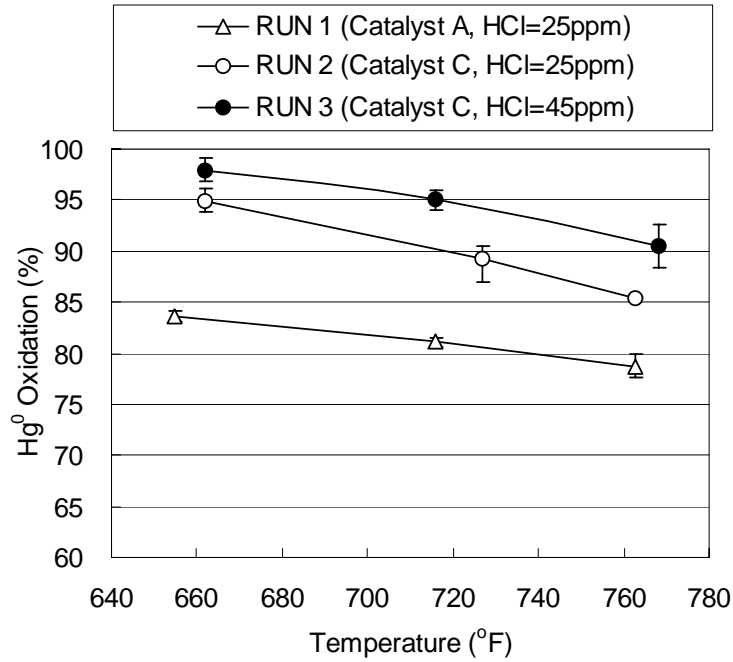
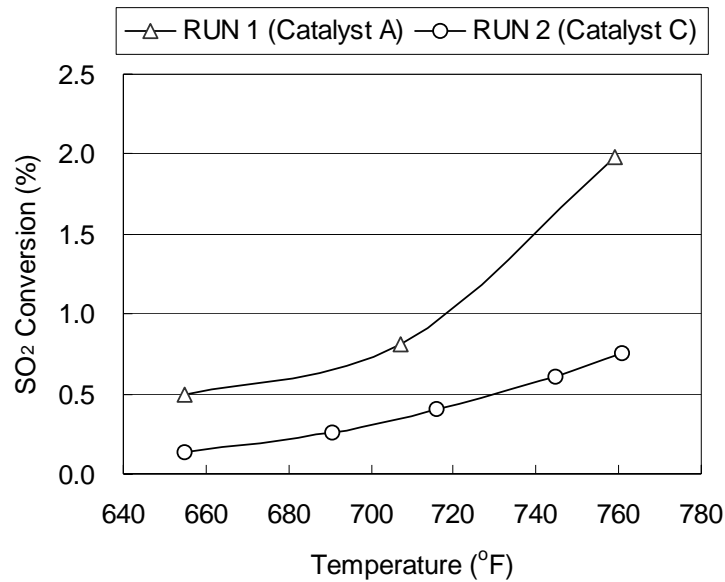


Figure 11: SO₂ to SO₃ Conversion of SCR Catalysts at Pilot-scale test facility



CONCLUSIONS

Babcock-Hitachi has developed a new-plate-type catalyst, which can achieve high Hg⁰ oxidation and low SO₂ to SO₃ conversion for power plants burning bituminous coal.

This catalyst should meet Hg⁰ oxidation targets of 95 % at a temperature of 716 °F, while keeping SO₂ to SO₃ conversion below 0.5 % at below 734 °F. Hg⁰ oxidation of 98 % can also be achieved at a temperature of 662 °F.

ACKNOWLEDGMENT

The measurement of mercury in the field-scale tests was supported in part by Louisville Gas and Electric Company. Mr. John W. Moffett, EON-US Services Inc, is gratefully acknowledged for the cooperation.

REFERENCE

1. Gretta, W., Morita, I and Moffett, J, *Mercury Oxidation Across SCR Catalyst at LG&E's Trimble County Unit 1*, Power Plant Air Pollutant Control Mega Symposium, Baltimore, MD, August 28-31, 2006.
2. 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*, 3rd International Air Quality Conference, Arlington, Virginia, September 9-12, 2002.
3. 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.
4. Constance L. Senior, ISSN 1047-3289 J. Air & Waste Manage. Assoc. 56:23-31.
5. Ghorishi, S.B.; Gullett, B.K.; Jozewicz, W. Waste Management Research. 1998, 16:6, 582-593.
6. 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.
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.

KEY WORDS

SCR catalyst, Mercury oxidation, SO₂ to SO₃ conversion