

NEW SCR CATALYST WITH IMPROVED MERCURY OXIDATION ACTIVITY FOR BITUMINOUS COAL-FIRED BOILERS

**Keichiro Kai*, Yasuyoshi Kato, Hirofumi Kikkawa, Naomi Imada, and Yoshinori Nagai
Babcock-Hitachi K.K.**

**Kure Research Laboratory, 3300, Kazahaya, Akitsu-cho,
Higashi-Hiroshima-shi, Hiroshima, 739-2403, JAPAN**

ABSTRACT

A new SCR catalyst with improved mercury (Hg^0) oxidation activity has been developed and evaluated using laboratory-scale test apparatus along with a pilot-scale test facility. Laboratory studies revealed that mercury oxidation rates across SCR catalyst decreased with increasing concentrations of H_2O and SO_2 , and the decline of mercury oxidation rate was especially prominent at high flue gas temperatures. The decline of mercury oxidation may be explained by the reduction of Hg^{2+} to Hg^0 , which is accelerated by H_2O and SO_2 , especially at high gas temperatures. Therefore, it is necessary to restrain the mercury reduction reaction in order to improve the overall mercury oxidation rate of SCR catalyst. The newly developed SCR catalyst has been designed to suppress the mercury reduction reaction with H_2O and SO_2 , by controlling the kinetics of competing mercury reactions. This catalyst has also been improved to have low SO_2 conversion rate for high sulfur bituminous coal applications. Laboratory scale tests showed that the Hg^0 oxidation activity of the developed catalyst was 1.5~2.0 times higher, and the SO_2 to SO_3 conversion activity was about half of that of conventional catalyst. Pilot-scale test results were in good agreement with the laboratory-scale test results and confirmed the Hg^0 oxidation activity of the developed catalyst was 1.4~1.7 times higher than that of conventional catalyst.

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 (NO_x) and sulfur oxides (SO_x) emissions contributed to high levels of ambient O_3 and $\text{PM}_{2.5}$. Currently, mercury (Hg) emissions from U.S. power plants are about 48 tons per year. CAMR will reduce the total national Hg emissions from power plants to 38 tons per year starting in 2010 and 15 tons per year starting in 2018.

Babcock-Hitachi (BHK) has been conducting extensive studies utilizing their in-house Air Quality Control Systems (AQCS) pilot test facility for evaluating technologies that can be applied to meet CAIR and CAMR requirements. This facility, located adjacent to BHK's catalyst manufacturing plant in Akitsu, Japan, includes air pollution control devices such as selective catalytic reduction (SCR), electrostatic precipitator (ESP) 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 SO_2 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 is SCR catalyst. Ideally, the SCR catalyst should produce high mercury oxidation, without increasing SO₂ oxidation, which forms SO₃ that can cause air heater fouling, flue corrosion and visible stack plumes. Several downstream SO₃ mitigation technologies have become commercially available in recent years ⁷, but these systems can have both high initial and operating costs, and maintenance concerns. Therefore advanced SCR catalyst, which can achieve high Hg⁰ oxidation with low SO₂ to SO₃ conversion, will be the most economical solution for bituminous coal-fired power plants.

SCR technology has become the preferred method for controlling NO_x emissions from coal-fired power plants. In addition to NO_x control, SCR catalyst has been found to affect the mercury speciation; the catalyst can convert elemental mercury (Hg⁰) to Hg²⁺ in coal combustion flue gases ¹⁻³. It is well known that increasing the proportion 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 ^{4, 5}. Therefore the co-benefit of mercury oxidation 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 Hg⁰ oxidation appears to be dependent on coal type. Power plants burning eastern bituminous coals, which generally contain high amounts of chlorine (Cl) and sulfur (S), tend to show relatively high Hg⁰ to Hg²⁺ conversion across the SCR catalyst compared with those burning PRB coals, because HCl can promote Hg⁰ oxidation. Other flue gas components such as NO, NH₃, H₂O and SO₂, however, decrease Hg⁰ oxidation within the typical SCR temperature range ⁶. In particular, SO₂ strongly reduces Hg⁰ oxidation at high temperatures (>662°F) ⁸. It will be therefore difficult to achieve high Hg⁰ oxidation efficiency through conventional SCR catalysts under high temperature and high SO₂ concentration conditions when firing eastern bituminous coals.

BHK has studied the impact of SO₂ gas toward Hg⁰ oxidation across SCR catalysts in a laboratory-scale apparatus. BHK has successfully developed a new type of SCR catalyst which satisfies the high Hg⁰ oxidation and low SO₂ oxidation requirements under high temperatures (716-770°F). The Hg⁰ oxidation performance of the new SCR catalyst has been tested in a laboratory-scale apparatus and also in a pilot-scale test facility.

EXPERIMENTS

Laboratory-scale Tests

Laboratory scale tests were conducted with simulated flue gas for studying Hg⁰ and SO₂ oxidation characteristics of SCR catalysts. A schematic diagram of test apparatus is shown in Fig. 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, together with HCl, was also supplied to the preheating furnace as HCl solution using a tube pump. NH₃ was directly injected upstream of the SCR catalysts. Mercury concentration was adjusted by adding a variable volume of mercury-saturated gas to the carrier gas.

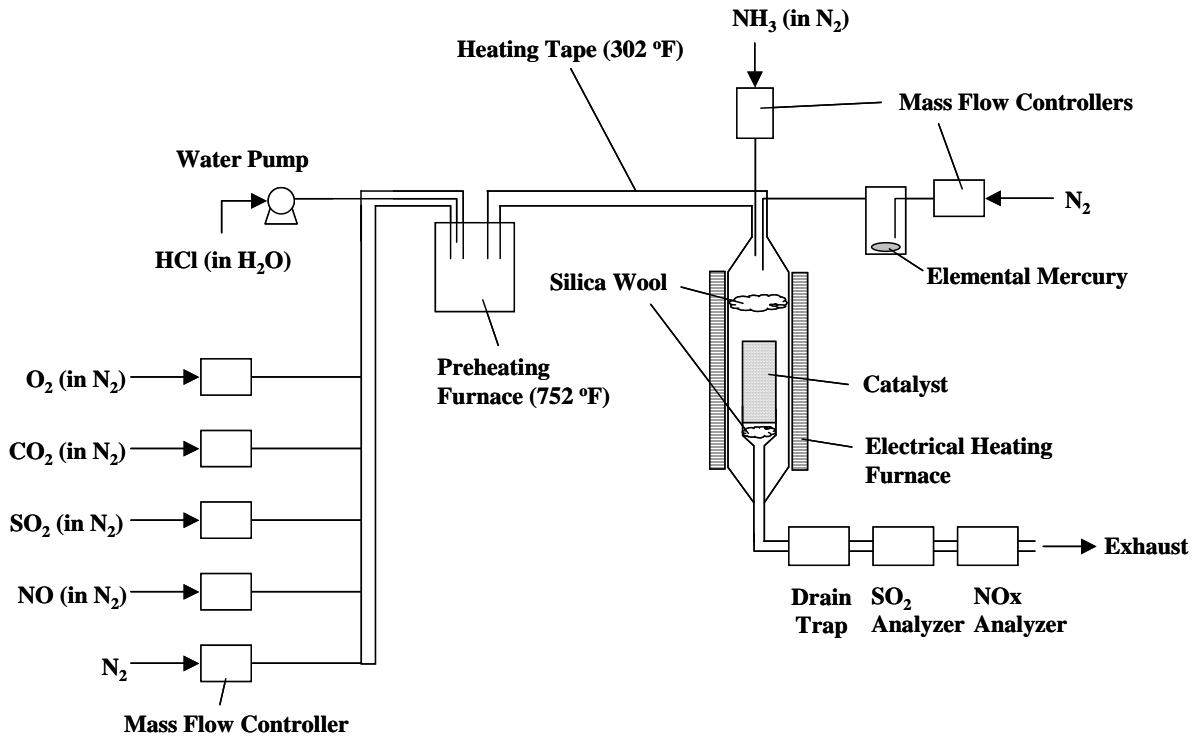


Fig. 1. Schematic of laboratory-scale apparatus to evaluate SCR catalysts

Pilot-scale Tests

New SCR catalyst and conventional catalysts were evaluated in the pilot-scale test facility, equipped with pollution control devices including SCR, DESP (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 of the pilot test facility is presented in Fig. 2.

The combustor is a vertical-type furnace with a burner installed at the top. The coal combustion rate was about 120-150 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 Fig. 2 indicate the sampling points.

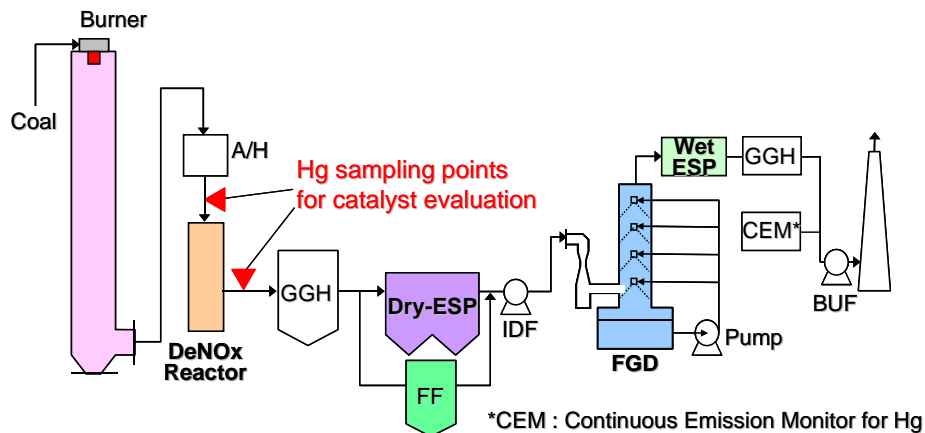


Fig. 2. Schematic Diagram of the Pilot Test Plant

Sampling and Analysis of Mercury

Figures 3 and 4 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 absorption (Nippon Instruments Corp. MA-1S+ MD-1). Isokinetic sampling rates were utilized based on the range of gas velocity at each point. Sample volumes were in the range of 50-100 liters which was 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 helped by an 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 the ESP and gypsum from the wet-FGD, 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.

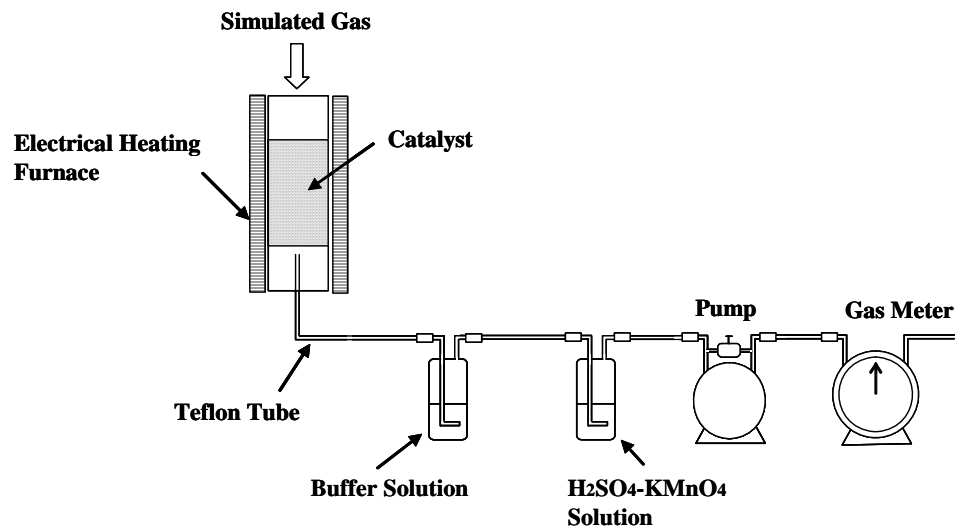


Fig. 3. Mercury Sampling Train for fundamental studies

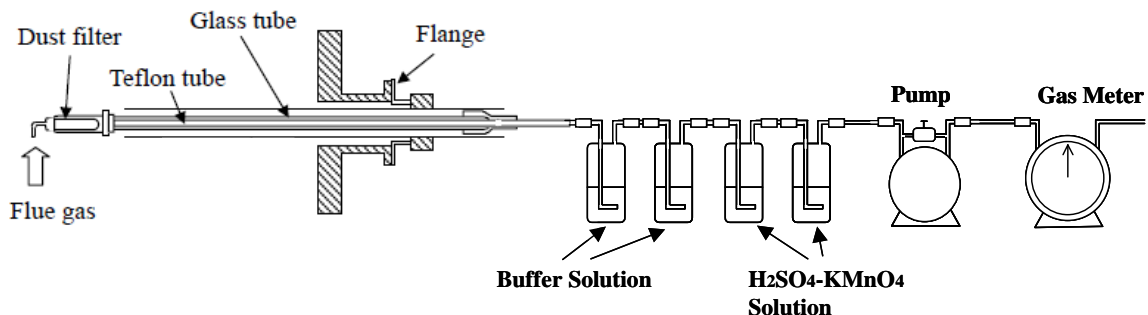


Fig. 4. Mercury Sampling Train for pilot tests

RESULTS AND DISCUSSION

Development of Catalyst for Mercury Oxidation

Ever since SCR was first applied in U.S. power plants firing bituminous fuels, BHK has made continuous efforts to improve the catalyst properties and to lower SO₂ to SO₃ conversion. Through these ongoing efforts, improved SCR catalyst has been applied for commercial use⁹, and resulting SO₂ conversion rates have decreased to about 20 % of the original values when SCR was first applied. All of these reductions have taken place with increasing NOx 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 NOx removal, but the SO₂ to SO₃ conversion activity is also dependent on the active composition of the catalyst. With conventional catalysts, by adding active components to increase Hg⁰ oxidation activity, the SO₂ to SO₃ conversion activity will also increase as shown in Fig. 5, because Hg⁰ oxidation and SO₂ oxidation are promoted by the same active sites in the catalysts.

The fundamental reaction mechanism of Hg⁰ oxidation and SO₂ to SO₃ conversion as well as the impact of SO₂ gas toward Hg⁰ oxidation across SCR catalysts was investigated in a laboratory-scale apparatus, to ascertain the most appropriate catalyst composition, conformation, and manufacturing methods for the new catalyst based on the characteristics of each reaction mechanism.

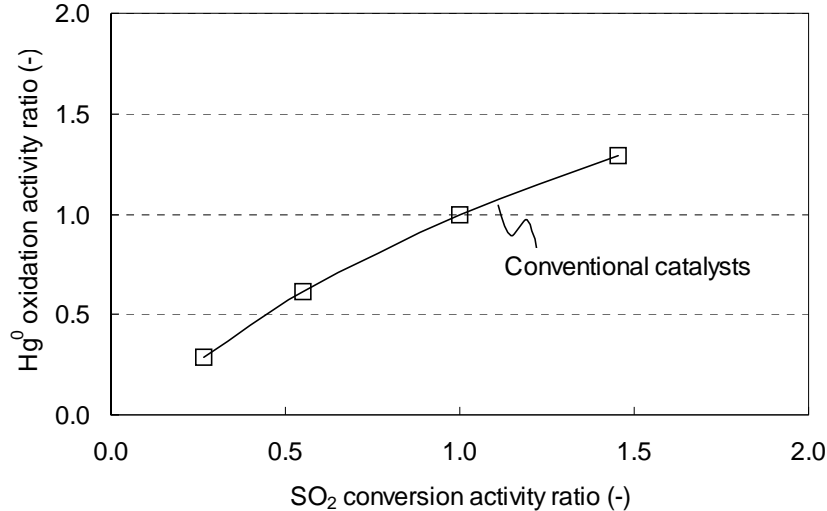


Fig. 5. Relationship between SO₂ conversion and Hg⁰ oxidation across catalysts

The laboratory-scale test results showed that the reaction mechanism of Hg⁰ oxidation differed from that of SO₂ to SO₃ conversion. Hg⁰ oxidation reaction across SCR catalysts can be generally expressed by the following reaction (1):



The reaction of Hg^0 oxidation with hydrogen chloride (HCl) and O_2 can be considered to be diffusion controlled reaction of Hg^0 in catalyst's pore because the reaction rate of Hg^0 oxidation is faster than the diffusion velocity of Hg^0 through the catalyst's pore. On the other hand, the 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 oxidation rate, which has a very close relationship with amounts of active components, that is, the number of active sites in the catalyst.



The effect of SO_2 on Hg^0 oxidation through SCR catalyst was subsequently studied using a conventional catalyst in the laboratory-scale test. Figure 6 shows the change in Hg^0 oxidation activity for the conventional catalyst by coexistence with SO_2 . The Hg^0 oxidation activity decreased in the presence of SO_2 ; this is consistent with the SO_2 effect on Hg^0 oxidation reported in some literature⁶. In the presence of SO_2 , HgCl_2 produced by Hg^0 oxidation, according to reaction (1), may be reduced back to Hg^0 by reacting with SO_2 and H_2O through SCR catalyst as shown in reaction equation (3). The rate of this reverse reaction on SCR catalyst depends on the concentrations of SO_2 and H_2O in the flue gas, and also depends on the flue gas temperature as indicated in Fig. 6. The overall Hg^0 oxidation activity across SCR catalyst is therefore determined by the competing reactions of Hg^0 oxidation with HCl and H_2O and of HgCl_2 reduction with SO_2 and H_2O at a given gas temperature.

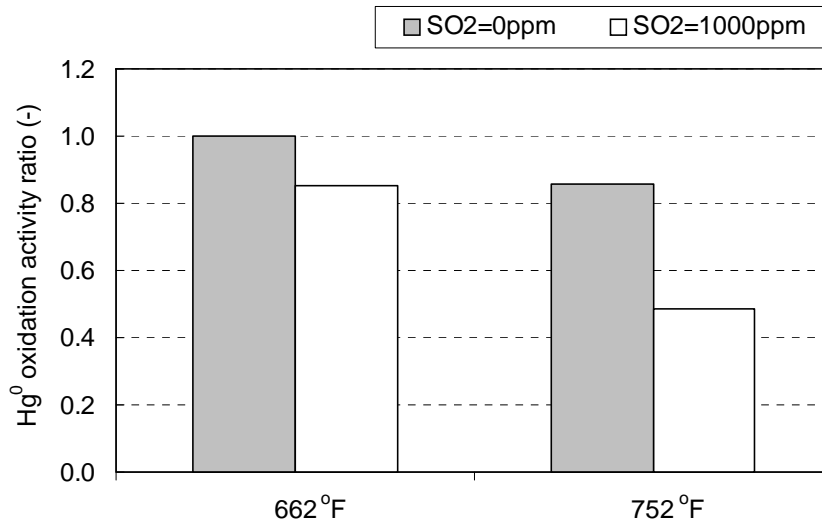
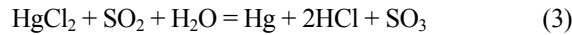


Fig. 6. Decrease of Hg^0 oxidation of conventional catalyst by coexistence with SO_2 gas

Hence enhancement of Hg^0 oxidation activity and simultaneous inhibition of both HgCl_2 reduction activity and SO_2 to SO_3 conversion activity are required to improve Hg^0 oxidation rate across SCR catalyst for bituminous coal-fired boilers where flue gas usually has high SO_2 concentrations. Therefore BHK studied the optimum catalyst composition in order to form the active sites that can preferentially promote Hg^0 oxidation. As a result, a new-type SCR catalyst, which shows higher Hg^0 oxidation activity without enhanced SO_2 conversion, has been successfully developed.

Figure 7 shows the temperature characteristics of Hg^0 oxidation activity, as well as the SO_2 to SO_3 conversion activity in the presence of SO_2 , NH_3 , and H_2O for the developed catalyst and the conventional catalyst evaluated at the laboratory-scale test apparatus. The Hg^0 oxidation activity of the developed catalyst is higher than that of the conventional catalyst at typical SCR temperature range. The developed catalyst also tends to maintain higher Hg^0 oxidation rate than the conventional catalyst at the high temperatures. Furthermore, the SO_2 to SO_3 conversion rate of developed catalyst is about half of that of conventional catalyst, as shown in Fig. 7.

Figure 8 shows the effect of SO_2 concentration on Hg^0 oxidation of the catalysts at two temperatures. At 752°F , Hg^0 oxidation activity of the conventional catalyst deteriorates very rapidly with increasing SO_2 concentration, while the decline of Hg^0 oxidation activity for the new catalyst is more moderate because of the improvement of Hg^0 oxidation activity and the inhibition of HgCl_2 reduction. At the lower temperature of 662°F , the developed catalyst maintains high Hg^0 oxidation activity over the entire tested SO_2 range.

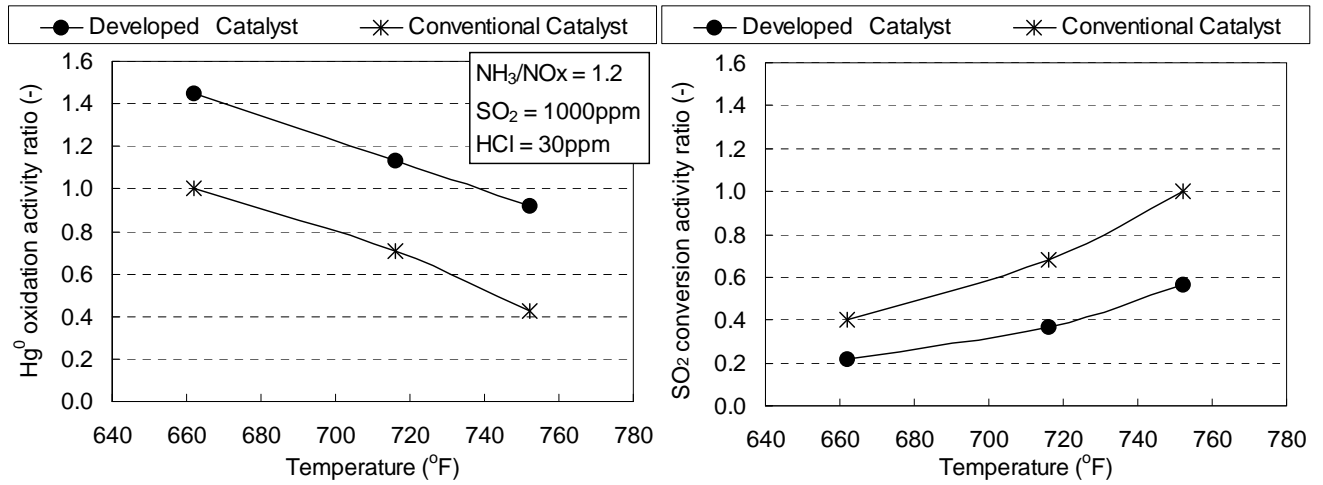


Fig. 7. Temperature characteristics of Hg^0 oxidation activity and SO_2 to SO_3 conversion activity for developed catalyst and conventional catalyst

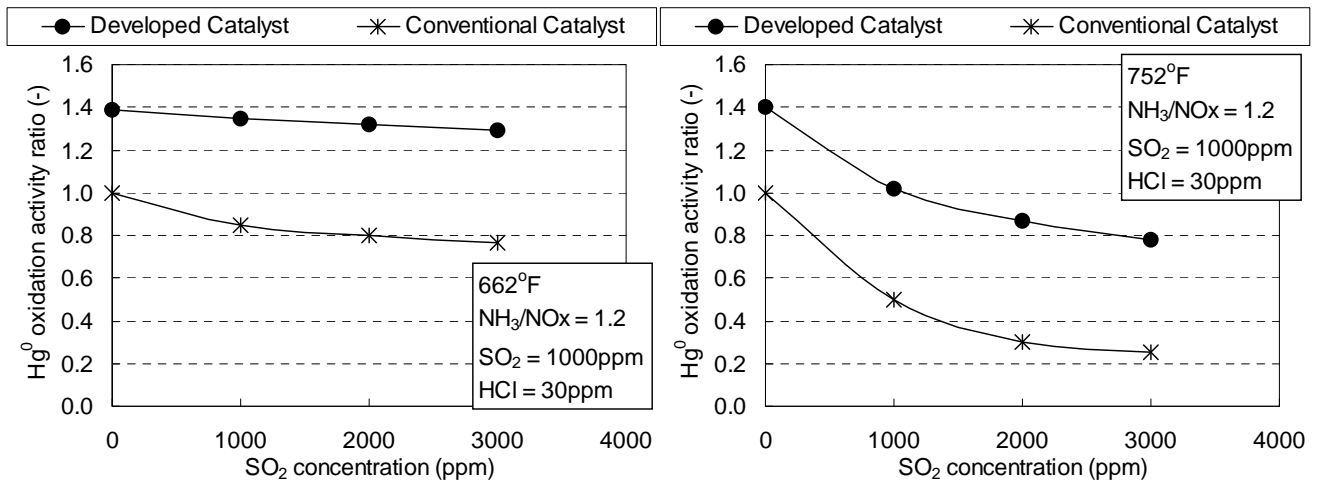


Fig. 8. Effect of SO_2 concentration for developed catalyst and conventional catalyst at each temperature

Pilot-scale Test Results of Developed Catalyst

The developed catalyst and conventional catalyst were evaluated in the pilot-scale test facility using two types of high-sulfur eastern bituminous coals. The operating conditions of the pilot tests are shown in Table 1. As shown in Table 1, all the tests were conducted under the constant condition of 90 % NO_x removal efficiency by controlling the NH₃/NO_x molar ratio to 0.9.

Figure 9 shows the test results for Hg⁰ oxidation of the developed catalyst and conventional catalyst at the pilot-scale test facility. As shown in Fig. 9, the Hg⁰ oxidation rate of the developed catalyst was higher than that of the conventional catalyst when firing coal type A. Furthermore, the developed catalyst was maintaining higher Hg⁰ oxidation rate (95%) at higher temperature when combusting coal type B, although SO₂ concentration in the flue gas was very high (ave.3800ppm). Results from the pilot-scale test are in good agreement with the laboratory-scale test results and indicate that the Hg⁰ oxidation activity of the developed catalyst was 1.4~1.7 times higher than that of the conventional catalyst for these tests with high sulfur coals.

Table 1. Operating Conditions of the Pilot Testing

Items		Units	Pilot Testing	
Coal Type		-	A	B
Flue Gas Temp.		°F	648 ~ 763	640 ~ 743
Inlet	NO _x	ppm	300	300
	O ₂	%	5	5
	SO ₂	ppm	1800 ~ 2000	3700 ~ 3900
	HCl	ppm	20 ~ 30	70 ~ 80
	Hg	μg/m ³ N	7 ~ 11	10 ~ 13
NH ₃ /NO _x ratio		-	0.9	0.9
NO _x Removal Efficiency		%	90	90

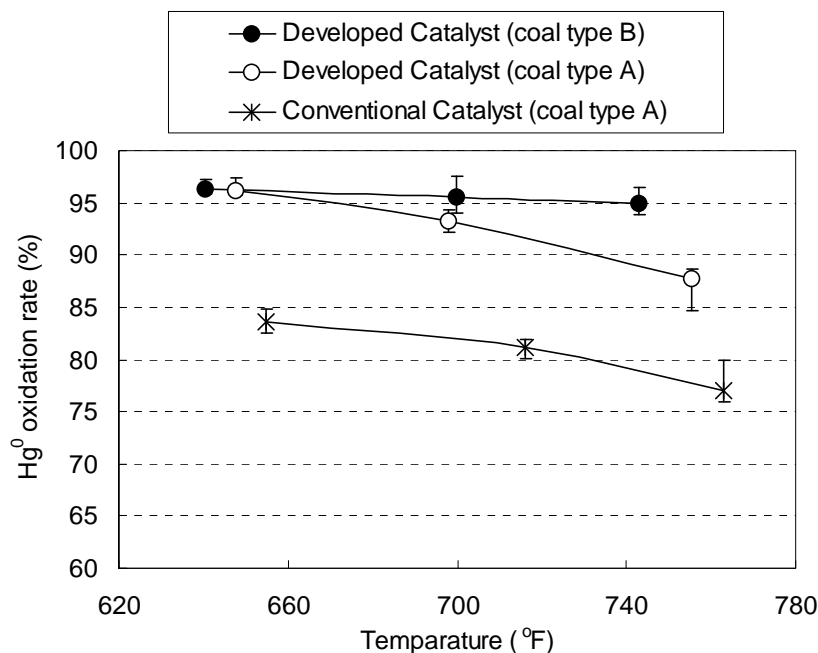


Fig. 9. Hg⁰ oxidation of Developed catalyst at Pilot-scale test facility
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CONCLUSIONS

Hitachi has developed a new plate-type catalyst, which can achieve high Hg^0 oxidation with low SO_2 to SO_3 conversion at high temperatures for power plants burning high sulfur bituminous coals. The Hg^0 oxidation activity of the developed catalyst in laboratory scale test was 1.5~2.0 times higher than that of the conventional catalyst and the SO_2 to SO_3 conversion activity was about half of conventional catalyst. Pilot-scale test results were in good agreement with the laboratory-scale test results and showed that the Hg^0 oxidation activity of the developed catalyst was 1.4~1.7 times higher than that of the conventional catalyst. The test data confirm that the developed catalyst has sufficiently robust catalytic performance to be applied to high sulfur bituminous coal-fired power plant applications.

REFERENCES

1. 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.
2. 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.
3. Constance L. Senior, ISSN 1047-3289 J. Air & Waste Manage. Assoc. 56:23-31.
4. Ghorishi, S.B.; Gullett, B.K.; Jozewicz, W. Waste Management Research. 1998, 16:6, 582-593.
5. 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.
6. Kai, K., Kikkawa, H., Kato, Y., Nagai, Y., Gretta, W., *SCR Catalyst with High Mercury Oxidation and Low SO_2 to SO_3 Conversion*, Power Plant Air Pollutant Control Mega Symposium, Baltimore, MD, August 28-31, 2006.
7. 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.
8. Jianrong Qiu, Richard O. Sterling, and Joseph J. Helble, 28th Int. Technical Conf. Coal Utilization Fuels Sys. 2003.
9. Favale, A, Morita, I, and Lin, C, *The Mitigation of SO_3 at AEP Gavin Unit 1 Following the SCR Installation*, Electric Power 2006, Atlanta, GA, May 2-4, 2006.
10. Kai, K., Kikkawa, H., Kato, Y., Nagai, Y., Gretta, W., *SCR Catalyst with High Mercury Oxidation and Low SO_2 Conversion*, 2006 MEGA Symposium, August 28-31, 2006.