

New Mercury Oxidation SCR Catalyst for Bituminous Coal-Fired Power Plants

William J. Gretta

Isato Morita

Song Wu

Hitachi Power Systems America, Ltd.
Basking Ridge, NJ

Keiichiro Kai

Yasuyoshi Kato

Hirofumi Kikkawa

Naomi Imada

Yoshinori Nagai

Babcock-Hitachi, K.K.
Kure, Japan

ABSTRACT

A new SCR catalyst has been developed for bituminous coal-fired boiler applications resulting in improved mercury (Hg^0) oxidation activity while maintaining low SO_2 to SO_3 conversion. The performance of this new catalyst has been confirmed using laboratory-scale test apparatus and a 1 MWt pilot plant. Recent laboratory studies revealed that mercury oxidation rates across the SCR catalyst decreased with increasing concentrations of H_2O and SO_2 , and the decline of mercury oxidation 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 new 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. 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 about half of conventional catalyst. Pilot-scale test results were in good agreement with the laboratory-scale test results and confirmed that the Hg^0 oxidation activity of the newly developed catalyst was 1.4~1.7 times higher than that of conventional SCR catalyst. Large test modules of this new catalyst have been installed as part of a full size SCR reactor in a power plant to determine long term catalyst performance. An update of this demonstration test program will be provided.

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 contribute to high levels of ambient O₃ and PM_{2.5}. CAMR separately addresses the reduction of mercury (Hg) emissions from U.S. power plants. Current emissions from U.S. power plants is about 48 tons per year and 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.

Although a number of technologies have been demonstrated to reduce mercury emissions such as activated carbon injection (ACI), it has been determined that significant Hg removal can be achieved in FGD systems. This removal, however, is significantly affected by the amount of oxidized mercury (Hg²⁺) entering the FGD. 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 FGD systems^{1,2}. Therefore, increased mercury oxidation upstream of the FGD system will facilitate higher overall mercury removal for the plant. Selective catalytic reduction (SCR) catalyst has been shown to significantly increase mercury oxidation by converting elemental mercury (Hg⁰) to Hg²⁺ in coal combustion flue gases³⁻⁵. Many U.S. plants either have SCR and FGD systems already in place, or will need to install these systems for future CAIR NO_x and SO₂ control requirements, respectively. Therefore, utilizing the co-benefits of this equipment for mercury removal can result in significant capital and operating cost savings as compared to other mercury control technologies such as ACI.

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^{7,9}, 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 with low SO₂ to SO₃ conversion, will be the most economical solution for bituminous 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^{6,10}. In particular, SO₂ strongly reduces Hg⁰ oxidation at high temperatures (>662°F)⁸. It will therefore be difficult to achieve high Hg⁰ oxidation efficiency

through conventional SCR catalysts under high temperature and high SO₂ concentration conditions when firing high-sulfur bituminous coals.

Since 2003, 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 the 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), fabric filter (FF) and wet flue-gas desulphurization (WFGD) systems. BHK has also studied the impact of SO₂ concentration and 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 the pilot-scale test facility.

EXPERIMENTS

Laboratory-scale Tests

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 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 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.

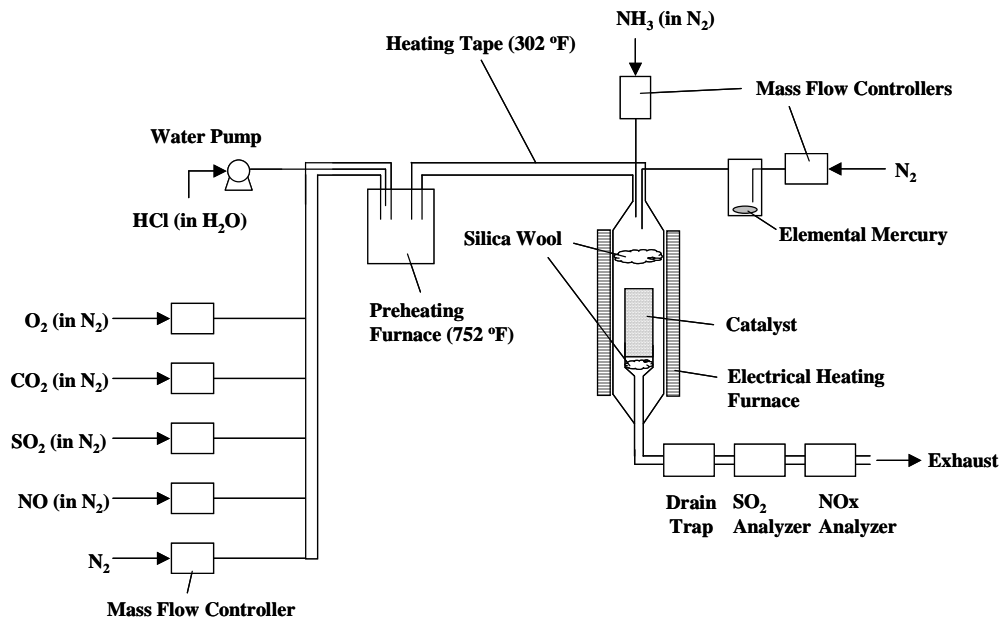


Fig. 1. Schematic of laboratory-scale apparatus to evaluate SCR catalysts

Pilot-scale Tests

The 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 contained 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) which was equivalent to roughly 1 MWt. The 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 seven 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) in Fig. 2 indicate the sampling points.

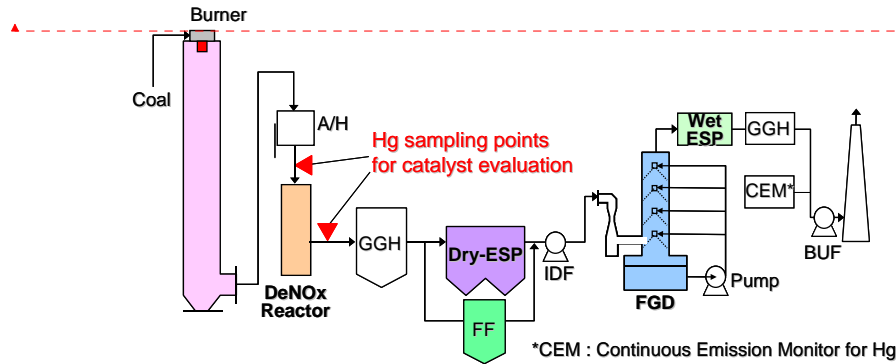


Fig. 2. Schematic Diagram of the Pilot Test Plant

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 tubing was used so that flue gas did not make contact with any metallic surfaces. Particle bound mercury and ash particles were collected in 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. 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 tubing was rinsed with a diluted nitric acid solution and pure water, and then the rinse was added to the buffer solution. 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, flyash 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.

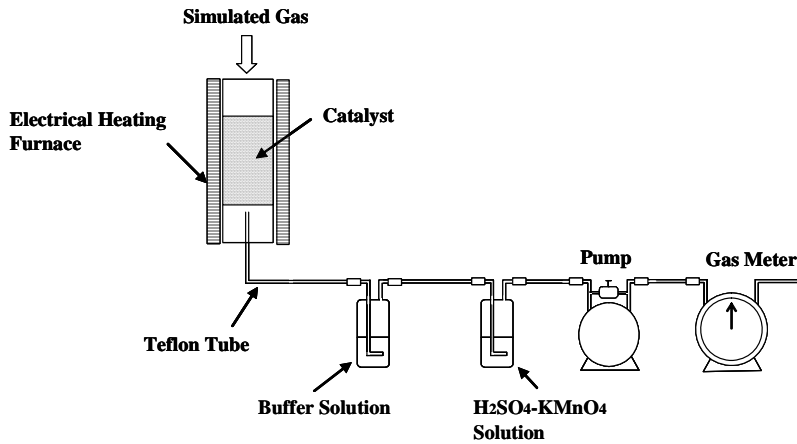


Fig. 3. Mercury Sampling Train for fundamental studies

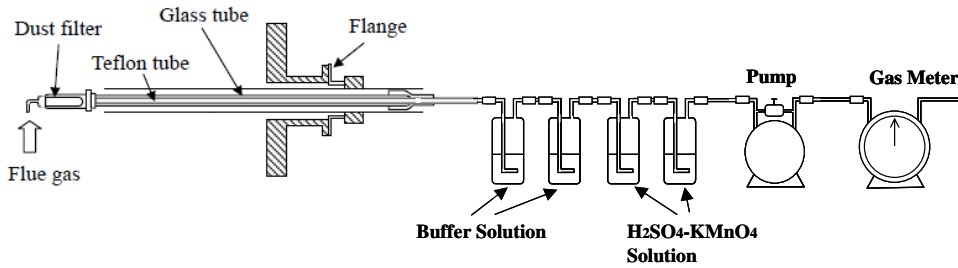


Fig. 4. Mercury Sampling Train for pilot tests

RESULTS AND DISCUSSION

Development of Catalyst for Mercury Oxidation

Ever since SCR was first applied in U.S. power plants firing bituminous fuels, Hitachi has made continuous efforts to improve the catalyst properties and to lower SO_2 to SO_3 conversion. Through these ongoing efforts, improved SCR catalyst has been applied for commercial use⁹, and resulting SO_2 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 NO_x removal requirements ($\geq 90\%$). This low SO_2 conversion, however, has also resulted in low Hg^0 oxidation because there is a close correlation between Hg^0 oxidation activity and SO_2 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. The Hg oxidation and DeNOx reactions take place exclusively on the surface of the catalyst, whereas SO₂ conversion rate is very slow and thus may increase with total active materials. 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 catalyst.

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

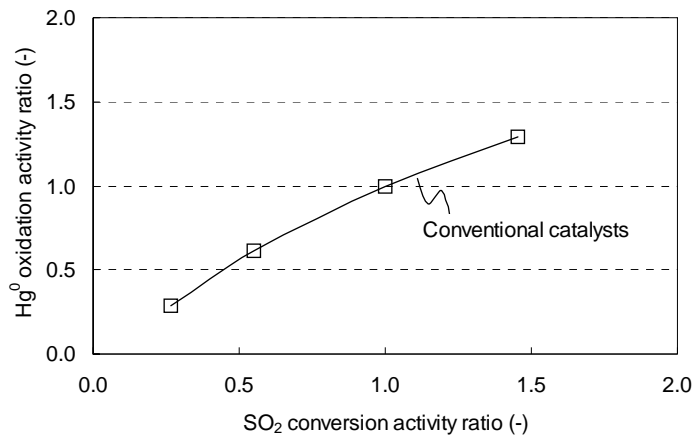


Fig. 5. Relationship between SO₂ conversion and Hg⁰ oxidation across catalyst

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 Hg⁰ oxidation with hydrogen chloride (HCl) and O₂ can be considered a diffusion-controlled reaction of Hg⁰ in the catalyst's pores because the reaction rate of Hg⁰ oxidation is faster than the diffusion velocity of Hg⁰ through the catalyst's pores. On the other hand, the reaction rate of SO₂ to SO₃ conversion, shown in equation (2), is slower than the diffusion velocity of SO₂ through the catalyst. In other words, the reaction of SO₂ 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.

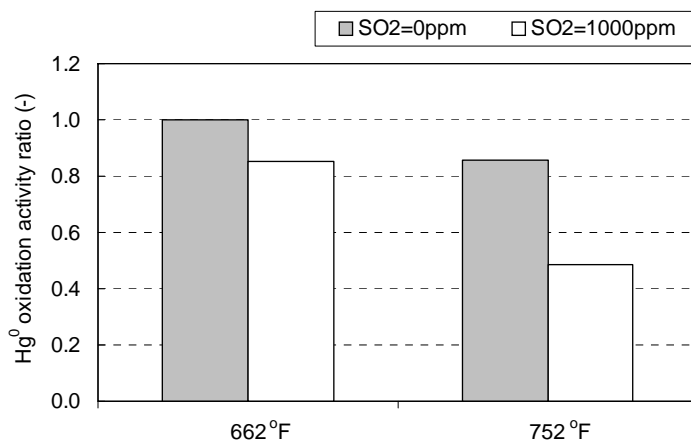
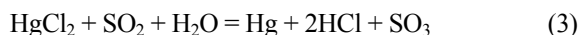


Fig. 6. Decrease of Hg^0 oxidation of conventional catalyst by coexistence with SO_2 gas

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 the Hg^0 oxidation rate across the SCR catalyst for bituminous coal-fired boilers where flue gas usually has high SO_2 concentrations. Thus, the optimum catalyst composition was evaluated in order to form the active sites that can preferentially promote Hg^0 oxidation. As a result, a new type of SCR catalyst has been developed, which shows higher Hg^0 oxidation activity without increased SO_2 conversion.

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 maintains higher Hg^0 oxidation rate than the conventional catalyst at high temperatures. Furthermore, the SO_2 to SO_3 conversion rate of developed catalyst is about half of that of conventional catalyst.

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.

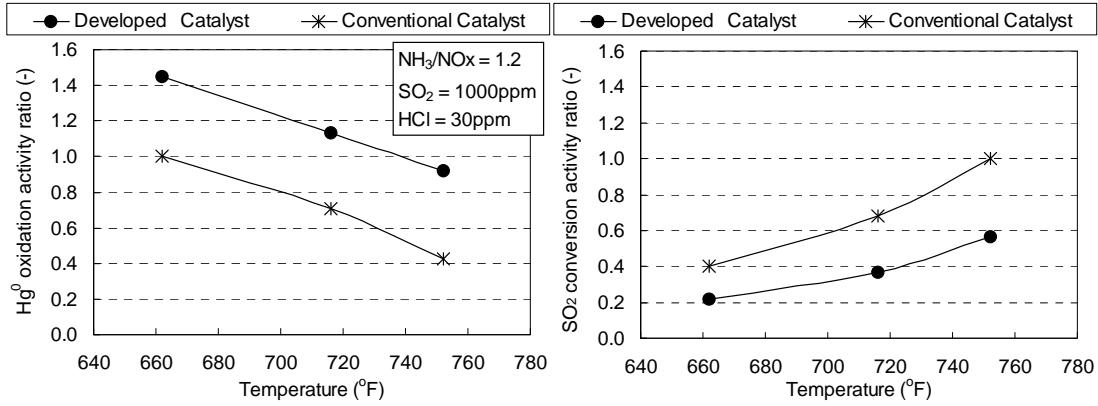


Fig. 7. Temperature characteristics of Hg⁰ oxidation activity and SO₂ to SO₃ conversion activity for developed catalyst and conventional catalyst

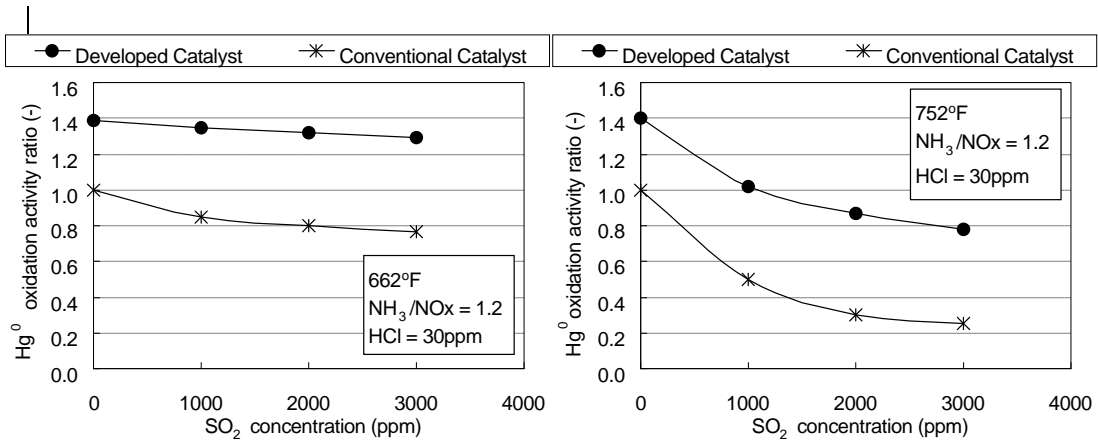


Fig. 8. Effect of SO₂ concentration for developed catalyst and conventional catalyst at each temperature

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) (this needs to be explained...are there impacts from HCl, Hg?). 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 for Pilot Testing

Parameters	Units	Operating Conditions
Coal Type	-	High sulfur bituminous coal
Flue Gas Temp.	°F	648 ~ 763
Inlet NO _x	ppm	300
O ₂	%	5
SO ₂	ppm	1800 ~ 2000
HCl	ppm	20 ~ 30
Hg	µg/m ³ N	7 ~ 11
NH ₃ /NO _x ratio	-	0.9
NO _x Removal Efficiency	%	90

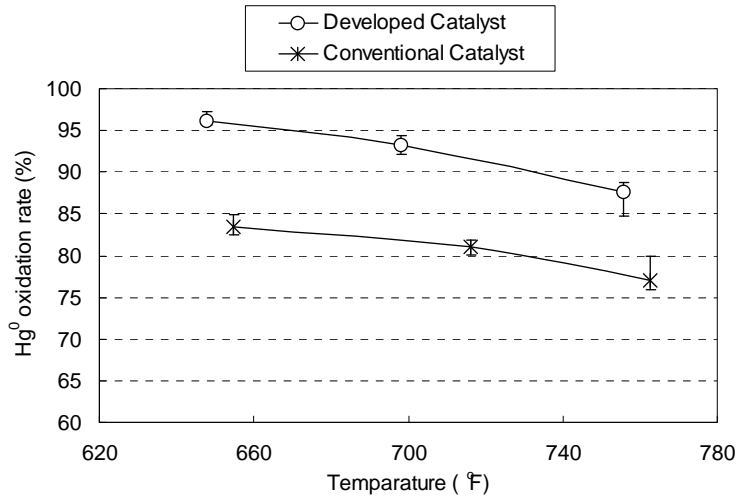


Fig. 9. Hg⁰ oxidation of Developed catalyst at Pilot-scale test facility

Development of Catalyst for Mercury Oxidation

In order to ascertain the performance of the developed catalyst in an actual operating unit, testing is underway at two U.S. plants burning high-sulfur coal. Table 2 shows the testing schedule.

Table 2 – Testing Schedule for New Mercury Oxidation Catalyst

Plant	Schedule			Note
	2007	2008	2009	
Plant A	Installation ▽	Test ▽ Test ▽	Test ▽	Module test
Plant B	Installation ▽	Sampling ▽	→	Sample test

Shown in Figure 10 is the arrangement of catalyst in an existing SCR reactor for Plant A. Basically, the reactor includes two modules (blocks) of the developed catalyst in both layers of the existing reactor. Above and below each catalyst layer is a partition plate that is used to separate the gas entering and leaving the test catalyst. This allows for a proper determination of the inlet and outlet flue composition which include the following measurements:

- NOx
- SO2
- SO3
- NH3
- Hg
- HCl

The testing will identify the mercury oxidation across the catalyst along with the resulting SO2 oxidation.

For Plant B, catalyst is installed in an operating SCR and catalyst plates will be periodically sampled and tested at BHK’s laboratory to confirm long term durability.

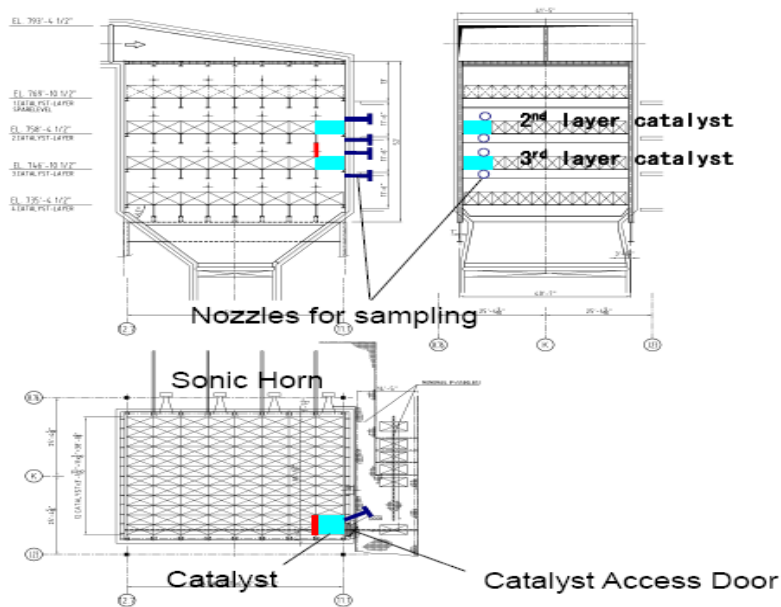


Figure 10 – Full-Scale Reactor Test Program (Plant A)

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 tests 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. Current full-scale testing is underway to determine the performance of the catalyst in an actual operating unit.

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