

# Development of NO<sub>x</sub> Removal SCR Catalyst for Low SO<sub>2</sub> Oxidation

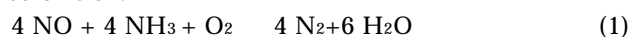
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We developed a selective catalytic reduction NO<sub>x</sub> catalyst for low SO<sub>2</sub> oxidation activity. This paper describes the cause of increase of SO<sub>2</sub> oxidation, the features of the improved SCR catalyst, and durability test results based on operation of a heavy oil fired unit.

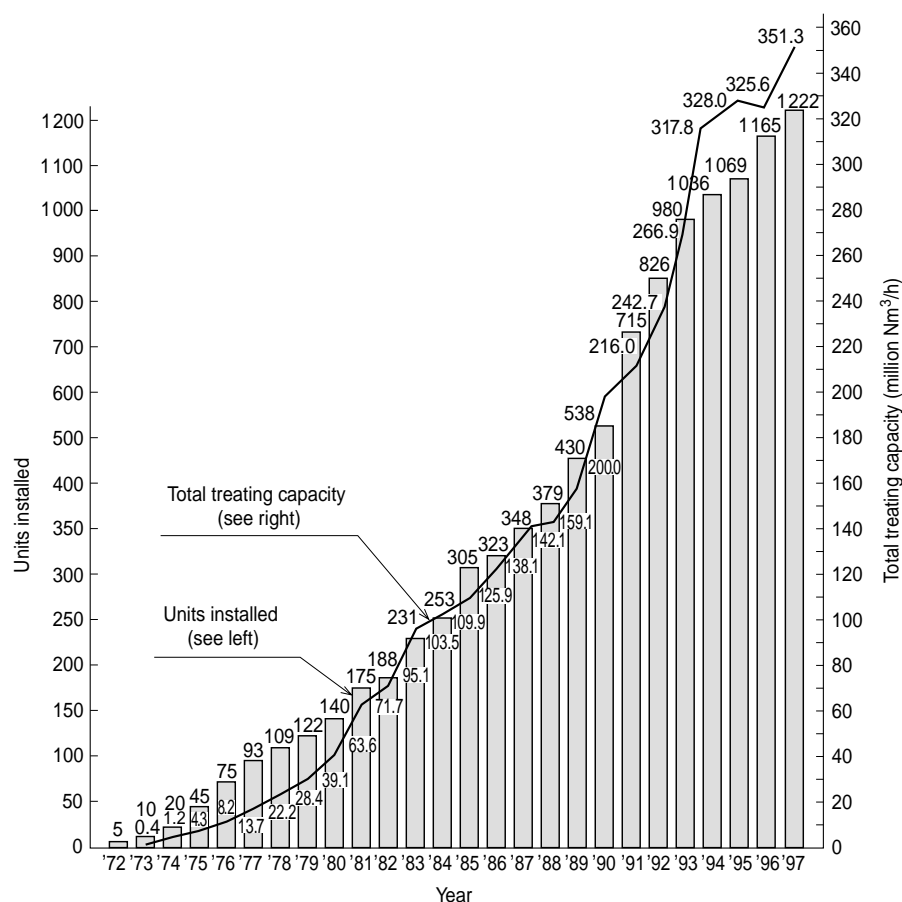
## 1. Introduction

More than a thousand units of flue gas denitrification systems have been in use in Japan for professional and industrial boilers since the first system for boilers started operation in the 1970s<sup>(1)</sup> (**Fig. 1**). Numerous flue gas denitrification techniques have been researched and developed so far, but most systems in operation are based on the selective catalytic reduction (SCR) method using NH<sub>3</sub> as reducing agent<sup>(2)</sup>. As the SCR method is employed widely, the catalysts have been improved to minimize deterioration of performance resulting from SO<sub>x</sub> contained in flue gas and alkali metals and others contained in

dust. Flue gases from heavy oil, coal and other fuels are being treated<sup>(3)</sup>. The de-NO<sub>x</sub> catalyst induces a selective catalytic reaction as shown in formula (1), and is also accompanied by SO<sub>2</sub> oxidative reaction shown in formula (2) as a side reaction in the presence of SO<sub>2</sub>.



Recently, boiler fuels of poor quality have come into use, including Orimulsion<sup>®</sup> and other high-sulfur heavy oils containing inorganics such as vanadium. This vanadium contained in the flue gas sticks to the de-NO<sub>x</sub> catalyst in the downstream apparatus, and causes a gradual increase in the SO<sub>2</sub> oxidation rate



**Fig. 1 Delivery record of SCR plants in Japan.**

More than 1000 units of flue gas denitrification systems are operating at present.

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of the catalyst. As a result, the  $\text{SO}_3$  produced by the  $\text{SO}_2$  oxidative reaction reacts with  $\text{NH}_3$  in the flue gas as shown in formula (3), and acid ammonium sulfate is produced.

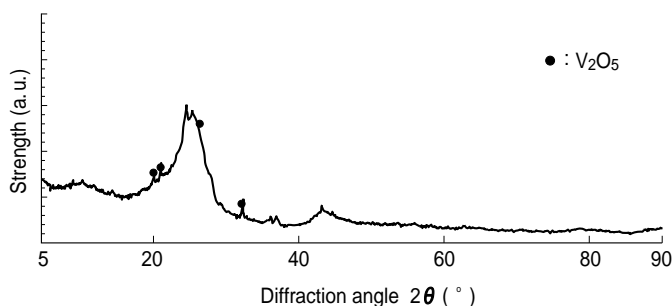


The increase of dust level resulting from acid ammonium sulfate has adverse effects that include corrosion, clogging and lowering of precipitation efficiency of downstream apparatus such as air preheater and electric dust precipitator, and an effective method for suppressing formation of  $\text{SO}_3$  has been required. Mitsubishi Heavy Industries, Ltd. (MHI) has been attempting to reduce the increased  $\text{SO}_2$  oxidation rate by removing the vanadium sticking to the de-NOx catalyst by chemical washing<sup>(4)</sup>. However, chemical washing of the catalyst requires frequent sampling exchanges at the time of shutting down the power plant, and involves very large expenses. In order to lessen the treatment process, there has been a need to develop a new de-NOx catalyst with lower  $\text{SO}_2$  oxidation rate.

MHI has already succeeded in developing a surface-treated catalyst for inhibiting permeation of vanadium compound into the catalyst, as a new de-NOx catalyst with lower  $\text{SO}_2$  oxidation rate. This paper reports on the history of research and development and the results of use of the new catalyst.

## 2. Mechanism of vanadium accumulation on de-NOx catalyst

Accumulation of vanadium on catalyst is believed to be caused when the vanadium contained in the dust collides with the catalyst. The results of X-ray diffraction analysis of the dust in flue gas of high sulfur heavy oil fired boiler, and the surface of the catalyst used in this operation are shown in **Fig. 2** and **Fig. 3**, respectively. From the X-ray diffraction pattern shown in Fig. 2, it has been ascertained that  $\text{V}_2\text{O}_5$  exists in the amorphous material due to unburnt carbon in the dust of flue gas. In the X-ray diffraction pattern of the surface of the de-NOx catalyst before and after the real gas durability test shown in Fig. 3, in the catalyst after 14 400 hours, diffraction peaks of  $\text{V}_2\text{O}_5$  and  $\text{VOSO}_4$  were noted aside from the peak of  $\text{TiO}_2$ . The existence of  $\text{VOSO}_4$  on the catalyst means



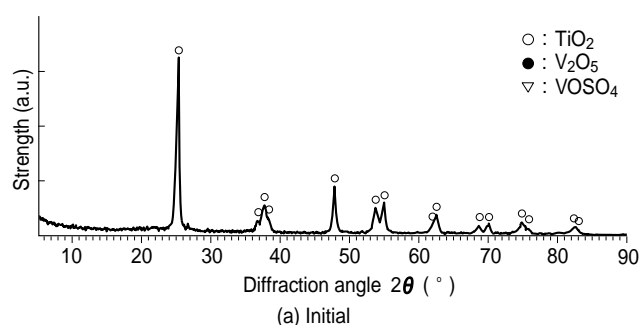
**Fig. 2 X-ray diffraction pattern of dust.**  
Dust contains  $\text{V}_2\text{O}_5$ .

that  $\text{V}_2\text{O}_5$  in the dust sticks to the catalyst to produce  $\text{VOSO}_4$  according to formula (4).

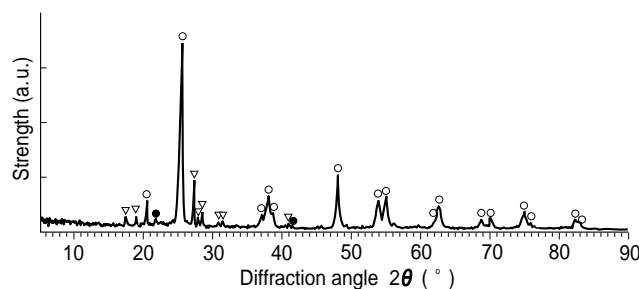


Consequently,  $\text{V}_2\text{O}_5$  and  $\text{VOSO}_4$  accumulated on the catalyst surface permeate into the catalyst in the presence of moisture, and the permeating vanadium appears to increase the  $\text{SO}_2$  oxidation rate.

Next, in various heavy oil fired power plants, the tendency of vanadium to accumulate on the catalyst and the tendency of the  $\text{SO}_2$  oxidation rate to increase were investigated. As is known from the relation between the operation time and vanadium accumulation amount (converted to  $\text{V}_2\text{O}_5$  amount) of the catalysts used in various power plants in **Fig. 4**, in all catalysts, the vanadium accumulation increases gradually



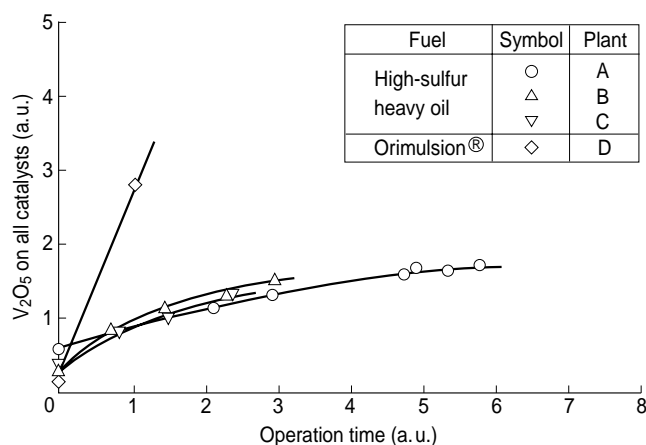
(a) Initial



(b) After 14 400 hours

**Fig. 3 X-ray diffraction patterns of de-NOx catalyst before and after durability test (14 400 hours).**

After durability test,  $\text{V}_2\text{O}_5$  and  $\text{VOSO}_4$  are accumulated on catalyst.



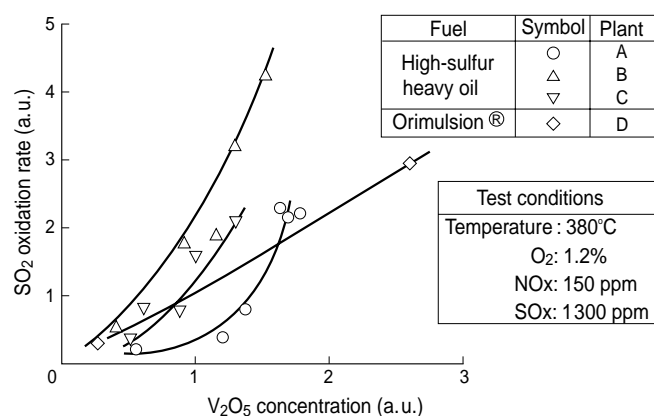
**Fig. 4 Time dependence of vanadium accumulation in de-NOx catalysts.**

Vanadium accumulates gradually on all catalysts.

in the course of time, and especially in power plant D using Orimulsion<sup>®</sup> of high content of  $V_2O_5$  as the fuel, the vanadium amount increases sharply due to real gas exposure. From the relation between the vanadium concentration and  $SO_2$  oxidation rate of the catalysts used in the actual plants shown in **Fig. 5**, it is known that in all catalysts the  $SO_2$  oxidation rate increases along with elevation of the vanadium concentration. In each catalyst, there is a difference in the increase rate of the  $SO_2$  oxidation with respect to the vanadium concentration, which is believed to be due to the difference in the state of accumulation of vanadium. Thus, in the catalyst with a larger increase rate of  $SO_2$  oxidation, the accumulated vanadium generally permeates into the catalyst, and is uniformly supported on the  $TiO_2$ , which is the principal component of the catalyst, while in the catalyst with a smaller increase rate, the accumulated vanadium often remains on the catalyst surface as crystalline matter.

### 3. Features of improved de-NOx catalyst

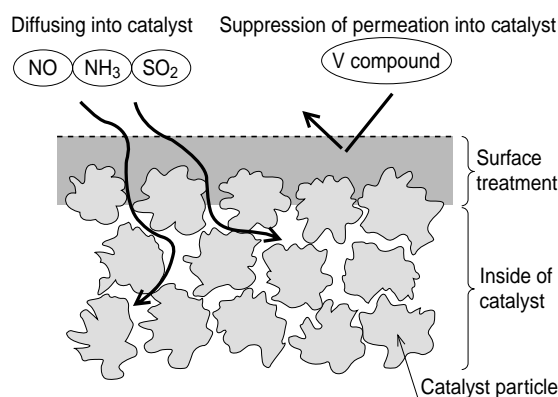
In order to suppress permeation of vanadium compounds such as  $VOSO_4$  and  $V_2O_5$  sticking to the



**Fig. 5 Relationship between  $V_2O_5$  concentration and  $SO_2$  oxidation activity of de-NOx catalysts.**

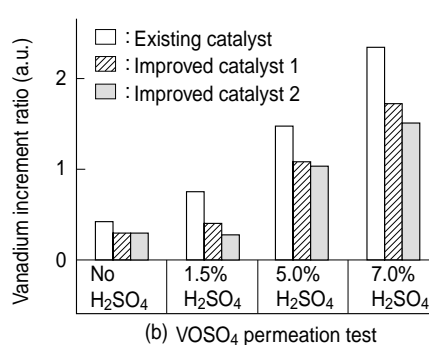
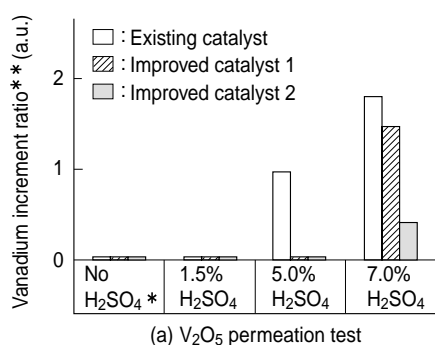
The higher the  $V_2O_5$  concentration, the higher the  $SO_2$  oxidation rate.

catalyst surface into the catalyst, an improved de-NOx catalyst with special surface treatment has been developed. A schematic model of this catalyst is shown in **Fig. 6**. This catalyst is prepared by treating the surface of the de-NOx catalyst, and it is characterized by sufficient diffusion of gas components such as NO and  $NH_3$  into the catalyst layer, and simultaneous suppression of permeation of  $V_2O_5$  or  $VOSO_4$  into the catalyst. Using this surface-treated improved de-NOx catalyst, permeation of  $V_2O_5$  and  $VOSO_4$  into the catalyst was tested by assuming dummy states of stopping and operation of the thermal power plant. In the dummy stopping conditions, the catalyst was held in a thermostatic oven (20°C, relative humidity 80%),  $V_2O_5$  or  $VOSO_4$  powder was applied and left over for a specified time, and the amount of vanadium permeating into the catalyst was analyzed. From the  $V_2O_5$  and  $VOSO_4$  permeation tests of 526 hours shown in **Fig. 7** (a), (b), it was ascertained in both cases that the vanadium accumulation tends to increase as the concentration of sulfuric acid contained in the catalyst becomes higher. As compared with  $V_2O_5$ , it is known that  $VOSO_4$  is more likely to permeate and accumulate in the catalyst. The reason seems to be



**Fig. 6 Structure model of improved de-NOx catalyst.**

Improved catalyst suppresses permeation of V compound into catalyst.

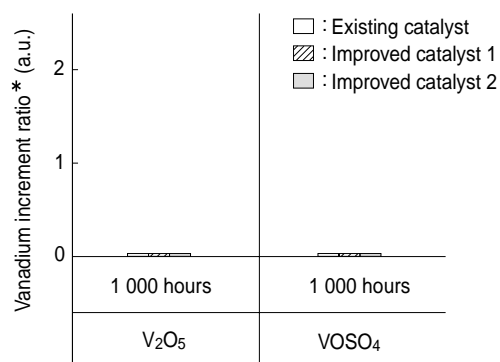


\*:  $H_2SO_4$  concentration refers to amount of addition to catalyst.

\*\* : On the basis of vanadium increment of 1 at  $H_2SO_4$  concentration 5.0% of existing catalyst in  $V_2O_5$  permeation test.

**Fig. 7 Test results of vanadium permeation into the improved catalyst in constant-temperature and -humidity chamber (526 hours).**

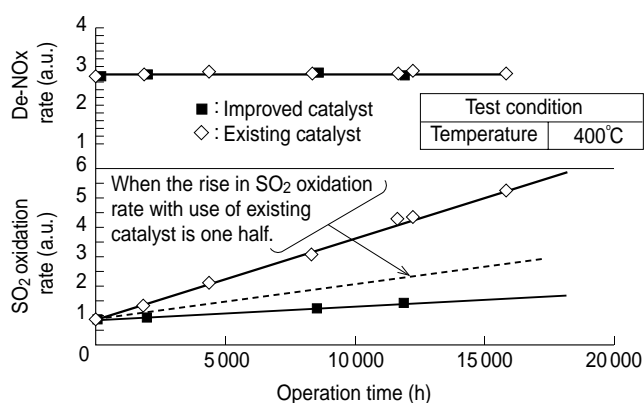
The improved catalyst is effective in suppressing permeation of both  $V_2O_5$  and  $VOSO_4$ .



\* : Vanadium increment ratio indicated is the same as in Fig. 7.

**Fig. 8 Test results of vanadium permeation into the improved catalyst in the heat of electric furnace**

Vanadium compounds do not permeate into the catalyst while they are heated in electric furnace at 400°C.

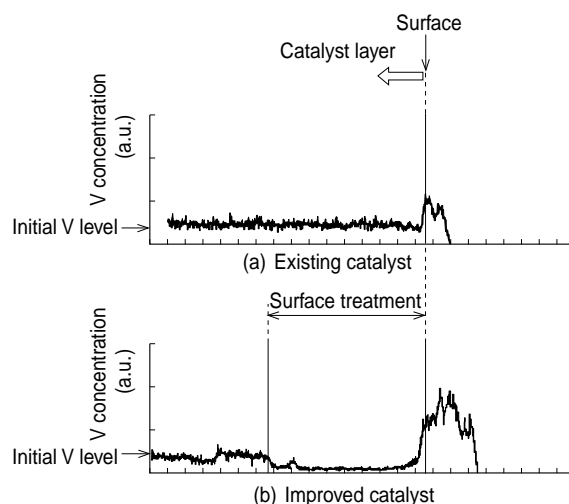


**Fig. 9 Durability test result of improved catalyst for heavy oil firing.**

The improved catalyst is more effective than conventional catalysts in retardation of SO<sub>2</sub> oxidation rate.

that VOSO<sub>4</sub> is more easily dissolved in water than V<sub>2</sub>O<sub>5</sub>, and hence permeates into the catalyst together with the moisture. In the improved catalyst, the vanadium increment is 5 to 80% of the existing catalyst in V<sub>2</sub>O<sub>5</sub>, and about 40 to 80% of the existing catalyst in VOSO<sub>4</sub>, and in both cases it has been ascertained that the improved catalyst is more effective in suppressing permeation of vanadium than the existing catalyst.

On the other hand, assuming actual operation, V<sub>2</sub>O<sub>5</sub> or VOSO<sub>4</sub> powder was applied on the catalyst, and left over for a specific time in an electric furnace at 400°C, and the amount of vanadium diffusing into the catalyst was analyzed. From an electric furnace heating test of V<sub>2</sub>O<sub>5</sub> and VOSO<sub>4</sub> of 1 000 hours as shown in Fig. 8, for both catalysts, no accumulation of vanadium in the catalyst was observed in either V<sub>2</sub>O<sub>5</sub> or VOSO<sub>4</sub>. This suggests that permeation into the catalyst of vanadium applied on the surface occurs mainly in the stopped state. Furthermore, permeation of vanadium into the catalyst in the stopped state seems to be caused mainly by transfor-



**Fig.10 Status of accumulation of vanadium composition into de-NOx catalyst (4 300 hours).**

The improved catalyst is effective in retarding permeation of vanadium into its catalyzing layer.

mation of the adsorbed SO<sub>3</sub> into sulfuric acid in the presence of moisture, and by this moisture allowing the vanadium compound to permeate into the catalyst.

#### 4. Real gas performance of improved de-NOx catalyst

Using the improved de-NOx catalyst whose effectiveness has been confirmed in the permeation test in chapter 3, a full-size catalyst was prepared, and evaluated in the real gas durability test at the plant. Fig. 9 shows the denitrification performance and the SO<sub>2</sub> oxidation rate of the existing catalyst and improved catalyst. It can be seen that the improved catalyst is roughly equal in denitrification performance to the existing catalyst, and that it is almost free from change in over 12 000 hours, while the elevation of the SO<sub>2</sub> oxidation rate is suppressed to less than 1/2 that of the existing catalyst.

Next, accumulation of vanadium on the real gas durable catalyst was observed. From an X-ray microanalyzer analysis of the catalyst layer section shown in Fig. 10, in the existing catalyst, vanadium is only slightly concentrated on the catalyst layer surface, and mostly permeates into the inside of the catalyst, whereas in the case of the improved catalyst it is mostly accumulated on the surface treatment layer and hardly permeates into the inside of the catalyst.

Meanwhile, as a recycling test of the improved catalyst developed after a real gas long-term durability test, an elution removal test of accumulated vanadium by chemical washing was attempted. As in the existing catalyst, vanadium elution removal was possible. It was regenerated to the level of initial

performance, and repeated recycling was also found to be possible.

From an evaluation of activities and properties, the surface-treated improved de-NO<sub>x</sub> catalyst has been shown to be effective in suppressing permeation of vanadium into the catalyst layer and suppressing gradual elevation of the SO<sub>2</sub> oxidation rate.

## 5. Conclusion

Surface-treated improved de-NO<sub>x</sub> catalysts were installed in high-sulfur heavy oil fired thermal power plants in 1998 and 2000, and are operating steadily at present. The new catalysts are expected to come into ever-greater demand in the future as de-NO<sub>x</sub> catalysts suited to the individual needs of users.

From the viewpoint of global environmental conservation, the necessity for denitrification systems is increasing, and is not limited to professional and industrial boilers. This technology is widely employed

in various flue gas treating facilities including refuse incinerators, electric furnaces, and sintering ovens. In this trend, the properties of fuel and flue gas are becoming more diversified, and there is a need for the development of new de-NO<sub>x</sub> catalysts with higher durability and reduced side reactions. Henceforth, MHI will continue its efforts to develop a more economical and reliable flue gas treatment technology in order to meet the various needs of a wide range of users.

## References

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