Verification of clean air technologies in GTCC

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Abstract

After 1960 in Japan, serious air polluting occurred especially in metropolitan areas. Even after 2000, NOx level in some areas are still over environmental criteria. Under these circumstances, it's quite difficult for power companies to plan and construct a new thermal power plant in those areas. This study shows the possibility of new power plants in city area. 99% of NOx can be removed with Selective catalyst reduction(SCR). When it goes with Gas Turbine Combined Cycle(GTCC), EPC (Engineering, Procurement and Construction) and location selecting would be much easier.

1. Introduction

In this IAIA16, we obtained an opportunity to release two articles about Gas Turbine Combined Cycle (hereinafter, referred to as GTCC).

In the 1960's-1970's, Japan achieved high economic growth. Due to such rapid economic growth, the electric power demand and the amount of electric energy generation were increased by 3-times in just ten years. At that time, the oil fired power generation was the main source of electric energy generation which discharges large amount of nitrogen oxide(NOx), sulfer oxide(SOx) and dusts. Air pollution was a serious problem especially Tokyo, Osaka and Nagoya. In the 1980's, Liquefied natural gas (hereinafter, referred to as LNG) fired power generation was gradually introduced and it contributed to the reduction of air pollution levels. But LNG fired power generation still has problem of NOx discharge.

In the past, various technologies have been examined to decrease NOx, which is the cause of acid rain. Acid rain is one of the global environmental issues. In metropolitan areas in Japan, our health and life have been suffered from it. Due to its economic efficiency and reliability, the ammonia selective catalyst reduction method (SCR method) is currently the main source of stationary flue gas denitrification.

In 1977, Sakai Chemical Industry Co., Ltd. succeeded, for the first time in the world, in the mass production of a NOx removal catalyst, a "titanium-base-honeycomb catalyst", which is the main element of this method. Sakai has achieved the position of the nation's largest supplier. Sakai Chemical Industry Co., Ltd. is the only enterprise that possesses rights to the entire process from the supply of titania which is the main raw material of the catalyst, to the de-NOx catalyst.

2. SCR Catalyst

2-1. De-NOx catalyst reaction

De-NOx catalysts reduce and eliminate nitrogen oxide generated through incineration processes at power plants and waste incineration facilities.

The denitrification reaction uses ammonia as a reducing agent and the representative equation is as follows.

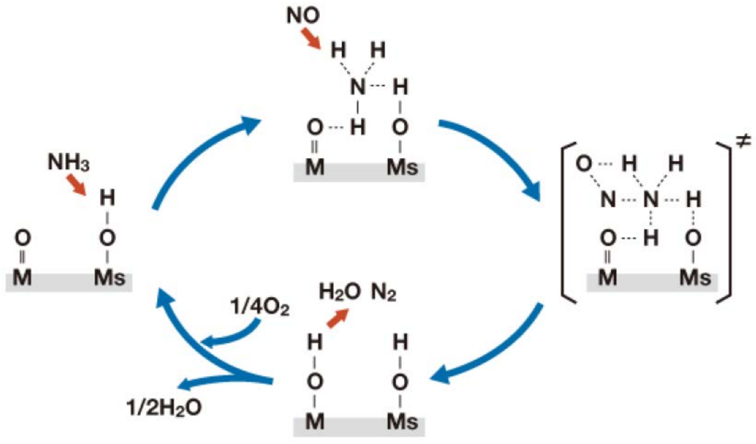
$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

The reaction mechanism of de-NOx reaction is as follows.

1) Diffusion of NH_3 from gas phase to catalyst surface
2) Diffusion of NH_3 into catalyst pore
3) NH3 adsorption on active site
4) NO diffusion from gas phase to adsorbed NH_3
5) Reaction of NO and NH_3 to N_2 and H_2O
6) Desorption of N_2 and H_2O to catalyst surface
7) Diffusion of N_2 and H_2O into gas phase

Figure 1 shows de-NOx reaction schematically.

Figure 1 : Mechanism of de-NOx reaction



The key points to the de-NOx reaction activity are the internal diffusion of the gas and the activity of the active point. When either is inhibited, the catalytic activity decreases.

The classification of the catalyst deterioration from reaction mechanism is as follows.

1) Pore confinement by acid ammonium sulfate, calcium sulfate, silica, the fine particles dust
2) Adhesion of alkali metals and the heavy metal at the active point
3) Change of catalyst in itself by the thermal influence

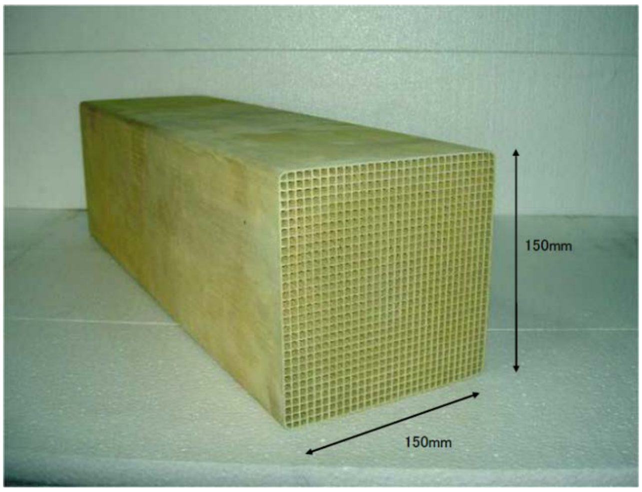
Generally, as for the catalyst performance drop, some factors are combined.

Pore confinement 1) is deterioration by the diffusion inhibition of the gas. It is particularly important, because the diffusion is a rate control process of the de-NOx reaction. Adhesion of metals 2) and the thermal influence 3) are the deactivation of the active point.

Initially, the shape of the de-NOx catalyst is mainly pellet type or the noodles type, because of easy manufacturing. But these types have the problem of high pressure drop and blowing. To solve these problems, the solid honeycomb type was developed and now widely used.

Figure 3 shows the image of honeycomb type catalyst.

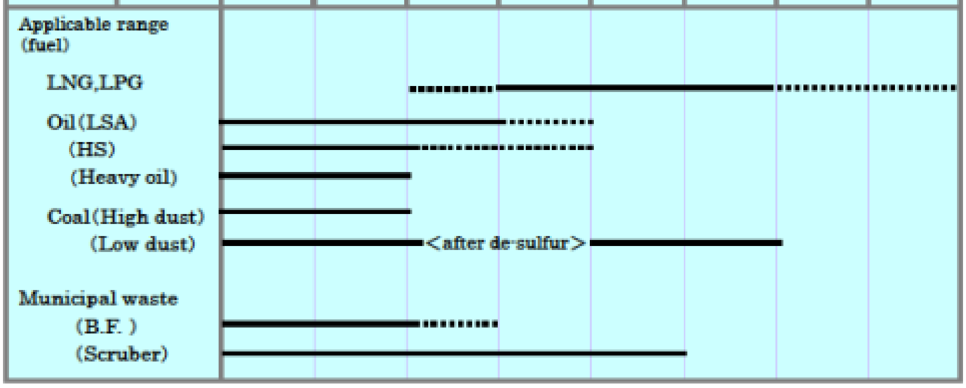
Figure 3 : Honeycomb type catalyst



The required cell number of the catalyst depends on the amount of the dust.
Table 1 shows the honeycomb catalyst dimension and applicable range.

Table1 : Honeycomb catalyst dimension and applicable range

Pitch	unit	7.4	6.0	5.0	4.2	3.7	3.3	3.0	2.5
External diameter	mm	150	150	150	150	150	150	150	150
Cell number	cell×cell	20×20	25×25	30×30	35×35	40×40	45×45	50×50	60×60



2-2. Characteristics of De-NOx catalyst

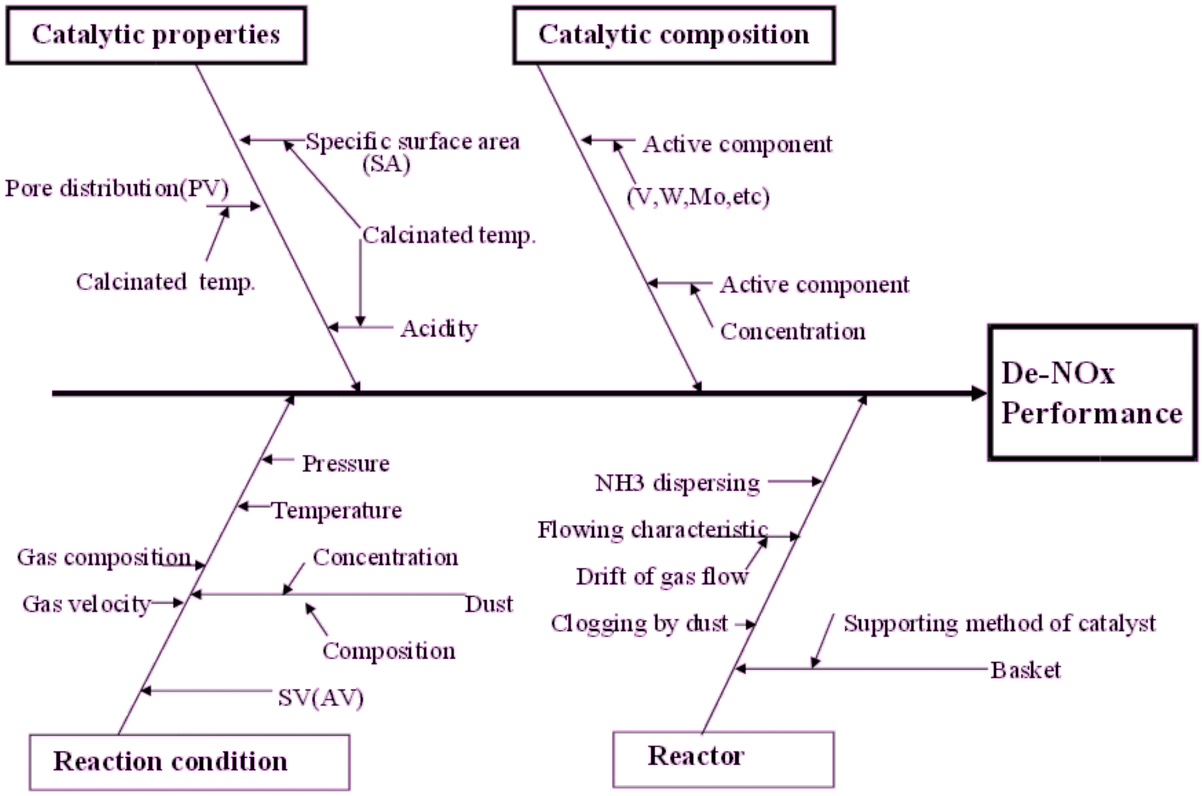
De-NOx catalyst is needed varies characteristics according to the gas composition and temperature.

Under the high dust and high SOx concentration conditions, it is needed not only the high de-NOx activity, but also the low SO_2 oxidation rate and the resistance of acid ammonium sulfate and alkali.

On the other hand, under low dust and low SOx concentration conditions like LNG combustion, it is mainly needed the high de-NOx activity.

Figure 4 shows the characteristic diagram for de-NOx performance.

Figure 4：Characteristic Diagram on De-NOx Performance



The pore volume affects the gas diffusion in the catalyst. The number of active sites in a given area is some extent proportional to the ratio specific surface area. But, without validation of conditions for de-NOx activity, making large specific surface area degrades performance of heat-resisting property. Therefore, to specify optimum calcination temperature and specific surface area is critical factor for de-NOx activity.

The composition of the catalyst is decided by gas temperature, SOx concentration and the amount of the dust.

The reaction condition is an important factor of the de-NOx activity and the catalyst life period. The lower NOx concentration, the lower de-NOx activity, because the de-NOx reaction activity depends on the diffusion of the gas. The de-NOx activity depends on the space velocity. The larger catalyst volume comes to the higher de-NOx activity. The influence of the gas composition on de-NOx activity is as follows.

The higher concentration of H2O, the lower de-NOx activity.

The higher concentration of O2, the higher de-NOx activity.

As for the reactor, it is necessary to consider about the gas drift and diffusion of the ammonia.

For high performance of the catalyst, it is necessary to optimize the catalyst property and composition, as well as the reaction condition and the reactor.

3. De-NOx Catalyst for New GTCC System

3-1 Application for New GTCC System

High de-NOx activity at low NOx concentration is needed for GTCCs application. Therefore, we have to consider for high de-NOx activity as follows:

1) lower pitch (high cell number) for increasing the gas contact area
2) thin wall thickness for low pressure drop
3) provision for the gas drift and diffusion of the ammonia

3-2 Test Results -Micro Scale and Actual Scale-

We tested in two conditions to verify NOx removal rate. The result showed 99% de-NOx activity in the micro scale and in the actual scale.

SV=45000l/h, Gas Velocity: Actual scale/Micro scale = 1.9

4. Conclusion

99% of NOx was removed with SCR at the low NOx concentration in the micro and actual scale test equipment.

EPC(engineering, Procurement and Construction) is facilitated with GTCC system for new power plants.

Location selecting is also much easier with GTCC system.

***Postscript**

We have already established a method for verifying the long-time performance of catalyst. This method is including a downsized test machine and test programs.

At this moment (June 2016), we are under preparation for International Patent on this method.

Reference

1. Japanese Government statistic and Website
2. Website: The federation of electric power companies of Japan
3. 50 years of company history on Kansai electric power company, 2002
4. 100 years of company history of Osaka Gas, 2005
5. Engineering and raw for preventing environmental pollution, new edition 2014
6. IAIA16 presentation #534 System developing from GTCC to GTCCs
7. A Gift from the Sun (Eco-support 2016)
8. Website of Eco-support: httep://www.plus-eco.com/