

7.9 Denitrification of Exhaust Gas

7.9.1 Introduction

Air pollution resulting from nitrogen oxides (NOx) in Japan, has been improved through the use of the low NOx combustion and the flue gas denitrification.

7.9.2 History of Flue Gas Denitrification Techniques in Japan

As previously mentioned, the incident where photochemical smog plagued the Risho High School in Tokyo in 1970 placed focus on NOx as an air pollutant. Along with the low NOx combustion techniques, research in flue gas denitrification techniques were also begun.

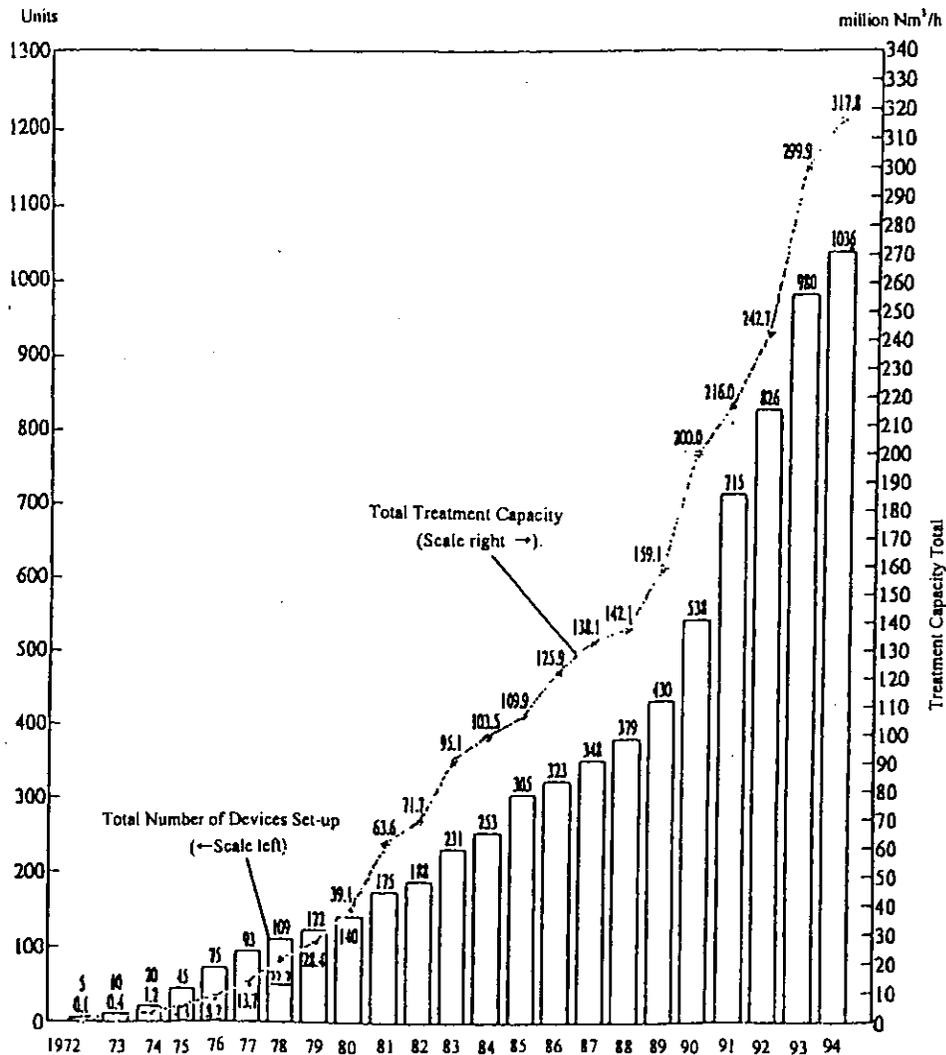
In the early stages, the catalytic cracking process, catalytic oxidation method, and non-selective catalytic reduction process were some of the dry process researched. Meanwhile, wet process such as the direct absorption method, oxidation absorption process, liquid phase absorption method, and complex salt creating absorption method were researched. However, the reaction of NO was poor and in the end these methods did not make it to the stage of practical use. The practically applied (includes substantive testing) flue gas denitrification process is illustrated in Table 7.9.1¹⁾. For the most part, the dry process is the mainstream in practical application in Japan.

Table 7.9.1 List of Denitrification Process

		Reaction Agent	Method	Status Practical Application
Dry method	Ammonia Catalytic Reduction Process	NH ₃ , (NH ₂) ₂ CO	Utilizes a catalyst, causes a reaction between ammonia and NOx, and separates the non-harmful nitrogen (N ₂) and water vapor (H ₂ O)	Used in boilers, gas turbine, diesel, garbage incinerator, and heating furnaces, accounts for over 90% of the denitrification devices currently in use
	Non-catalytic Reduction Method	NH ₃ , (NH ₂) ₂ CO	Uses ammonia as a reduction agent, which is then sprayed into the exhaust gas, reduces NOx into N ₂ using a gas phase non-catalyst	Used in petroleum heating furnaces, garbage incinerators. Denitrification rate is low and there are many non-reacting reduction agents, therefore there are only a few points of application.
	Activated Carbon (simultaneous desulfurization · denitrification)	NH ₃	Absorbs SOx from the exhaust gas using activated carbon (or activated cokes), the NOx is decomposed to N ₂ by the NH ₃ agent utilizing activated carbon (activated cokes) as its catalyst.	Used in boilers and incinerators. It is also being used as a simultaneous desulfurization/denitrification unit in industrial fluidized bed boilers.
	Electron Beam Irradiation Method (simultaneous desulfurization · denitrification)	NH ₃	NH ₃ is added to the exhaust gas and irradiated with an electron beam. The SOx is converted into ammonium sulfate and the NOx is converted into ammonium nitrate.	US and Germany have long performed testing for verification of the method. Testing also being done in Japan. Hopes for use in boilers and incinerators.
Wet method	Oxidation Reduction Method	O ₃ , ClO ₂ , Na ₂ SO ₃	NO is oxidized using ozone or chlorine dioxide and adsorbed by a soda solution.	Several units being used in relatively small boilers and heater furnaces. Not easily used for large-scale facilities as the oxidizing agents such as ozone and chlorine dioxide are expensive.

Among dry process, the ammonia catalytic reduction process is the most widely used and accounts for about 90% of the total in treatment capacity²⁾. Also, in regards to the flue gas processing system which has made possible in recent years the ability to simultaneously perform both denitrification and desulfurization, substantive testing is being run and the development of this technique is continuing.

As shown in Fig.7.9.1³⁾, the flue gas denitrification system began to be implemented from around 1972. By the end of fiscal 1994, there were 1,036 units in operation. The total treatment capacity of exhaust gas is 317.8 million m³N/h, which exceeds that of flue gas desulfurization systems.



Note: The values shown are those current as of January 1, for the years up to 1982. For the years starting from 1983, the values shown are those which were current as of March 31.

Source: Environment Agency

Fig.7.9.1, Status Reports for Flue Gas Denitrification Devices based on Year

7.9.3 Recent trends in Flue Gas Denitrification Technology in Japan

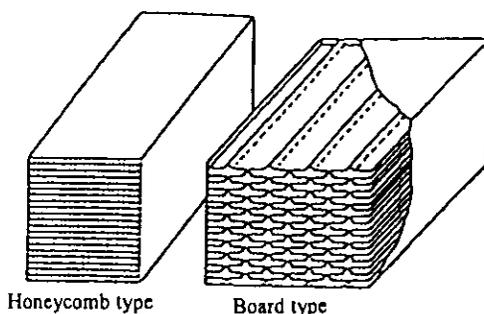
(1) Ammonia Catalytic Reduction Method

NH₃ is injected into the exhaust gas and due to the function of the catalyst, the NO_x in the gas is decomposed to N₂ and H₂O. This basic reaction is shown as follows in Eq. (1) and (2):



The catalyst which is currently being used, uses TiO₂, which receives little toxicity from SO_x, as a catalyst support and V₂O₅, WO₃, etc. as active bodies. Depending upon its use, a number of substances with different component make-up are used. In order to prevent the catalyst from losing pressure to some extent, the shape of the medium is either the honeycomb type and the board shaped parallel flow type. (refer to Fig.7.9.2⁴⁾)

As a result of all the technological development that has been done up until now, denitrification systems based on the ammonia catalytic reduction process are now able to run stably on automatic pilot. They are widely used in power generator boilers, diesel engines, gas turbines, and garbage furnaces. At present, the ammonia catalytic reduction method is the most popular technology used in the denitrification units.



The ordinary dimensions of the honeycomb type are 150 mm × 150 mm, and 500-1,000 mm long. The board type comes in various sizes.

Source: Junpei Ando: Exhaust Gas Purification Technology of the World, Coal Technology Research Center, 141 (1990)

Fig.7.9.2 Typical shapes of catalysts

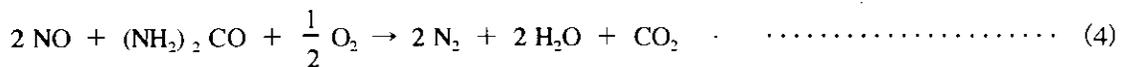
(2) Non-catalytic Reduction Process

This method is based on the theory that by using ammonia or urea water as a denitrification reducing agent and spraying it into exhaust combustion gas in the temperature range of 800~1,000°C where both NO_x and O₂ exist, NO would be selectively reduced. The basic reaction is illustrated in Eq. (3) and (4).

• In the case of ammonia



• In the case of urea water



As clearly seen in the reaction equations, in order to perform the non-catalyst reduction method, the existence of oxygen in the exhaust combustion gas is indispensable. However, if the coexisting oxygen concentration exceeds 1% or more then the rate of denitrification will indicate a maximal value at a certain density as the production of the NO by-product increases due to the oxidation of the ammonia near 900°C.

This method is used in boilers, garbage incinerators, etc. However, the rate of denitrification is not very high, at around 30~40%. In particular, in the case of garbage incinerators, it is widely used as a method of reduction when NOx reaches its peak concentration.

(3) Techniques for Simultaneous Desulfurization and Denitrification⁵⁾

As flue gas process techniques, there are already established techniques, the lime-gypsum wet process for desulfurization and the ammonia catalyst reduction process for denitrification. Both these methods are in practical use. However, focus has centered on promoting the development of a dry process which implements simultaneous desulfurization and denitrification techniques due to problems such as the need for a vast amount of water when using the lime-gypsum wet process. Or in the case of the ammonia catalyst reduction process, the need for measures to prevent the clogging of the latter portion of the equipment due to the life span of the catalyst or ammonia leaks.

① Activated Carbon Method⁶⁾

This process utilizes activated carbon (or activated cokes) in order to adsorb the SOx out of the exhaust gas. Also due to the catalytic effects of the activated carbon, NH₃ decomposes NOx to N₂, and both desulfurization and denitrification occur at the same time. Besides being used in several incinerator units, it was put into operation as the denitrification unit for the fluidized bed boiler (350 MW) at the Electric Power Development Co., Ltd., Takehara thermal power plant which began operation in 1995.

In this method, the SOx in the exhaust gas is easily adsorbed by the activated carbon in the desulfurization tower. It is captured in the form of sulfuric acid or ammonium sulfate (hereafter abbreviated as (NH₄)₂SO₄) (when injected with ammonia.) However, the adsorption capacity of activated carbon is limited and regeneration is necessary. Therefore, the activated carbon is used as a moving bed, shifted to a regeneration system where it is regenerated and then circulated around for use once again.

Also, activated carbon is the same as the metallic catalyst which is used in the ammonia catalyst reduction method, it works as a reduction and decomposing catalyst due to the existence of the ammonia. Also, it is believed to have the ability to remove NOx due to the denitrification reaction caused by the reducing substance on the surface of the activated carbon or the adsorption.

② Electron Beam Irradiation Process⁷⁾

This technology achieves simultaneous desulfurization and denitrification by adding NH₃ to the exhaust gas, using an electron beam to irradiate the substance changing the SOx into (NH₄)₂SO₄ and the NOx into ammonium

nitrate. This method has cleared the substantive testing level where it was used in boilers of coal-fired thermal power stations and is in the stages prior to actual application.

Firstly, a dry type electrostatic precipitator is used to roughly collect the dust in exhaust gas of about 130°C. After this the gas is passed through a GGH where it is cooled down to about 110°C. Furthermore it is cooled down to around 60~70°C in the cooling tower, a temperature which is suited for the desulfurization reaction. It is then irradiated by electron beam in the reaction chamber.

By submitting gas to an electron beam for irradiation, radicals with extremely strong oxidation properties such as O*, OH*, HO₂*, are created from the elements O₂ and H₂O found in the exhaust gas. It is due to these radicals that SO_x and NO_x are oxidized down to H₂SO₄ and HNO₃. These strong acids react with the previously added NH₃ to create (NH₄)₂SO₄ and ammonium nitrate.

7.9.4 Specified Issues

Looking from the standpoint of the reexamination of worldwide and Japanese energy demand, accompanying the increase in usage of fossil fuels, especially coal combustion, there will be further calls for the reduction of total exhaust for SO_x and NO_x.

In addition, due to the recent global environmental issues, there is a need to make consideration toward the reduction of CO₂. By putting dust collector, flue gas desulfurization units, and denitrification devices into operation at thermal power generators, this only results in a decrease in the efficient transmission of electricity. There needs to be technological development in the future which is geared to the construction of an overall optimum flue gas processing system which also takes into consideration CO₂ exhaust.