

NO_x ABATEMENT FOR STATIONARY SOURCES IN JAPAN

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NO_x ABATEMENT FOR STATIONARY SOURCES IN JAPAN

by

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ABSTRACT

Strict ambient air quality standards for SO_2 and NO_x in Japan mandate the use of various air pollution control technologies. This report is a compilation of information on the current status of NO_x abatement technologies for stationary sources in Japan. The author obtained this information from electric power companies, various industries, and developers of numerous technology processes, as well as from his own original research in the field. The report focuses on the combustion modification (CM) and Selective Catalytic Reduction (SCR) NO_x abatement technologies. Information is provided on the development status, pilot and demonstration plant tests, technological problems, and costs associated with the use of these technologies in Japan. Detailed operation data is given to describe the commercial operation of SCR plants.

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SUMMARY

NO_x Standards and Ambient Concentrations

Recent air pollution control efforts in Japan have concentrated on NO_x abatement, since ambient SO₂ concentrations already have been drastically reduced in response to stringent standards. In 1978, the ambient air quality standard for NO₂ was amended from 0.02 ppm to the range of 0.04 to 0.06 ppm as a daily average. In regions with NO₂ concentrations above 0.06 ppm, the concentration will be reduced to 0.06 ppm by 1985. In regions where NO₂ concentrations range from 0.04 to 0.06 ppm, efforts will be made to keep the concentrations from substantially exceeding the present level. In areas where the concentration falls below 0.04, efforts must be made to keep at that level. The new NO₂ standard is relaxed compared with the previous standard, 0.02 ppm as a daily average, but is still more stringent than the U.S. standard of 0.05 ppm as a yearly average.

In regions with large cities such as Tokyo and Osaka, ambient NO₂ concentrations often exceed the standards, reaching 0.07-0.08 ppm as daily averages. The prefectural governments of Chiba, Kanagawa, and Mie have established even more stringent regulations and plan to reduce NO₂ concentrations to 0.04 ppm from the current 0.05-0.06 ppm level. Even in regions with NO₂ concentrations below 0.04 ppm, NO_x reduction is often required by local governments to prevent any further increase.

Nearly 2 million tons/year of NO_x is emitted in Japan, 60% of which is derived from stationary sources and the rest from mobile sources. In large cities such as Tokyo and Osaka, about 60% of the NO_x is emitted from mobile sources.

NO_x emissions from gasoline engine passenger cars manufactured since 1978 have been controlled by stringent regulations. The current limit is 0.25 gram/km, which amounts to 8% of the NO_x emissions from cars in 1973. NO_x emissions from diesel-engined buses and trucks have been reduced to about 50% of the 1974 level. For stationary combustion sources, emission standards based on advanced combustion modification technology has been applied to reduce NO_x by 30-70%.

With these efforts, ambient NO₂ concentrations are no longer increasing despite a continuing increase in the number of stationary and mobile sources. However, it is difficult to lower current NO₂ concentrations in large cities and industrial regions without more effective emission controls for diesel engine cars and stationary sources.

NO_x Reduction for Stationary Sources

Nearly all NO_x emissions are produced by the combustion of fossil fuels. In Japan, the major combustion fuel is heavy oil. This residue of the atmospheric distillation of crude oil has been used at the rate of nearly 200 million kiloliters per year. Coal use decreased markedly between 1965 and 1975 and currently accounts for only 3% of the nation's total energy supply. However, coal consumption is expected to triple in the next 10 years. Imported LNG also accounts for about 3% of the energy currently used and is expected to nearly triple in 10 years.

Large stationary sources such as utility boilers have reduced NO_x emissions 50-70% by applying combustion modifications (CM) including low excess air combustion, staged combustion, flue gas recirculation and low-NO_x burners. As a result, the NO_x concentration in flue gas from utility boilers is minimal---150-300 ppm for coal, 80-120 ppm for oil, and 40-60 ppm for gas firing. Smaller boilers and furnaces have reduced NO_x 30-50% by using low-NO_x burners or by switching from heavy oil to kerosene fuel.

For additional NO_x abatement, several flue gas treatment (FGT) processes have been developed. Of all the processes, selective catalytic

reduction (SCR) which uses ammonia and a catalyst at 300-400°C to control NO_x, is presently the most advanced technology. Over 150 commercial SCR plants are in operation to remove 80-90% of the NO_x emissions. Selective noncatalytic reduction (SNR) which uses ammonia at 800-1,000°C to remove 30-50% of NO_x emissions has been developed and applied to about 20 furnaces and industrial boilers. Wet and dry simultaneous SO_x and NO_x removal processes also have been developed but have not been applied commercially except for several small units.

SCR has been used most often for flue gas treatment because of its simplicity (which enables unattended operation), relatively high NO_x removal efficiency (80-90%), and relatively low cost. Most of the new coal-fired utility boilers being planned will have SCR units. SCR will also be needed for some of the existing boilers even in regions with NO_x concentrations below a 0.04 ppm daily average, due to local policies which forbid any increase in NO_x levels. For example, when a new boiler is installed at a power station, not only the new boiler, but also some of the existing boilers will be required to have SCR units so that total NO_x emissions from the station do not increase.

SCR is usually used with CM. For most boilers and furnaces, CM is applied first, followed by SCR in order to meet the stringent regulations. For over 90% NO_x reduction, the combination of CM (to reduce 35-50% of the NO_x emissions) and SCR (to remove 80-85% of the remaining NO_x) is usually more economical than SCR by itself.

Typical examples of uncontrolled and controlled NO_x concentrations in utility boiler flue gas are shown in Table S-1. Examples of NO_x regulations and emissions from utility boilers are shown in Table S-2.

A new combustion process, in-furnace NO_x removal, has been developed to remove about 50% of NO_x by injecting a small portion of the fuel above the flame, followed by air addition to assure complete combustion. By using this process along with CM for utility boilers, NO_x may be reduced to 100 ppm for coal, 50 ppm for oil, and 20 ppm for gas.

TABLE S-1. EXAMPLES OF CONTROLLED AND UNCONTROLLED NO_x CONCENTRATIONS IN UTILITY BOILER FLUE GAS

Fuel	Without Control, ppm	Outlet NO _x Concentration (ppm)		Percent Control		TOTAL % CONTROL
		Controlled By CM	Controlled By CM and SCR	by CM	by SCR	
Gas	200	50	10	70	83	95
Oil	300	100	20	67	80	93
Coal	600	250	50	58	80	91

TABLE S-2. EXAMPLES OF NO_x REGULATIONS AND EMISSIONS FROM UTILITY BOILERS (ppm)

Fuel	Boiler	Central Government	Local Agreement	Actual Emission
Gas	Existing	100	60	60 ^a
Gas	New	60	10	8 ^b
Oil	Existing	150	100	100 ^a
Oil	New	130	25	20 ^b
Coal	Existing	400	159 ^d	170 ^a
Coal	New	400	170	160 ^c

^aBy combustion modification (CM).

^bBy CM and selective catalytic reduction (SCR).

^cBy CM and partial SCR.

^dDesired by local government.

Fluidized bed combustion, gasification, and liquefaction of coal all have been tested in Japan, but these technologies are not as advanced there as they are in the U.S. This is because Japan must import coal and because these technologies are unable to meet the stringent Japanese NO_x emission regulations. Most of the new coal-fired boilers in Japan will use conventional pulverized coal combustion with CM, SCR and FGD.

SCR and SCR/FGD Characteristics

In the past SCR has experienced several problems, but these have been solved by recent improvements. The major problems were: 1) poisoning of the catalyst by SO_x in the gas, 2) dust plugging of the catalyst, and 3) deposition of ammonium bisulfate in the air preheater downstream of the SCR reactor. Catalyst poisoning has been eliminated by using catalysts based on TiO_2 instead of Al_2O_3 or Fe_2O_3 . The use of parallel-flow honeycomb, tube or plate catalysts or a parallel passage reactor eliminates dust plugging. Ammonium deposits can be prevented by maintaining the concentration of unreacted ammonia in the reactor outlet gas below 5 ppm and using a low-oxidation catalyst. To do this, 0.82-0.95 mole NH_3 is usually used per mole NO_x to obtain 80-90% NO_x removal with less than 5 ppm unreacted NH_3 , while SO_2 oxidation is kept below 1%.

SCR and FGD system applications to boilers and other gas sources are schematically shown in Figure S-1. SCR is easily applied to boiler economizer outlet gas at 300-400°C as shown in the A portion of the figure. For SO_x -rich gases, FGD may be applied downstream of SCR as shown in B. At an early stage of development, SCR was applied downstream of FGD systems, as shown in C, to protect the catalyst from SO_x attack. System C, however, is expensive since it requires large amounts of energy for gas reheating. System B has become popular as SO_x -resistant catalysts have been developed.

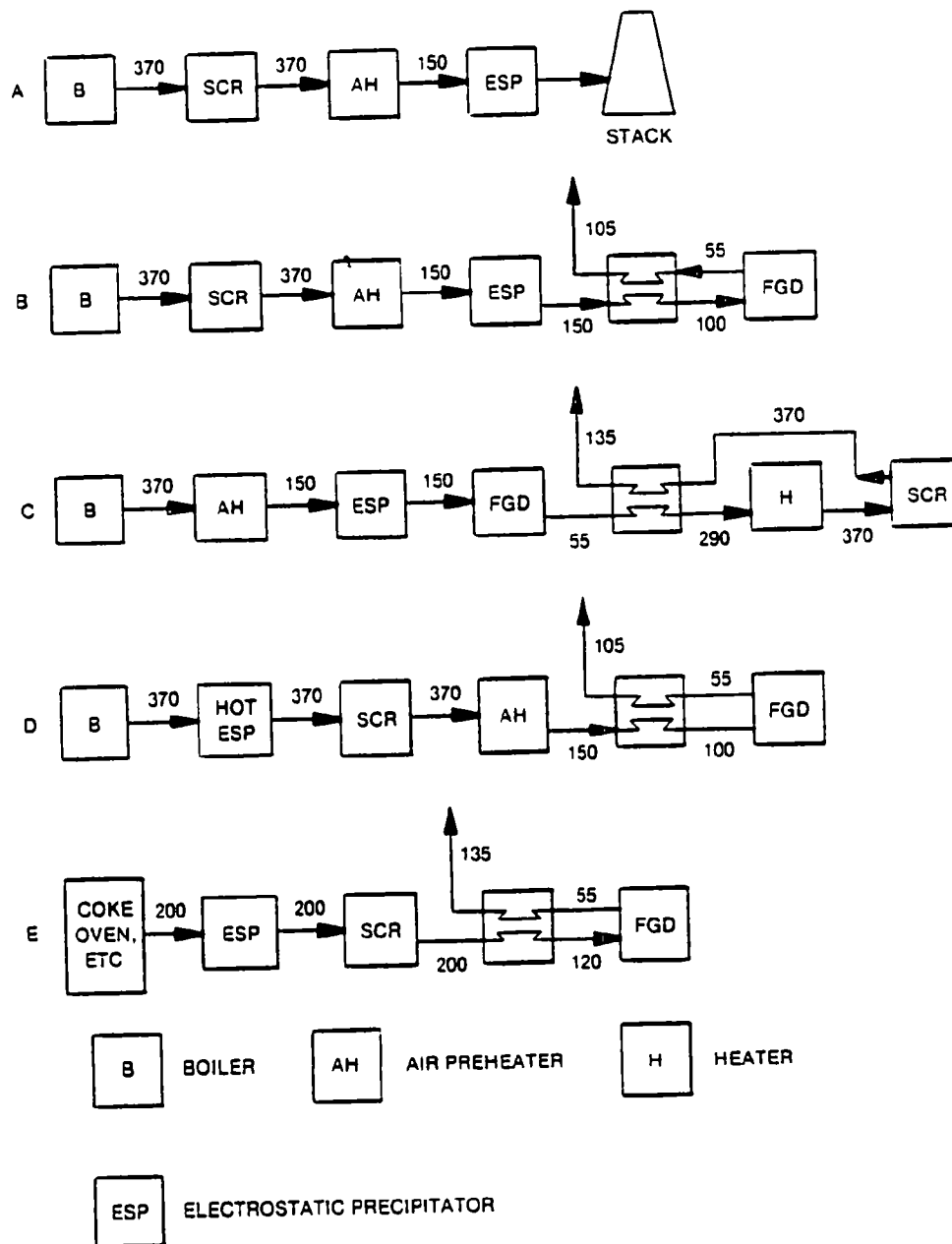


Figure S-1 SCR and FGD System Arrangements in Use in Japan.
(numbers indicate gas temperature in °C)

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System D is often used for flue gas from a low-sulfur coal. In this system, the boiler economizer outlet gas is first treated by a hot electrostatic precipitator (ESP) and then by SCR and FGD. A cold ESP is not highly efficient for flue gas from low-sulfur coal. For high-and medium-sulfur coals, system B is preferable. System B may also be useful for low-sulfur coal provided that both the cold ESP and the FGD unit are designed for sufficient dust removal.

Low-temperature catalysts have been used for 200-250°C gases such as that produced by coke ovens, as shown in system E of Figure S-1. Since ammonium bisulfate deposits on the catalyst at these low-temperatures, the catalyst requires occasional heating to 400°C to remove the bisulfate.

When wet FGD is applied downstream of SCR or SNR, the ammonia present in the reactor outlet is caught by the FGD system and goes into the wastewater. In some cases it may be necessary to use the activated sludge process to remove ammonia from the wastewater.

Cost of NO_x Abatement for Stationary Sources

The investment cost for a combustion modification system is shown in Table S-3. Costs range from ¥400 to 800 per Nm³ of flue gas or ¥1,200-2,400/kW for 55-70% reduction using a combined low-NO_x burner, staged combustion, and flue-gas recirculation system.

TABLE S-3. CM INVESTMENT COST

Method	NO _x removal (%)	Yen/Nm ³	Yen/Kw	\$/Kw ^a
Low-NO _x burner	20-40	100-200	300-600	1.2-2.4
Combined System ^b	50-70	400-800	1200-2400	4.8-9.6

^a\$1 = ¥ 250

^bLow-NO_x burner, staged combustion and flue gas recirculation

SCR costs for new 700 MW gas-, oil-, and coal-fired utility boilers are shown in Table S-4. For cost estimation purposes, it was assumed that flue gases leaving the boiler economizer at 330-400°C are treated in two equal size reactors in parallel and that unreacted NH_3 is kept below 5 ppm. The investment cost for 80% NO_x removal is about ¥2,500/kW for gas, ¥4,100-6,200/kW for oil, and ¥6,700-8,400/kW for coal. The cost differences are due to the varying amounts of catalyst required. For example, a small amount of a very active catalyst is used for gas streams while a larger amount of a less active catalyst which is resistant to SO_x and dust erosion is used for dirty flue gas (oil or coal streams). Compared with 80% removal, 90% removal costs 15% more for gas, 25-30% more for oil, and 30% more for coal. The investment cost of an SCR system for an existing boiler is 10-50% more than for a new boiler.

The dirtier the gas, the shorter the life of the catalyst. Therefore, the annualized SCR cost/kWhr is higher when SCR is used with dirty gas. On the other hand, the annualized cost per pound of NO_x removed is lower with NO_x rich gas. The cost per pound for 80% removal is 10-17 percent lower than the cost for 90% removal. Ninety percent NO_x removal with a low level of unreacted NH_3 (about 5 ppm) is not easy to obtain with a large amount of gas from a utility boiler. The reason for this is that both gas velocity and NO_x concentrations vary across the duct at the reactor inlet.

The investment and annualized SCR costs for 80% SO_2 removal for coal-fired boilers are about one-third of those for 90% SO_2 removal using the wet lime/limestone FGD process. On the other hand, SCR is more expensive than CM. Although the investment cost of SCR for a gas-fired boiler is similar to that of CM in the combined system (Table S-3), the annualized cost of SCR may be considerably higher than CM, which has low operating costs. Therefore, for NO_x abatement, CM should be used first and SCR should be used in combination with CM when CM alone is not sufficient to meet control regulations. One CM technique, flue gas recirculation, is relatively expensive and is not highly efficient for coal. For this reason, flue gas recirculation may not be useful when SCR is applied to coal-fired boilers.

TABLE 8-4. SCR COST FOR 700 MW NEW BOILER (1981 COST)
(70% BOILER UTILIZATION 4,292,000 Mwhr/year)

Fuel	Gas		Low-S Oil		High-S Oil		Low-S Coal		High-S Coal		High-S Coal	
Inlet NO _x ppm	60		100		200		300		300		600	
Catalyst Type	pellet		Honeycomb		Honeycomb		Honeycomb		Honeycomb		Honeycomb	
Cost, 10 ⁴ yen/m ³	3.0		3.3		3.3		3.5		3.5		3.5	
Life, year	4		3		3		2		2		2	
NO _x removal, percent	80	90	80	90	80	90	80	90	80	90	80	90
Investment Cost ^a (1,000 ₀ yen/kW)	2.47	2.80	4.13	5.11	6.23	7.93	6.69	8.51	7.26	9.10	8.44	10.76
Annualized cost ^b (yen/kWhr)	0.17	0.20	0.28	0.35	0.44	0.56	0.59	0.76	0.65	0.82	0.81	1.04

^aIncluding initial charge of catalyst, civil engineering, and test operation.

^bIncluding 10% interest and 7 years depreciation

The costs of other FGT processes are uncertain because they have not been used widely in continuous commercial operation. However, experience with Thermal DeNO_x, a type of SNR used with an oil-fired utility boiler, indicates that its cost is about half that of SCR although the NO_x removal efficiency is also half as much (40% versus 80%).

SECTION 1

NO_x EMISSIONS AND CONTROL

1.1 ENERGY AND NO_x EMISSIONS

Between 1960 and 1973 the energy supply in Japan increased sharply and then dropped slightly during the 1974 oil crisis. Since 1975 the energy supply has been increasing steadily (Figure 1-1). In 1980, 66.4% of Japan's total primary energy supply was dependent on imported oil (Table 1-1). The Japanese government intends to restrict oil imports to 366 million kiloliters after 1985, and to increase the use of other fuels, mainly atomic power and coal. By 1990, 50% of the nation's total energy supply will come from sources other than imported oil.

Japan's supply of domestic coal cannot exceed 20 million tons annually because of its deep and small native mines; this necessitates the importation of coal. In 1980, imported coal exceeded 70 million tons; nearly all of it was used for coke production in the steel industry. Imported coal for fuel is expected to increase rapidly in the next few years, reaching 22 million tons in 1985, and 53 million tons in 1990.

Man-made NO_x emissions in Japan total about 2 million tons annually. About 60% of the total emissions are derived from stationary sources and the rest from mobile sources; in large cities, as much as 50-60% of the NO_x comes from mobile sources.

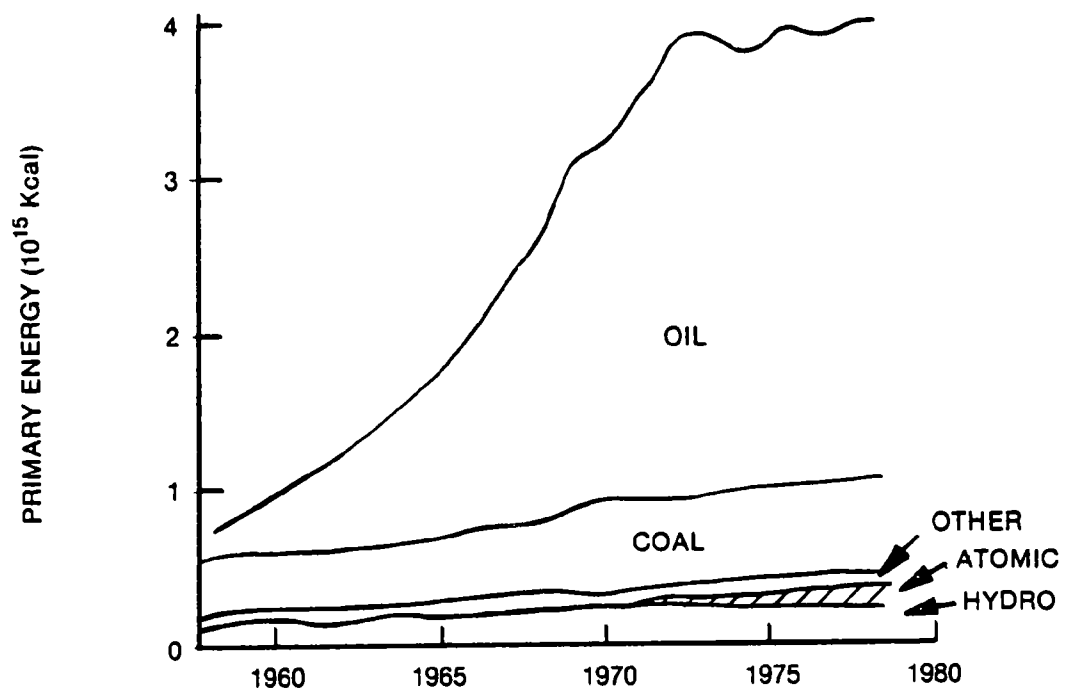


Figure 1-1 Primary Energy Supply in Japan: 1960 - 1980.

TABLE 1-1. JAPAN'S ENERGY SUPPLY: 1980-2000 (MITI, 1982)

	1980		1990		2000	
	Amount	(%)	Amount	(%)	Amount	(%)
Coal, total (10 ⁶ t)	92.4	(16.7)	153	(19.5)	200	(19.0)
Domestic	18.1		18~20			
Imported	74.3		133~135			
For Power Generation	21.3		66			
Atomic Power (10 ⁶ kW)	15.7	(5.0)	46	(11.3)	90	(18.0)
Natural Gas, total (10 ⁶ kl) ^a	25.9	(6.0)	68	(11.5)	82	(11.0)
Domestic (10 ⁹ m ³)	2.2		7.3			
LNG (10 ⁶ t)	16.8		43			
Hydro Power (10 ⁶ kW)	29.8	(5.6)	45.5	(5.0)	63	(5.0)
Geothermal (10 ⁶ kl) ^a	0.3	(0.1)	6	(1.0)	15	(2.0)
New Energy, etc. (10 ⁶ kl) ^b	0.7	(0.2)	15	(2.5)	65	(8.0)
Oil, total (10 ⁶ kl)	286.6	(66.4)	290	(49.2)	290	(37.0)
Domestic	0.5		1.9		—	
TOTAL (10 ⁶ kl)	429	(100)	590	(100)	770	(100)

^aCounted as oil energy^bIncluding solar energy, coal gasification, charcoal, etc.

Figure 1-2 shows annual NO_x emissions from large stationary sources. The emissions from utility boilers add up to about 310,000 tons which account for 34% of the emissions from large sources. As larger amounts of coal are used the emissions from utilities may increase significantly (Figure 1-3). Although extensive efforts have been made to reduce NO_x from both mobile and stationary sources, further NO_x abatement efforts will be needed for future coal-fired boilers.

New coal usage techniques, fluidized-bed combustion (FBC), and coal gasification and liquefaction have been tested by many Japanese organizations. Figure 1-4 shows the Japanese Government's 1978 preliminary plan for development of coal gasification and liquefaction. Called the Sunshine Project, this work is being carried out in cooperation with various industries under the leadership of the Japanese government. In addition, private companies have been trying to develop these technologies by themselves or through international cooperation.

Development of FBC and coal liquefaction and gasification is not as advanced in Japan as it is in the U.S. Japan is handicapped by the necessity of importing coal and by stringent NO_x emission regulations. These regulations often require NO_x removal from the exit flue gases of FBC or coal gasification and liquefaction systems. In addition, each process has the following disadvantages.

FBC: Japan has no land available for disposal of the process' throwaway ash containing lime and calcium sulfate. Although the absorbent may be regenerated and recycled, this approach may be too costly.

Gasification: For utility boilers, conventional pulverized coal combustion with flue gas treatment by SCR of NO_x, ESP, and FGD may be less costly and more reliable than gasification with combined cycle power generation; both FGD and SCR have proved to be highly reliable in Japan. For industry, there has been little need to use gas produced from coal. Japan plans to import increasing amounts of LNG, a large portion of which will be burned at power

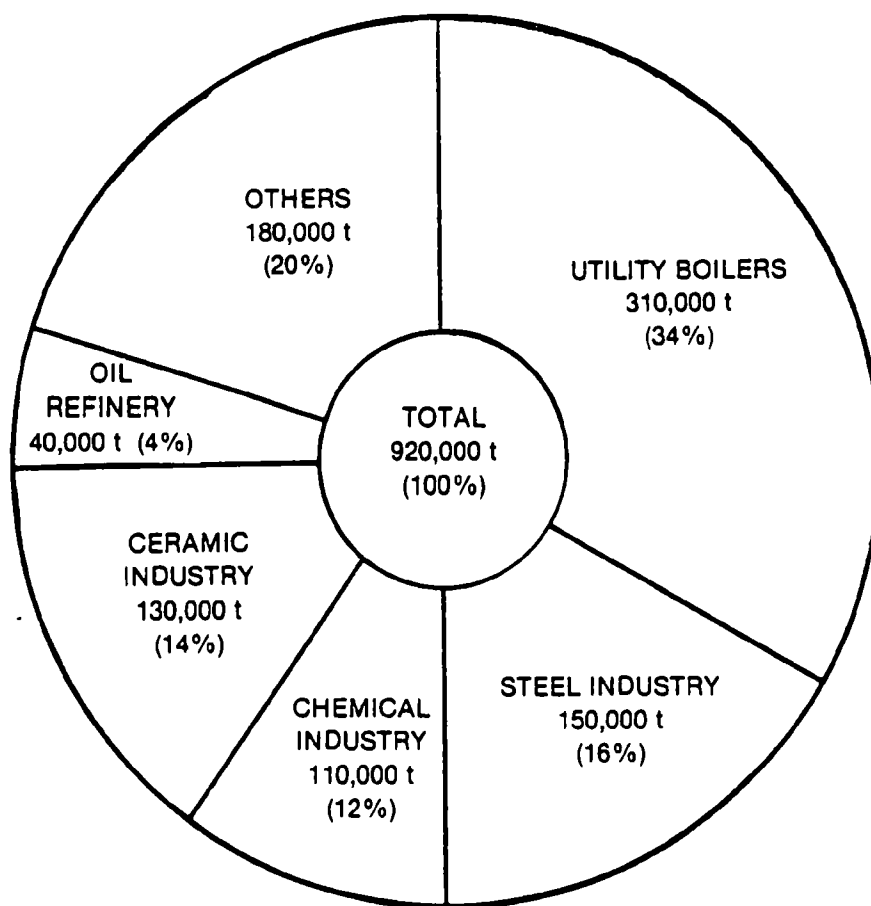


Figure 1-2 Annual NO_x Emissions from Stationary Sources.

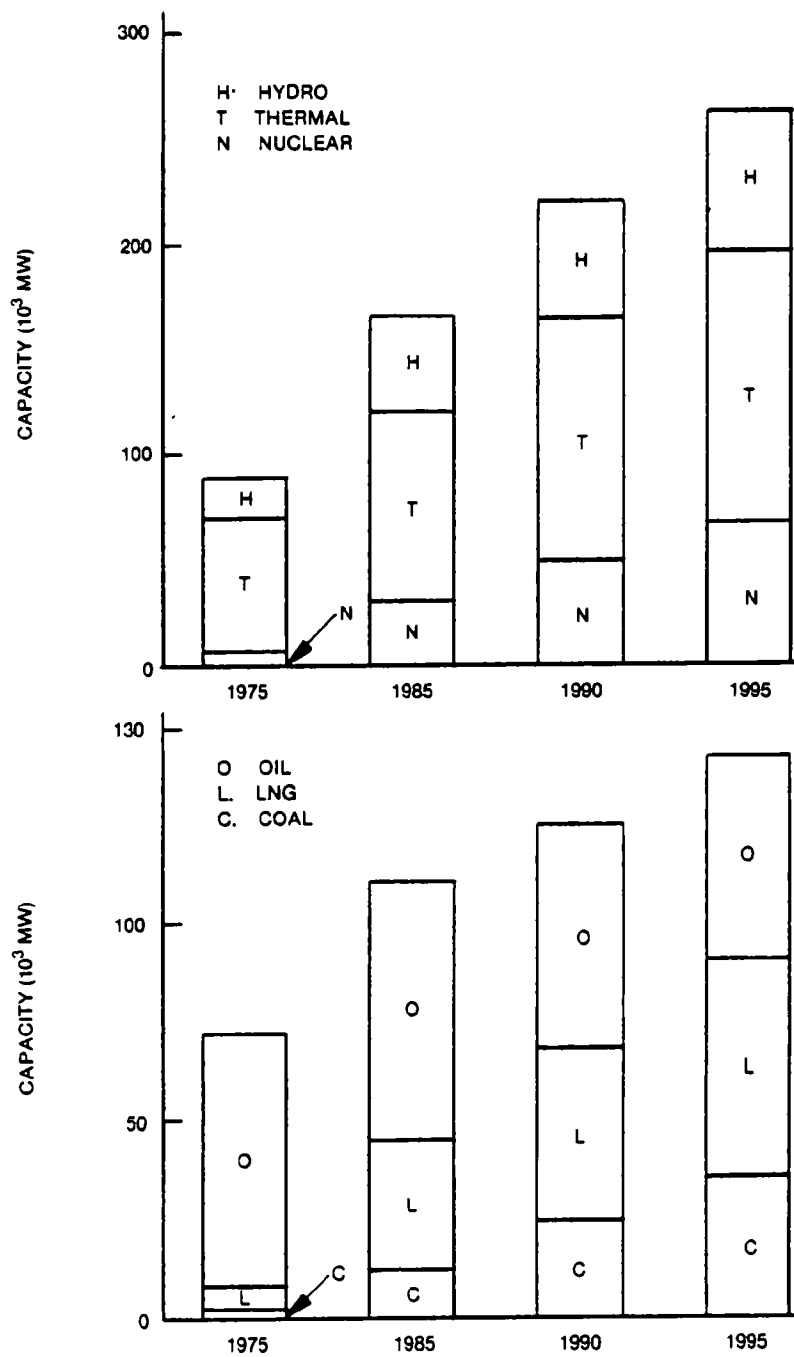


Figure 1-3 Estimated Increase in Electrical Power Generation Capacity.

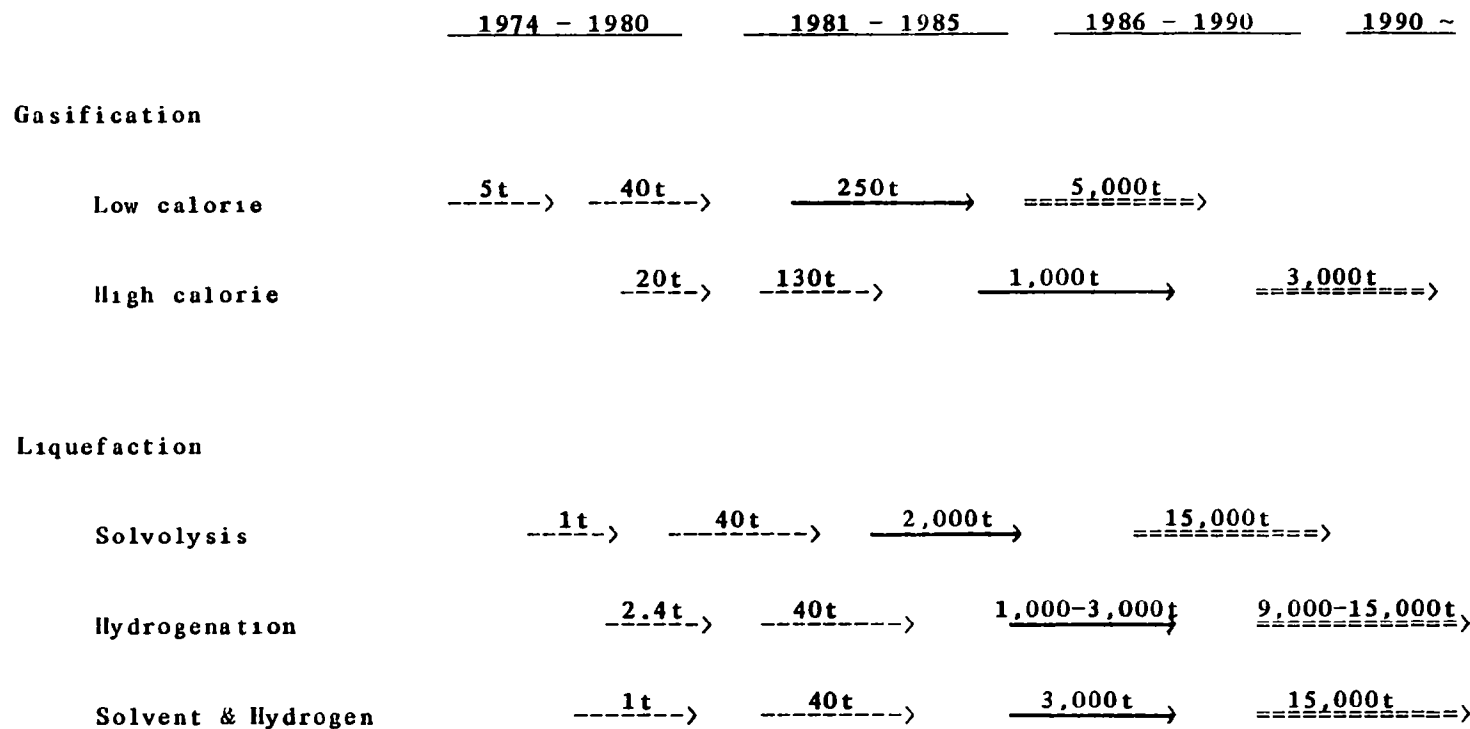


Figure 1-4. Preliminary Plan for Development of Coal Gasification and Liquefaction by the Sunshine Project (Arrows Show Construction Periods of Plants and Coal Treating Capacities per Day).

-----> Pilot Plant —————> Demonstration Plant =====> Commercial Plant

plants (Table 1-1 and Figure 1-3). It may be more appropriate for power plants to use more coal so that industry and cities can use larger amounts of LNG.

Liquefaction: It is not economically feasible to construct a liquefaction plant to produce fuel oil in Japan because of the necessity of importing coal. The primary objective of the liquefaction tests in Japan has been to produce a binder for coke production. When fuel oil from coal becomes necessary in the future, it would be more practical for liquefaction plants to be constructed abroad near large coal mines and the fuel oil exported to Japan.

Given these disadvantages as well as the technical and environmental problems, the Sunshine project plans shown in Figure 1-4 have been delayed, or in some cases, terminated. Although gasification and liquefaction may be needed in the future when the supply of oil and LNG becomes limited, further technological and economic improvements are needed before these technologies can be commercialized in Japan.

Many coal-fired boilers presently planned or under construction will use pulverized coal. Most of these boilers will use a wet limestone-gypsum FGD process and many will also use SCR.

1.2 AMBIENT NO₂ STANDARDS

The environmental quality standard for NO₂ in Japan was amended in 1978 from 0.02 ppm as a daily average to a new criterion of "within the range of 0.04-0.06 ppm as a daily average." The old standard was found to be overly stringent and not achievable in industrial regions and large cities. Under the new standard, NO₂ concentrations above 0.06 ppm, must be reduced to 0.06 ppm by 1985. In regions with NO₂ concentrations below 0.04 ppm, efforts must be made to keep NO₂ from exceeding 0.04 ppm.

The new daily average standards correspond to the annual NO₂ average of 0.02-0.03 ppm, a criterion proposed by the Expert Subcommittee on NO₂ of the Central Council for Environmental Pollution Control. At the same time it is

expected that an hourly average of 0.1-0.2 ppm, a short term criterion of the Subcommittee, can be met by the new standards.

There has been some criticism regarding the relaxation of the standards. The new standards, however, are still much more stringent than those of the U.S. and West Germany, which are equivalent to 0.05 ppm as a yearly average or 0.1 ppm as a daily average. As shown in Figures 1-5 and 1-6 and Table 1-2, NO₂ concentrations at some Japanese monitoring stations exceed the new standards although they meet the U.S. standards (based on the new Saltzman coefficient). Some of the prefectural governments have established more strict ambient air quality standards for NO₂—0.04 ppm as a daily average—and have been trying to reduce NO₂ levels from the current 0.05-0.07 ppm to 0.04 ppm. Extensive NO_x abatement efforts have been made so that both stationary and mobile sources can meet these standards.

1.3 NO_x EMISSION STANDARDS FOR STATIONARY SOURCES

The NO_x emission standards for stationary sources were first promulgated by the Central Government in 1973 to apply to large boilers and furnaces. These standards were revised in 1975, 1977, and 1979 to become more stringent and to cover a larger, more diverse number of emission sources (Table 1-3).

The NO_x emission standards for major stationary sources are shown in Table 1-4. In addition to those shown in the table, emission standards have been applied to many other sources such as driers, calciners, smelters, reformers, generators, etc. Except in the case of nitric acid plants, NO_x from these sources are derived from combustion, and therefore, the standards are based on the improved technology of combustion control described in Section 2. Industrial efforts described in the following sections have enabled these standards to be met.

Even with extensive NO_x control for stationary sources and automobile exhausts (Section 1.4), it is not possible to meet the NO₂ ambient air quality standard in several regions which include large cities such as Tokyo and

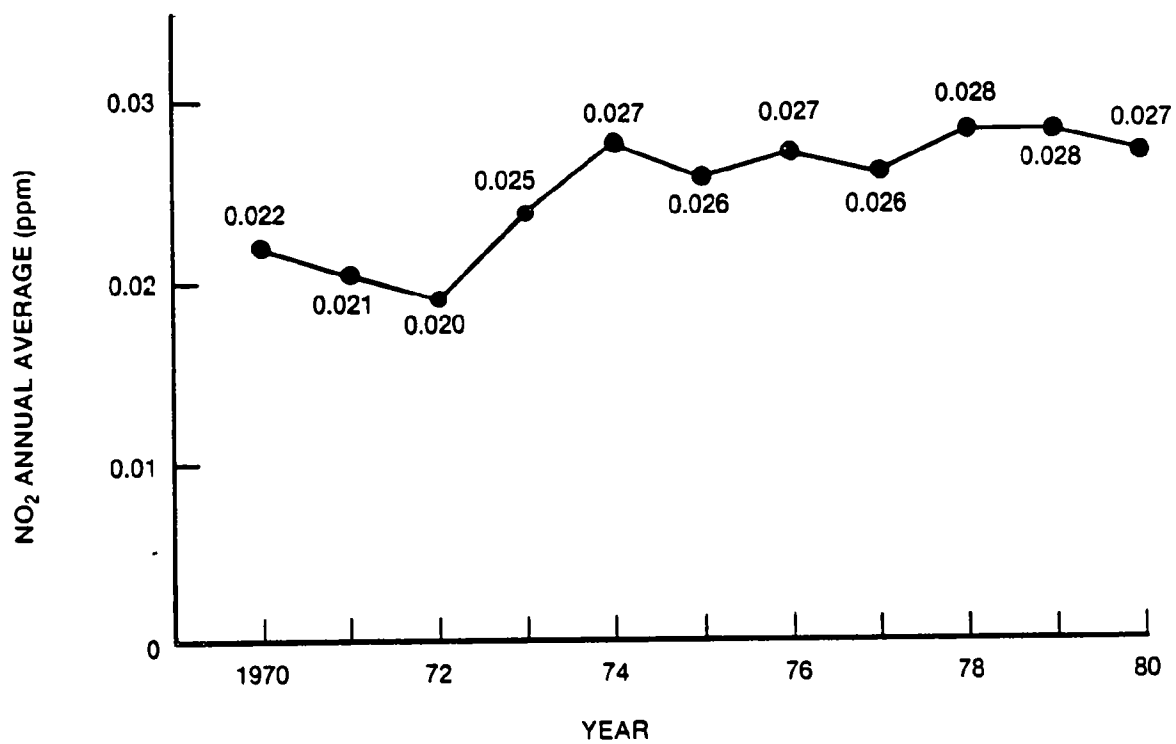


Figure 1-5 Changes in Annual Average Concentration of NO₂. (Average of those recorded at 15 general air pollution monitoring stations) (1).

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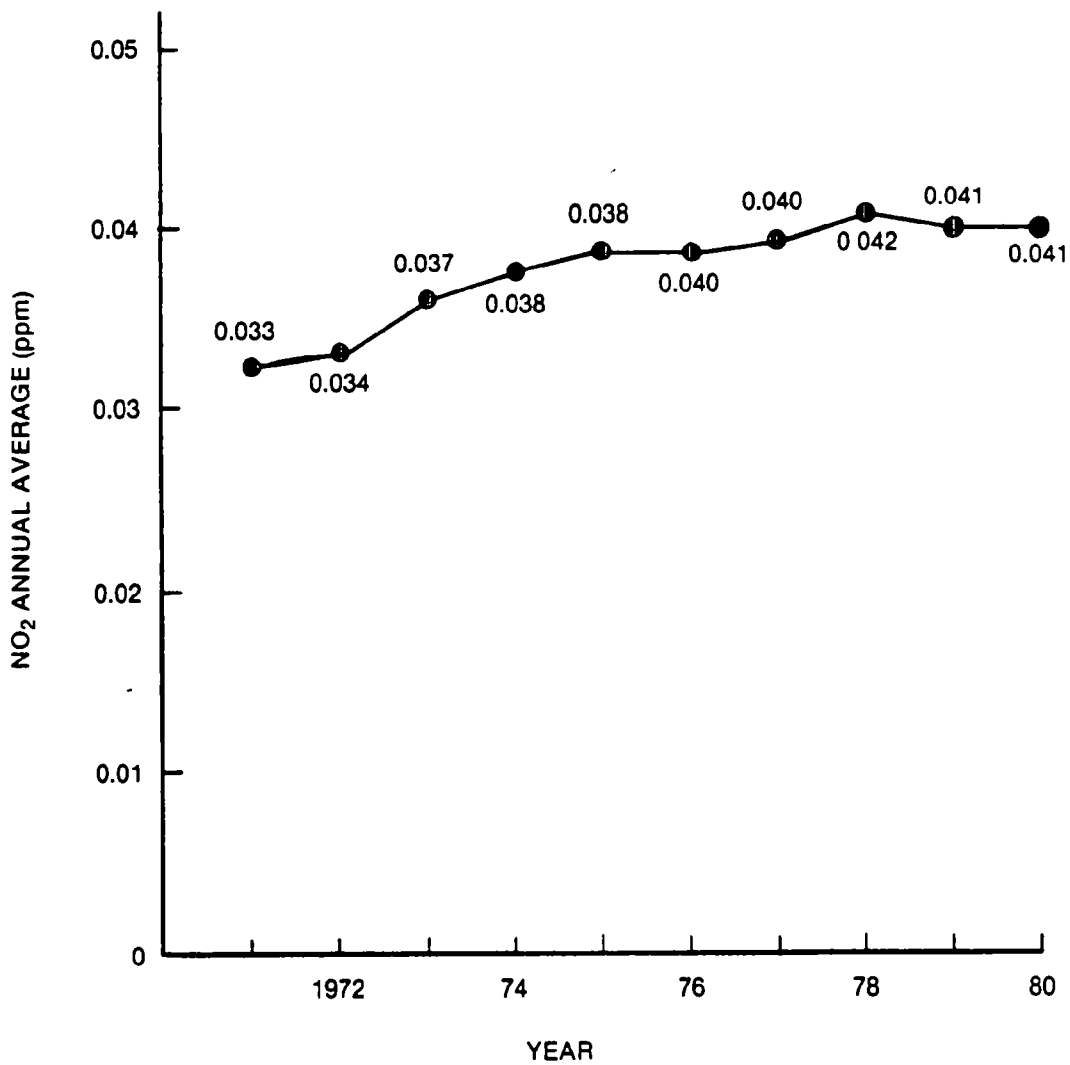


Figure 1-6 Changes in Annual Average Concentration of Nitrogen Dioxide.
(average of 26 automobile pollution monitoring stations) (1)

TABLE 1-2. STATE OF COMPLIANCE WITH THE NEW NITROGEN DIOXIDE ENVIRONMENTAL QUALITY STANDARD IN 1978 (The data correspond to 98% of total readings)

Descriptions of data corresponding to 98% of the total readings	Type of Monitoring Station			
	General Air Pollution Monitoring Station		Automobile Pollution Monitoring Station	
	Number of stations	Percentage	Number of stations	Percentage
Recordings exceeding 0.06 ppm	75	7.6	77	40.5
Recordings in the range 0.04 - 0.06 ppm	233	23.8	92	48.4
Recordings below 0.04 ppm	673	68.6	21	11.1
Total	981	100	190	100

Source: Environment Agency, Japan

TABLE 1-3. EXPANSION OF NO_x CONTROL FOR STATIONARY SOURCES

	1973	1975	1977	1979
NO _x sources controlled (additions each year)	Large boilers and furnaces HNO ₃ plants.	Medium sized boilers and furnaces. Large cement kilns and coke ovens.	Relatively small boilers and furnaces. Medium sized cement kilns and coke ovens. Waste incinerators.	Small boilers and furnaces. Metal heating furnaces. Gas generators, calciners, etc.
Number of sources controlled (total)	1,500	3,400	13,000	105,000
NO _x emitted from the controlled sources (percent of total NO _x from all stationary sources)	38	44	73	95

TABLE 1-4. NO_x EMISSION STANDARDS FOR MAJOR STATIONARY SOURCES (ppm)

Sources (%)	Capacity (1000 Nm ³ /hr)	~1973	73-75	75-77	77-79	1979~
Boiler (gas) (5%)	>500	130	130	100	60	60
	100-500	130	130	100	100	100
	40-100	130	130	130	100	100
	10-40	150	150	130	130	130
	<10	150	150	150	150	150
Boiler (oil) (4%)	>500	180	180	150	130	130
	100-500	170	180	150	150	150
	40-100	190	180	150	150	150
	10-40	210	230	150	150	150
	5-10	250	250 ^a	250	180	180
	<5	250 ^a	250 ^a	250 ^a	180	180
Boiler (coal) (6%)	>100	480	400	400	400	400
	40-100	600	480	480	400	400
	11-40	600	600	480	400	400
	5-10	480	480 ^a	480 ^a	400	400
	<5	680 ^a	480 ^a	480 ^a	400	400
Sintering Machine	>100	260	260	260	220	220
	10-100	270 ^b	270 ^b	270 ^b	220 ^b	220
	<10	300 ^b	300 ^b	300 ^b	300 ^b	220
Metal heating furnace (Radiant type) (11%)	>100	200	200	100	100	100
	40-100	200	200	150	150	150
	10-40	200	200	150	150	150
	5-10	200 ^b	200 ^b	200 ^b	150	150
	<5	200 ^b	200 ^b	200 ^b	180	180
Petroleum heating furnace (6%)	>40	170	170	100	100	100
	10-40	180	150	150	130	130
	5-10	180	180	180	150	150
	<5	200	200	200	180	180
Cement Kiln (10%)	>100	480	480	250	250	250
	<100	480	480	480	350	350
Glass furnace (15%)		500	500	500	500	450
Waste incinerator (12%)	>40	300 ^b	300 ^b	300 ^b	250 ^b	250
	<40	300 ^b	300 ^b	300 ^b	300 ^b	250
Coke oven (7%)	>100	350	350	200	170	170
	<100	350	350	350	170	170
Nitric acid plant		200	200	200	200	200

^aTo be met by 1984.^bTo be met by 1982.

Osaka. Therefore, the Central Government (Environment Agency) decided to apply total emission regulations to Tokyo, Osaka, and Yokohama in order to further increase NO_x abatement and meet the air quality standard. Similar total emission regulations for SO_x have been successfully applied in several regions and have resulted in the attainment of the SO₂ air quality standard. The NO_x regulations are more difficult to attain because over 50% of NO_x emissions in most large cities are derived from mobile sources, while most SO_x emissions are from stationary sources. With implementation of the total emission regulations as well as stringent local regulations, flue gas treatment for NO_x removal will be needed in addition to combustion modification.

1.4 NO_x CONTROL FOR MOBILE SOURCES

The emission standards for gasoline engine passenger cars are shown in Table 1-5. According to the 1978 standards, NO_x discharge is controlled below 0.25 g/km, on the average. Accordingly, permissible limits are set at 0.48 g/km, as shown in Table 1-5. At the same time, those in 11 modes are limited to 6.0 g/test (average discharge 4.4 g/test). The 1978 standard is responsible for a 60-70 percent reduction in NO_x discharge compared with the 1976 regulations and to over a 90 percent reduction compared with the time when there were no regulations. The 1978 standards are much more stringent than similar standards in the U.S. (Table 1-6).

It was predicted that automobile performance and fuel economy would decline measurably with enactment of the 1978 standards. However, strenuous efforts have been made to maintain and even to improve fuel economy while maintaining performance. As the result of these efforts, fuel consumption rates have improved considerably in the vehicles which satisfy the 1978 standards. Fuel economy for some models is lower than that of automobiles which complied with the 1973 standards.

The NO_x regulations for heavy duty diesel engine vehicles (buses and trucks) have also been tightened (Table 1-7). Under the 1977 regulation, NO_x emissions from diesel vehicles were reduced by about 30% while those

TABLE 1-5. AUTOMOBILE EMISSION STANDARDS IN JAPAN^a

	HC (g/km)	CO (g/km)	NO _x (g/km)
1973	3.80 (2.94)	28.00 (18.40)	3.00 (2.18)
1975	0.39 (0.25)	2.70 (2.10)	1.60 (1.20)
1976	0.39 (0.25)	2.70 (2.10)	0.84 (0.60)
1978	0.39 (0.25)	2.70 (2.10)	0.48 (0.25)

^aFigures show allowable limits; those in parentheses indicate average emissions.

TABLE 1-6. AUTOMOBILE EMISSION STANDARDS IN THE UNITED STATES^a

	HC (g/km)	CO (g/km)	NO _x (g/km)
1978	0.94	9.4	1.25
1979	0.94	9.4	1.25
1980	0.26	4.4	1.25
1981	0.26	2.1	0.63

^aEstablished by the Clean Air Act of 1977.

from gasoline engine and LPG engine heavy duty vehicles were reduced by about 45%—as compared with the uncontrolled emissions in 1973.

With these regulations and efforts to reduce traffic by 10%, the NO_x emissions from automobiles will be reduced by about 40% by 1983; but will increase after 1984 due to projected increases in traffic (Figure 1-7). The 1978 standard for gasoline engine passenger cars will not be amended. However, NO_x control for diesel engine vehicles will be tightened (Tables 1-7 and 1-8).

TABLE 1-7. EMISSION STANDARDS FOR DIESEL ENGINE HEAVY DUTY VEHICLES (PPM)

	CO	HC	NO _x	
			Auxiliary Chamber Type	Direct Injection Type
1974	980	670	590	1000
1977	980	670	500	850
1979	980	670	450	700
1981			450	540
1983			290	470

TABLE 1-8. NO_x CONTROL FOR DIESEL ENGINE PASSENGER CARS (g/km)

	Current Regulation	Interim Target	Target
Medium Size	1.2	0.9	0.6
Small Size	1.0	0.7	0.5

1.5 METHODS OF NO_x ABATEMENT FOR STATIONARY SOURCES

The major methods of NO_x abatement for stationary sources are classified in Table 1-9.

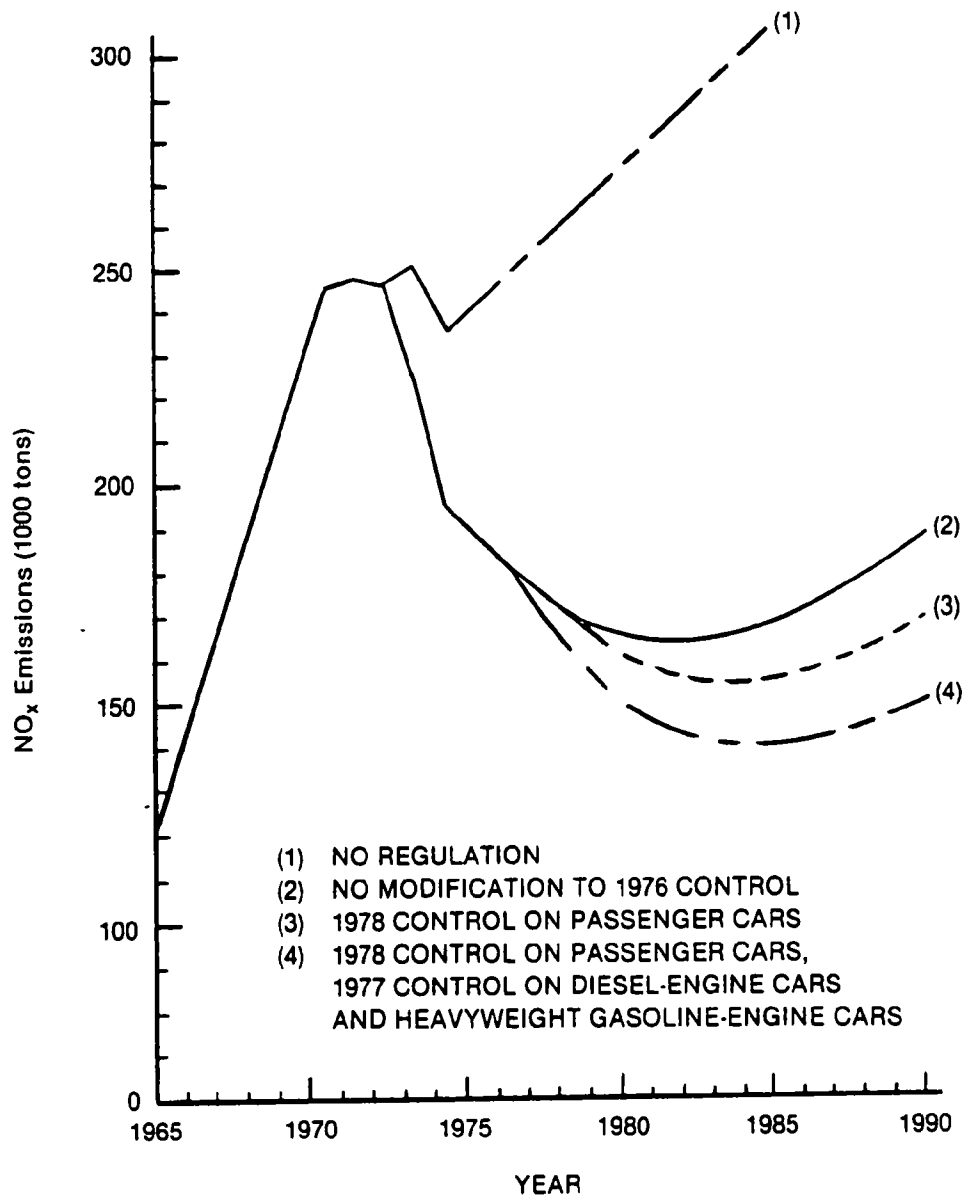


Figure 1-7 Estimated Total Amount of NO_x Emissions from Road Traffic in the Tokyo Bay Area. (2)

TABLE 1-9. CLASSIFICATION OF NO_x ABATEMENT METHODS

Reduction of Formation	[Combustion Modification	[Low Oxygen Combustion Flue Gas Recirculation Staged Combustion Off-Stoichiometric Combustion Low NO _x Burners
		Use of Low-Nitrogen Fuel	[Change of Fuel Nitrogen Removal from Fuel
NO _x Removal	[Dry Process	[NO _x only
			[SO _x and NO _x
			[Selective Catalytic Reduction (SNR) Selective Noncatalytic Reduction (SNR) In-furnace Reduction
	[Wet Process	[Carbon Adsorption Copper Oxide Adsorption Electron Beam Radiation
			[NO _x only
			[SO _x and NO _x
			[Oxidation Absorption Oxidation Reduction Absorption Reduction

Combustion modification is the most reasonable first step for stationary source NO_x abatement. It is described in more detail in Section 2. Combustion modification has been widely applied in Japan and has reduced NO_x by 20-70 percent from each stationary source.

A widespread switch from high-nitrogen to low-nitrogen fuel has occurred in Japan. Heavy oil, now the major fuel, usually contains 0.2-0.3 percent nitrogen, and its combustion gas contains 100-130 ppm of NO_x using the best combustion control. Hydrodesulfurization of heavy oil, which removes 70-90 percent of sulfur, also removes 20-30 percent of the nitrogen and contributes to NO_x reduction by 20-30 ppm. Kerosene is used in many small stationary sources.

A considerable number of power plants constructed recently near large cities burn LNG (imported liquid natural gas), which produces only 30-40 ppm of NO_x using the best combustion control. However, there is, a limit to the supply of such clean fuel, and it is expensive as well.

Recently it has become necessary to use increasing amounts of coal, particularly for power generation. Since coal contains over 1% nitrogen and produces flue gas with about 200 ppm NO_x , even using combustion modification, flue gas treatment may be needed for further NO_x reduction.

Many processes have been developed to remove NO_x from flue gas. Of these, a selective catalytic reduction (SCR) process that uses NH_3 and a catalyst at 300-400°C to reduce NO_x to N_2 has been the most widely used. SCR is simple, has a high NO_x removal efficiency of 80-90%, and does not produce by-products which present difficult disposal problems. Although NO_x can be reduced to N_2 by other reducing agent gases such as H_2 , CO, and CH_4 , large amounts of these gases are consumed by reacting with the O_2 in flue gas. The use of NH_3 is more suitable because it selectively reacts with NO_x (Section 3). SCR was initially applied to industrial boilers and furnaces (Figure 1-8). Since 1978, many large SCR units have been constructed for utility boilers (Table 4-1, Section 4).

Selective noncatalytic reduction (SNR), NH_3 reduction without a catalyst, also has been used commercially. SNR is simpler than SCR, but its NO_x removal efficiency rarely exceeds 50 percent and a considerable amount of NH_3 is emitted (see Section 6.2).

In-furnace NO_x reduction has been developed recently and applied to small oil-fired utility boilers to remove about 50% of NO_x . With this process, a small amount of fuel, about 10% of that used for the boiler, is injected above the flame in the furnace and then has air added to it for complete combustion. The size of this furnace is 10 to 20% larger than a conventional furnace (see Section 6.4).

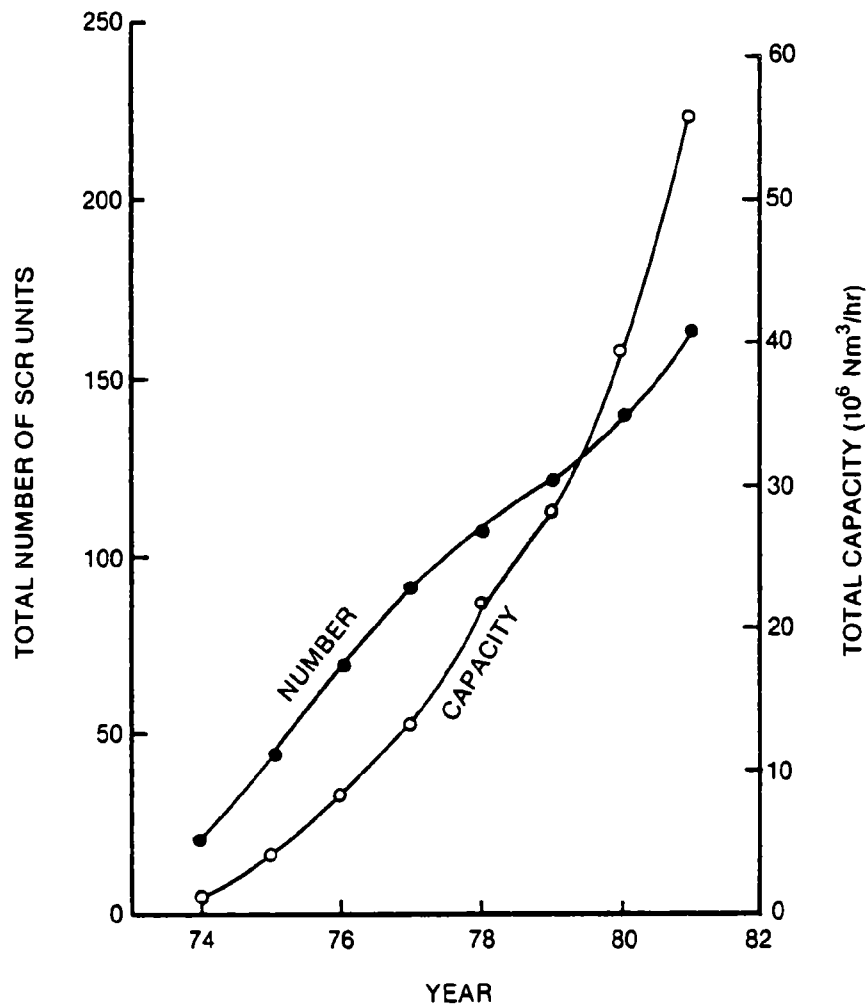


Figure 1-8 Number and Total Capacity of NO_x Selective Catalytic Reduction (SCR) Plants: 1974 - 1981.

Among dry SO_x and NO_x removal processes, carbon adsorption and electron beam processes have been tested at a pilot plant while a copper oxide adsorption process has been used for an industrial boiler. The carbon and copper oxide processes use ammonia to decompose NO_x to N₂ and H₂O; the electron beam process forms ammonium nitrate and ammonium sulfate byproducts which are used for fertilizer.

The disadvantage of wet processes is that they require extensive wastewater treatment to eliminate nitrate and other compounds. Efforts have been made to recover useful byproducts and to minimize the amount of wastewater produced.

1.6 LOCAL REGULATIONS AND NO_x ABATEMENT

1.6.1 Introduction

Prefectural governments and large city authorities have established pollution control ordinances for stationary sources which are usually much more stringent than those set by the Central Government. In addition, city authorities and citizens groups often make agreements with industries for further pollution control. A good example of the way in which local pollution control regulatory agencies operate is the Kanagawa Prefecture.

Kanagawa Prefecture adjacent to Tokyo has an area of 2,391 km² and three major cities—Yokohama, Kawasaki, and Yokosuka with populations of about 4 million, 1 million, and 400,000, respectively (Figure 1-9). These cities have numerous industries including several electric power stations, steel works, and oil refineries.

The first step towards pollution control was taken in 1951 with the enactment of the Kanagawa Prefectural Workshop Pollution Prevention Ordinance. The ordinance was revised in 1955, 1971, and 1978 to comprise the present Kanagawa Prefectural Ordinance for Pollution Control.

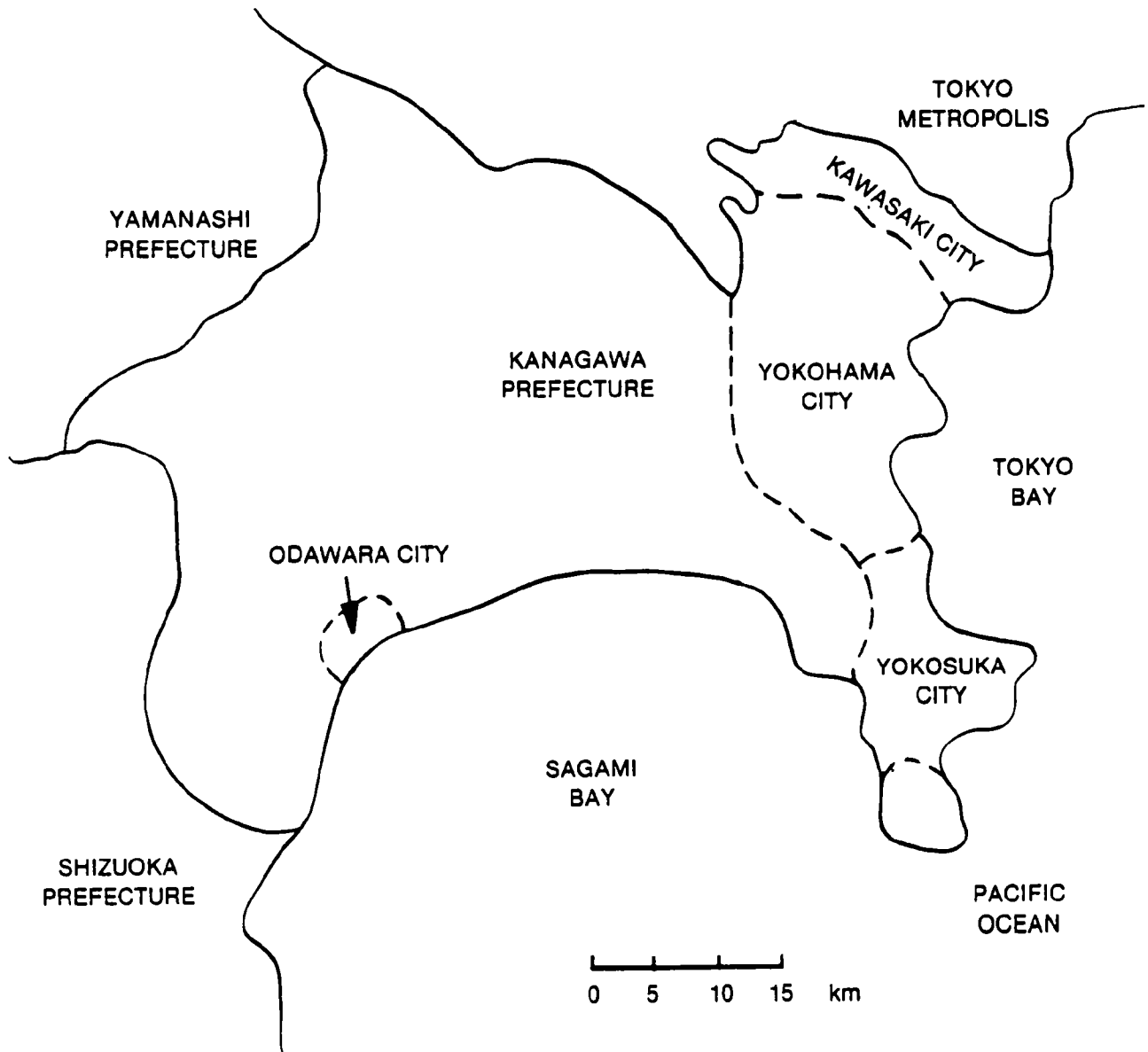


Figure 1-9 Kanagawa Prefecture and its Major Cities.

1.6.2 Air Quality Monitoring Systems in the Kanagawa Prefecture

The three major cities in Kanagawa have installed their own monitoring systems with automatic analyzer-telemeter-computer systems for measuring, recording, and analyzing pollutants in ambient air, automobile exhausts, and stack emissions. For example, Yokohama City has 12 ambient air monitoring stations for measuring SO₂, suspended particulates, NO, NO₂, and oxidants as well as wind velocity and direction; eight automobile exhaust monitoring stations for suspended particulates, CO, NO, NO₂, HC, oxidants, as well as the number of passing cars; and stack gas monitoring systems to analyze SO_x, NO_x, and particulates at 40 major stationary sources. All of the analytical results are transmitted to the Yokohama City Office on an hourly basis.

In addition, Kanagawa Prefecture has its own ambient air and automobile exhaust monitoring stations in areas other than the three cities. Information from a total of 72 monitoring stations, including the stations owned by the cities, are transmitted to the Prefecture's air monitoring center. The annual costs for the center are shown in Table 1-10.

The initial air quality control efforts in Kanagawa focused on SO_x abatement. Since the ambient SO₂ concentrations now have been reduced to meet the standard (0.04 ppm daily average) at most of the monitoring stations, recent efforts have been concentrated on NO_x control.

The daily average NO₂ concentrations at some of the stations in the three cities sometimes exceeds the 0.06 ppm national standard. Kanagawa Prefecture has been making efforts to reduce the concentrations to 0.04 ppm by extensive NO_x reduction.

1.6.3 NO_x Emissions and Control in Kanagawa Prefecture

In the city of Yokohama, about 65% of the total NO_x emissions are derived from stationary sources while about 30% come from automobiles. The latter is controlled by the national regulation; stationary source emissions are regulated by prefectural ordinances and agreements between the Prefecture or

TABLE 1-10. TOTAL COST FOR KANAGAWA CONTINUOUS AIR MONITORING CENTER (1970-1980)

Items/Year	Measuring Sets		Telemetry		Others		TOTAL
	Purchase Cost (\$1,000)	Operating Cost (\$1,000)	Purchase Cost (\$1,000)	Operating Cost (\$1,000)	Purchase Cost (\$1,000)	Operating Cost (\$1,000)	
1970	1624	—	23	—	50	—	1,697
1971	307	109	169	22	—	1	608
1972	192	144	670	26	154	2	1,183
1973	172	220	947	13	—	9	1,361
1974	144	176	74	23	4	30	451
1975	21	326	—	123	—	35	505
1976	29	304	—	133	—	35	501
1977	455	361	—	158	32	33	1,039
1978	672	361	—	160	8	36	1,237
1979	301	399	—	149	7	39	1,108
1980	166	444	402	141	—	39	1,192
TOTAL	4,083	2,844	2,498	948	255	259	10,887
TOTAL	6,927		3,446		514		10,887

City and industry. Yokohama has 1,165 plants which use more than 1 kiloliter of oil per hour including 13 large plants (three utility power stations, three oil refineries, two glass plants, etc.) that emit about 95% of the NO_x from all stationary sources. As a whole, a 64% reduction of the 1974 NO_x emissions must be achieved to attain 0.04 ppm as a daily average. Therefore, 60-70% NO_x reduction of the 1974 emissions is requested of the large plants and a 30-50% reduction of the smaller plants. Since these reductions are not easily achieved by combustion modification, a considerable number of plants must remove NO_x from flue gas. According to the City's initial plan, the reduction was to be achieved by 1981. This time limit has been postponed 2 years because it was too difficult to meet.

Yokohama has 3 power stations—Yokohama Power Station which burns oil and Minamiyokohama Power Station (LNG), both belonging to Tokyo Electric, and EPDC's Isogo Power Station which burns coal. The NO_x emissions and regulations which apply to these utility boilers are compared in Table 1-11.

TABLE 1-11. NO_x EMISSIONS AND REGULATIONS FOR EXISTING UTILITY BOILERS IN YOKOHAMA CITY

Fuel	YOKOHAMA CITY (PPM)			
	Before NO _x abatement	Present level ^a	Central government	Yokohama (Target)
Gas	150-250	40-80	130	50
Oil	250-350	80-150	180	80
Coal	400-600	160-200	400	159

^aAchieved by combustion modification

The target NO_x concentration chosen by Yokohama City is less than one-half the emission standard set by the Central Government and is not easily achievable by combustion modification alone. Yokosuka and Kawasaki Cities also have set similarly stringent NO_x target concentrations. In order to meet these targets, 7 SCR plants are in operation for various gas sources,

TABLE 1-12. NO_x REMOVAL PLANTS IN KANAGAWA PREFECTURE

Owner	Plant Site	Gas Source	Gas Treated (1,000 Nm ³ /hr)	Process	Year Completed
Asahi Glass	Yokohama	Glass furnace	75	SCR ^a	1976
Tokyo Electric	Yokohama	Oil-fired boiler	500	SNR ^b +SCR	1978 ^d
" "	Yokosuka	"	1060	SNR+SCR	1978 ^d
Nippon Kokan	Kawasaki	Sintering machine	1300	SCR	1979
Ajinomoto	Kawasaki	Oil-fired boiler	180	SCR	1978
Nippon Yakin	Kawasaki	Oil-fired boiler	15	SCR	1976
Toho Gas	Kawasaki	Gas generator	10	SCR	1976
Tonen Sekiyu Kagaku	Kawasaki	Oil-fired boiler	423	SNR ^c	1976
Tonen Sekiyu Kagaku	Kawasaki	Oil-fired boiler	423	SNR ^c	1977
Toa Nenryo	Kawasaki	CO boiler	314	SNR ^c	1978
Toa Nenryo	Kawasaki	Pipestill furnace	254	SNR ^c	1978

^aSelective catalytic reduction^bSelective noncatalytic reduction^cSelective noncatalytic reduction for emergency use^dDemonstration Plant. The SNR system was removed in 1980.

while four plants using selective noncatalytic reduction (Thermal DeNO_x) have been installed for emergency use (Table 1-12).

The NO_x concentrations in the flue gas from the coal-fired boilers at EDPC's Isogo Station, has been lowered from 400-500 ppm to 160-180 ppm by combustion modification. Although the City has requested further NO_x reduction the power station has no space to install a NO_x removal facility because FGD plants were retrofitted in the narrow space beside the boilers. Therefore, efforts have been continued for further NO_x abatement by combustion modification.

1.7 AIR POLLUTION PROBLEMS RELATED TO NO_x

In Japan, ambient SO₂ concentrations have been lowered substantially in order to meet the stringent standards (Figure 1-10 and Table 1-13). On the other hand, the number of designated air pollution patients have increased (Figure 1-10). Designated patients are the inhabitants of specific polluted regions such as Yokohama, Kawasaki, Amagasaki and portions of Tokyo and Osaka who have been diagnosed as air pollution victims. They receive compensation from the government for medical care and living expenses.

TABLE 1-13. AMBIENT AIR QUALITY STANDARDS (ppm)

	SO ₂		NO ₂	
	Daily	Yearly	Daily	Yearly
Japan	0.04	(0.02)	0.02 ^a 0.04-0.06 ^b	0.01 ^a (0.02-0.03) ^b
U.S.A.		0.03		0.05
West Germany		0.05		0.05

^a1973-1978

^bSince 1979

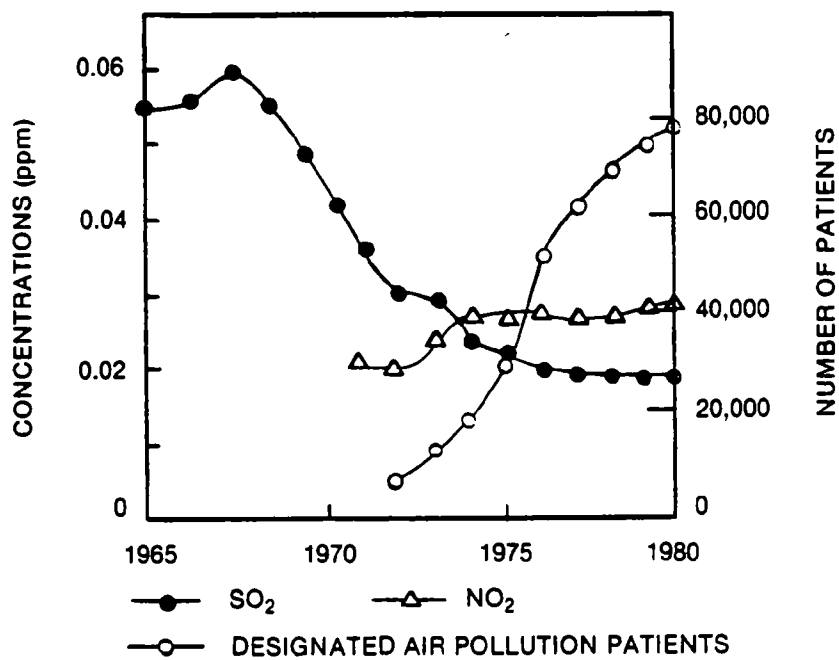


Figure 1-10 Annual Average Ambient SO₂ Concentrations in 15 Major Cities and Industrial Regions and Number of Designated Air Pollution Patients.

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The major reason for the increase in patients is the expansion of the designated regions to include several regions of Tokyo and Osaka. As ambient NO_2 concentrations have increased considerably between 1970 and 1974 and slightly since 1978, some people claim that the increase in patients is caused by ambient NO_2 concentrations. Although the NO_2 concentrations exceed the standard in several regions, NO_2 may not be the direct cause of patient increases; the concentrations are well below the U.S. standard.

A number of problems with photochemical smog were encountered in 1973-1974 but these have decreased since that time (Table 1-14). The decrease may be related to the decrease in hydrocarbon emissions (Table 1-15). Particulate emissions from stationary sources also have been reduced substantially.

It should be noted that the annual average ambient sulfate concentrations in five major cities (Tokyo, Kawasaki, Osaka, Amagasaki, and Kitakyushu), decreased from $30\mu\text{g}/\text{m}^3$ in 1970 to $13\mu\text{g}/\text{m}^3$ in 1973. Since then the concentrations have increased slightly to $15\mu\text{g}/\text{m}^3$ in 1979, despite an on-going decrease in ambient SO_2 concentrations. This may be due to the increase in diesel cars which emit sulfuric acid mists and also possibly to the slight increase in NO_x which tends to promote the oxidation of SO_2 to sulfate.

Although sulfate concentrations since 1973 have not been high, the sulfuric acid mists from diesel cars may affect human health in Japan where there are many diesel buses and trucks and the sulfur content in the light oil for diesel engines already is high (0.4% as compared with about 0.2% in the U.S.). Sulfur abatement of the light oil and further control of particulates for diesel-engine exhausts may be needed.

TABLE 1-14. NUMBER OF DAYS IN WHICH PHOTOCHEMICAL SMOG WARNINGS WERE ISSUED (1)

Area	Prefecture	1970	'71	'72	'73	'74	'75	'76	'77	'78	'79	'80	'81
Tokyo Bay	Saitama		23	15	45	29	44	15	26	36	8	15	8
	Chiba		19	21	28	26	33	21	7	14	11	13	8
	Tokyo	7	33	33	45	26	41	17	21	22	12	13	14
	Kanagawa		11	31	30	26	27	17	12	18	19	10	11
Osaka Bay	Kyoto			7	17	17	11	6	9	5	1	5	3
	Osaka		4	18	26	27	23	25	25	16	12	10	12
	Ilyogo		7	19	23	19	11	3	4	2	1	1	1
	Nara			1	6	3	9	3	3	3		1	
Seto Inland Sea	Okayama			3	14	16	5	1	5	8	1	1	
	Hirashima				9	18	4		6	9	1	1	
	Yamaguchi					5	1		5	3			
	Tokushima					2	2		3	1			
	Kagawa				1	4	1			6			
	Ehime			2	2	13	1	4	7	1	2	1	
Ise Bay	Aichi		1	5	8	2	6	3	2		1		
	Mie			4	6	7		3	1				
TOTAL*		7	98	176	328	288	260	150	187	189	84	72	57

*Including other prefectures

TABLE 1-15. GASEOUS HYDROCARBON EMISSIONS FROM STATIONARY SOURCES (1)

		1973			1978		
Sources		Amount (t)	Ratio (% of total)	Ratio (%)	Amount (t)	Ratio (%)	Ratio (%)
Petroleum	Refinery	67,000	5.2		42,400	4.0	
	Service Tank	68,100	5.2	15.2	41,800	3.7	14.6
	Service Station	62,800	4.8		78,500	6.9	
	Others	100			100		
Petrochemical	Plant	69,800	5.4	5.8	27,000	2.4	
	Tank	4,900	0.4		3,600	0.3	2.7
Painting	Production	1,600	0.1		1,500	0.1	
	Car Painting	37,500	2.9		45,400	4.1	
	Ship Painting	19,900	1.5	47.9	16,700	1.5	55.2
	Others	564,500	43.4		552,800	49.5	
Inks		109,800	8.4	8.4	81,100	7.2	7.2
Other Solvents	Cementing	42,500	3.3		32,800	2.9	
	Metal degreasing	85,000	6.5		52,800	4.7	
	Cleaning	116,500	9.0	22.7	106,000	9.5	20.3
	Rubber	51,200	3.9		35,000	3.1	
TOTAL		1,301,200	100.0	100.0	1,117,600	100.0	100.0

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1. Environment Agency. White Paper on Environment, 1982 (in Japanese).
2. Environment Agency. Recent Countermeasures for Air Pollution Control in Japan, 1977 (After OECD Review of Japanese Environmental Politics in 1976).

SECTION 2

NO_x ABATEMENT BY COMBUSTION MODIFICATION (CM)

2.1 INTRODUCTION

2.1.1 Classification of Combustion Modification (CM) Techniques

NO_x emissions from combustion processes consist of thermal NO_x formed by the oxidation of nitrogen in air at high temperatures and fuel NO_x derived from nitrogen compounds in fuel. Thermal NO_x can be reduced by combustion modifications, such as decreasing the oxygen concentration in the combustion regions; shortening the residence time of combustion gases in high temperature zones; or lowering the flame temperature. Fuel NO_x emissions can be reduced by decreasing the oxygen concentration in the combustion reaction zone and by switching to a low-nitrogen fuel.

Combustion modification techniques used widely in Japan for NO_x control can be grouped into four categories:

- Modified operating conditions
 - 1) Low-excess-air combustion
 - 2) Change of fuel/air contacting in the combustion chamber
 - 3) Reduction of heat load in combustion chamber (reduction of output power)
 - 4) Lowering of air preheating temperature
- Burner design modification

- Modifications in combustion system design
 - 1) Reduction of heat density in combustion chamber (increased furnace volume)
 - 2) Staged combustion
 - 3) Flue gas recirculation
 - 4) Water or steam injection

- Other methods
 - 1) Fuel switching
 - 2) Firing modification

Many combinations of the above techniques have also been used. Although operating conditions can be changed relatively easily in existing installations, the changes usually reduce NO_x emissions only slightly and often cause operating problems. On the other hand, modifications in burner and combustion system design are promising control techniques. Fewer problems are encountered when design modifications are incorporated in new plants; relatively large reconstruction costs are required when the modifications are applied to existing installations.

In Japan, NO_x emission limits have been applied to over 100,000 sources including boilers, various furnaces and kilns, heaters, and incinerators, representing about 95% of the total emissions from all stationary sources (Section 1.3). Virtually all of these sources have reduced NO_x emissions by combustion modification. Larger sources use the combination of staged combustion, flue gas recirculation (gas mixing) and low-NO_x burners (Table 2-1) while smaller sources reduce NO_x primarily with low-NO_x burners and fuel switching.

With these efforts, NO_x concentrations in boiler flue gases have been maintained at 30-120 ppm for gas-, 60-200 ppm for oil-, and 150-400 ppm for coal-firing to meet the national emission standards and the more stringent local regulations (Table 2-1). For further NO_x reduction, over 160 SCR plants are in operation or under construction. Normally SCR is applied in combination with combustion modification.

TABLE 2-1. NUMBER OF BOILERS AND COMBUSTION MODIFICATIONS APPLIED FOR OIL AND GAS AS OF APRIL 1981 (TOKYO ELECTRIC)

Methods of Combustion Modification	Number of Boilers	Total Generating Output (MW)
FGR ^a only	15	1,857
FGR + Two stage combustion	12	5,289
FGR + Low NO _x burner	9	2,710
FGR + Two stage combustion + Low NO _x burner	<u>32</u>	<u>13,605</u>
Total	68	23,461

^aFlue Gas Recirculation

TABLE 2-2. NO_x ABATEMENT BY COMBUSTION MODIFICATION (CM) FOR UTILITY BOILERS

	GAS	OIL	COAL
NO Control	200-300	250-350	500-800
GM ^a	150-200	180-250	400-600
TSC ^b	150-250	180-250	300-500
GM + TSC	100-150	120-200	250-400
GM + TSC + LNB ^c	50-90	80-140	150-300

^aGas Mixing (Flue Gas Recirculation)

^bTwo-Stage Combustion

^cLow-NO_x Burner

Combustion modification has also been applied extensively in the U.S. and European countries. Combustion modification technology is similar in most of these countries. This section describes combustion modification with emphasis on low-NO_x burners developed and used in Japan.

In addition, an advanced combustion modification process has been developed which reduces about 50% of the NO_x emissions by injecting about 10% of the fuel above the flame followed by air addition to assure complete combustion. The process is also considered to be a flue gas treatment process and is described in Section 6.4.

2.1.2 NO_x from Pulverized Coal Burning

The reduction of NO_x in flue gas from pulverized coal combustion has become very important in Japan because of the rapid increase in coal consumption and high NO_x concentrations in the combustion gas. Reduction of fuel NO_x is of particular importance because coal contains much larger amounts of nitrogen (1-3%) than does oil (0.1-0.5%). The fuel NO_x from coal consists of volatile NO_x derived from volatile nitrogen compounds in the coal and char NO_x derived from residual nitrogen compounds in the char. Abatement of the volatile NO_x can be accomplished efficiently by combustion control. Char NO_x control may not be accomplished as easily since it is less sensitive to injection design modifications in the early stage of combustion.

Staged combustion is highly effective for NO_x abatement for pulverized coal flue gas because it reduces both fuel and thermal NO_x. On the other hand, flue gas recirculation (gas mixing) is less effective because it reduces thermal NO_x which is not as much of a problem for coal-burning facilities.

Various types of low-NO_x burners have been developed and used in combination with other combustion modification techniques such as staged combustion and flue gas recirculation as shown in Table 2-3.

TABLE 2-3. EXAMPLES OF COMBUSTION MODIFICATION FOR COAL-FIRED UTILITY BOILERS

Station (Company)	Boiler (MW)	Coal Source	Burner Type	NO _x (ppm)
ISOGO (EPDC)	265 ^a	Domestic	DF-CN ^c	150-200
Tomato-Atsuma (Hokkaido)	350 ^b	Domestic	Dual Air Register ^d	200
Matsushima (EPDC)	500 ^b	Imported	SGR ^e	200-280

^a Staged combustion is used.

^b Staged combustion and flue gas recirculation are used.

^c See Section 2.2.

^d See Section 2.3.

^e See Section 2.4.

2.2 NO_x ABATEMENT BY IHI-FW DF-CN COAL BURNER (1, 2, 3)

2.2.1 IHI-FW DF-CN Burner

Ishikawajima-Harima Heavy Industries (IHI) and Foster Wheeler Corporation of the U. S. have developed a low-NO_x burner called the IHI-FW DF-CN (Dual Flow Convergent Fuel Nozzle) burner. It is based on the following principles for NO_x reduction:

- 1) Minimum primary/secondary mixing prior to completion of the combustion of volatile fraction.
- 2) Ignition stability at the injector.
- 3) Dilution of the secondary air with recirculating combustion products.

The configuration of the burner is shown in Figure 2-1. The secondary air sharing the largest portion of total combustion air is divided into an outer and inner flow by an annular flow divider located between the outer sleeve of the coal nozzle and throat ring. The flow quantity and/or the swirl intensity of inner air is controlled by changing the opening of the circularly-linkaged inner vane located just downstream of the secondary air vane. The inner swirled air is supplied mainly to the burner axis zone, where the fuel-rich combustion of volatile matter takes place and stabilizes the flame. The outer swirled air is supplied along the periphery of the burner throat and controls the mixing with char particles as well as strengthening the external recirculation flow of combustion products.

The pulverized fuel is injected through a ring-shaped convergent nozzle, so that fuel-rich combustion on the burner axis can take place. The inner sleeve of the fuel nozzle can be moved toward and away from the furnace. The velocity of the injected fuel may be varied to some extent by moving the inner sleeve, and thus the initial mixing of fuel and air may be controlled.

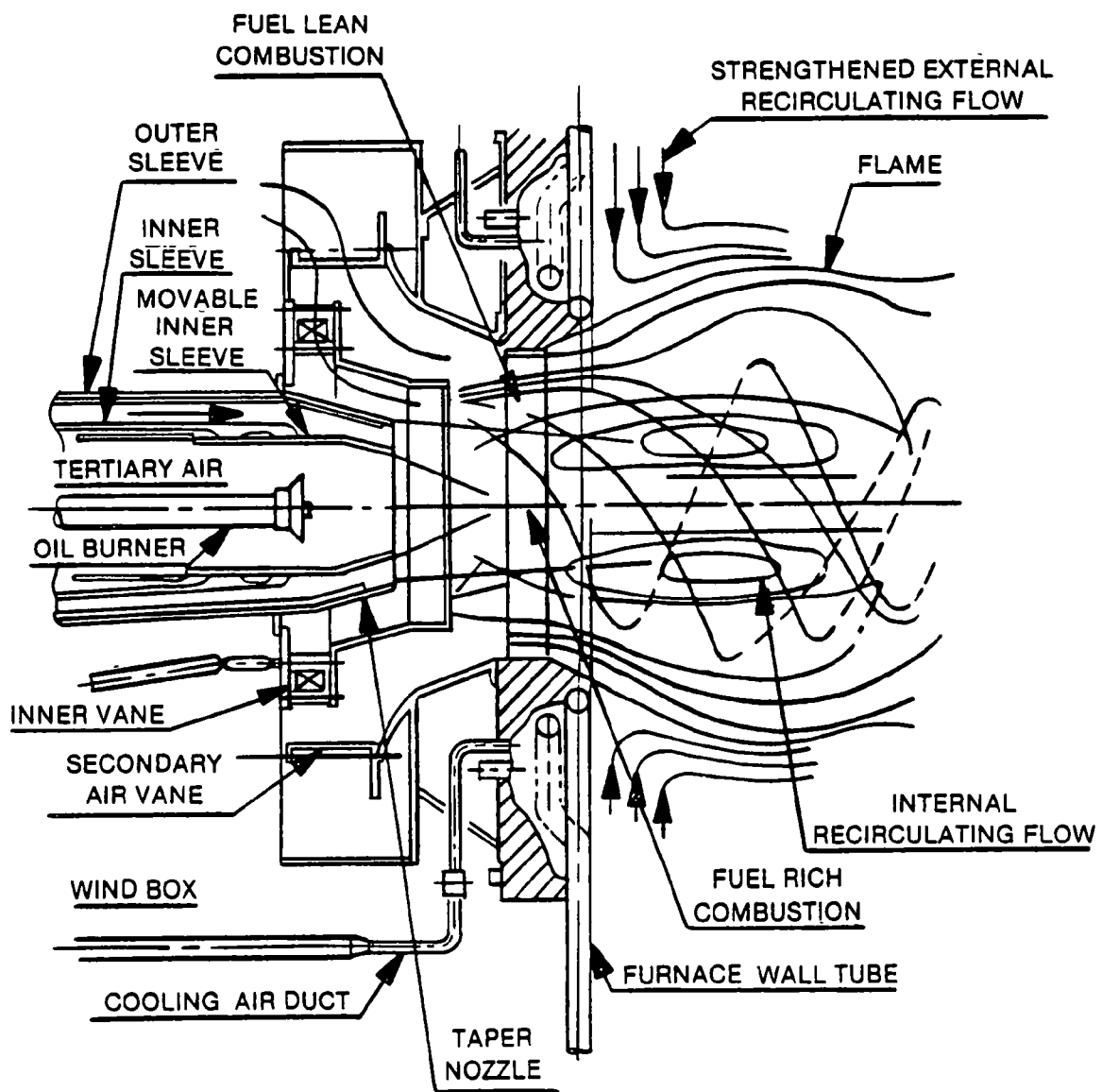


Figure 2-1 DF-CN Burner.

2.2.2 Test Furnace and Coal Composition

IHI conducted a combustion test using DF-CN type burners with a capacity of 2,000 kg/hr on a test furnace installed at IHI's Aioi Works. The study consisted of two stages. During the first stage, the characteristics of the DF-CN burner were investigated. During the second stage, other combustion modifications such as staged combustion and/or flue gas recirculation were examined for use with the DF-CN burner. The test furnace is illustrated in Figure 2-2. It was designed to have a geometrical similarity to the actual furnace of the coal-fired boiler. Single-burner and overfire-air ports (OAP) for staged combustion were installed on the front wall. Maximum heat input to the furnace is approximately 11×10^6 kcal/hr. Secondary air is preheated by a tubular gas-air heater to a wind box air temperature of almost 300°C.

The compositions of the coals used for these tests are shown in Table 2-4.

2.2.3 Test Results

The results of tests conducted with Japanese coal A are shown in Figures 2-3 through 2-6. The O_2 concentration in the flue gas was about 4%.

Figure 2-3 shows that NO_x decreases as the swirl intensity of secondary air is reduced by the opening of the secondary air vane. Figure 2-4 shows that NO_x decreases sharply when the opening of the inner vane is reduced; it reaches a minimum before the vane is entirely closed. Figure 2-5 indicates that the tertiary air stream has a strong effect on NO_x . The increase in fuel injection velocity assisted by tertiary air is assumed to be the cause of the decrease in NO_x emissions.

The primary air/coal ratio and the position of the inner sleeve influence NO_x emissions by changing the fuel injection velocity. The effect of the injection velocity on NO_x removal is shown in Figure 2-6.

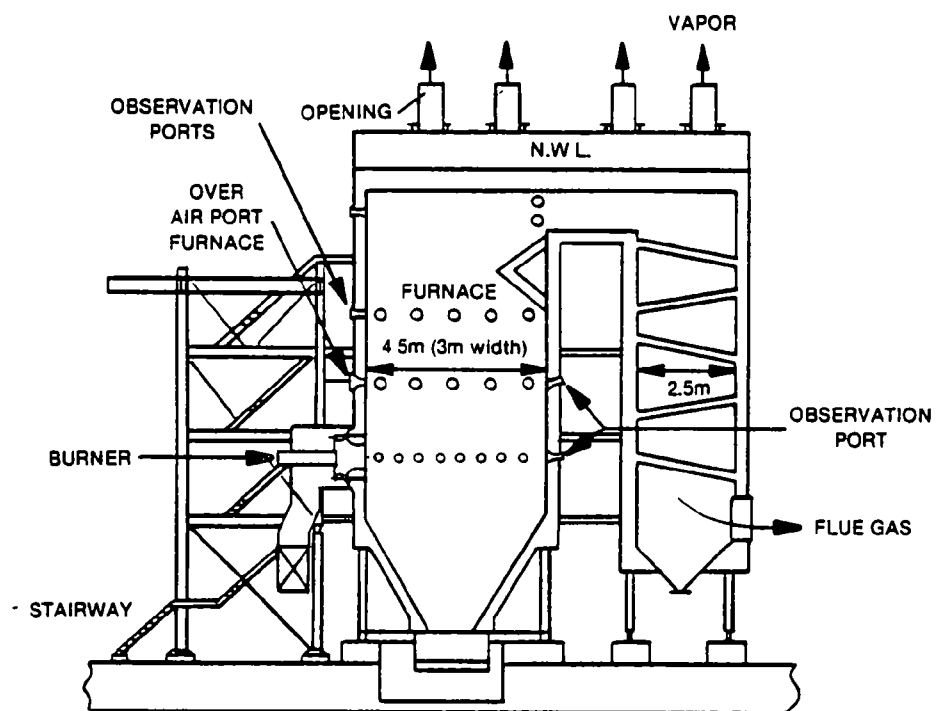


Figure 2-2 Cross-section View of Test Furnace.

TABLE 2-4. COMPOSITIONS OF COALS TESTED

Kind of Coal	Japanese Coal			Imported Coal			
	A	B	C	A	B	C	D
<u>Proximate Analysis</u>							
Higher Heating Value (kcal/kg)	6,200	6,600	5,410	6,870	7,220	6,740	6,460
Inherent Moisture, %	5.29	1.61	1.72	3.72	4.06	3.13	4.53
Volatile Matter, %	43.9	39.1	35.8	28.7	41.4	34.6	32.5
Ash, %	13.9	18.4	31.1	10.4	5.44	12.7	12.8
Fixed Carbon, %	36.9	40.9	31.3	57.2	49.1	49.6	50.2
<u>Ultimate Analysis</u>							
C, %	62.9	66.6	52.7	72.8	71.8	68.0	65.2
H, %	5.1	5.0	4.4	4.1	5.0	4.3	4.1
N, %	1.1	0.9	0.7	1.0	1.4	1.4	2.3
S, %	0.26	2.31	1.37	0.81	0.43	0.60	0.98
O, %	10.66	4.84	7.45	6.74	11.62	9.44	9.43

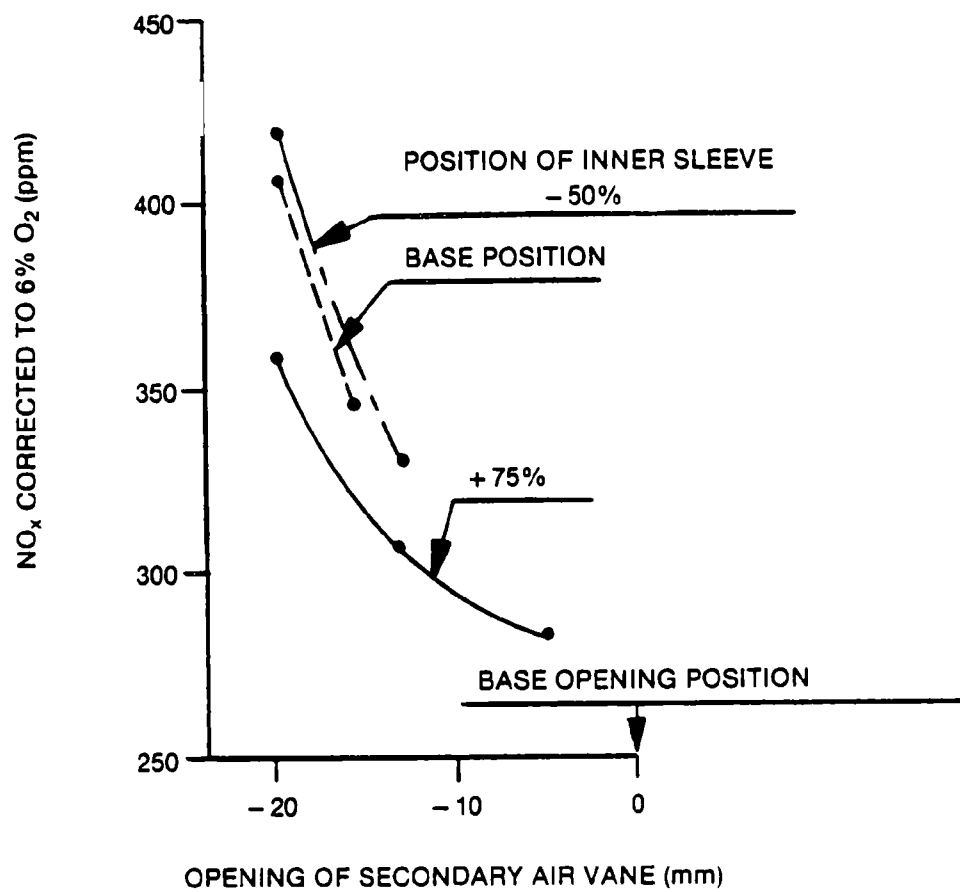


Figure 2-3 Secondary Air Vane Opening vs. NO_x.

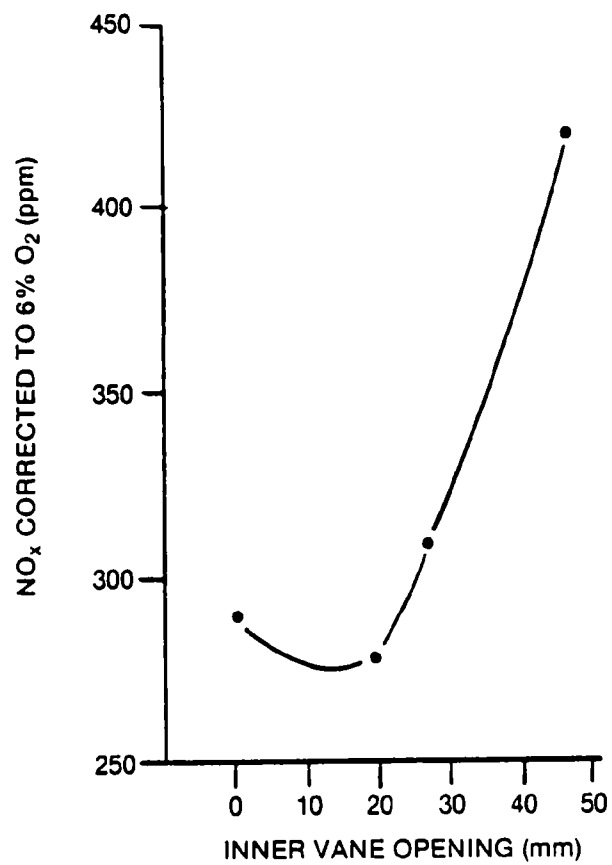


Figure 2-4 Inner Vane Opening vs. NO_x.

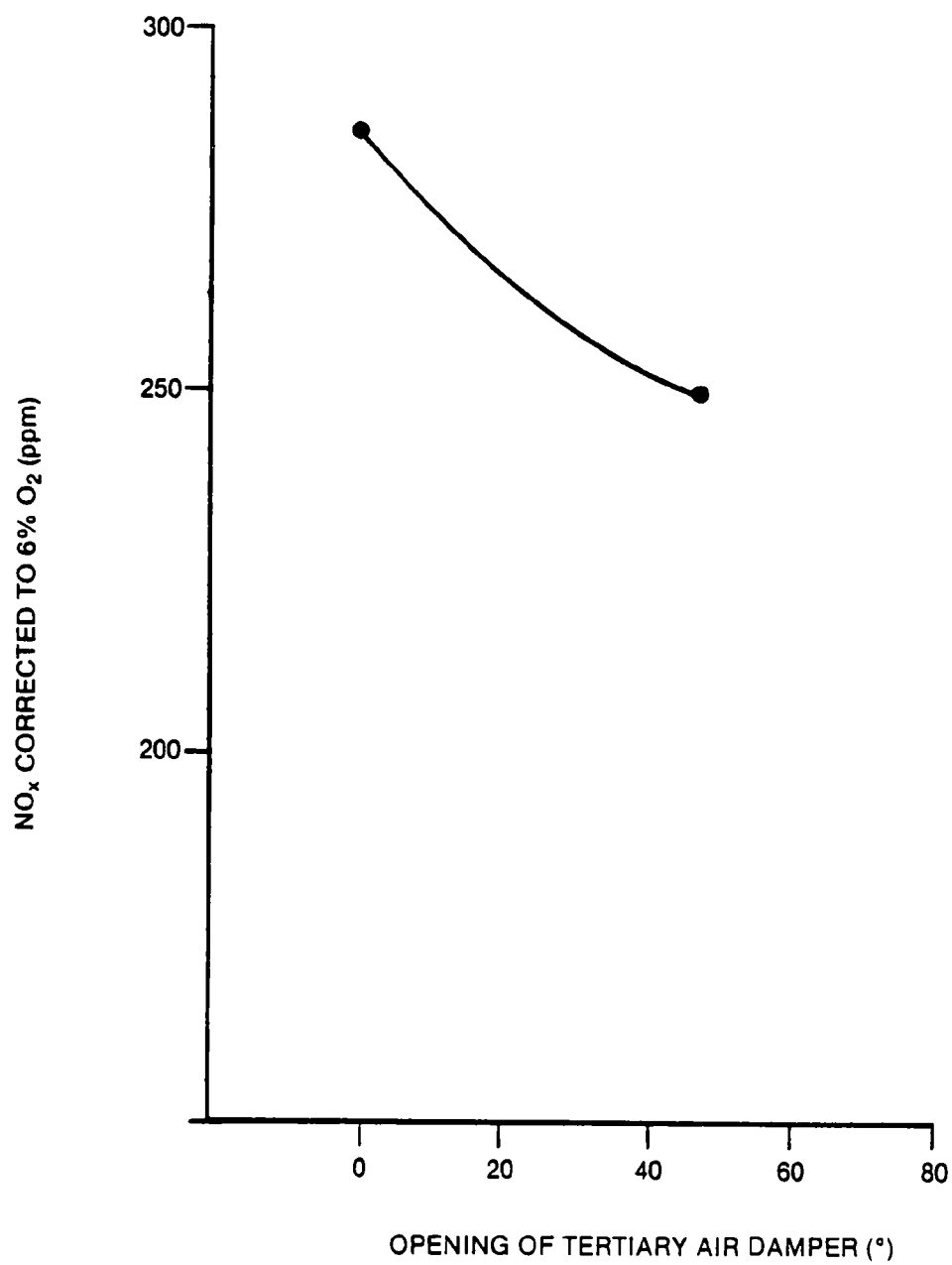


Figure 2-5 Opening of Tertiary Air Damper vs. NO_x.

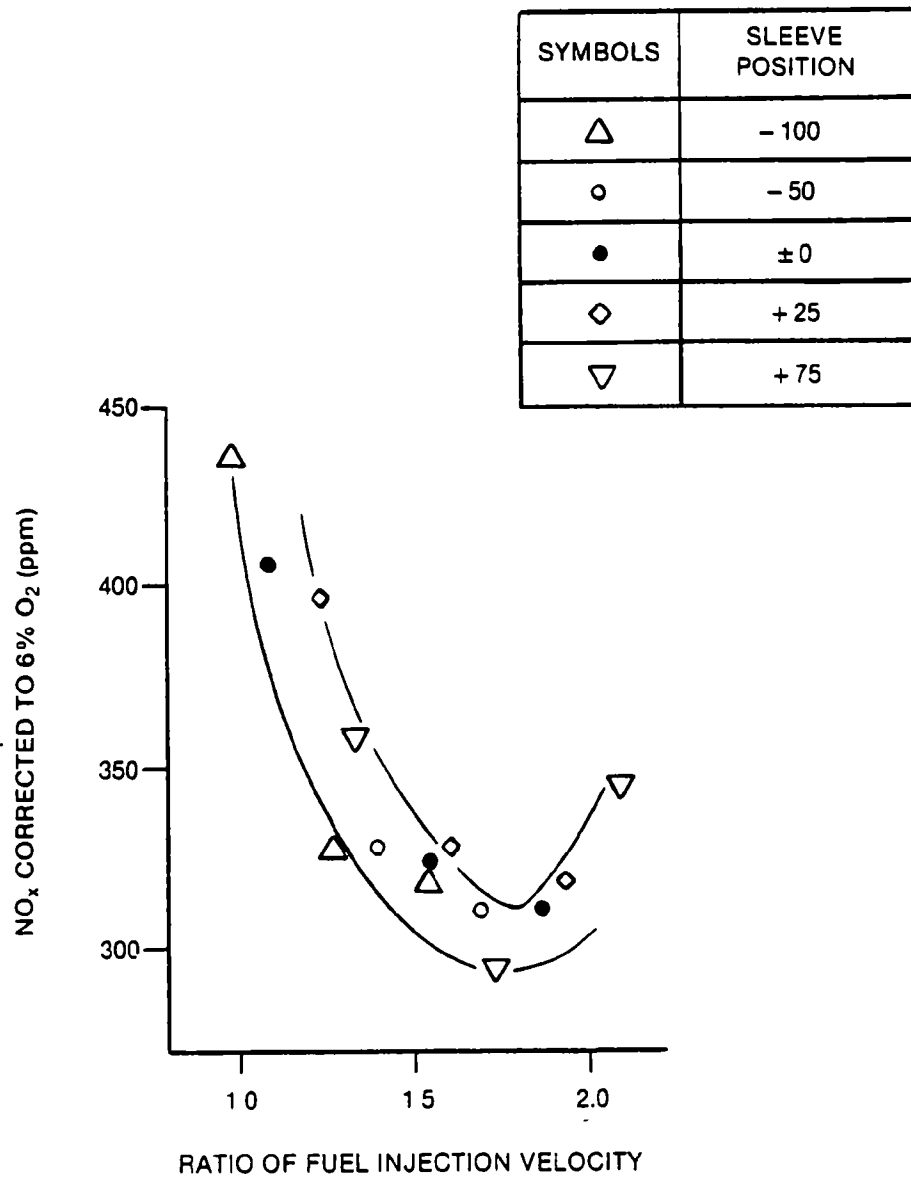


Figure 2-6 Effect of Fuel Injection Velocity on NO_x.

The effects of staged combustion and flue gas recirculation on the performance of the low- NO_x burner were also studied. Three over-fire air ports were installed—one of them straight above the burner and the others on either side of the air port. Figure 2-7 shows that NO_x was reduced substantially by lowering the burner stoichiometry; it reached about 150 ppm at 0.8 stoichiometry. The relationship between the nitrogen content of the coal and the NO_x concentration at different burner stoichiometries is shown in Figure 2-8. By using a lower stoichiometry, most of the fuel NO_x can be reduced to N_2 which reduces NO_x to a low level even with a high-nitrogen coal. Figure 2-9 shows the effect of flue gas recirculation on NO_x concentration. By using the combination of a low- NO_x burner, staged combustion, and flue gas recirculation, NO_x was reduced to about 100 ppm, even with high-nitrogen coal.

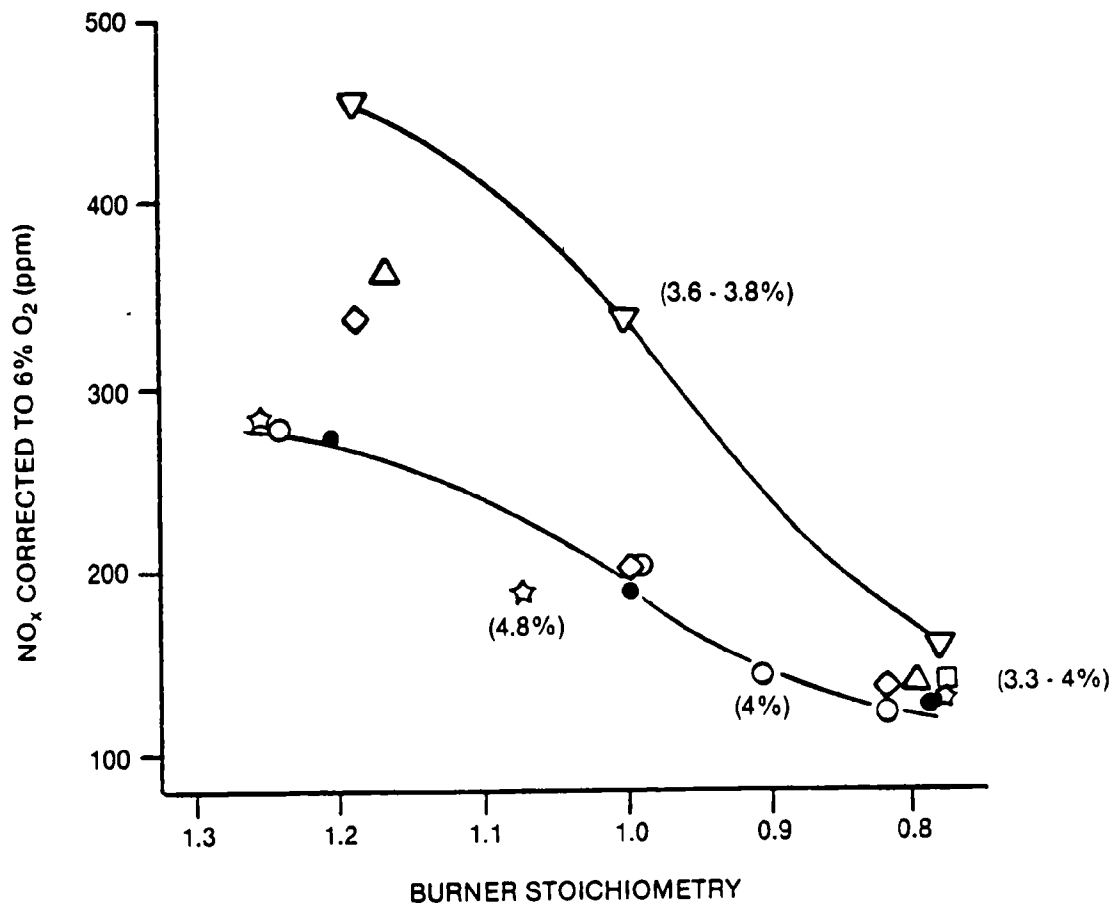
Commercial application of the burner is described in Section 2.6.3.

2.3 NO_x ABATEMENT BY BHK LOW- NO_x COAL BURNER (4,5,6)

2.3.1 Primary Gas Dual Air Register Burner

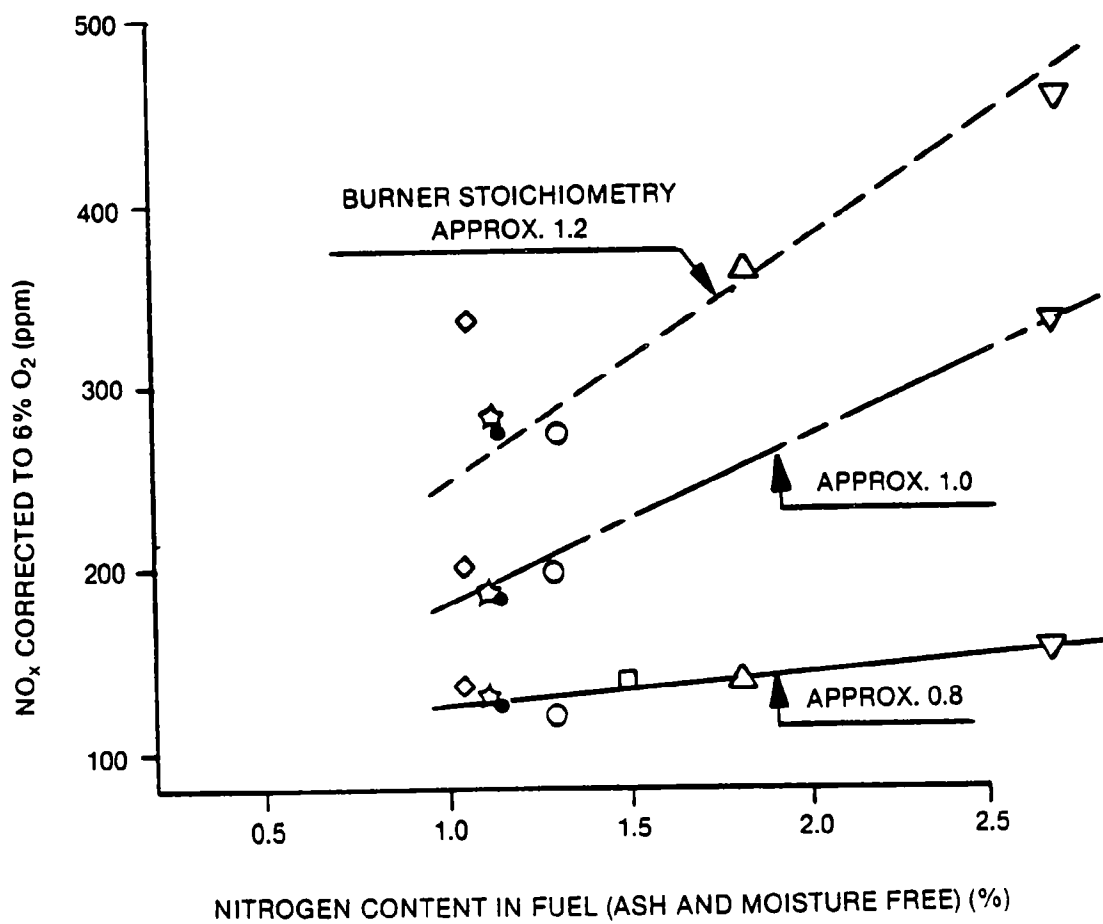
This low- NO_x burner is based on the dual air register burner developed by Babcock and Wilcox of the U.S. with an improvement made by Babcock-Hitachi K.K. (BHK). The major difference between this burner and the dual air register burner is that the former has a primary gas (PG) port for injection of recirculated flue gas to reduce NO_x formation. Figure 2-10 shows the construction of the burner. The nozzle for pulverized coal is located in the center of the air register and allows injection of pulverized coal which is mixed with air (primary air) and sent into the furnace. The pulverized coal injection nozzle has two concentric cylindrical sleeves. The inner of the cylindrical paths formed by them is called the primary gas port and the outer is called the secondary air port. The cylindrical path formed by the outer sleeve of the secondary air port and the burner throat is called the tertiary air port.

○	JAPANESE COAL	A
☆		B
◇		C
●	IMPORTED COAL	A
□		B
△		C
▽		D



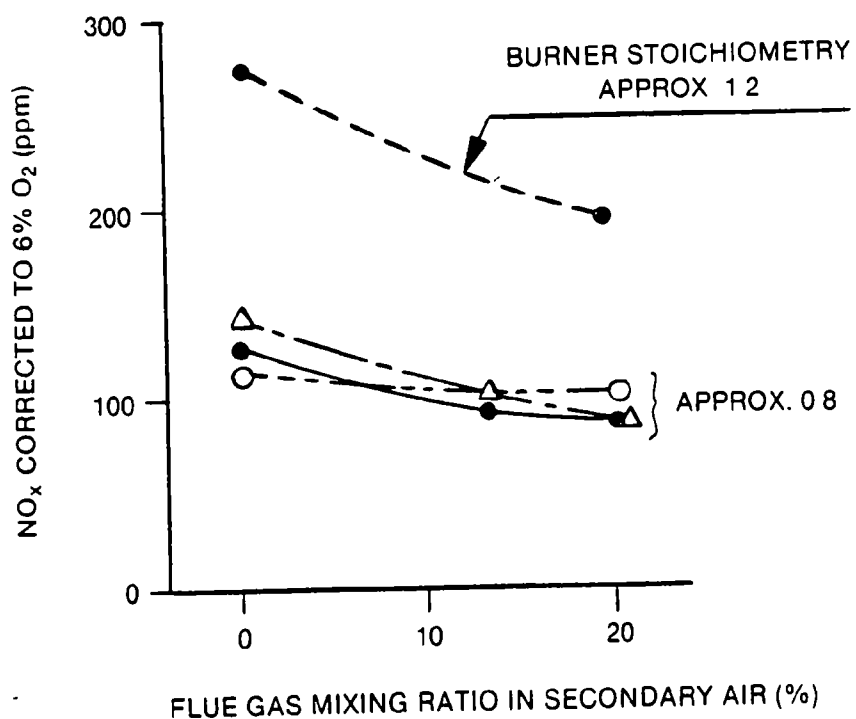
NOTE: Figures in Parentheses indicate Exhaust Gas O₂.

Figure 2-7 NO_x Reduction by Low-NO_x Burner and Two-staged Combustion.



NOTE. Symbols in This Figure are the same as those in Figure 2-7.

Figure 2-8 Nitrogen Content in Fuel vs. NO_x.



NOTE: Symbols in this Figure are the same as those in Figure 2-7.

Figure 2-9 NO_x Reduction by Flue Gas Recirculation.

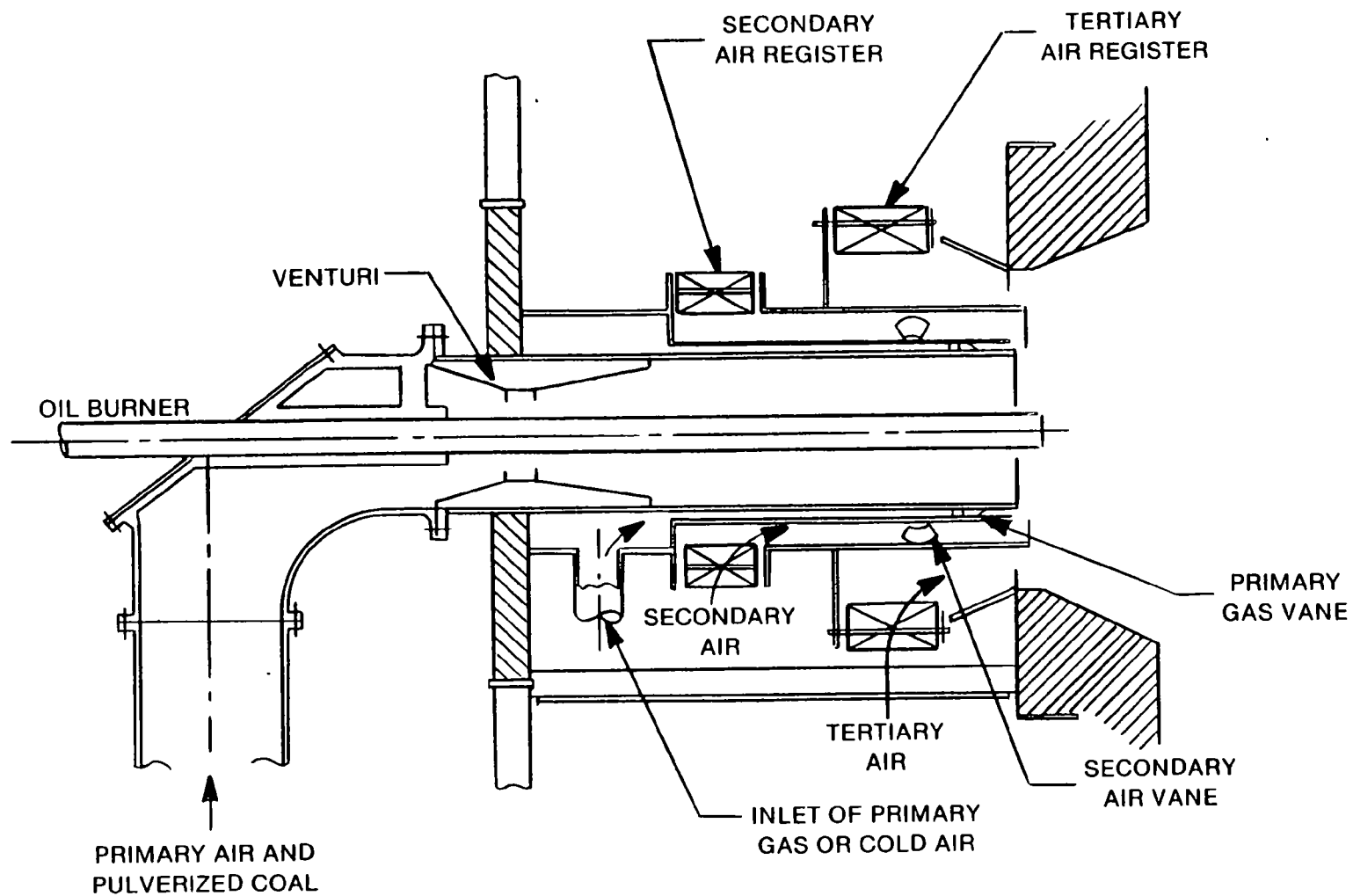


Figure 2-10 PG Dual-Air Register Burner.

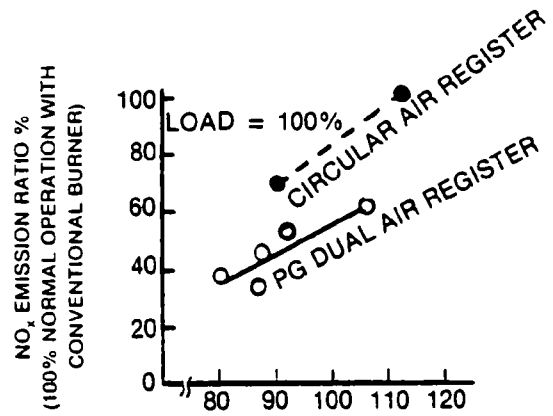
Combustion air from the windbox is supplied to the secondary and tertiary air ports. Each port is equipped at its inlet with louvre dampers, called secondary and tertiary registers, for distributing the air flow among these ports. Each of the nozzles accommodates a specific amount of combustion air. In addition, the PG type burner uses a primary gas port to introduce flue gas from the economizer outlet and slow the rapid mixing of the fuel-rich flame with secondary air.

2.3.2 Test Results

Results of tests with a 250 MW natural circulation coal-fired boiler are shown in Figure 2-11. The A portion of the figure shows the relationship between the two-stage combustion ratio (air through the burner throat/theoretical air) and the NO_x concentrations for a conventional circular burner and the PG dual air register burner. Assuming that the NO_x concentration with the conventional burner without two-stage combustion is 100%, the reduction ratio was 31% with two-stage combustion, 39% with the use of the PG dual air register burner, and 63% with the combination of two-stage combustion and the PG burner.

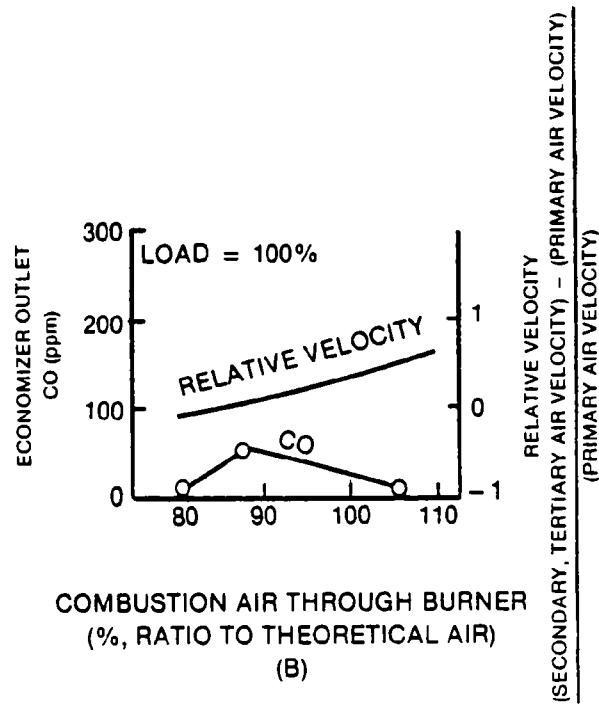
Figure 2-11 B gives an example of the relationship between CO concentration and the two-stage combustion ratio. CO emissions increased up to the two-stage combustion ratio of 87 and then decreased. The variation in two-stage combustion ratios causes variation in the flow ratios of the secondary and tertiary air. Because of this variation the injection speed of the combustion air at the burner throat also varies. On the other hand, the relative speed between the air side and fuel side at the burner throat varies because the fuel injection speed (primary air) is constant. The concentration of CO seems to increase at zero relative speed.

Figures 2-12 and 2-13 show the effects of O_2 levels in flue gas and boiler loads on NO_x emission levels. Figure 2-14 illustrates the results of using different coals in a test furnace as shown in Table 2-5. The application of primary gas along with staged combustion and flue gas recirculation



COMBUSTION AIR THROUGH BURNER
(%, RATIO TO THEORETICAL AIR)

(A)



COMBUSTION AIR THROUGH BURNER
(%, RATIO TO THEORETICAL AIR)

(B)

Figure 2-11 Results of Two-Staged Combustion Test: NO_x and CO.

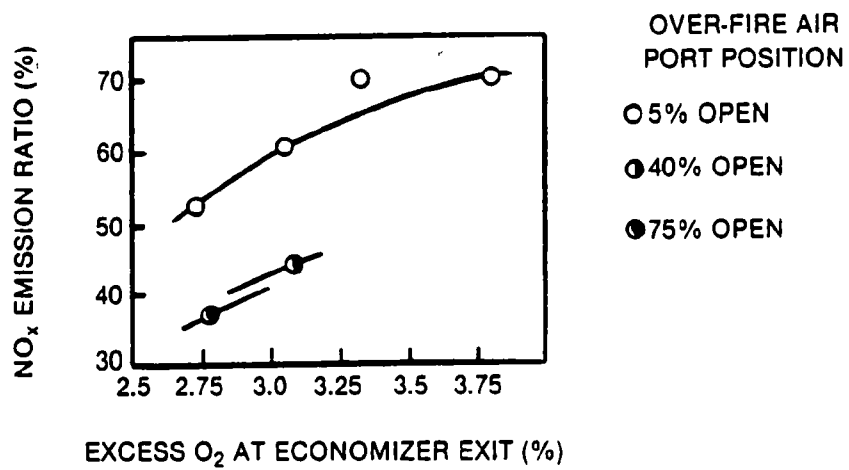


Figure 2-12 Effect of Flue Gas O₂ Level on NO_x Emissions in PG Dual Register Burner.

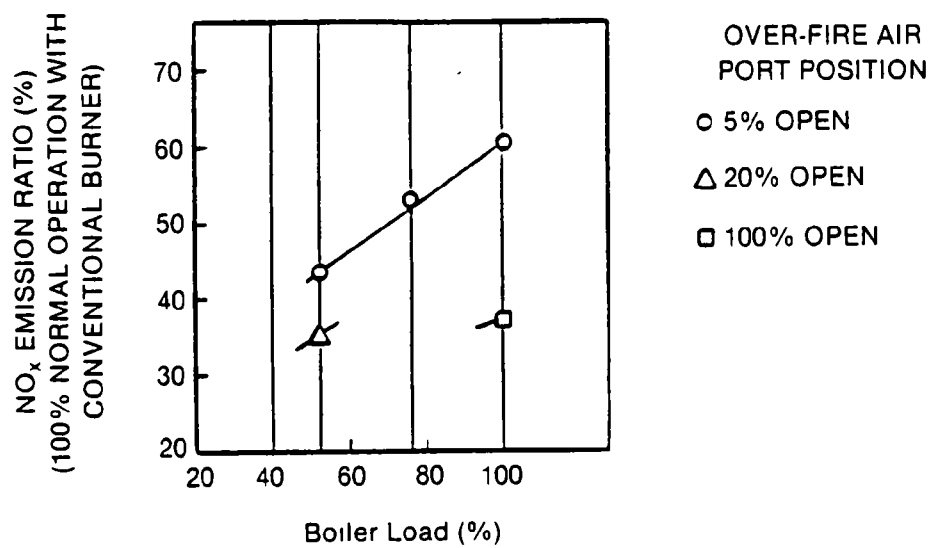


Figure 2-13 Effect of Boiler Load on NO_x Emissions in PG Dual Register Burner.

BURNER TYPE	COAL	NO OTHER CONTROL	2 STAGE COMBUSTION	2 STAGE + GM	2 STAGE + GM + PG
DUAL AIR REGISTER	JAPANESE	X			
PG DUAL AIR REGISTER	JAPANESE	○	●	●	●
	OVERSEAS A	△	△	△	△
	OVERSEAS B	□	□	■	■

2 STAGE COMBUSTION: 85% BURNER STOICHIOMETRY

GM = GAS MIXING (FLUE GAS RECIRCULATION)

PG = FLUE GAS (6.5%) FED THROUGH THE BURNER

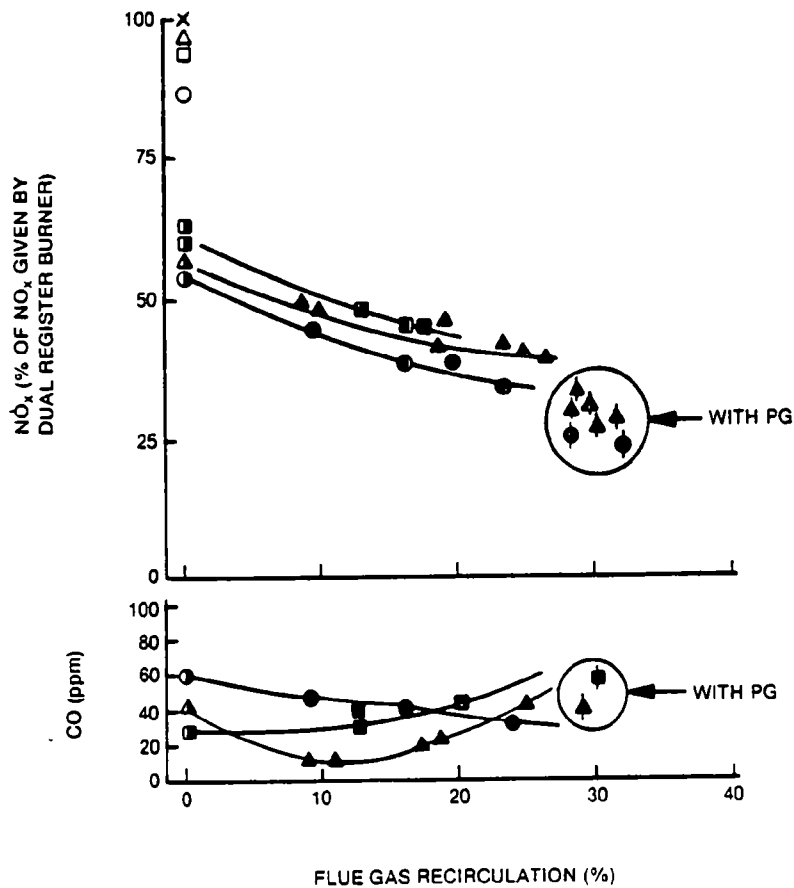


Figure 2-14 Performance of the PG Dual Register Burner In the Test Furnace

TABLE 2-5. COMBUSTION FURNACE TEST CONDITIONS FOR FACTORY TEST

1. Furnace
 - Type: Horizontal water-cooled cylinder
 - Size: Inner diameter 2.2m
 - Length 9.0m
 - Combustion capacity:
 - max. 13×10^6 kcal/h
2. Type of burner
 - (1) Dual air register
 - (2) P.G. Dual air register
3. Type of coal
 - (1) Japanese coal: 1,000 kg/h
 - (2) Overseas coal A: 930 kg/h
 - (3) Overseas coal B: 870 kg/h
4. Air temperature: 300°C
5. Furnace outlet O₂: 3.0%
6. Fuel analysis:

Type of Coal	Japanese Coal		Overseas Coal	
			A	B
<u>Proximate Analysis</u>				
GCV (Dry Base)	kcal/kg	6,040	6,494	6,900
Moisture	%	1.90	2.04	2.60
Volatile matter	%	32.29	25.64	28.20
Fixed carbon	%	40.91	55.74	57.30
Ash	%	24.90	16.58	12.00
<u>Ultimate Analysis</u>				
Total sulfur	%	1.0	0.83	0.70
Carbon	%	59.86	67.76	71.98
Hydrogen	%	4.08	3.53	4.12
Nitrogen	%	1.09	1.61	0.90
Oxygen	%	8.07	8.41	10.02
Sulfur	%	0.64	0.53	0.42
Fluorine	ppm	106	1,581	—

reduced NO_x to about 25% of the level obtained with conventional combustion. CO was not increased by using primary gas.

The performance of the PG-type burner will be discussed in Section 2.6 (Figure 2-35).

2.4 MHI LOW- NO_x COAL BURNERS (7,8,9)

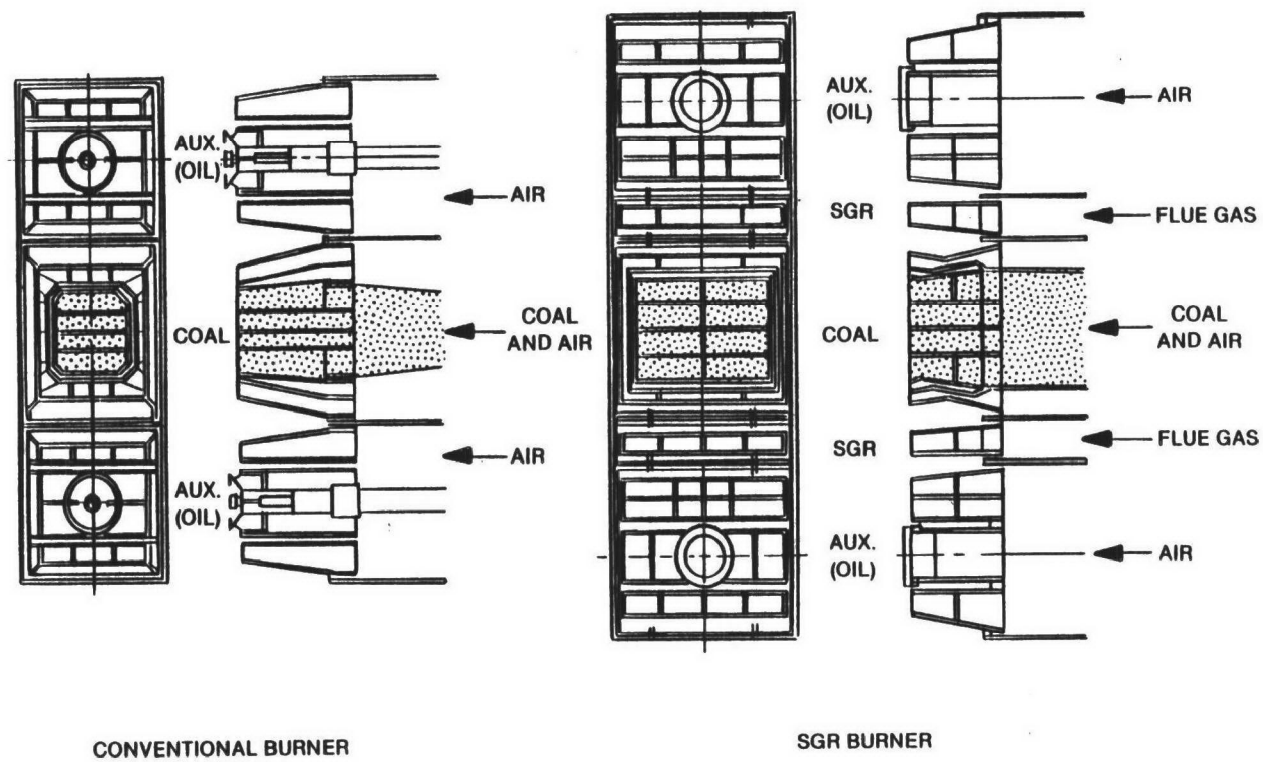
2.4.1 Separate Gas Recirculation Burner

Mitsubishi Heavy Industries (MHI) developed a low- NO_x separate gas recirculation (SGR) burner, which is used with the new 500 MW coal-fired boiler at EPDC's Matsushima Station. Recently MHI further improved the SGR burner to produce a PM coal burner.

By conducting extensive fundamental studies, MHI has found the following conditions to be important for NO_x abatement.

- 1) The temperature in the volatile matter combustion zone should be kept as high as possible and the combustibles should stay in this zone as long as practicable.
- 2) The temperature of the char combustion zone should be appropriately low and combustion should be completed in this zone.

Figure 2-15 compares the SGR burner with a conventional burner. The SGR burner has several features to satisfy the conditions described above. A flame holder is provided at the outlet of the coal nozzle to maintain a stable ignition and expedite the combustion of volatile matter. The coal nozzle and each auxiliary air nozzle are located apart from one another and SGR nozzles are placed between them to retard the diffusion of secondary air to the volatile matter combustion zone.



(Oil Burners are for Start-up)

Figure 2-15 Configurations of Conventional and SGR Burners.

Extensive combustion tests have been carried out with a test furnace shown in Figure 2-16 and described in Table 2-6, using coals shown in Table 2-7. As shown in Figure 2-17, NO_x concentrations were 30-50% lower with the SGR burner than with a conventional burner. NO_x abatement was more pronounced with the Japanese coal which had a low fixed carbon (FC)/volatile matter (VM) ratio. As will be shown in Figure 2-24, data obtained with the test furnace agree well with the data from commercial boilers.

2.4.2 PM Burner for Pulverized Coal

Figure 2-18 indicates that the NO_x concentration falls as the primary air/coal ratio (kg/kg) decreases from 3 to 1. Figure 2-19 shows that the NO_x concentration is also lowered when the ratio increases from 3 to 7.

As shown in Figure 2-20, a ratio of 3~4 approximately corresponds to the theoretical air for volatile matter in coal. NO_x concentrations are lowered with the smaller ratio because of the deficiency of O_2 . On the other hand, the ratio 7~8 corresponds to the theoretical air for coal. With the ratio of between 3~4 and 7~8, fixed carbon in coal burns with deficient O_2 to form NO_x .

A conventional burner may produce a primary air/coal ratio of 2~3 as shown in Figure 2-20. If the primary air-coal supply is divided into two streams with different ratios— C_1 for a coal-rich concentrated nozzle and C_2 for coal-lean weak nozzle—for separate burning, the average NO_x value should be $(\text{NO}_x)\text{PM}$ as shown in the figure. This is the weighted mean of $(\text{NO}_x)C_1$ and $(\text{NO}_x)C_2$ and is substantially lower than $(\text{NO}_x)C_0$. The combined use of the concentrated flame and weak flame may result in low- NO_x combustion.

Figure 2-21 shows the configuration of the Pollution Minimum (PM) burner for use with coal. The performance of the PM burner in the test furnace is shown in Figures 2-22 and 2-23. A low NO_x concentration, about 100 ppm or below, was achieved by the furnace.

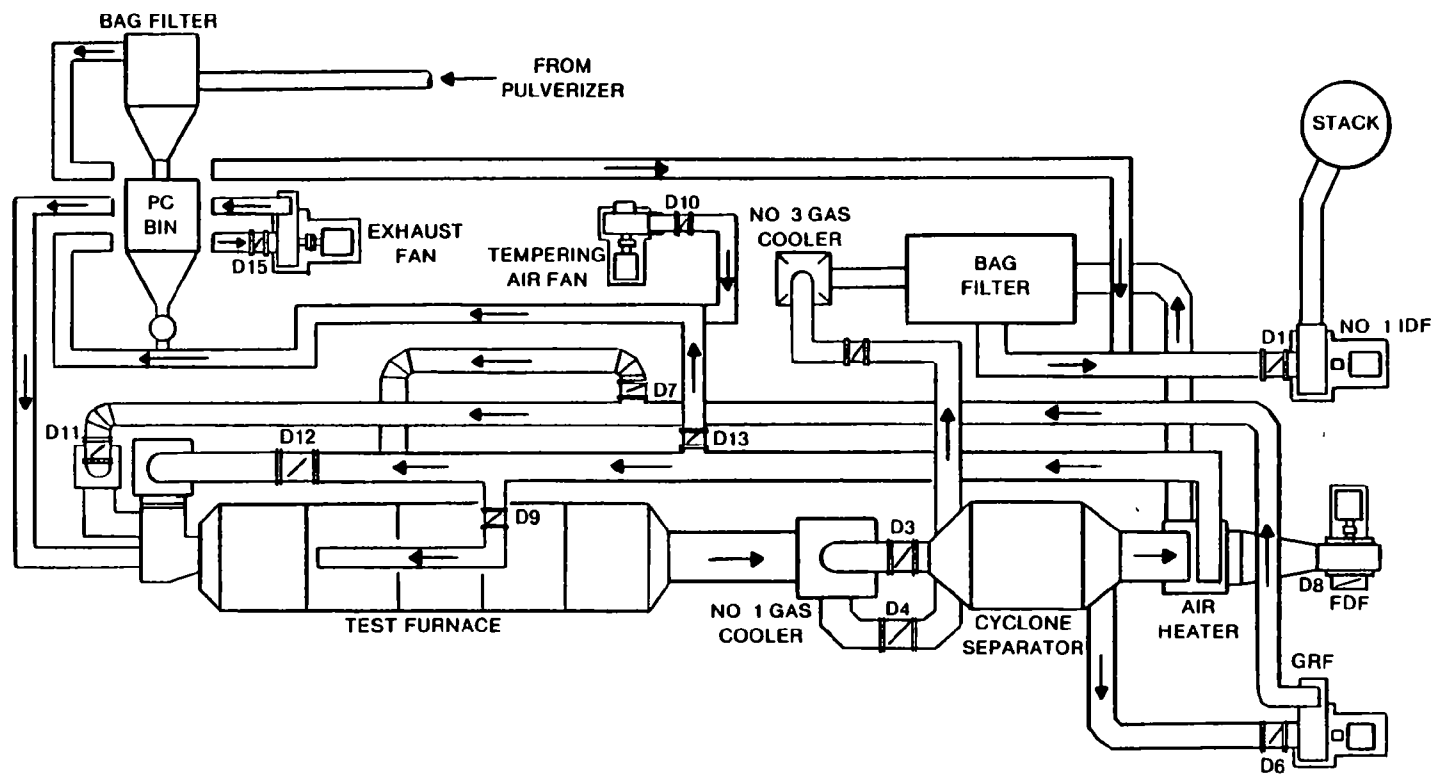


Figure 2-16 Flowsheet of the 4t/hr Test Furnace

TABLE 2-6. MAIN FEATURES OF MHI TEST FURNACE (4 t/hr Test Furnace)

Equipment		Technical details
Test furnace		Horizontally installed, water cooled, circular-walled steel construction. 4.4 diameter, 20 m length
Fan	F.D. fan	Capacity: 920m ³ /min x 800mmAq at 20°C, Motor: 160kw
	No. 1 I.D. fan	Capacity: 1140m ³ /min x 800mmAq at 100°C, Motor: 330kw
	No. 2 I.D. fan	Capacity: 200m ³ /min x 320mmAq at 100°C, Motor: 30 kw
	Exhaust fan	Capacity: 260m ³ /min x 700mmAq at 100°C, Motor: 90kw
	G.R. fan	Capacity: 760m ³ /min x 600 mmAq at 350°C, Motor: 165kw
Air Heater		Ljungstrom type, Capacity: 750Nm ³ /min x (25 350°C)
Gas	No. 1 Gas cooler	Water-cooled tubular type, Capacity: 750nm ³ /min x (800 500°C)
Cooler	No. 2 Gas cooler	Water-cooled tubular type, Capacity: 200nm ³ /min x (700 120°C)
	No. 3 Gas cooler	Water cooled tubular type, Capacity: 100nm ³ /min x (700 350°C)
Ash	Cyclone separator	Multi-cyclone type, Capacity: 1000nm ³ /min x 500°C
disposal	Bag filter	Gas area 613m ² , Capacity: 1200nm ³ /min x 120°C
	Precipitator	Gas velocity: 1~1.5m/s, Capacity: 2500nm ³ /h
Fuel feed	Coal pulverizer	Bowl mill type, Capacity: 2300hg/h x 8000m ³ /h x 600mmAg
assembly	P.C. bin	Capacity: 20m ³
	P.C. feeder	Table feeder type, Capacity: Max 4500kg/h

TABLE 2-7. ANALYSIS OF COALS USED WITH MHI TEST BURNER

Coals	Marks	Proximate analysis (surface moisture free)				Ultimate Analysis (dry base)			HHV (surface moisture free) kcal/kg
		Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	FC/VM (-)	N (%)	O (%)	O/N (-)	
Japanese	II	42.8	40.2	11.2	0.94	1.1	13.9	11.0	6390
	I	31.6	46.0	20.5	1.46	1.0	6.6	6.6	6450
	J	26.3	59.7	7.5	2.27	1.7	11.5	7.2	6710
	K	35.7	50.6	10.1	1.42	1.4	11.0	7.86	6930
Australian	L	28.6	50.6	17.8	1.77	1.5	8.1	5.40	6410
	M	34.6	52.6	10.9	1.50	1.5	8.3	5.53	7120
	N	30.8	54.1	14.1	1.77	1.1	5.8	5.3	6730
Chinese	O	27.4	60.6	8.8	2.21	0.86	9.8	10.2	7100
	P	25.2	56.1	15.5	2.23	1.9	8.4	4.42	6520
South African	Q	33.9	49.4	12.8	1.46	1.7	10.9	6.41	6540
	R	24.1	57.6	15.2	2.39	1.5	8.1	6.95	6490
	S	23.7	57.9	14.2	2.44	1.6	9.3	7.05	6350
U.S.	T	36.9	47.0	9.9	1.27	1.1	13.4	12.2	6060

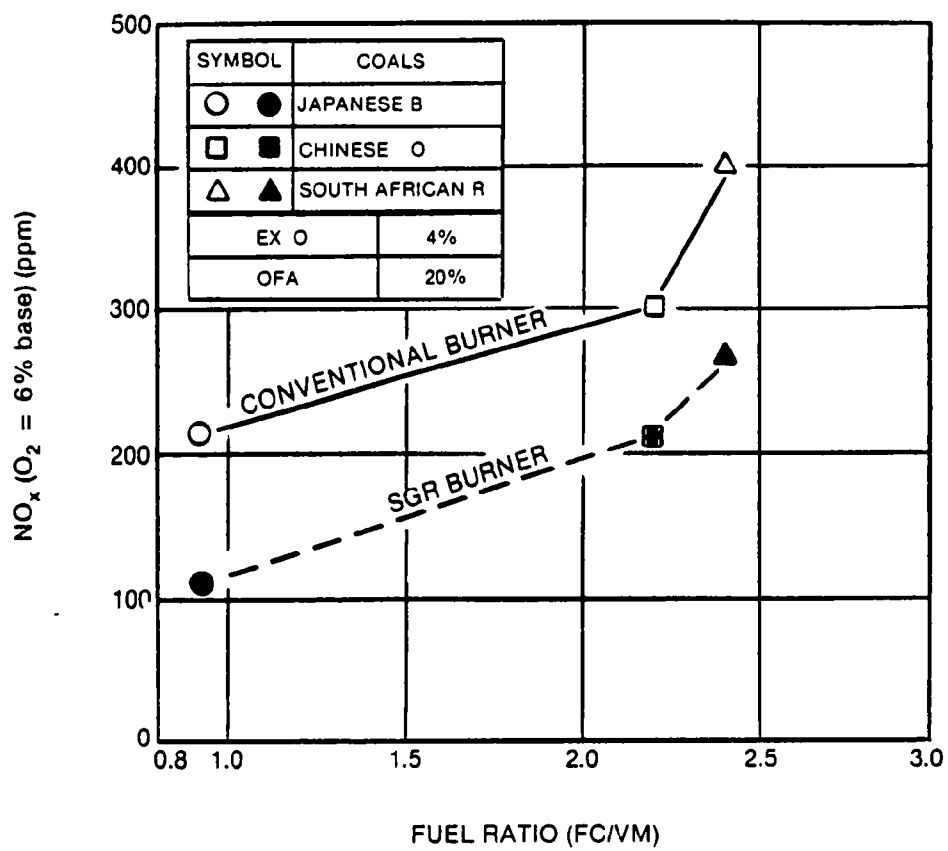


Figure 2-17 Comparison of NO_x Formation with SGR Burner and Conventional Burner.

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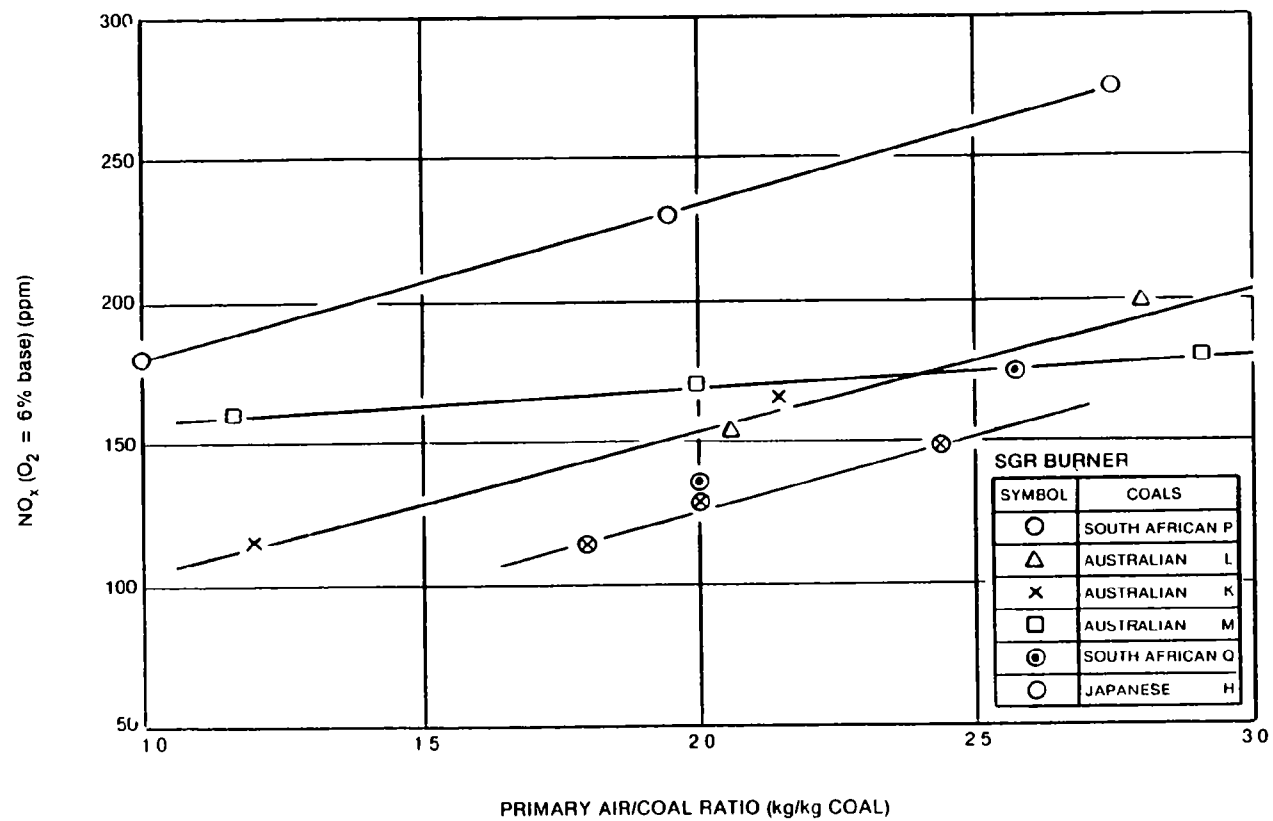


Figure 2 18 Effect of Primary Stage Stoichiometry on NO_x (Fuel-rich side)

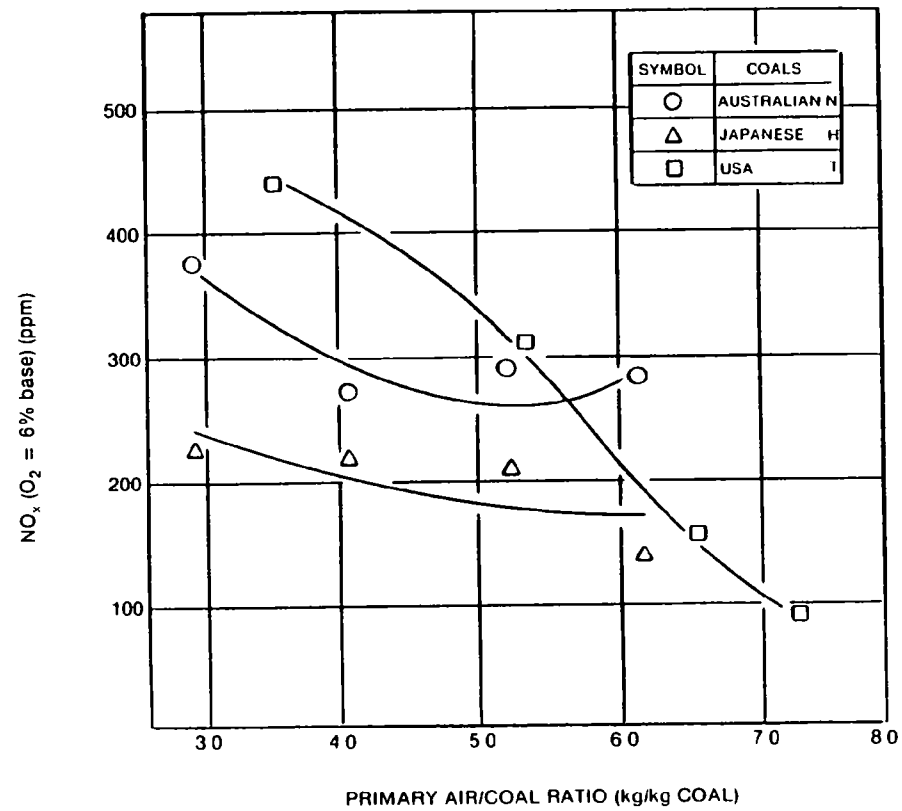


Figure 2-19 Effect of Primary Stage Stoichiometry on NO_x (Fuel lean side)

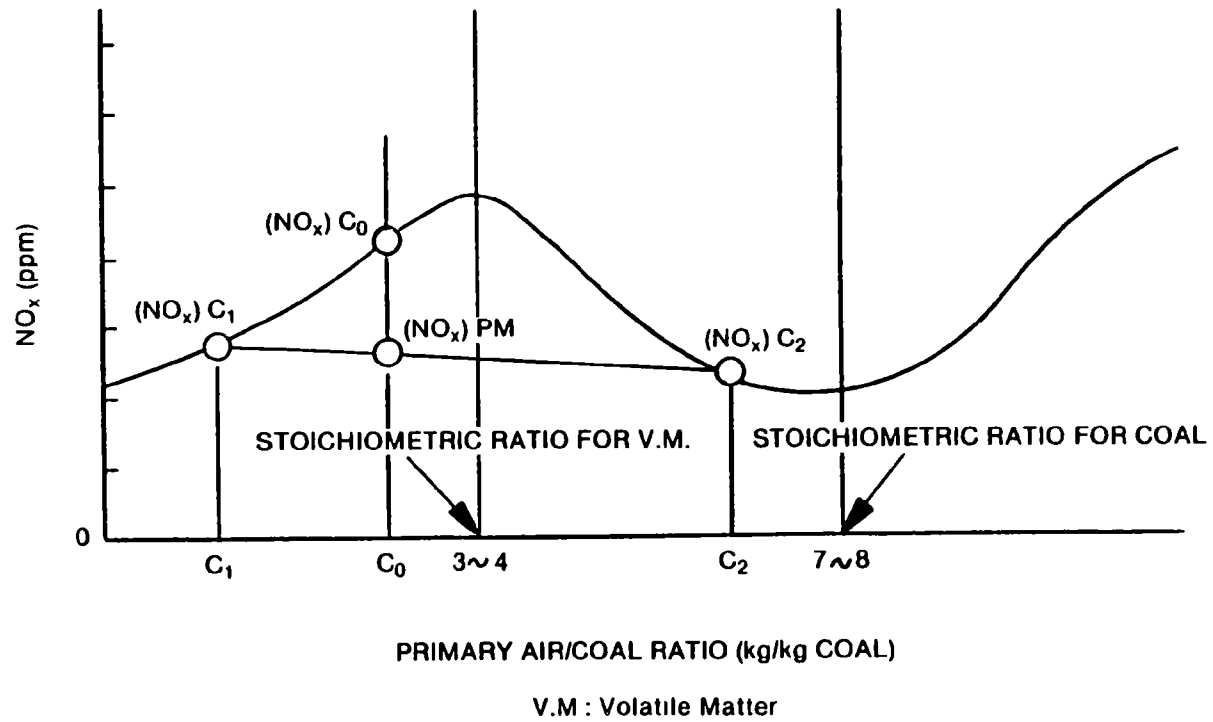


Figure 2-20 Concept of Pulverized Coal-fired Low NO_x PM Burner.

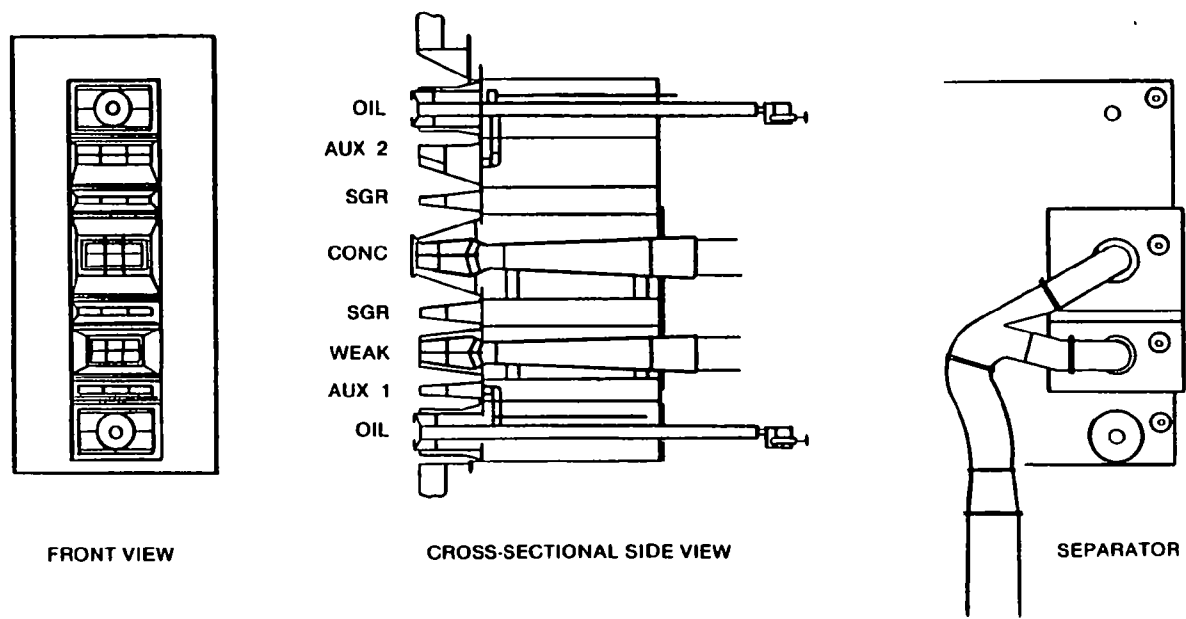


Figure 2-21 Structure of the Coal-fired PM Burner

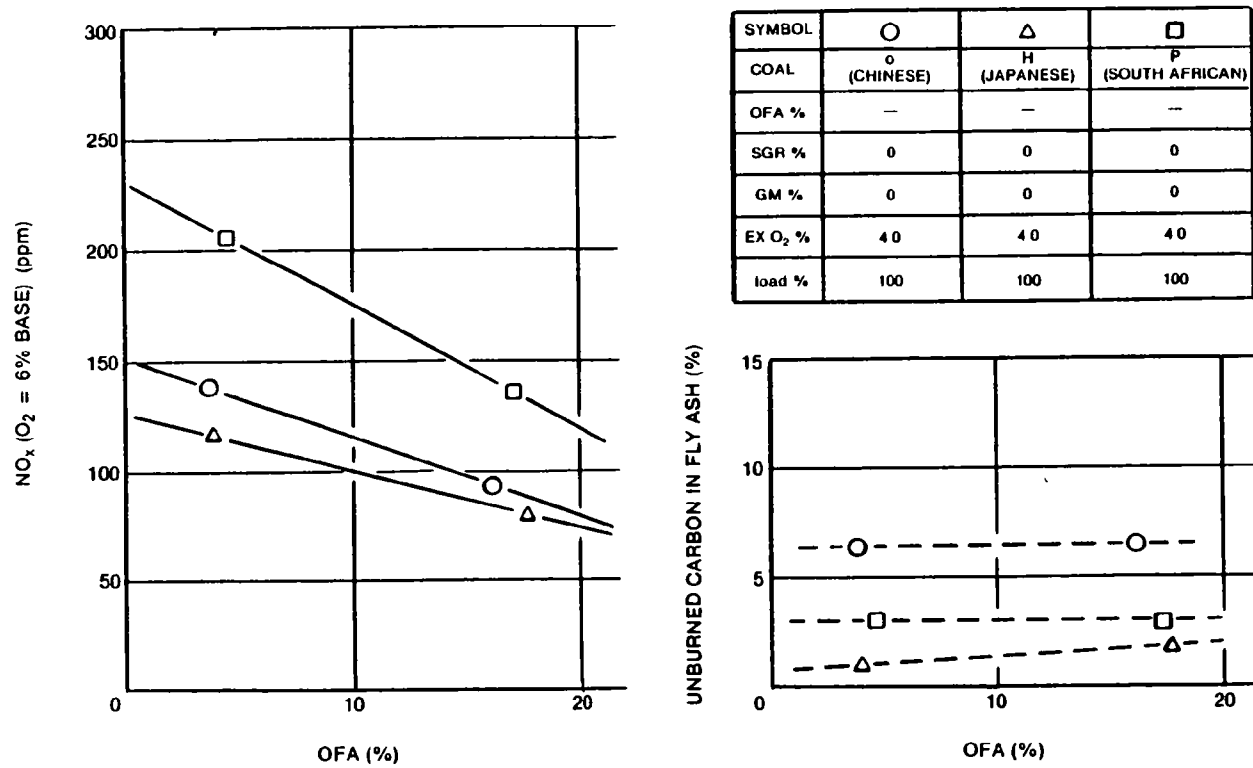
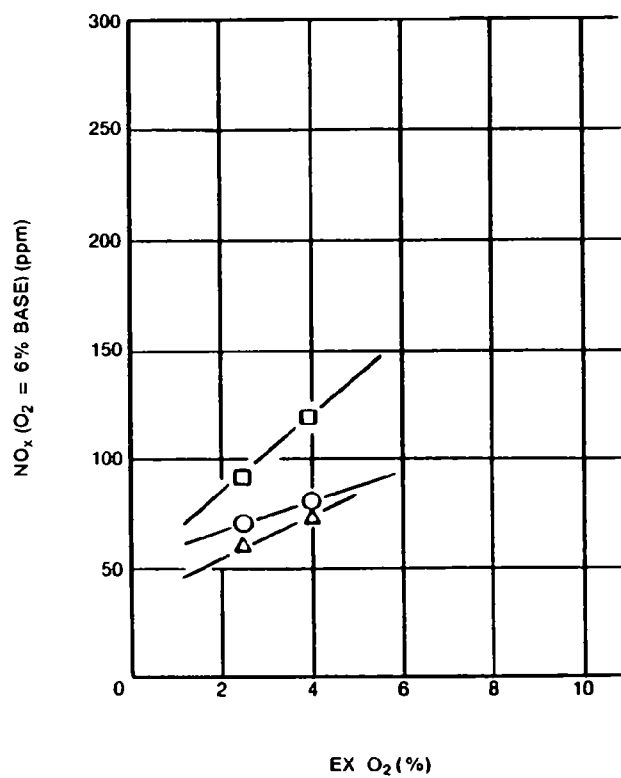


Figure 2-22 NO_x and Unburned Carbon in Fly Ash vs. OFA. (PM Burner)



SYMBOL	○	△	□
COAL	O (CHINESE)	H (JAPANESE)	P (SOUTH AFRICAN)
OFA %	20	20	20
SGR %	0	0	0
GM %	0	0	0
EX O_2 %	—	—	—
LOAD %	100	100	100

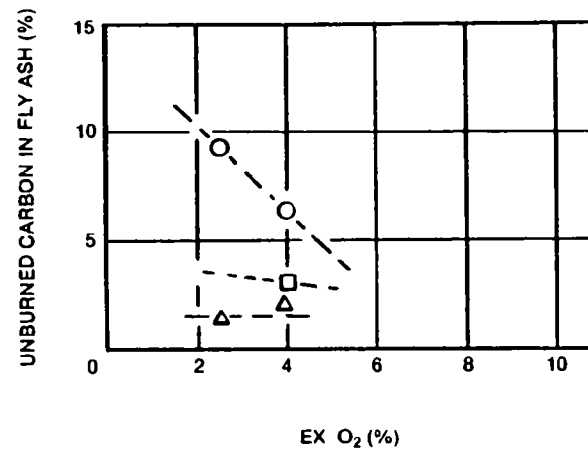


Figure 2-23 NO_x and Unburned Carbon in Fly Ash vs. EX O_2 . (PM Burner)

Figure 2-24 compares the NO_x concentrations for a Combustion Engineering (CE) conventional burner, SGR burner and PM burner when used for tangential-firing commercial boilers and the test furnace. Since NO_x concentrations for test boilers agree well with those for commercial boilers, it is expected that with use of a commercial PM burner, NO_x concentrations may be reduced to 60-80 ppm with Japanese coals and 100-150 ppm with imported coals.

2.5 KHI LOW- NO_x COAL BURNER (11,12)

2.5.1 Structure and Combustion Model

Kawasaki Heavy Industries (KHI) initially developed a low- NO_x coal burner for pulverized coal as shown in Figure 2-25. Later KHI improved the burner design and developed a vortex diffuse (VD) burner as shown in Figure 2-26.

KHI's burners are designed to reduce NO_x efficiently by using low- NO_x burners in combination with staged combustion. The primary air is swirled intensely; much larger amounts of secondary and tertiary air are introduced to provide slow contacting with the coal and the partial combustion products.

A combustion model is shown in Figure 2-27. In the primary combustion zone (I of the figure), volatile matter begins to burn, producing high concentrations of NO_x due to the combustion of nitrogen compounds in the coal. In the secondary zone (II), the volatile matter continues to burn, the char begins to burn, and O_2 concentrations decrease, producing a reducing atmosphere which causes the decomposition of the NO_x to N_2 . The reducing atmosphere also exists in the tertiary zone (III), where the NO_x concentrations reach a minimum just before the over-fire air port for staged combustion. The CO concentration remains high.

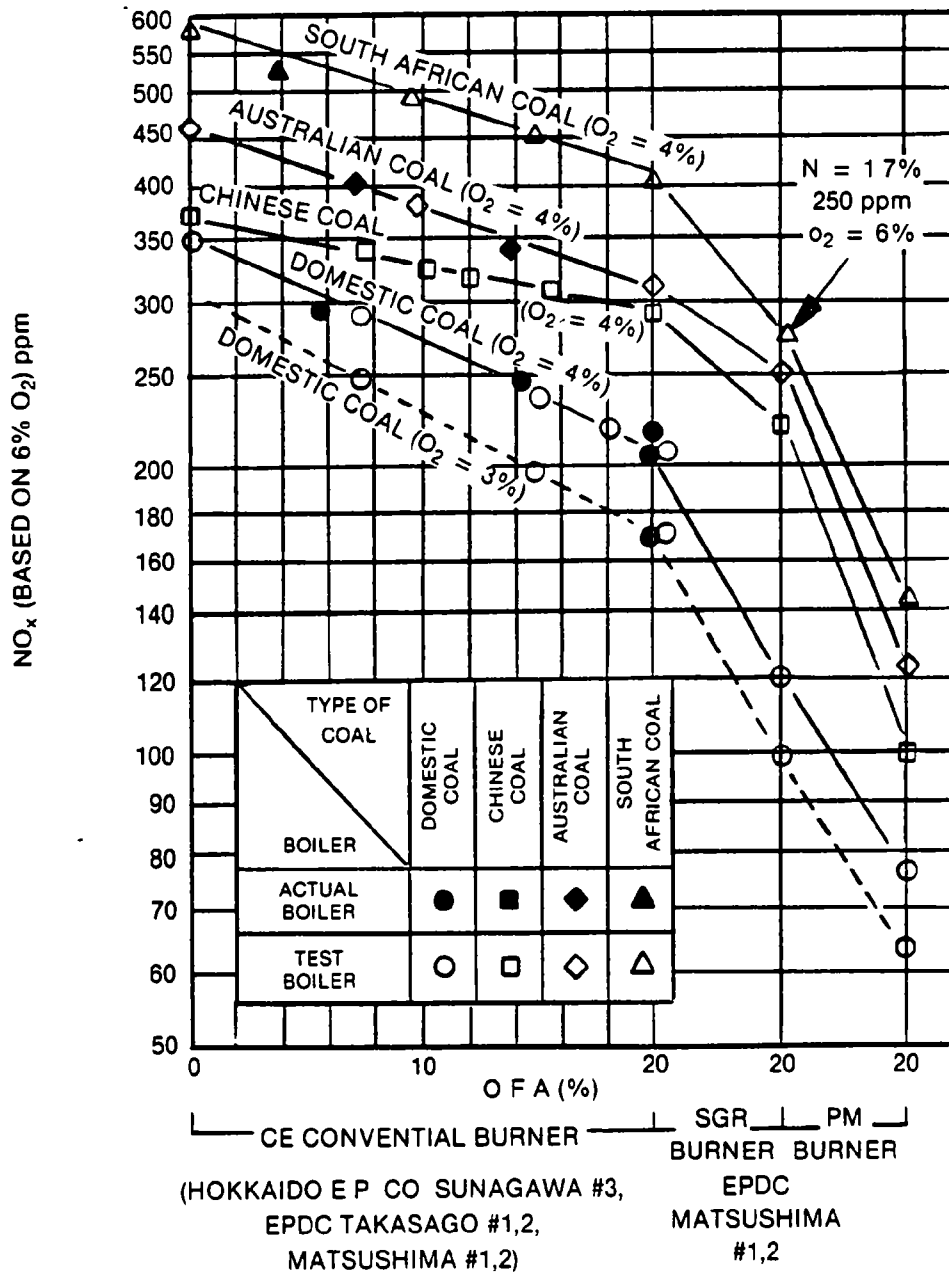


Figure 2-24 Comparison of NO_x Emissions: Laboratory Test Results vs. Field Data. (10)

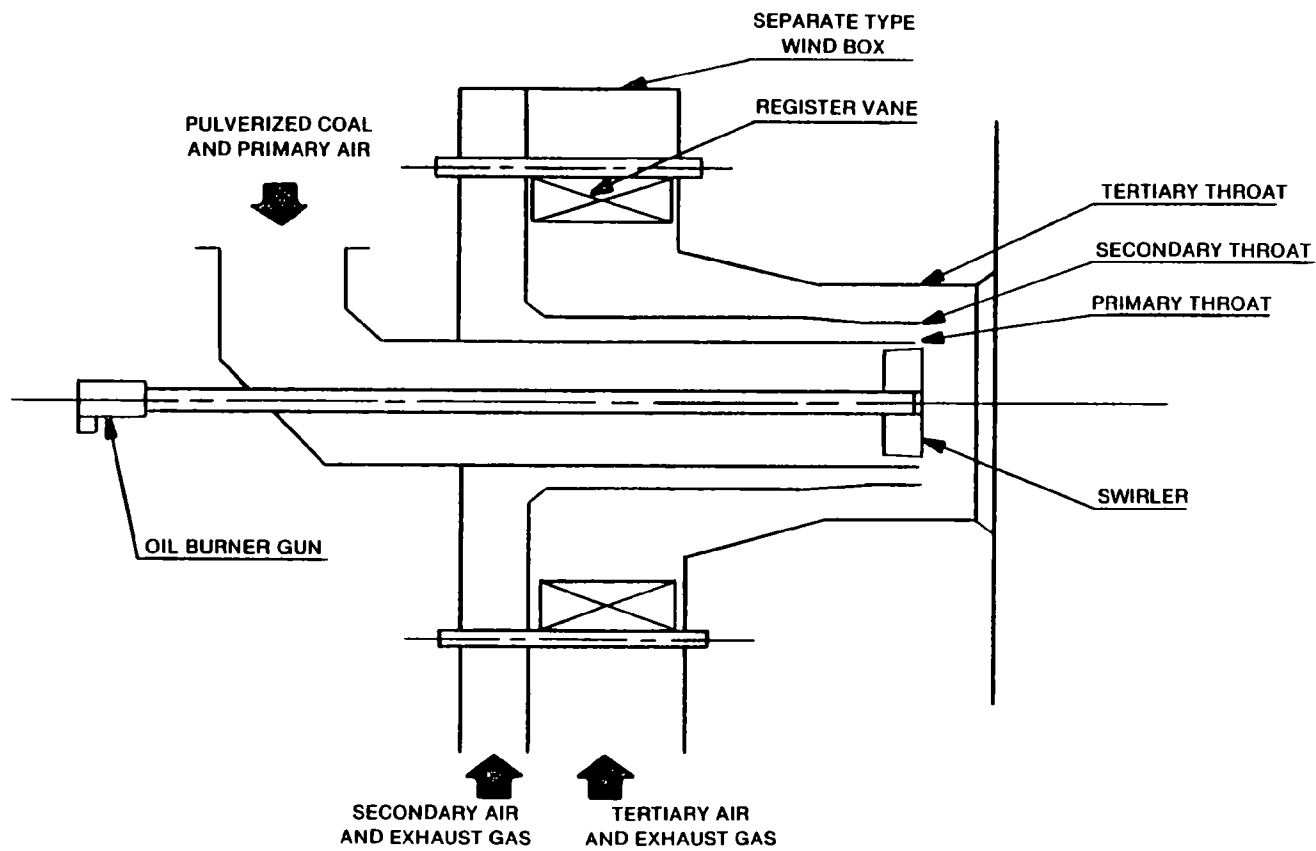


Figure 2 25 Structure of Original KHI Low-NO_x Burner

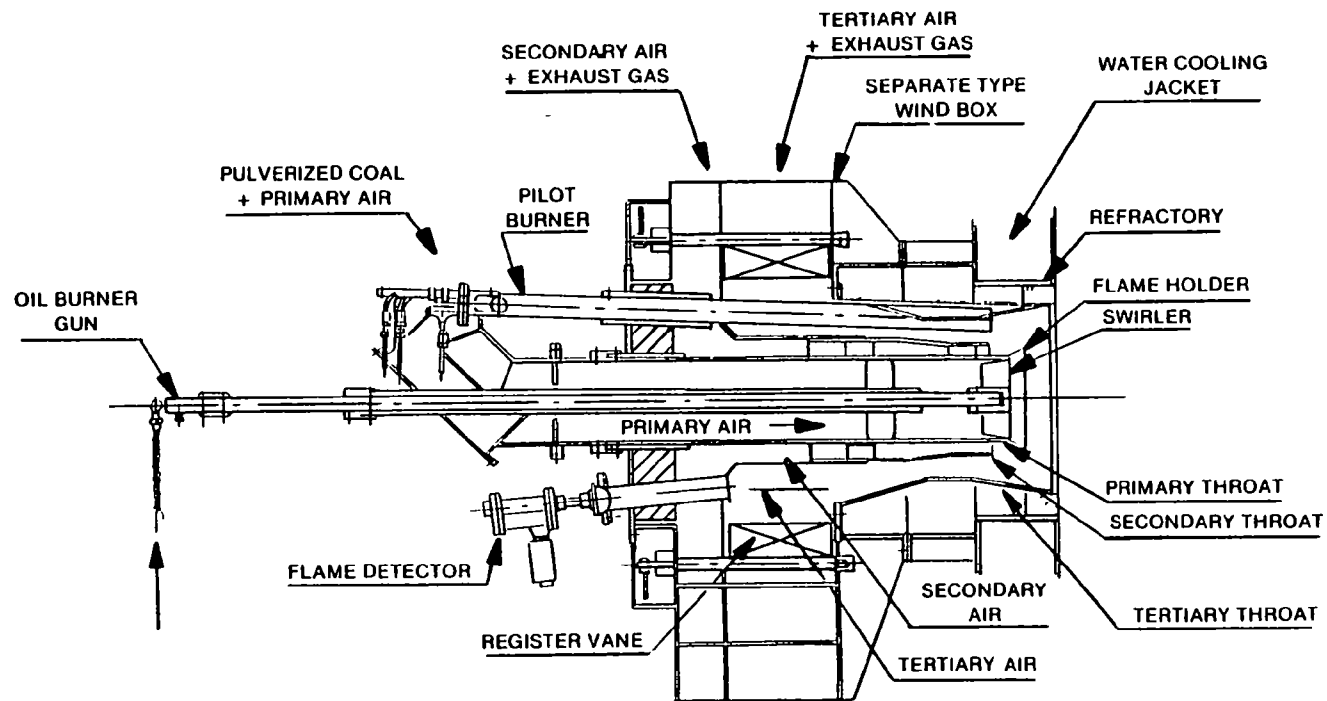


Figure 2-26 Structure of VD Low-NO_x Pulverized Coal Burner

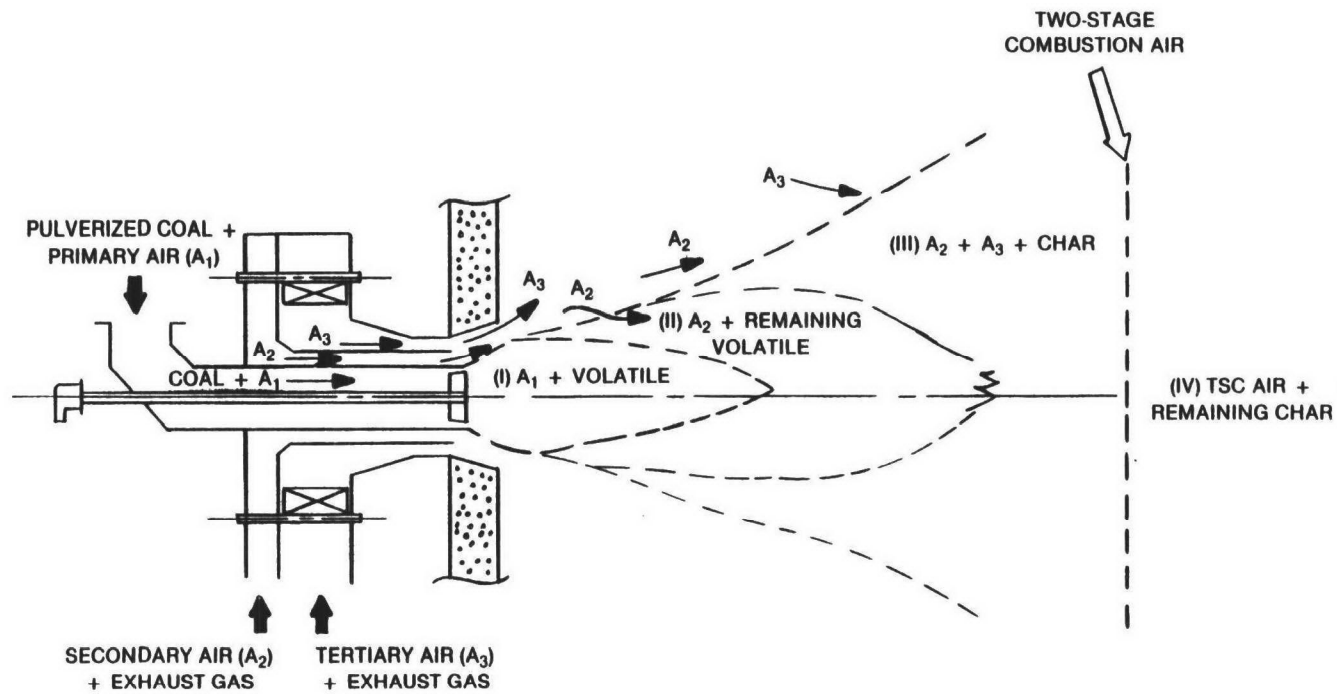


Figure 2-27 Model of Low- NO_x Pulverized Coal Combustion.

Upon injection of the staged air (IV), the remaining char, CO and other reducing gases are burned. However, no significant amounts of fuel NO_x or thermal NO_x are formed during the complete combustion because: 1) virtually all of the nitrogen compounds in the coal already have been decomposed, and 2) the combustion temperature is not very high.

Figure 2-28 shows the test results using the original burner with Japanese coal at the 3t/hr test furnace. The figure clearly illustrates the efficient NO_x reduction of the burner when used in combination with staged combustion. Flue gas recirculation (gas mixing) further reduced NO_x concentrations.

Figure 2-29 compares the performance of the original burner with that of the improved VD burner. In the VD burner, the effect of the combined use of staged combustion and gas mixing is greater; a very low NO_x concentration, below 100 ppm, was achieved. Although the CO concentration in the flue gas increased appreciably, it remained in an acceptable range.

2.6 EPDC'S NO_x ABATEMENT BY COMBUSTION MODIFICATION (10)

2.6.1 Introduction

Electric Power Development Co. (EPDC) is a joint venture of the Japanese Government and nine major power companies. One of its objectives is the consumption of domestic coal. EPDC has three power stations which use domestic coal and recently constructed a new station (Matsushima) to use imported coals. The stations and applicable NO_x regulations are shown in Table 2-8.

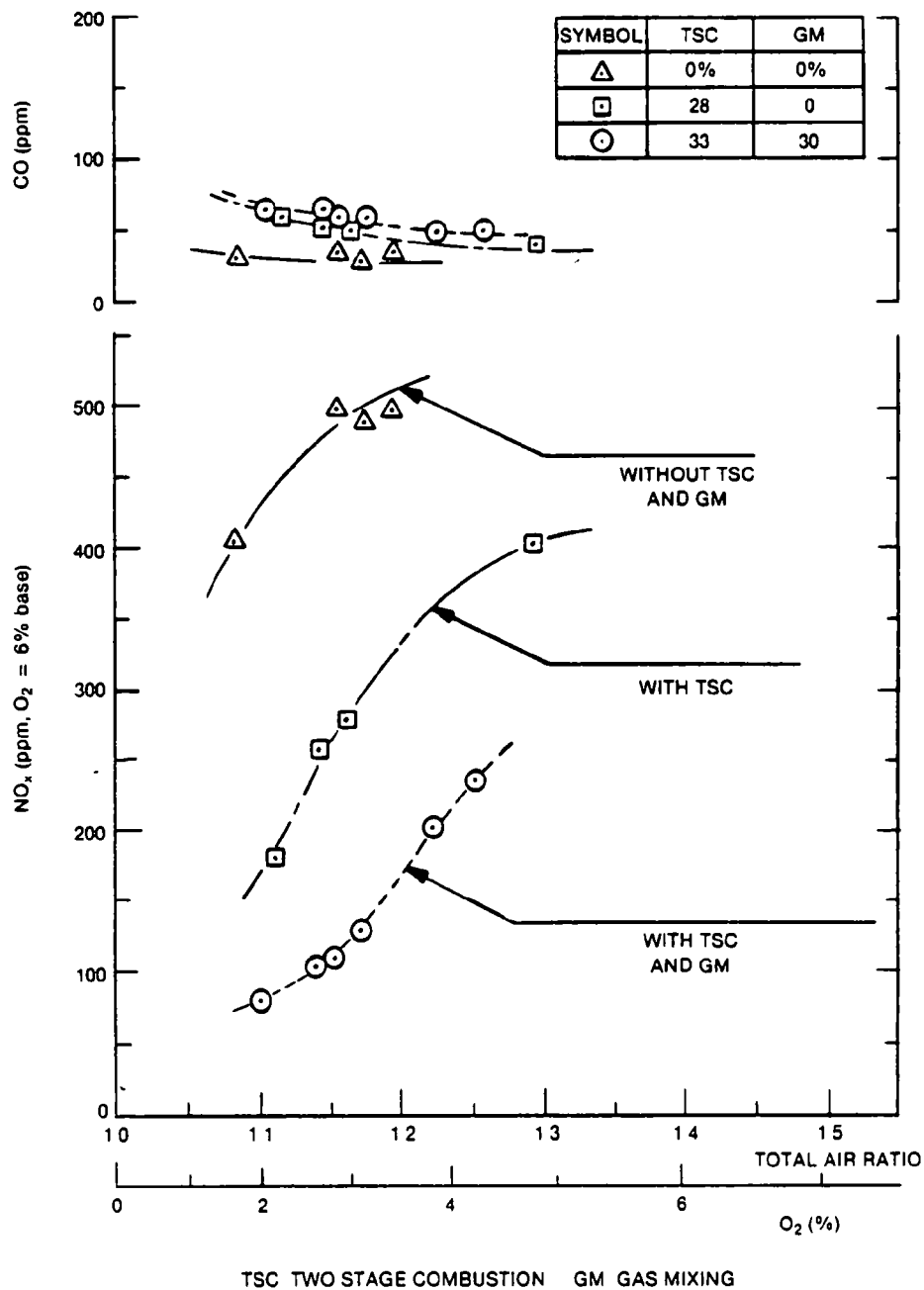


Figure 2-28 NO_x Emission Characteristics of Original KHI Burner.

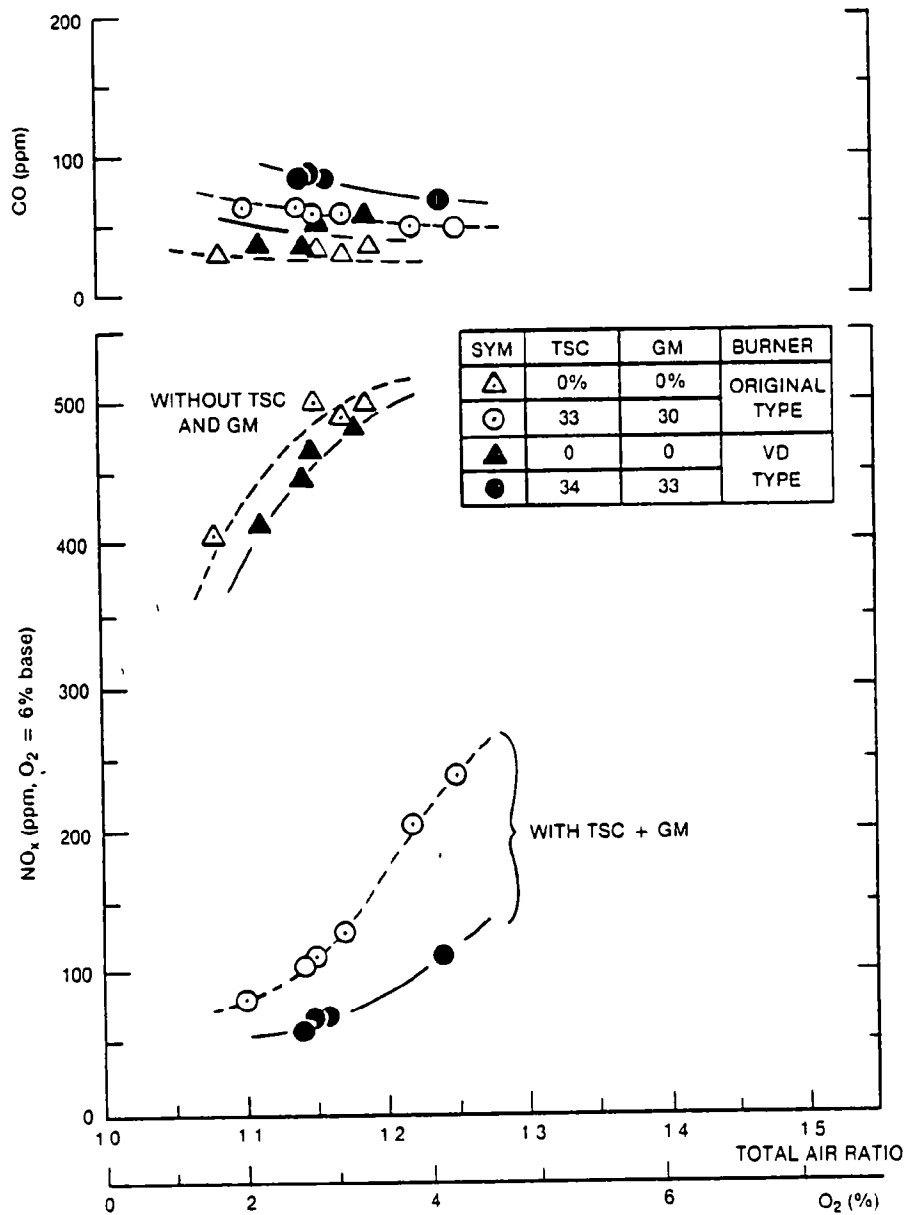


Figure 2-29 Comparison of NO_x Emissions in VD and Original Burners.

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TABLE 2-8. EPDC'S POWER STATIONS AND NO_x REGULATIONS

Power Station	Isogo		Takasago		Takehara		Matsushima	
Boiler No.	No.1	No.2	No.1	No.2	No.1	No.3	No.1	No.2
Capacity, MW	265	265	250	250	250	700	500	500
Year completed	1967	1969	1968	1969	1967	1983	1980	1981
Type of coal	Domestic		Domestic		Domestic	Imported	Imported	
NO _x regulation, ppm								
Emission standard	400		400		400 ^b	400 ^b	400	
Local agreement	159 ^a		300		112 ^b	60 ^b	300	
Actual	150-180		Below 300				240-280	

^aUnder negotiation.^bAfter the completion of the No. 3 boiler in 1982. SCR is to be applied.

2.6.2 Tests of NO_x Abatement by Combustion Modification

EPDC has conducted extensive tests of combustion modification for NO_x abatement jointly with major boiler manufacturers including Mitsubishi Heavy Industries (MHI), Babcock Hitachi, Ltd (BHK), Ishikawajima-Harima Heavy Industries (IHI) and Kawasaki Heavy Industries (KHI). Some of the test results are shown in Figure 2-30. Those tests indicate that by using a combination of low-NO_x burners with staged combustion and flue gas recirculation, NO_x can be reduced by 60-70%---to 100-150 ppm with low-nitrogen coal and to 150-200 ppm with a nitrogen-rich coal. A test conducted jointly with a company C indicated that flue gas recirculation was not effective for NO_x abatement with coal, and that unburned carbon increased with the application of staged combustion.

The relationship between polycyclic organic matter (POM) concentrations and NO_x concentrations is shown in Figure 2-31. POM generally increased with the decrease in NO_x caused by combustion modification. Table 2-9 shows the POM compounds and their relationship to combustion modification.

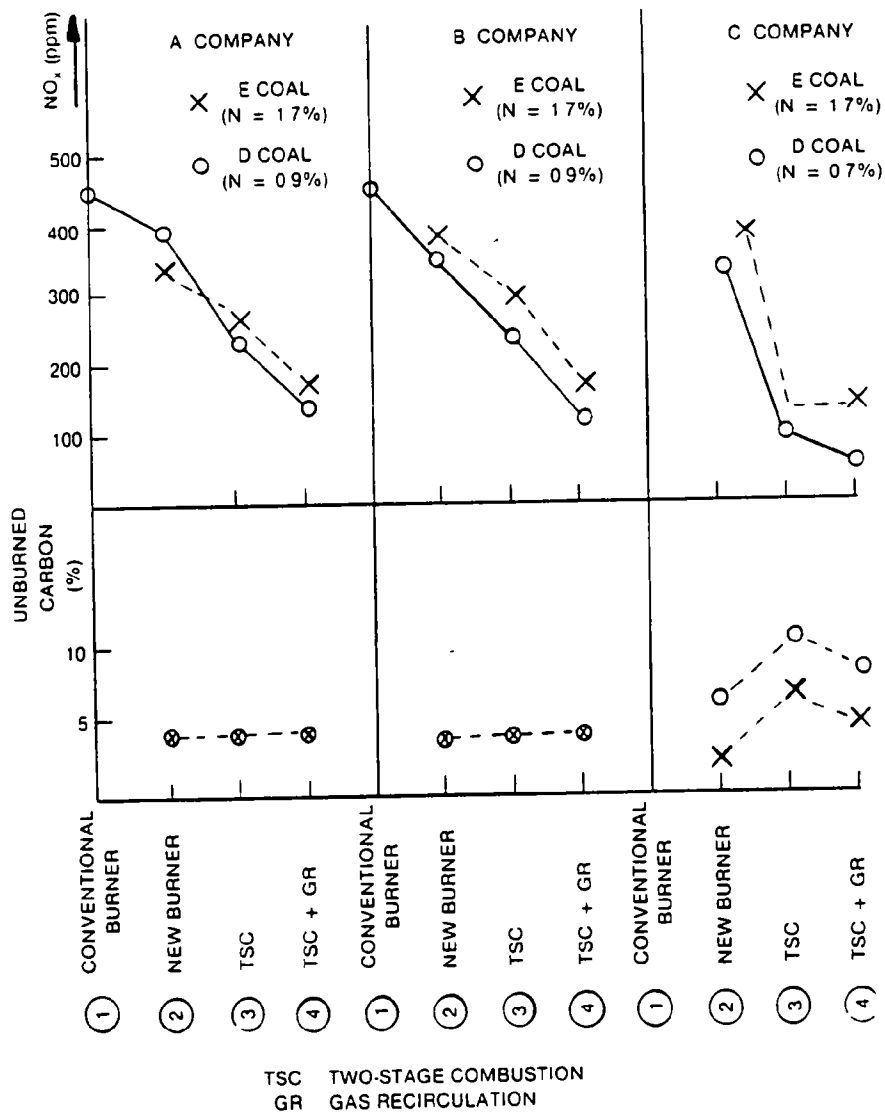
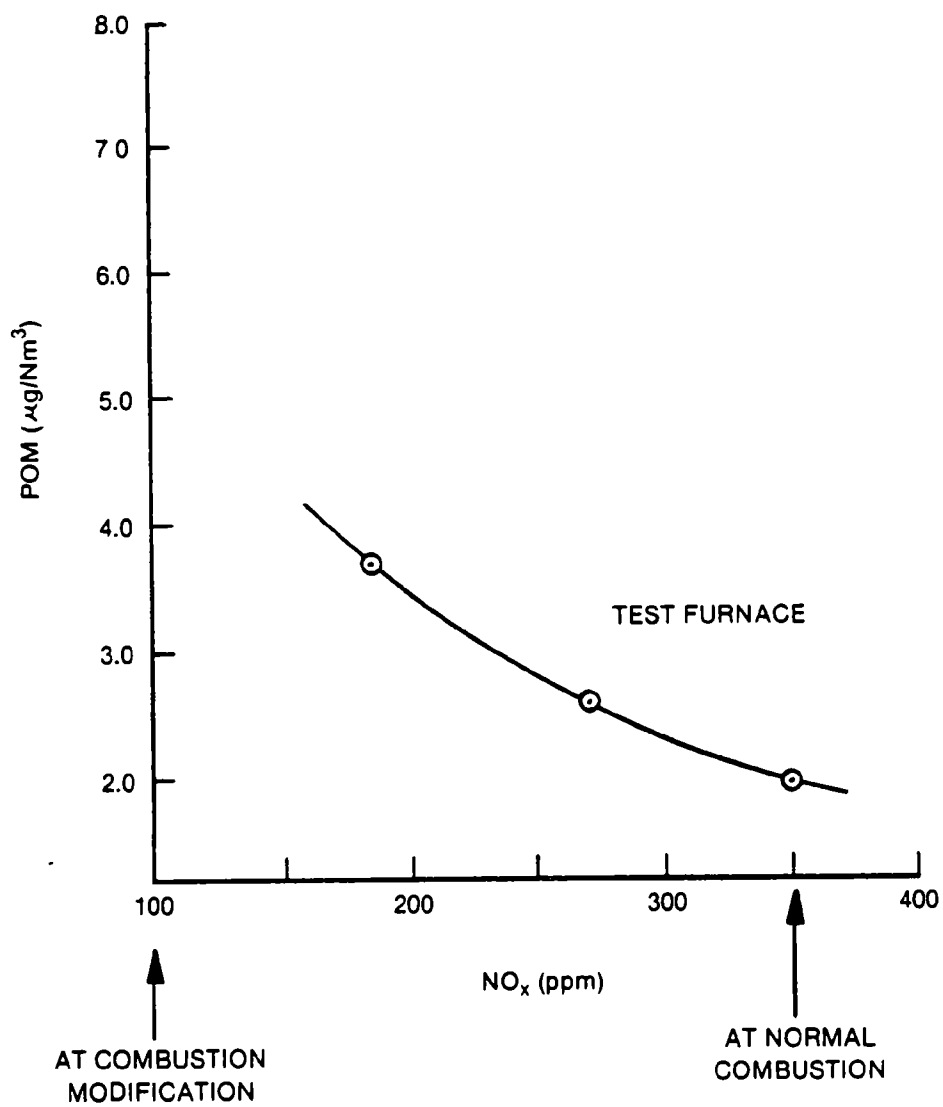


Figure 2-30 Examples of Combustion Modification Tests Conducted by EPDC and Boiler Manufacturers.



(NO_x concentration in test furnace is the average value of maximum and minimum values.)

Figure 2-31 NO_x Concentration vs. P.O.M. Emission.

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TABLE 2-9. MEASUREMENT RESULTS OF POM AT FURNACES (Unit $\mu\text{g}/\text{Nm}^3$)

POM Component	Combustion Condition	Normal Combustion	2 Stage Combustion	2 Stage + FG Mix + Primary Gas	PGM	Partial Load
Naphthalene		0.22	0.18	0.22	0.24	0.24
Fluoranthene		--	0.40	0.88	0.78	0.84
Pyrene		0.65	0.64	0.87	0.87	0.84
Benzo (a) pyrene		0.48	0.59	0.66	0.58	0.62
Total POM (Percentage when Normal combustion is 100)		1.99 (100)	2.62 (132)	2.46 (124)	3.15 (158)	3.49 (175)

Although the POM concentration increased with combustion modification, it reached a much lower level than the values reported in the U.S. POM was measured using the EPA No. 5 sampling method, modified by Battelle, and a liquid chromatography analyzer. It is not clear whether the difference in values is due to the analytical method (GC-MS was used in the U.S.) or to differences in the type of coal and the size of boiler used.

2.6.3 Combustion Modification at Isogo Power Station

The Isogo Power Station, located in Yokohama City (population 4 million) was asked by the city to reduce NO_x emissions as much as possible. The station had no space to install SCR units because FGD plants had already been retrofitted in the narrow spaces beside the boilers. Therefore, extensive efforts have been made to reduce NO_x by combustion modification.

The specifications of the Isogo boilers are given in Table 2-10. The boilers burn domestic low-sulfur coal which is relatively low in nitrogen and volatile matter and is suitable for NO_x abatement (Table 2-11).

TABLE 2-10. SPECIFICATIONS FOR ISOGO 265 MW PULVERIZED COAL-FIRED BOILER

Type:	IHI-FW single drum, radiant type, natural circulation, reheat boiler (indoor service)
Evaporation (at M.C.R.):	840,000 kg/h
Steam pressure (at M.C.R.)	
Superheater outlet:	176 kg/cm ² g
Reheater outlet:	34 kg/cm ² g
Steam temperature (at M.C.R.)	
Superheater outlet	571°C
Reheater outlet	571°C
Fuel:	Bituminous coal (equipped with 50% MCR heavy oil firing system)
Number of burners:	24 set (4 rows and 3 stages on boiler front and rear walls)
Draft System:	Balance draft system

The boilers were completed in 1967 and 1969, and were modified in 1973 with an over-fire air port system for NO_x abatement. As a second step to meet the increasingly stringent NO_x regulation, an IHI-FW DF-CN burner (Section 2.2) and a boundary air system (Figure 2-32) were applied to the No. 1 boiler in 1976 and to the No. 2 boiler in 1977. The boundary air prevents the melting of the ash. As a third step, burners out of service (BOOS) and steam injection from oil guns were tested on the No. 2 boiler in 1978. Eight additional over-fire air ports also were installed near the side walls and a division wall, based on tests conducted by IHI. In addition, steam injection was carried out through oil burner guns for the No. 2 boiler. These modifications were made in the spring of 1979 to reduce NO_x below 180 ppm (at 6% O₂) under routine operating conditions. The same modifications were made on the No. 1 boiler in 1980. The results of these modifications are summarized in Table 2-12.

TABLE 2-11. TYPICAL ANALYSIS OF COAL USED AT ISOGO STATION

Higher heating value	6,200 kcal/kg
Ash	16.5%
Volatile matter	39.6%
Fixed carbon	39.4%
Sulfur	0.4%
Hydrogen	5.5%
Nitrogen	1.0%

TABLE 2-12. MODIFICATIONS MADE FOR INCREASED NO_x CONTROL AT THE ISOGO POWER UNIT

Month, Year	NO _x Emission Level by Regulation, etc. (ppm)	Achieved NO _x Level (ppm)	Modifications
Before May 1973	600	570	None
June, 1973	600	380 ~ 510	Two-Stage combustion
April, 1977	480	240 ~ 250	Low-NO _x burner Curtain Air
April, 1979	400	170 ~ 190	More rigorous Two-Stage combustion, etc
April, 1980	159 ^a	170 ~ 190	

^aYokohama City's Requirement

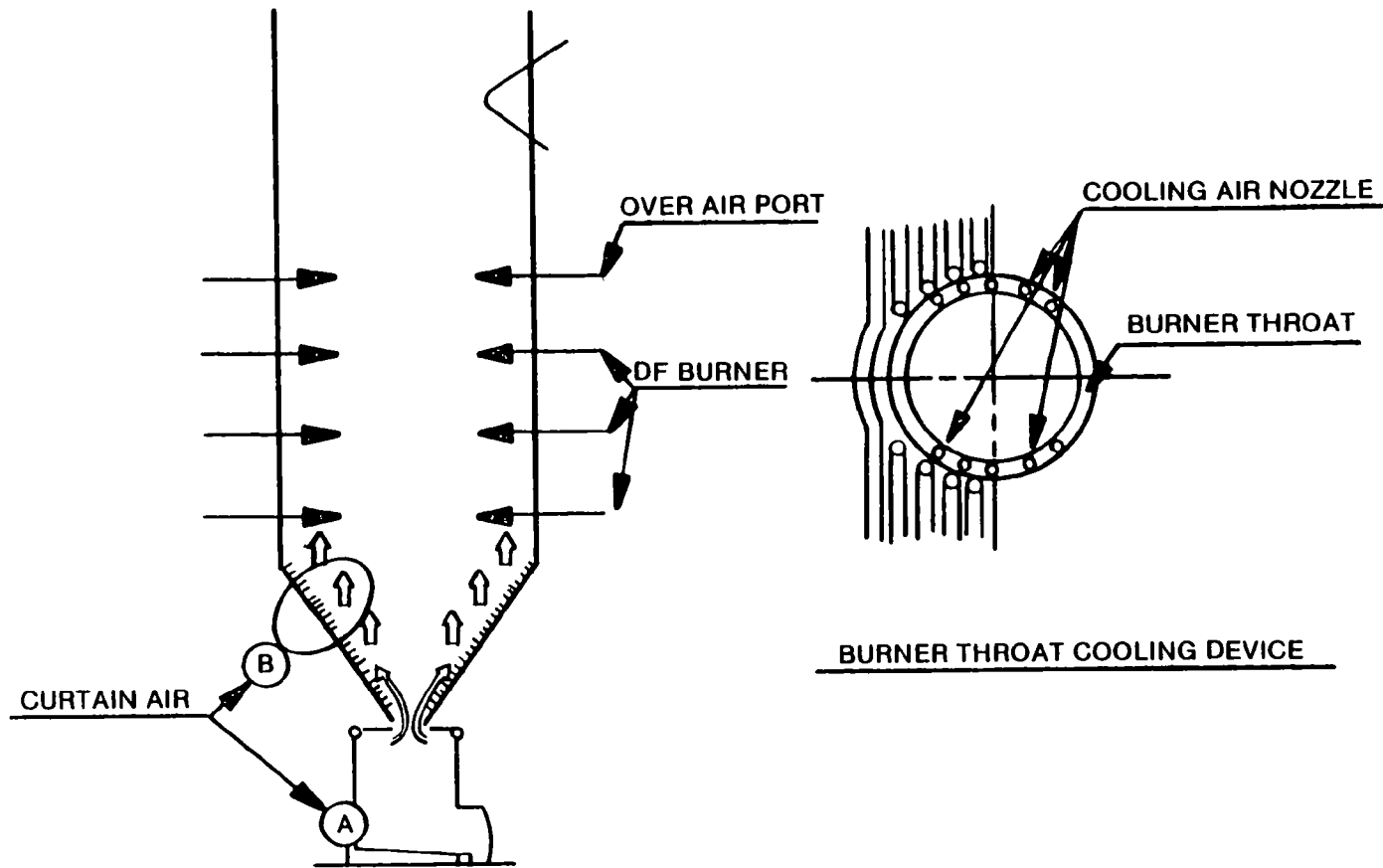


Figure 2-32 IHI's Boundary Air System and Burner Throat Cooling Device.

Figure 2-33 shows the relationship between the overfire air port open ratio and NO_x emissions. With the 50% opening, NO_x is reduced to 150-180 ppm. By increasing the size of the opening, NO_x can be further lowered, but the super-heater tube metal temperature becomes excessively high. To prevent overheating of the superheater, methods of modifying the superheater layout, were tested; unfortunately test results were not very successful. Figure 2-34 shows NO_x and O₂ concentrations during the actual operation of the boiler. NO_x is maintained around 170 ppm at full load and 140 ppm at the reduced load. Although the NO_x concentration increased during the load change, it seldom exceeded 200 ppm.

2.6.4 Matsushima Power Station

Two new 500 MW coal-fired boilers were completed at the Matsushima Station in late 1980, and went into commercial operation in 1981. The boilers were constructed by MHI using tangential-firing and SGR burners (Section 2.4.1). The specifications of the boilers are shown in Table 2-13. NO_x concentrations of 200-290 ppm were attained during test operation using imported coal containing 1.7% nitrogen. In commercial operation, NO_x has been kept below 290 ppm to meet the local agreement of 300 ppm.

TABLE 2-13. SPECIFICATIONS OF BOILERS AT MATSUSHIMA POWER STATION

Output, MW	500 x 2 unit
Fuel	Coal (imported)
Boiler Manufacturer	MHI
Type of Boiler	Supercritical pressure reheat type U.P. boiler
NO _x (guaranteed), ppm	285 (O ₂ = 6%) (N = 1.7%)
NO _x (target)	same as guaranteed
Burner type	SGR burner (illustrated in Section 2.4.1)

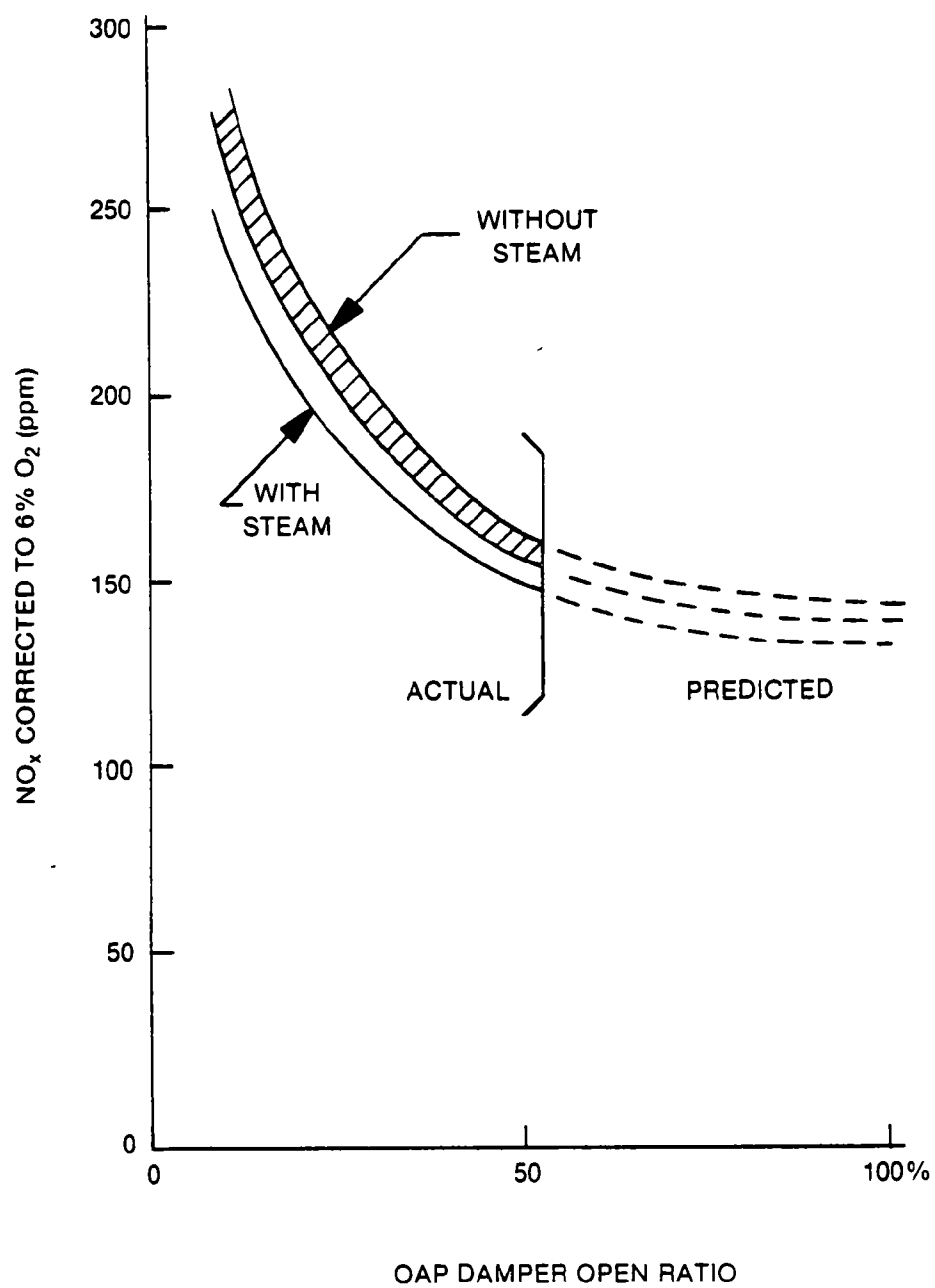


Figure 2-33 Damper Open Ratio and NO_x Concentration. (Isogo)

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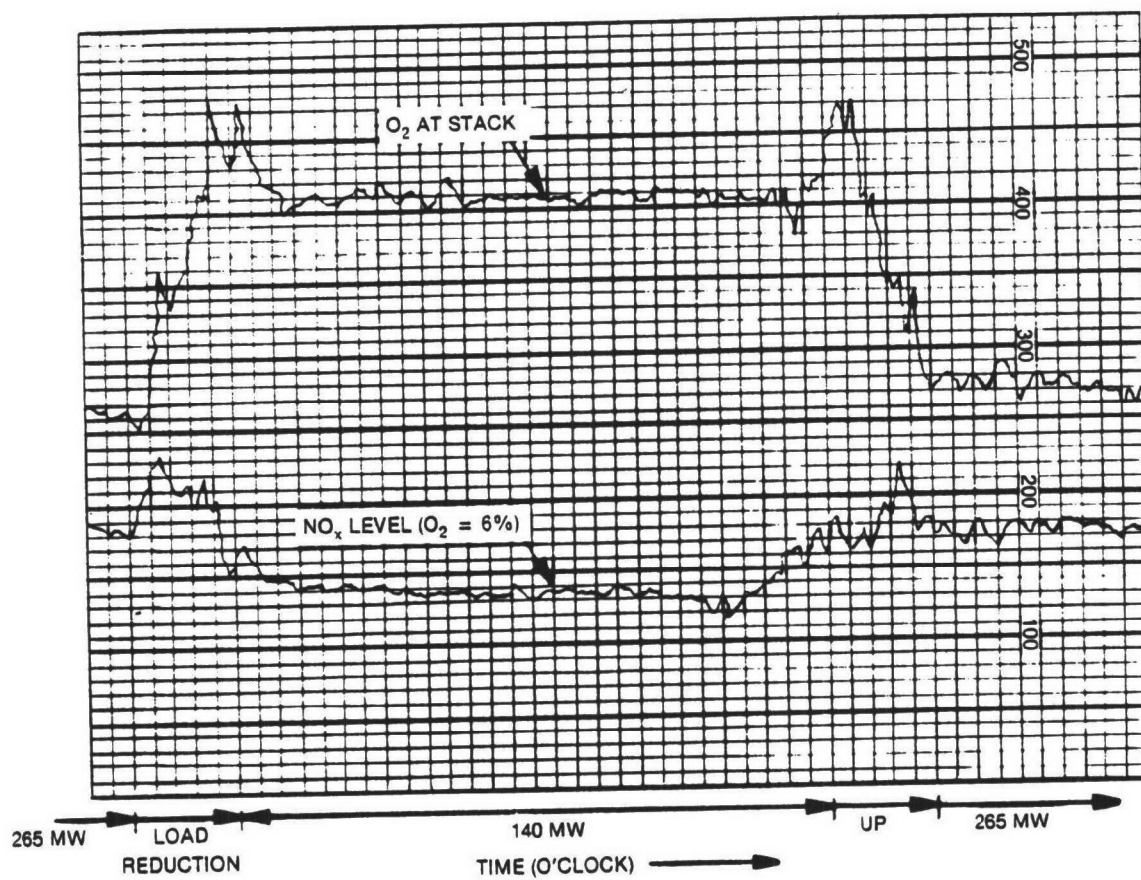


Figure 2-34 NO_x Concentrations During Boiler Operation. (Isogo)

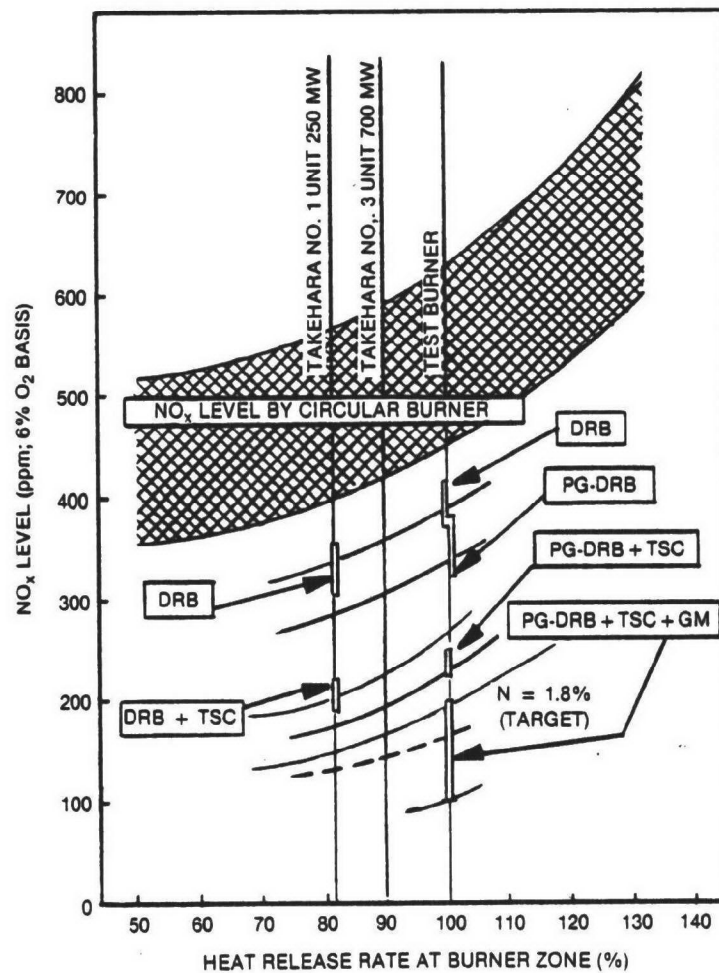
2.6.5 Takehara Power Station

The Takehara Station has a 250 MW coal-fired boiler (No. 1) and a 350 MW oil-fired boiler (No. 2). In addition, EPDC has begun construction of the No. 3 Unit, a 700 MW coal-fired boiler. Many NO_x abatement techniques for the coal-fired boilers are planned, including the application of SCR. Specifications for the No. 3 boiler are shown in Table 2-14. The boiler is being constructed by Babcock-Hitachi (BHK) and is scheduled for completion late in 1982; it will begin commercial operation in March 1983.

TABLE 2-14. SPECIFICATIONS OF NO. 3 BOILER OF TAKEHARA STATION

Output, MW	700 x 1 unit
Fuel	Coal (imported coal)
Boiler Manufacturer	BHK
SCR Manufacturer	BHK
Type of Boiler	B&W Supercritical pressure reheat type UP boiler
NO _x (guaranteed at boiler), ppm	250 (O ₂ = 6%, N = 1.8%)
NO _x (target at boiler), ppm	200 (O ₂ = 6%, N = 1.8%)
NO _x (guaranteed at stack), ppm	60 and below (O ₂ = 6%, N = 1.8%)
Burner type	PG dual burner

The Takehara Power Station uses PG dual-air register burners (Section 2.3). Figure 2-35 shows the relationship between the heat release rate at the burner zone and NO_x concentrations with three types of burners—conventional circular-air register, dual-air register, and PG dual-air register—with or without two-stage combustion and gas mixing. The No. 1 boiler uses a dual-air register burner and produces about 200 ppm NO_x using two-stage combustion, and about 300-360 ppm NO_x without two-stage combustion. A test furnace with a higher heat release rate produced about 400 ppm NO_x with the dual-air register burner and around 350 ppm NO_x with the PG-type burner when staged combustion was not applied; it produced 100-200 ppm NO_x with the



CB: CIRCULAR AIR
REGISTER BURNER
DRB: DUAL AIR
REGISTER BURNER
PG-DRB: PG TYPE-DRB
TSC: TWO-STAGE COMBUSTION
GM: GAS MIXING TO
SECONDARY AIR

Figure 2-35 Heat Release Rate at Boiler Zone. (%)

PG-type burner with staged combustion and gas mixing. Since the heat release rate of the No. 3 boiler falls between that of the No. 1 boiler and the test furnace, a NO_x concentration about 150 ppm or below is expected.

2.7 LOW-NO_x BURNERS FOR GAS AND OIL FIRING

2.7.1 Introduction

Various types of low-NO_x burners for gas- and oil-fired boilers have been developed and used in Japan. These burners may be classified into the following categories according to the principles of NO_x abatement employed.

- (1) High-mixing
- (2) Divided-flame
- (3) Self-recirculating
- (4) Staged-combustion
- (5) Off-stoichiometric-combustion
- (6) Water-injection
- (7) Combination

This section describes the major low-NO_x burners available for commercial gas- and oil-firing applications.

2.7.2 High-Mixing Burner

A high-mixing burner developed by Nippon Furnace Kogyo Kaisha, Ltd. is shown in Figure 2-36. It is called a NFK-TRW burner, because it was developed by Nippon Furnace jointly with TRW Inc. of the U.S., under a licensing agreement with Civiltech Corp. of the U.S.

NO_x concentrations for the burner using oil under various operating conditions are shown in Figure 2-37. This burner reduces the formation of thermal NO_x by shortening the residence time of the combustion gas in high-temperature zones.

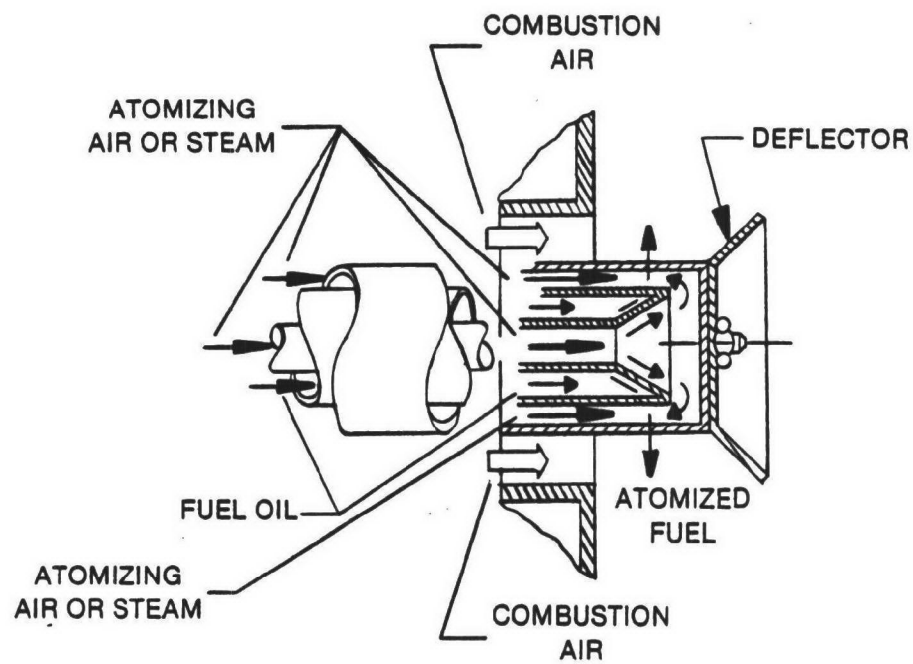
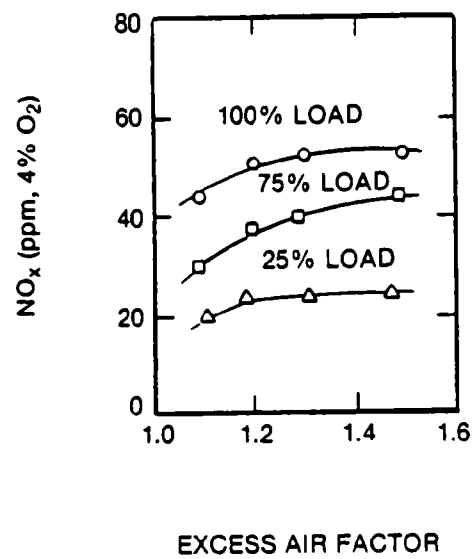


Figure 2-36 NFK-TRW Burner.



(Fuel: Grade A fuel oil; air temperature: 25°C;
maximum fuel flow rate: 380 l/hr)

Figure 2-37 Effect of NFK-TRW Burner on NO_x Concentrations.

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2.7.3 Divided-flame Burner

A divided-flame burner developed by IHI is shown in Figure 2-38. In this burner the flame is divided into several small flames by means of grooved nozzle tips. This reduces the flame temperature and residence time in high-temperature zones, thus reducing thermal NO_x (13).

2.7.4 Self-recirculating Burner

In the self-circulating burner, a portion of the hot combustion gas is recirculated to the initial stage of combustion by the jet force of the fuel and/or air injection. Thus vaporization and burning of the fuel oil in a low O_2 concentration are achieved. Various burners of this type have been produced by many manufacturers.

Figure 2-39 shows the configuration of the burner developed by Daido Tokushuko (Special Steel) Co. The NO_x concentration with this burner is shown in Figure 2-40. The burner was originally developed for metal-heating furnaces firing oil or gas. A similar burner called the SPP has been developed by the Volcano Company.

The burner shown in Figure 2-41 produces a circulating flow of combustion gas in the precombustion chamber by means of orienting the air flow with intense swirls to the axis of the atomizer. It is called a voltmetric burner and was commercialized by Nippon S. T. Johnson Shokai Co., Ltd.

Similar burners, designed for kerosene firing, are shown in Figures 2-42 and 2-43. The NPL burner was developed by Chugairo Kogyo, Ltd., and the YLAP burner by Yokoi Kikai Kosakujō, Ltd. The NO_x levels with the NPL burner are shown in Figure 2-44. These burners use low air-pressure atomizers with various burner tile configurations.

Figure 2-45 shows the ONR burner with a rotary atomizer, developed by Sanrey Reinetsu Co., Ltd. Combustion gas is recirculated by the secondary air jet at a high velocity. The burner's performance is shown in Figure 2-46.

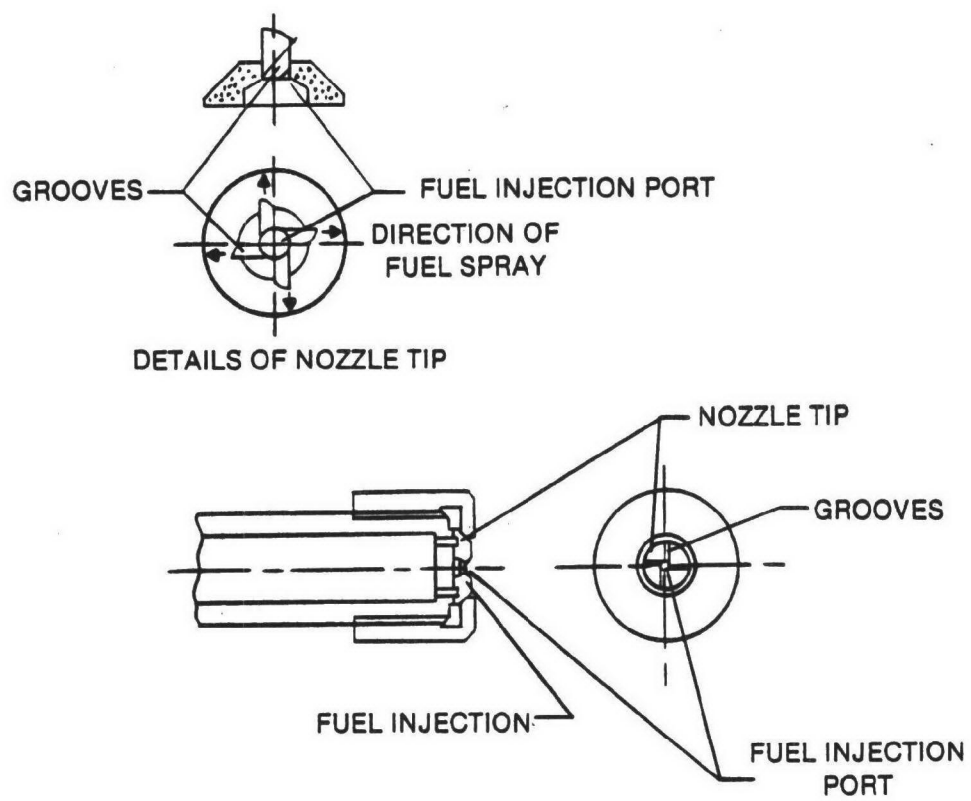


Figure 2-38 IHI Divided Flame Burner.

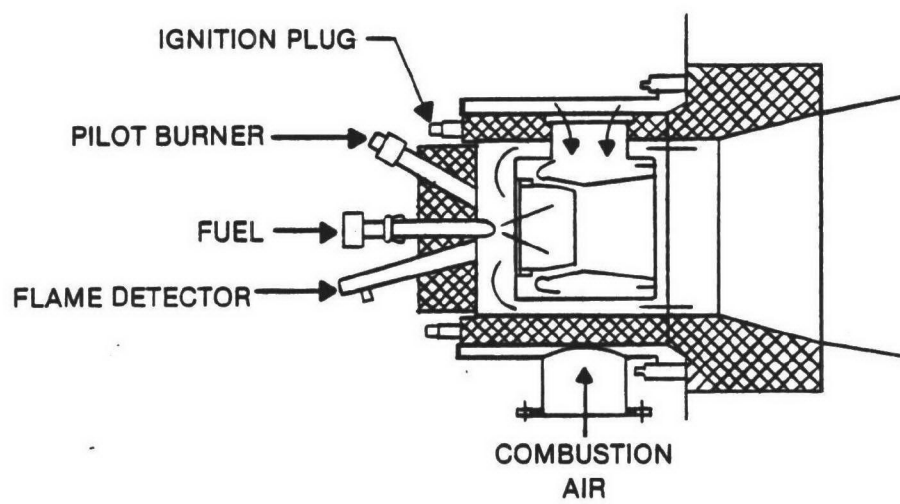
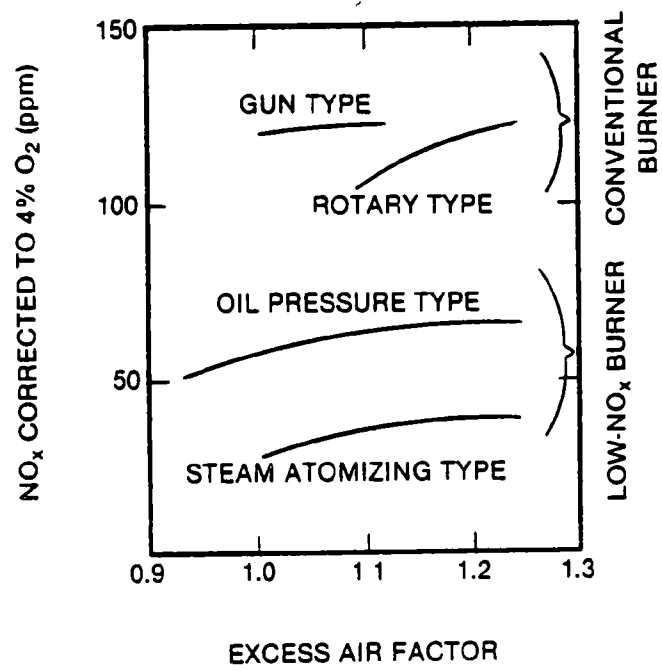


Figure 2-39 Daido Tokushuko Self-recirculation Burner.



(Fuel: Grade A oil; fuel flow rate: 100 l/hr)

Figure 2-40 Effect of Self-recirculation Burner on NO_x Reduction.

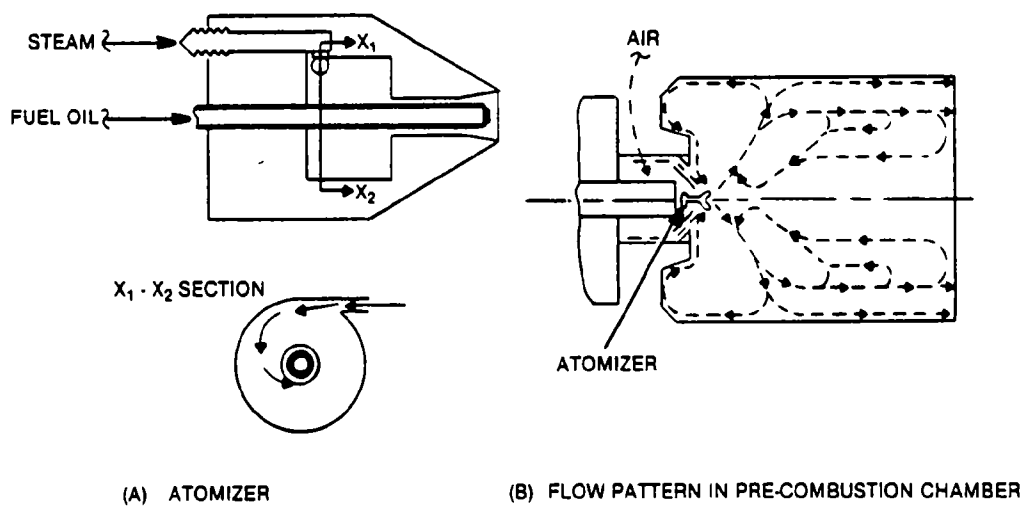


Figure 2-41 Schematic Diagram of the Voltmetric Burner (Nippon S.T. Johnson).

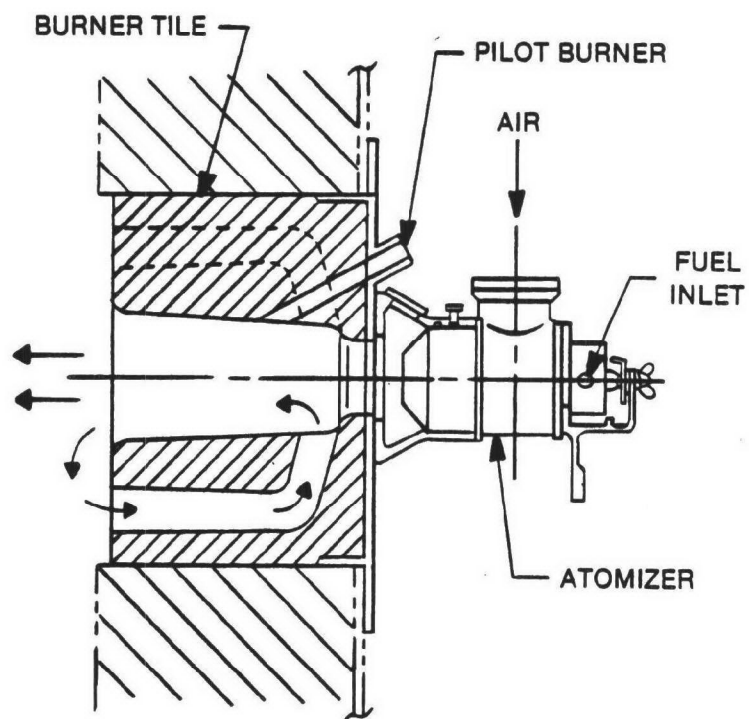


Figure 2-42 NPL Burner (Chugairo Kogyo).

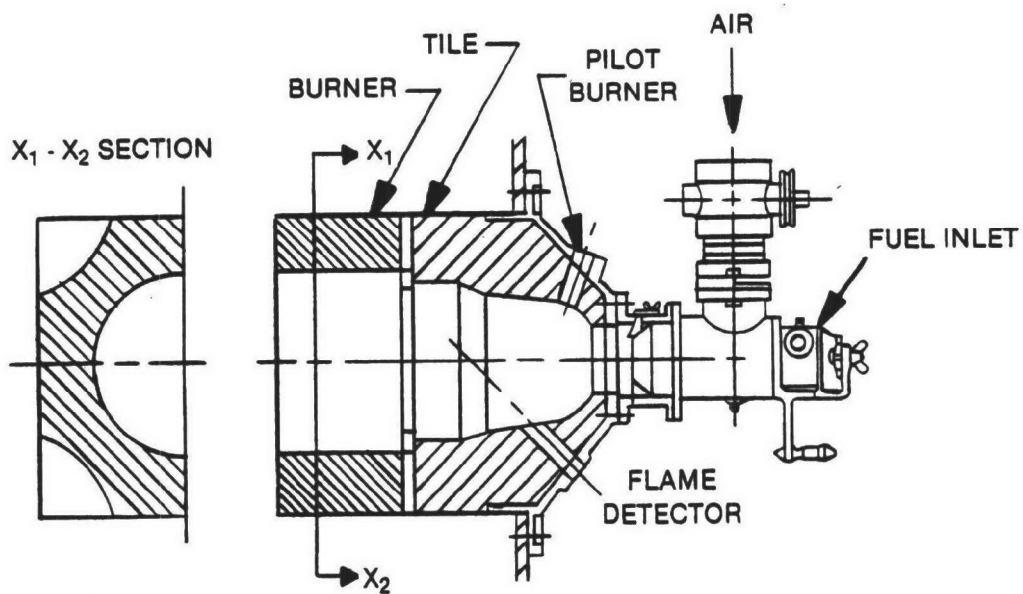
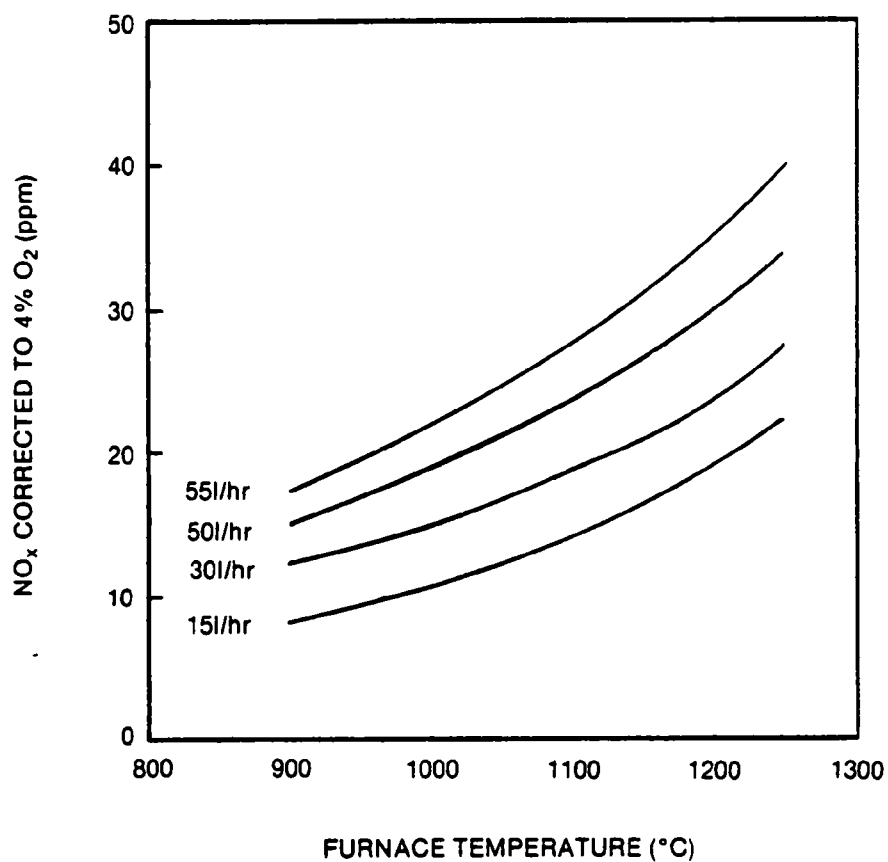


Figure 2-43 YLAP Burner (Yokoi Kikai Kosakujo).



(Fuel: kerosene; oxygen concentration in the outlet of test furnace: 3%, fuel flow rate: 15 l/hr - 55 l/hr)

Figure 2-44 Effect of NPL Burner on NO_x Emissions.

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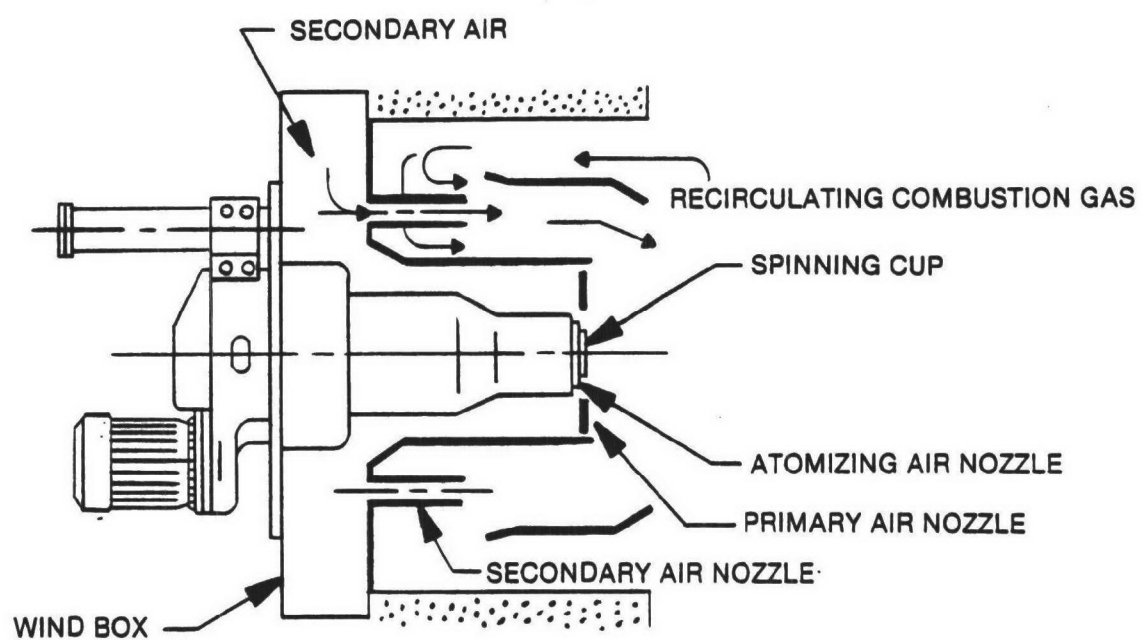
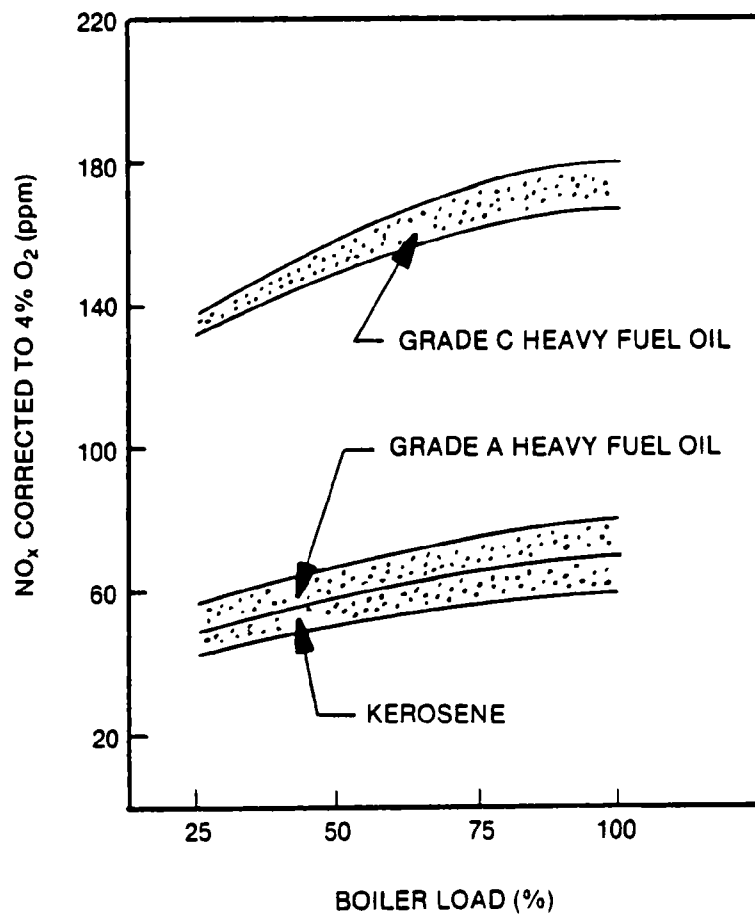


Figure 2-45 ONR Burner (Sanrey ReInetsu).



(Fuel flow rate: 700-1000 kg/hr; excess air factor: 1.10-1.15;
combustion air temperature: 20°C)

Figure 2-46 NO_x Emission Level of ONR Burner.

Figure 2-47 shows the RSNT burner designed by Rozai Kogyo Co. for oil and gas firing. An intense swirling flow of secondary air causes the recirculation of the combustion gas in the narrow space confined by the burner tile. NO_x emission levels by fuel type are shown in Figure 2-48.

Figure 2-49 shows the XB burner developed by Osaka Gas Co. jointly with Sanrei Reinetsu Co. for gas-firing applications. Several fuel injection nozzles are arranged circularly to shorten the flame. A low NO_x level, 20-40 ppm, is achieved, as shown in Figure 2-50.

The High Speed burner, developed by Tokyo Gas Co., is shown in Figure 2-51. Flue gas is recirculated by the momentum of the fuel flow and a large amount of combustion gas is entrained by the high-velocity gas flow.

2.7.5 Staged-Combustion Burner

The staged-combustion burner may be classified according to the composition of the first-stage flame into two types: fuel-rich and air-rich. The fuel-rich burner is similar to the standard staged combustion burner. Both fuel NO_x and thermal NO_x are lowered by fuel-rich combustion followed by complete combustion at relatively low temperatures. With the air-rich burner, the first stage has an excessive O₂ concentration and additional fuel is injected during the second stage.

Fuel-Rich Type

Figure 2-52 shows the APOC burner developed by Tokyo Gas Company for gas-firing applications. In the pre-combustion chamber, an excess air factor of 0.5 to 0.7 is used. NO_x concentrations in the flue gas after complete combustion are about 35 ppm (corrected to 5% O₂).

Figures 2-53 and 2-54 show the FH burner developed by Chugairo Kogyo, Ltd., and its performance. A high NO_x reduction efficiency, 75-80%, can be achieved with this burner when used with certain types of furnaces.

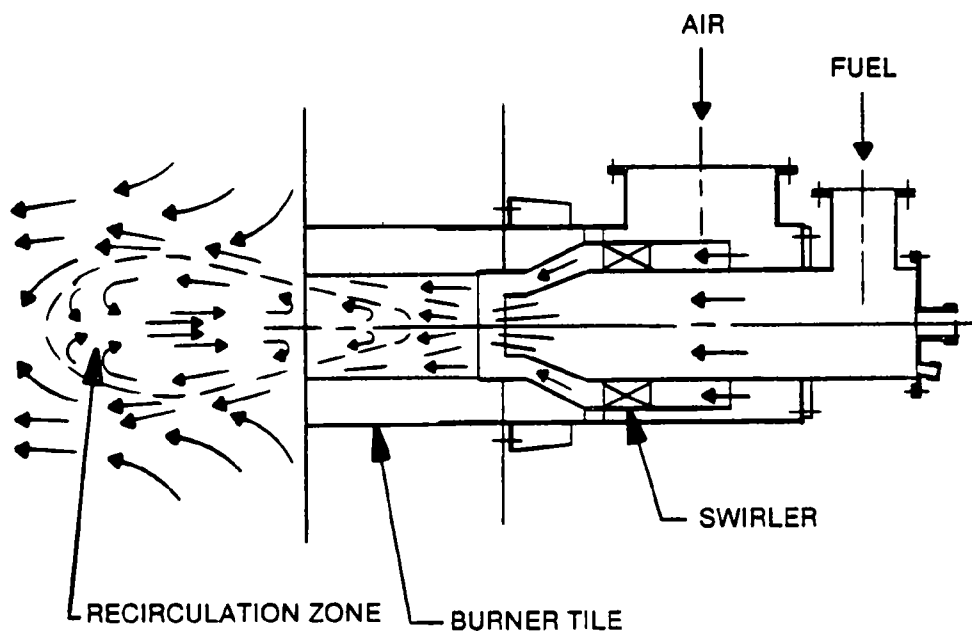


Figure 2-47 RSNT Burner (Rozai Kogyo).

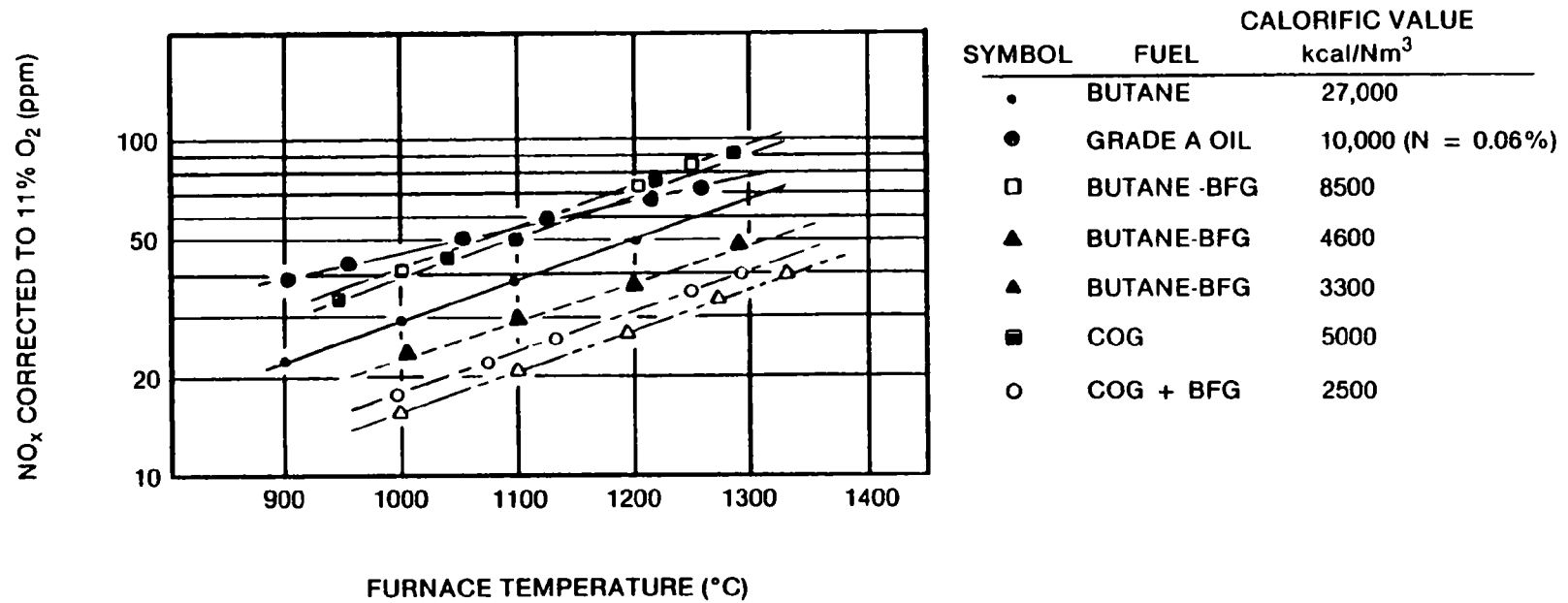


Figure 2-48 NO_x Emission Levels of the RSNT Burner. (Thermal input: 2.4×10^6 kcal/h; excess air factor: 1.1; combustion air temperature: 250-350°C).

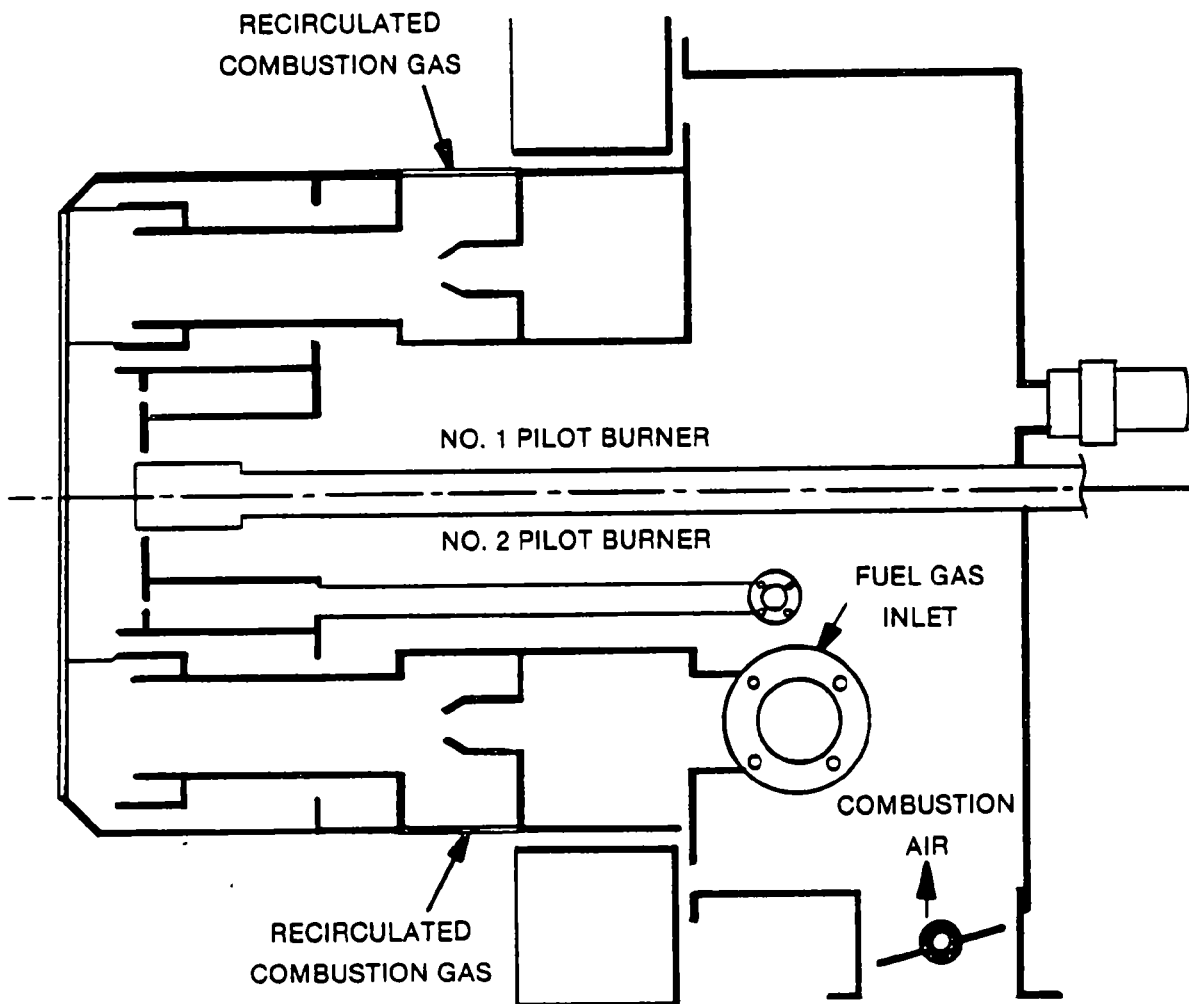


Figure 2-49 XB Burner (Osaka Gas).

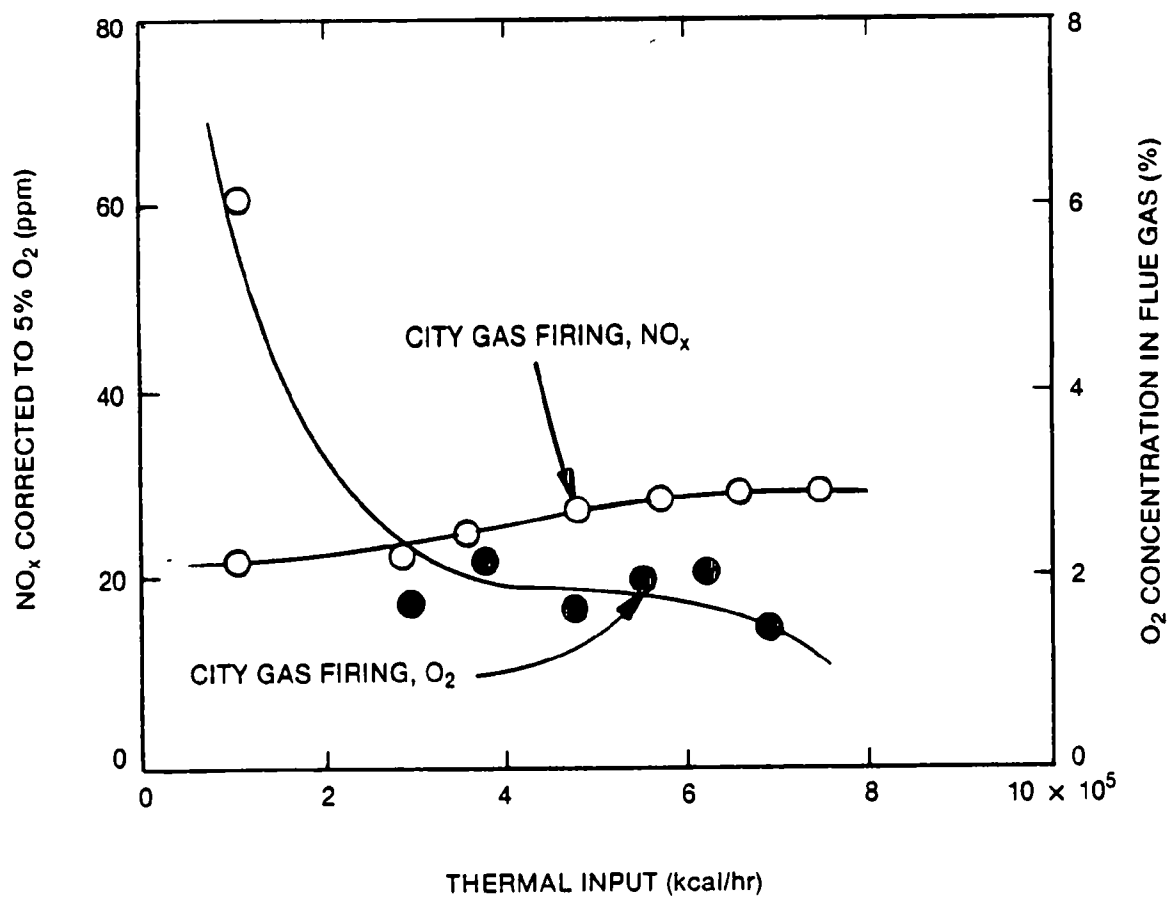


Figure 2-50 Effect of XB Burner on NO_x Emission Levels.

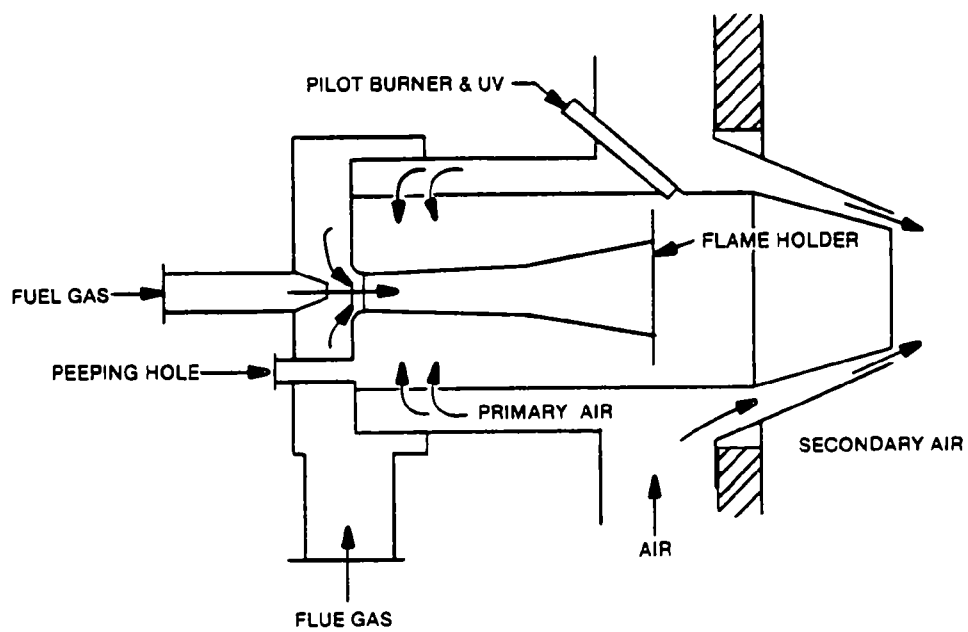


Figure 2-51 High Speed Burner (Tokyo Gas).

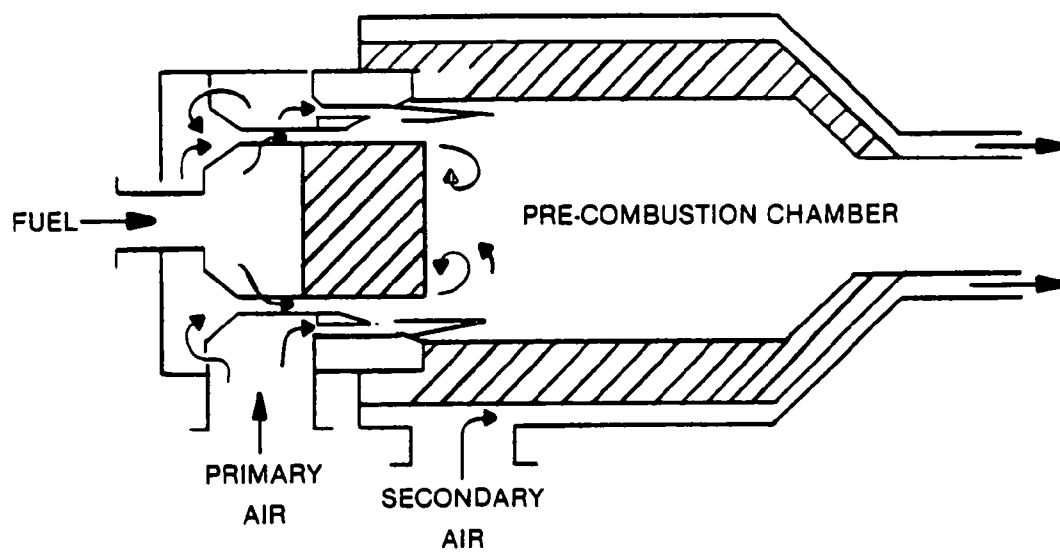


Figure 2-52 APOC Burner (Tokyo Gas).

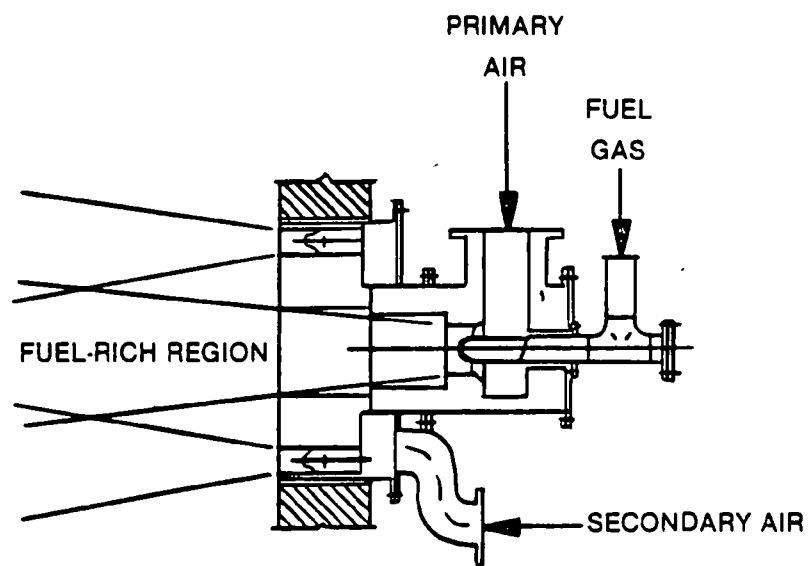


Figure 2-53 Schematic of FH Burner (Chugairo Kogyo).

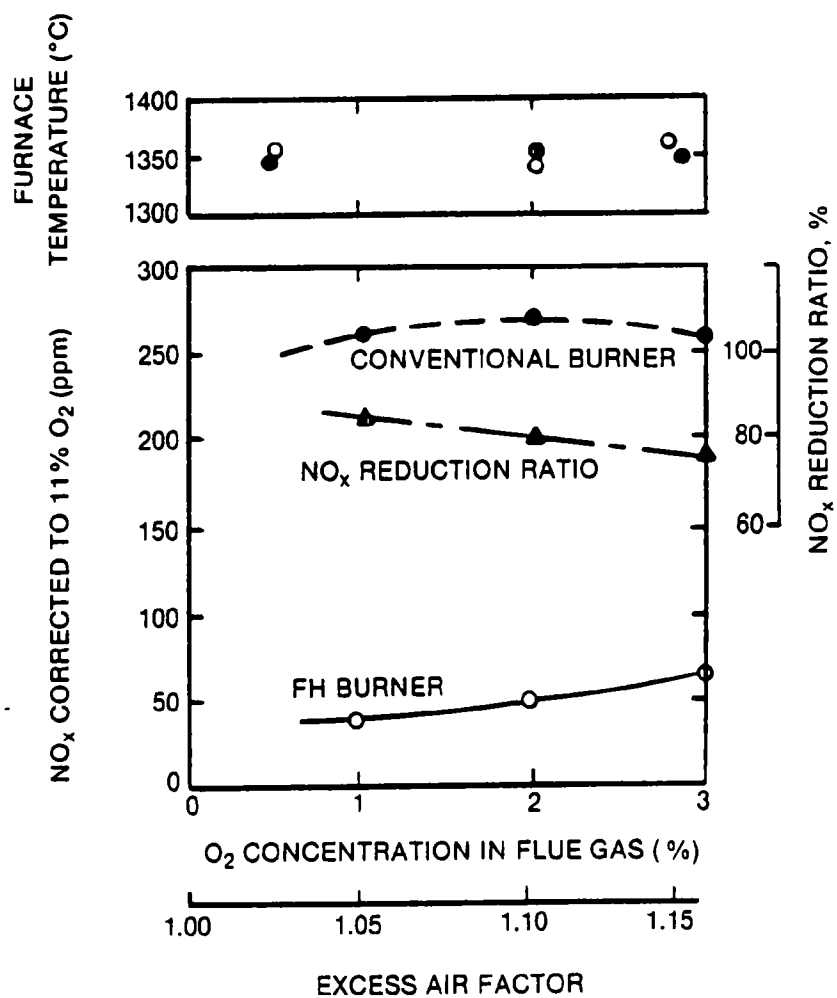


FIGURE 2-54 Effect of the FH Burner on NO_x Reduction.

Figure 2-55 shows the MR burner developed by MHI for package boilers with a capacity of up to 30 t/hr. In addition to producing the effect of staged combustion, this burner also reduces NO_x by cooling the flame with an adjacent water tube. The NO_x levels guaranteed by MHI are shown in Table 2-15.

The TS burner developed by Osaka Gas Co. and its performance are shown in Figures 2-56 and 2-57.

TABLE 2-15. NO_x EMISSION LEVELS GUARANTEED WITH THE MR BURNER FOR SMALL SCALE BOILERS

Fuel	Nitrogen Content in Fuel (%)	NO _x Emission Level (ppm)
Grade C Oil	0.20	150 ^a
Grade B Oil	0.14	130 ^a
Grade A Oil	0.03	65-90 ^a
Kerosene	0.01	60-70 ^a
Gas	—	50 ^b

^aCorrected to 4% O₂.

^bCorrected to 5% O₂.

Air-Rich Type

Figure 2-58 shows the TGS burner developed by the Tokyo Gas Company. The primary fuel gas is premixed with a large amount of excess air. The rest of the gas is then added to the flame. The burner shows an appreciable NO_x reduction as illustrated in Figure 2-59.

Figure 2-60 shows the TZ burner developed by the Daido Sanso Company. In the primary combustion chamber, 40-60% of the fuel is fired with a large amount of excess air—a factor of 1.6 to 2.4—and the secondary fuel injected into the furnace is burned with an O₂ concentration of 7-14%. The overall excess air ratio is kept between 1.05 and 1.2. The performance of the burner is shown in Figure 2-61.

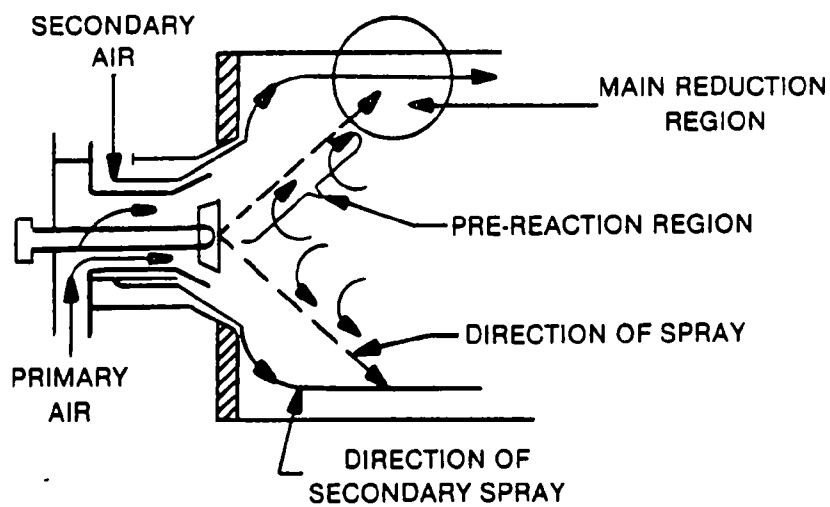


Figure 2-55 **Schematic of MR Burner (Mitsubishi Heavy Industries).**

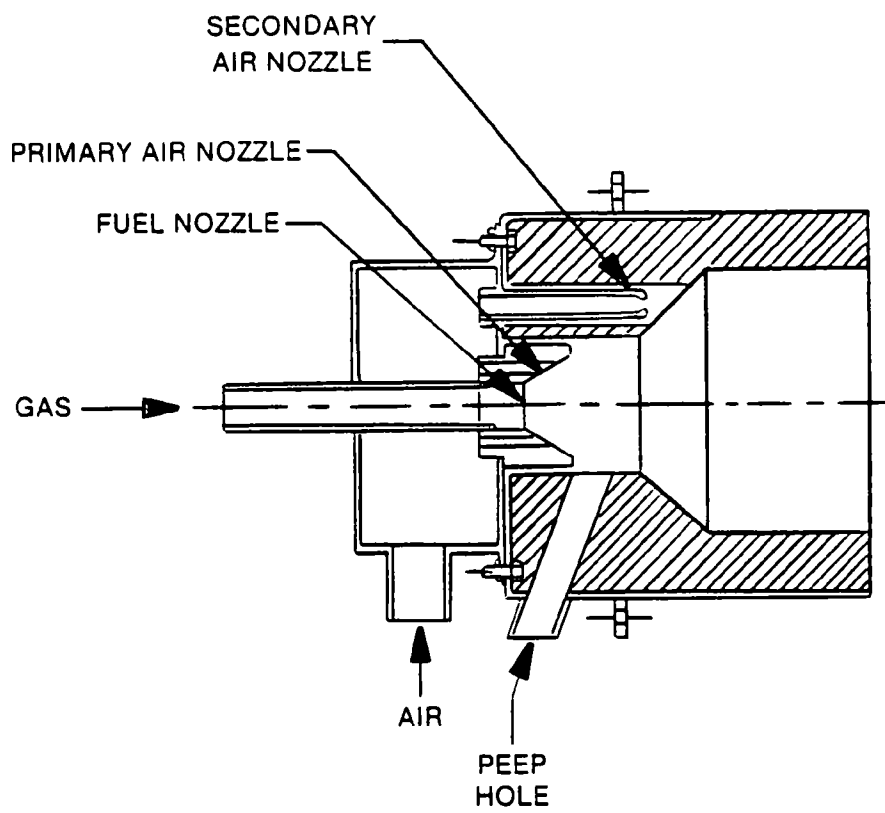
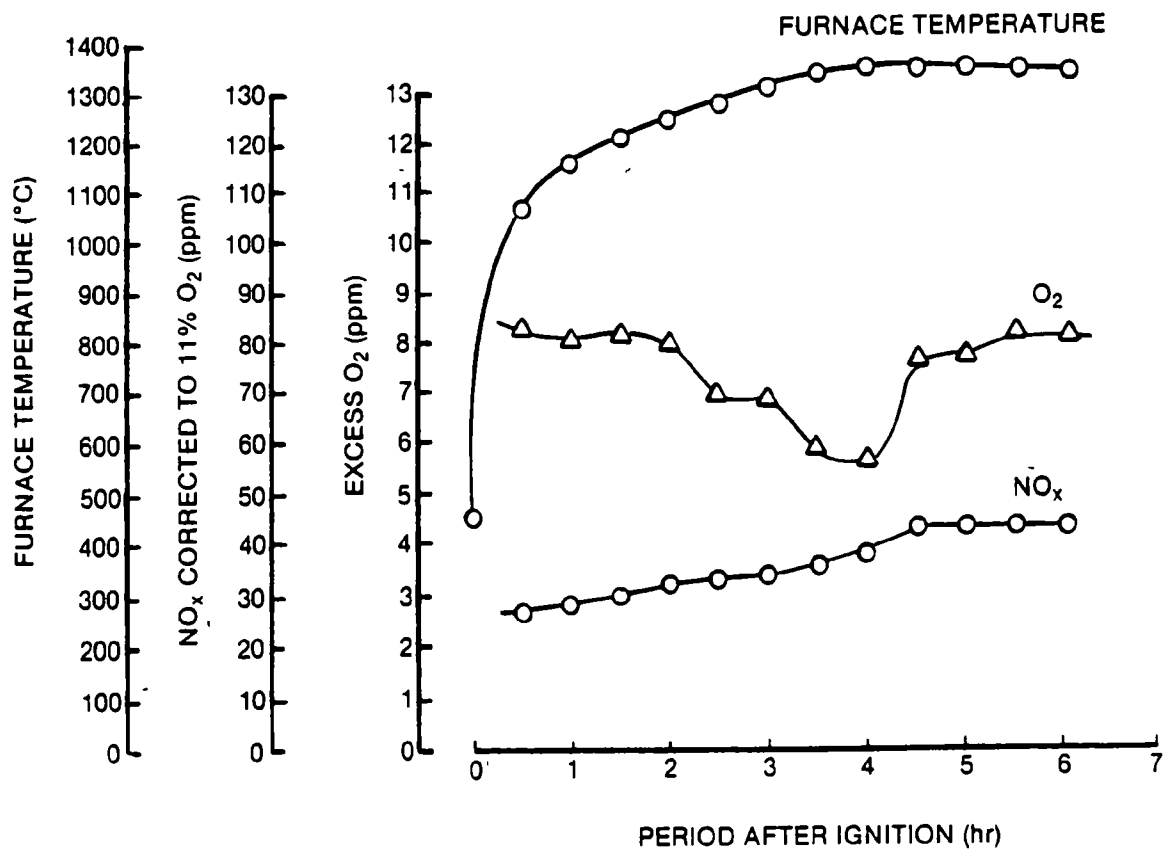


Figure 2-56 TS Burner.



(Fuel: city gas; calorific value: 5000 kcal/Nm³;
number of burners: 6 units)

Figure 2-57 NO_x Emission Level of the TS Burner in a Batch Forging Furnace with a Capacity of 20 t/charge.

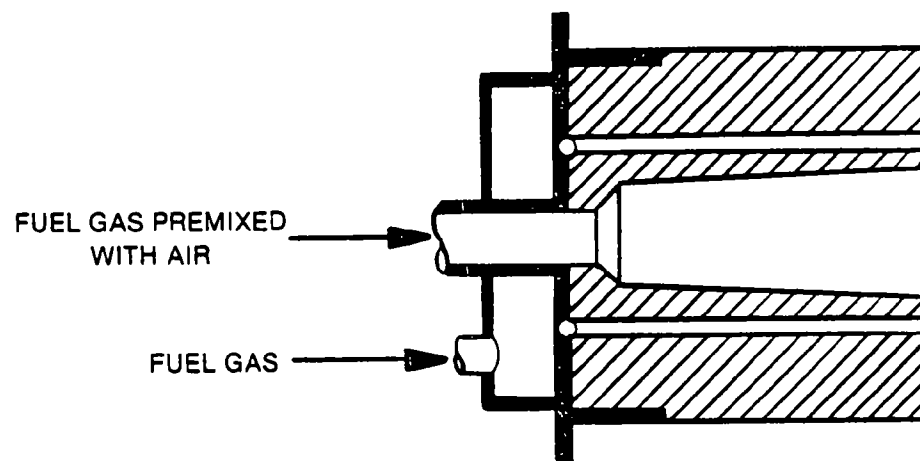
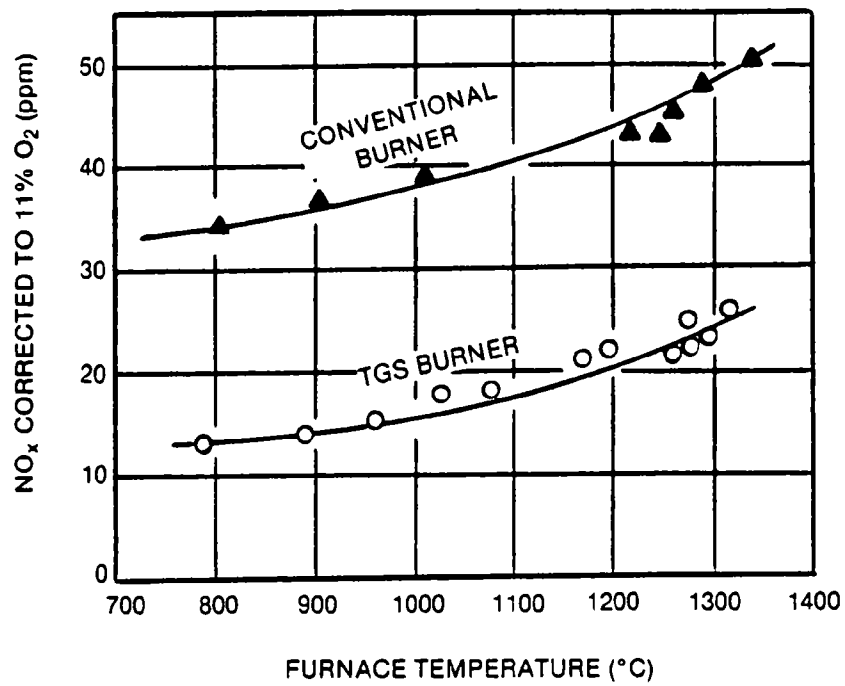


Figure 2-58 Schematic of TGS Burner.



(Fuel: city gas; calorific value: 5000 kcal/Nm³; number of burners: 4 units; thermal input: 2.4×10^5 kcal/hr)

Figure 2-59 NO_x Reduction Effects of TGS Burner in a Batch Forging Furnace with a Capacity of 2t/charge.

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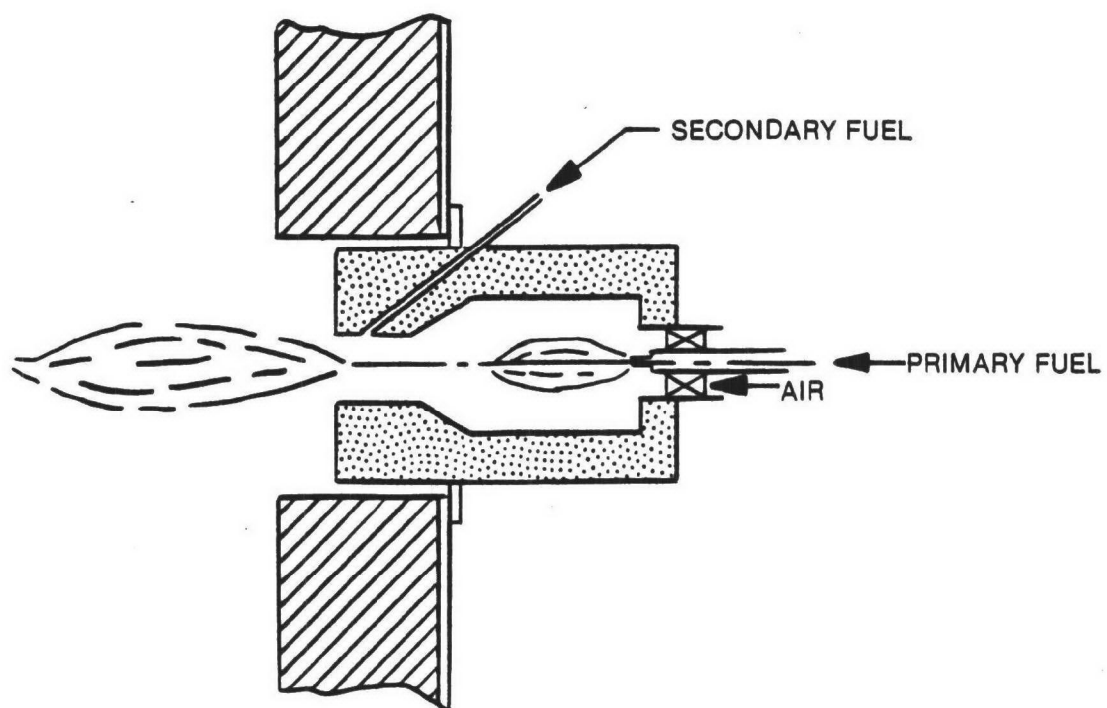
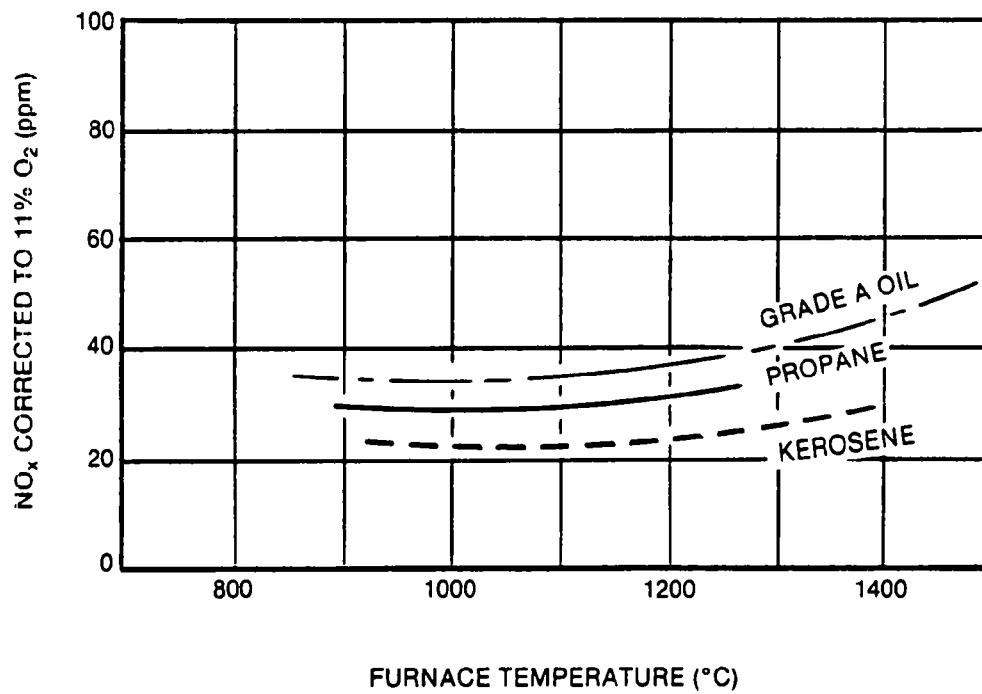


Figure 2-60 Schematic of TZ Burner (Daido Sanso).



(Total emission factor: 1.1, thermal input: 1.0×10^5 - 1.5×10^5 kcal/hr)

Figure 2-61 **NO_x Emission Levels with the TZ Burner.**

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2.7.6 Off-Stoichiometric-Combustion Burners

This type of burner first produces fuel-rich and fuel-lean flames both of which have low NO_x concentrations. The two flames are then mixed for complete combustion.

Figure 2-62 shows the DLS burner developed by Osaka Gas Company for gas-firing metal-heating furnaces. Its performance is shown in Figure 2-63. Compared with the TS burner (Figures 2-56 and 2-57), the fuel gas in the DLS burner is burned with much less excess O_2 , and NO_x concentrations are almost constant during the operation period.

Figures 2-64 and 2-65 show the improved smokeless PM burner developed by MHI, and its performance. Recirculated flue gas is injected between the air-rich and fuel-rich flames to retard the mixing of the flames, thus causing greater NO_x reduction. Particulates, as well as NO_x , can be reduced by this burner.

Off-stoichiometric combustion can be attained by a special arrangement of the fuel injection holes in a burner. Figure 2-66 shows such an arrangement in the burner developed by the Volcano Company. The larger holes produce the fuel-rich flame while the smaller holes produce the fuel-lean flame.

Figure 2-67 shows the I-type throat in the dual-air register burner developed by Babcock Hitachi, Ltd. (Section 2.3). From 25-40% of the combustion air is fed through the grooved parts while the rest is fed through the circular part to achieve the off-stoichiometric combustion. The effect of the I-type throat using the off-stoichiometric-combustion type atomizer with an OSC tip is shown in Figure 2-68.

2.7.7 Water-Injection Burner

Water-injection burners have been used extensively in Japan because they reduce NO_x by lowering the flame temperature and, to some extent, produce effects similar to emulsified oil (Section 2.8.4).

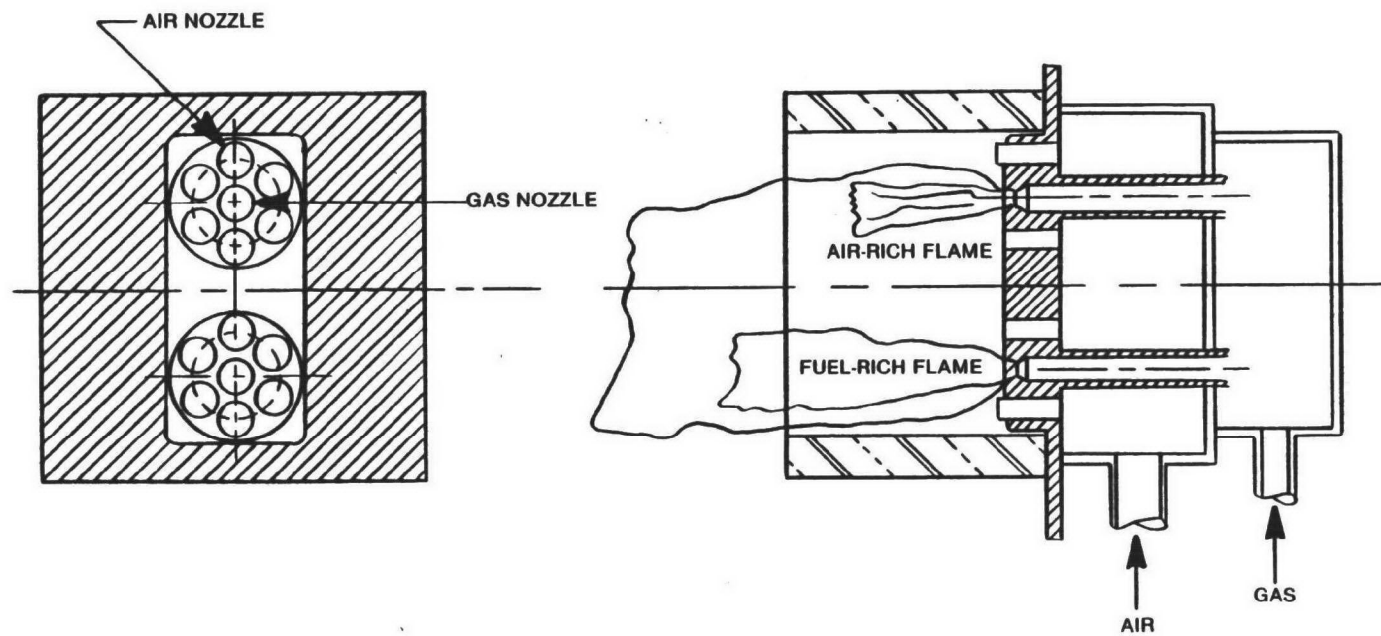
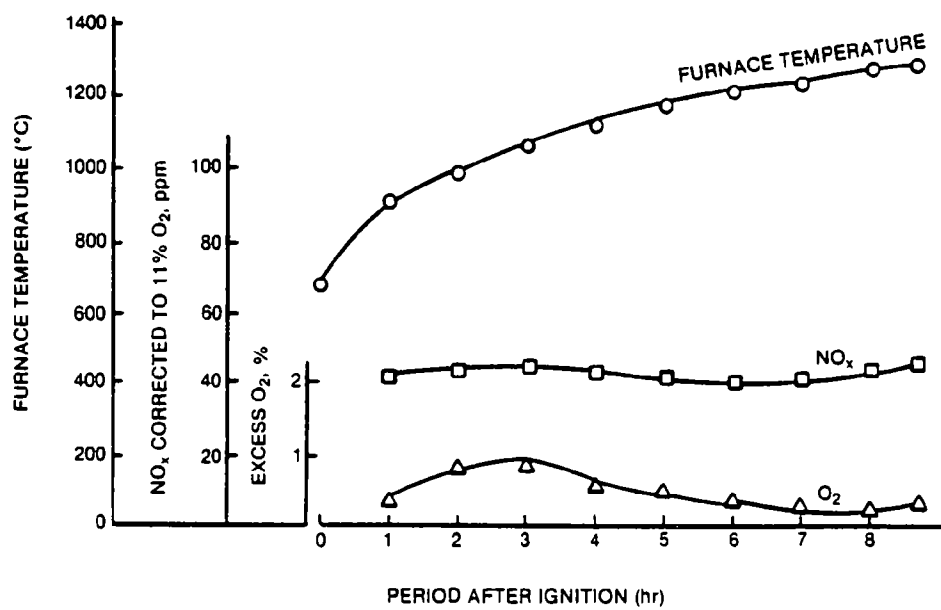


Figure 2-62 Schematic of the DLS Burner (Osaka Gas).



(Fuel city gas, calorific value 5000 kcal/Nm³)

Figure 2-63 NO_x Emission Levels with the DLS Burner in a Batch Forging Furnace with a Capacity of 2t/charge.

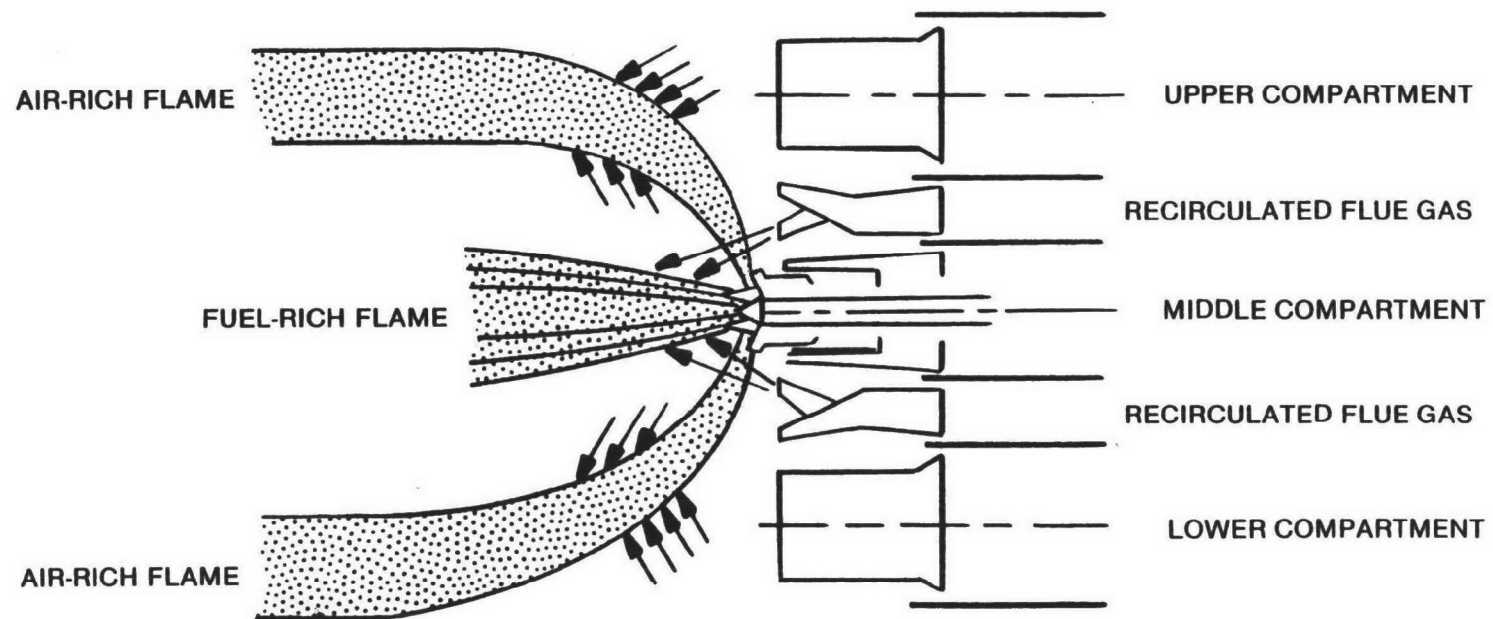
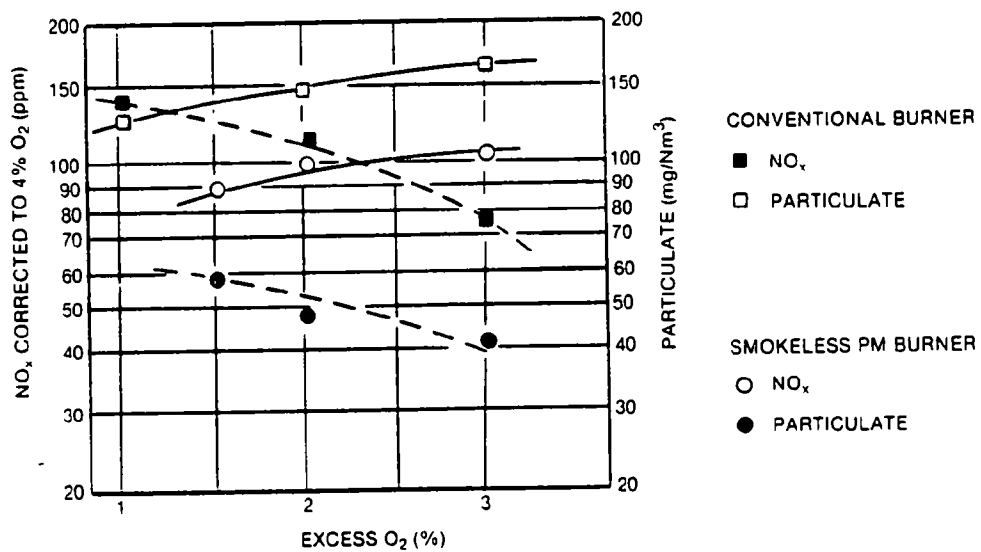


Figure 2-64 Smokeless PM Burner (MHI).



(Fuel grade B heavy fuel oil, nitrogen content 0.13%, fire air about 5%, recirculated flue gas including flue-gas recirculation 10%)

Figure 2-65 NO_x and Particulate Reduction with the Smokeless PM Burner.

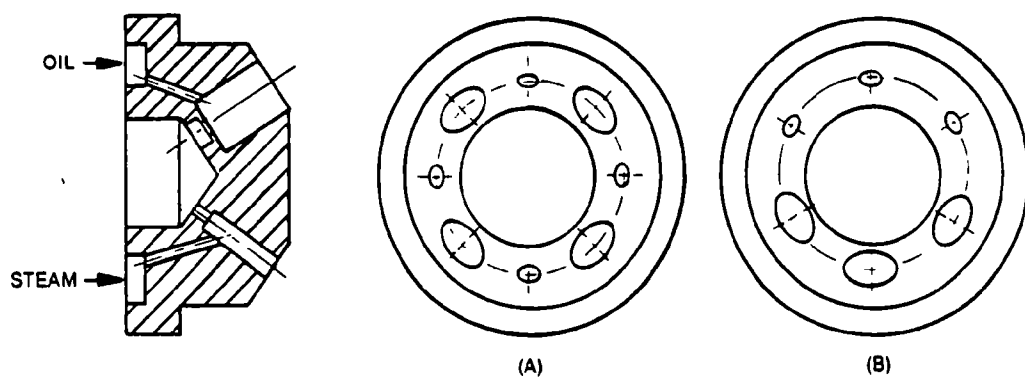


Figure 2-66 Atomizing Nozzles in the Off-stoichiometric-combustion Low- NO_x Burner for Oil (Volcano Co.).

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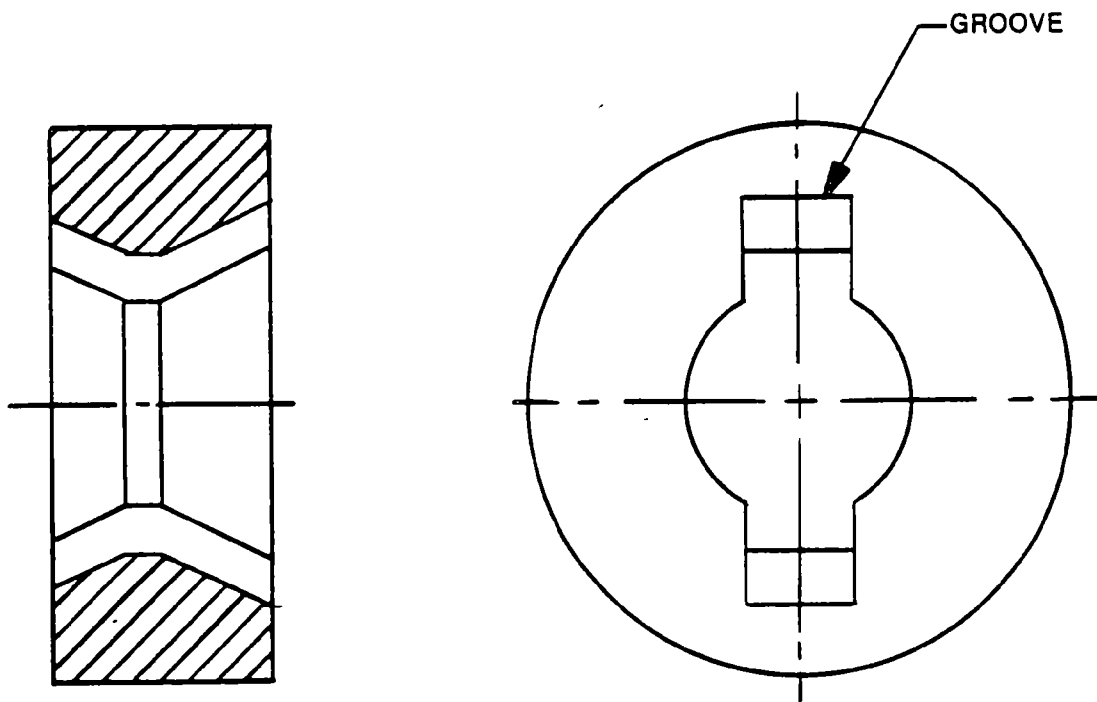
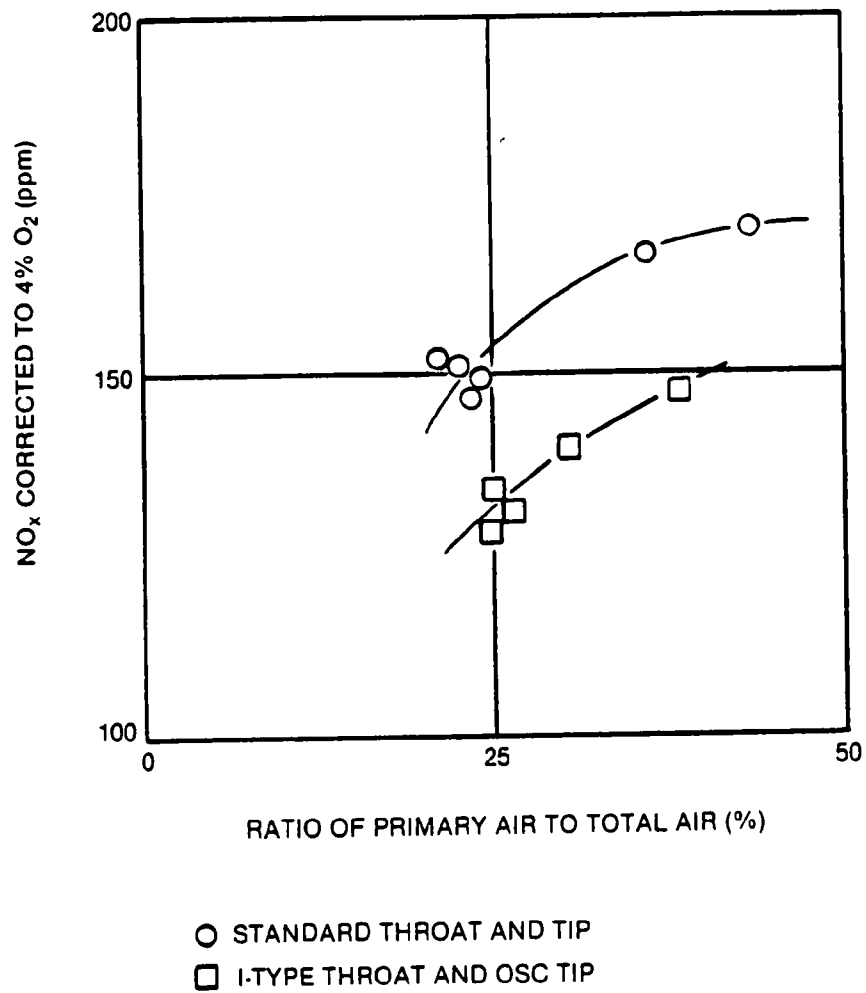


Figure 2-67 I-Type Throat in the Dual-Air Register Burner.

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(Fuel, grade C oil, thermal input 3.4×10^5 kcal/hr)

Figure 2-68 NO_x Reduction of the OSC Burner with I-Type Throat in a Watertube Boiler (15 t/hr).

Burner tips for water injection, developed by Asahi Chemical Industry jointly with Nippon Plant Engineering Co., are shown in Figure 2-69. Oil and water are ejected with steam in different ways with various types of tips. The type-C tip generally gives the best results, reducing both NO_x and particulates as shown in Figure 2-70. Similar types of tips also are used by Osaka Gas Co.

The JSR burner, developed by the Japan Synthetic Rubber Company, injects water and oil from separate holes as shown in Figure 2-71. NO_x reduction with the burner is shown in Figure 2-72. The NO_x reduction is caused not only by the lowering of the flame temperature which reduces thermal NO_x , but also by the atmosphere produced by the reaction of water and oil which reduces the fuel NO_x .

The UN burner, shown in Figure 2-73, injects water into the atomizing air pressurized at 1 to 2 kg/cm^2 . The relationship between the water-injected burner and NO_x emissions is shown in Figure 2-74. In addition, water injection reduces soot formation and thus enables low excess air combustion, sometimes resulting in energy savings.

2.7.8 Combination Burner

There are several low- NO_x burners which use a combination of the above NO_x reduction principles. For example, the SRG burner (Figure 2-75), developed by Nippon Furnace Kogyo Kaisha, Ltd., applies two-stage combustion and self recirculation of flue gas. The self recirculation is attained by the Coanda effect of the high-velocity combustion gas. These burners have been used mainly for oil- and gas-fired furnaces at chemical plants and refineries. NO_x levels produced by the SRG burner, in comparison with conventional Tandem burners, are shown in Figure 2-76.

The CVS Voltmetric burner, shown in Figure 2-77, was developed by Chugairo Kogyo and is based on a similar NO_x reduction principle.

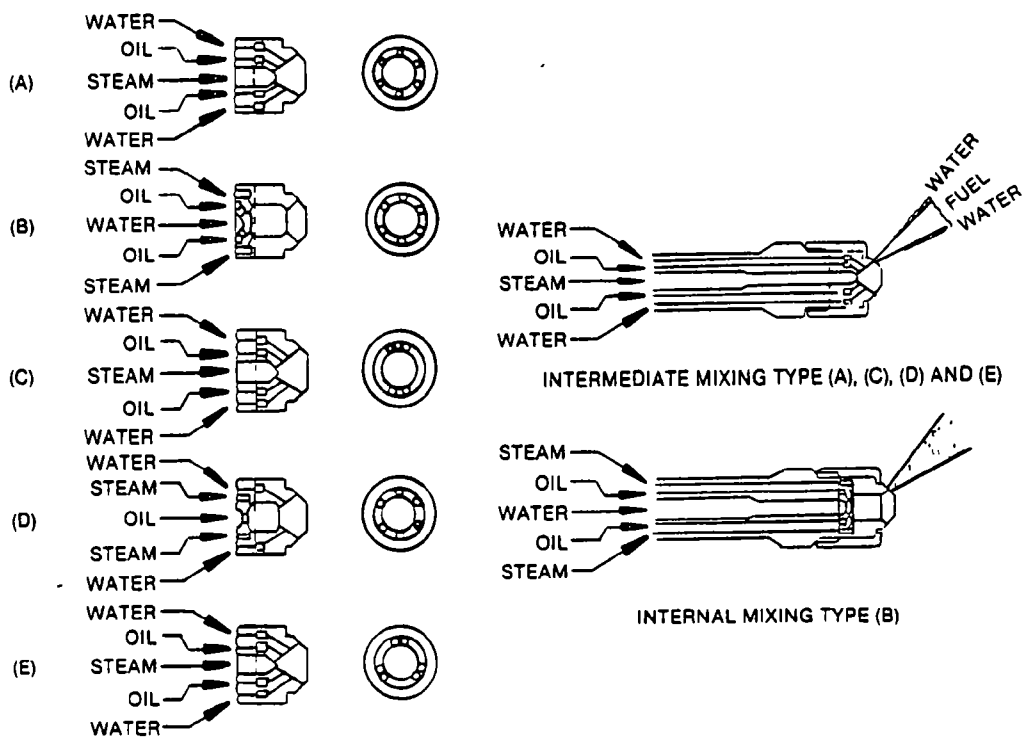
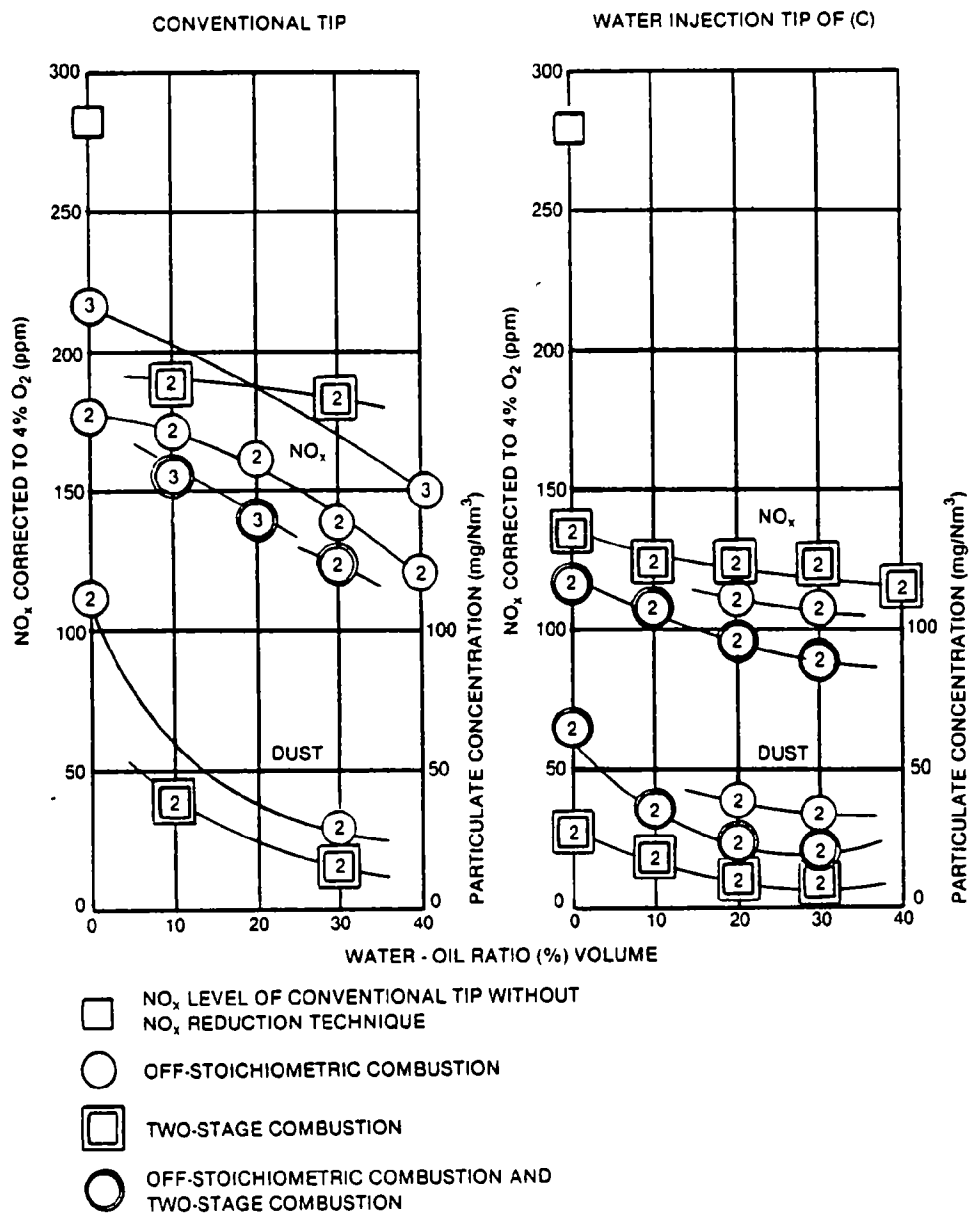


Figure 2-69 Atomizer Tips and Distribution of Water Particles.



(Fuel grade C oil, fuel flow rate 11 t/h, number of burners 9 units, firing type front firing, combustion air temperature 115°C)

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Figure 2-70 NO_x Reduction by Water-Injection Atomizer Tip in a Boiler with a Capacity of 162 t/hr

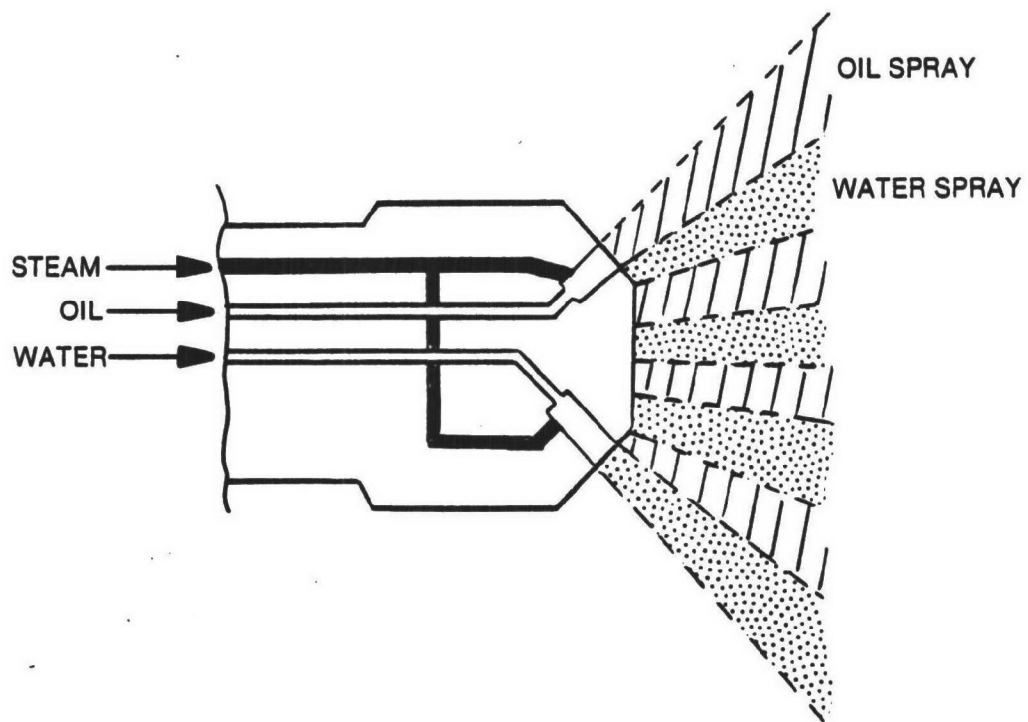
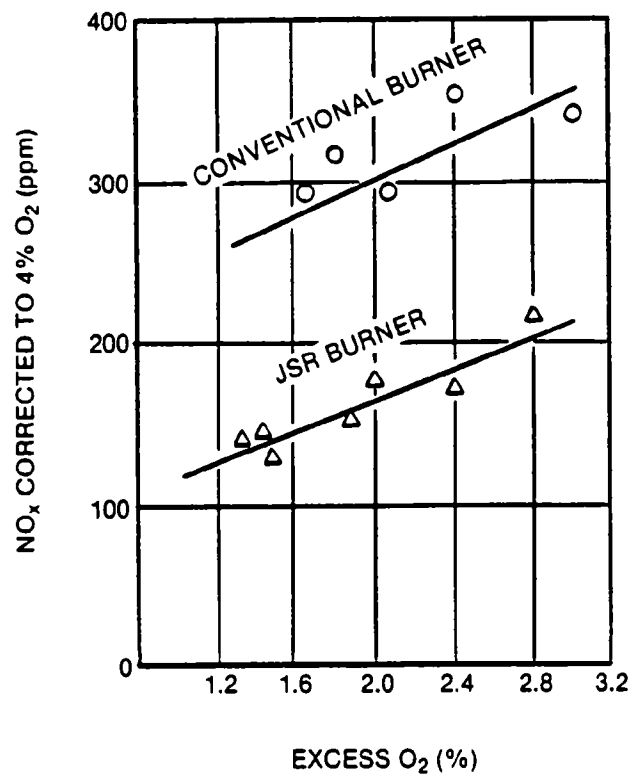


Figure 2-71 **Schematic of JSR Burner (Japan Synthetic Rubber).**



(Fuel: grade C oil; firing type: front firing)

Figure 2-72 NO_x Reduction with JSR Burner in a Boiler with a Capacity of 130 t/hr.

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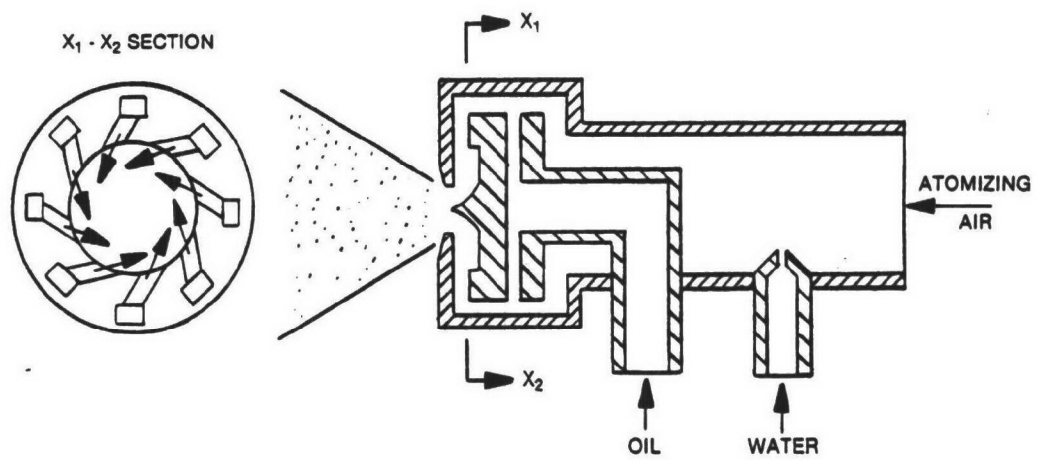


Figure 2-73 Schematic of UN Burner.

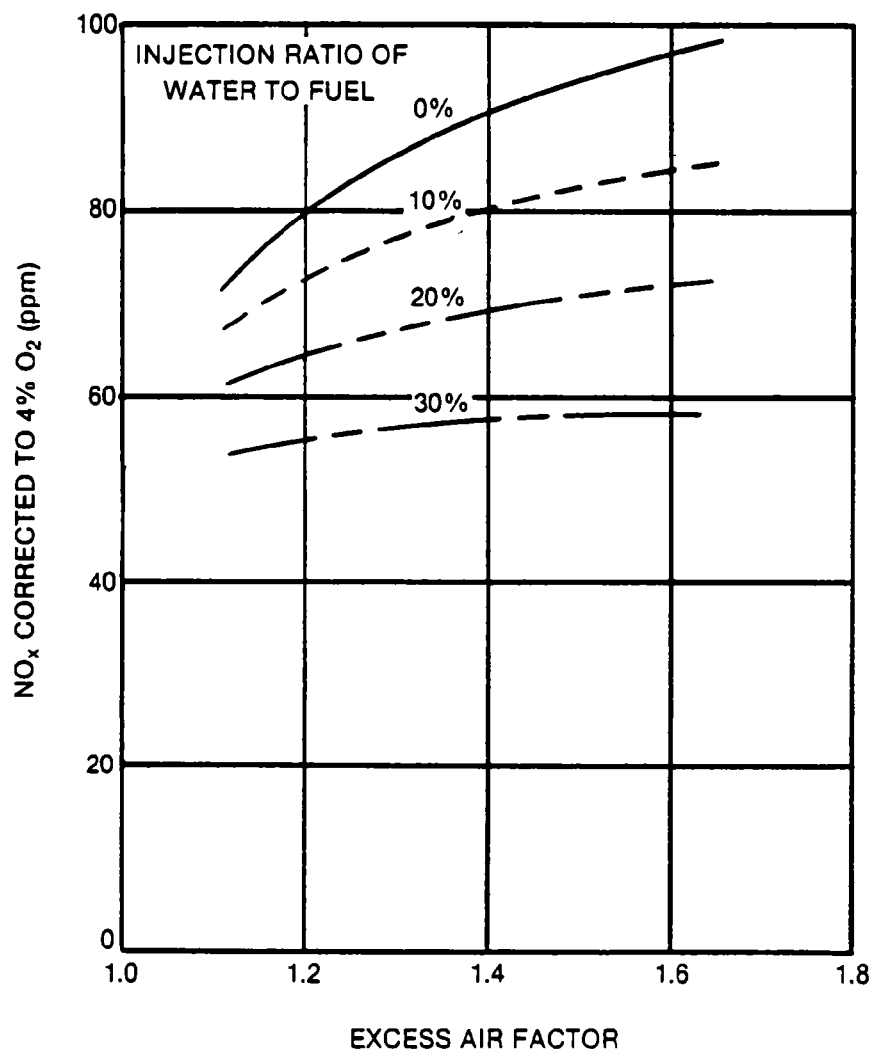


Figure 2-74 NO_x Emission Levels with UN Burner.

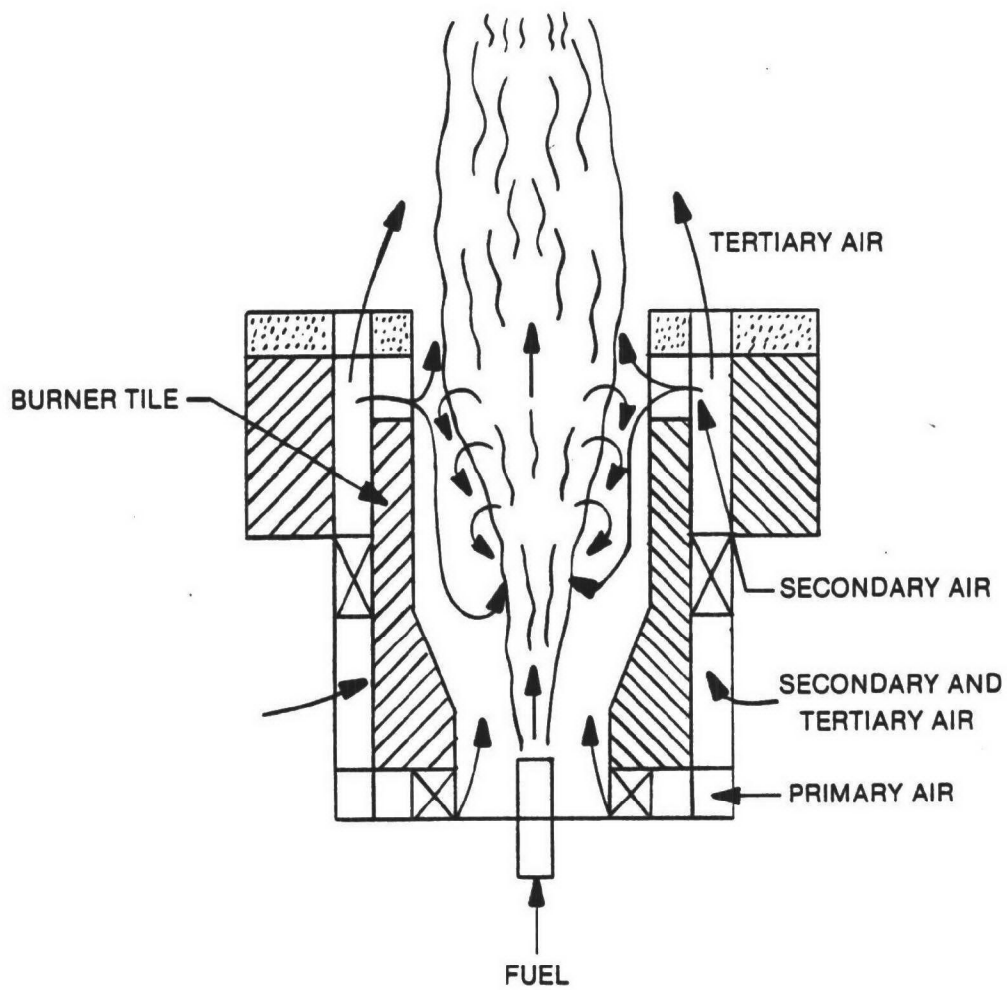


Figure 2-75 Schematic of SRG Burner. (Nippon Furnace Kogyo Kaisha)

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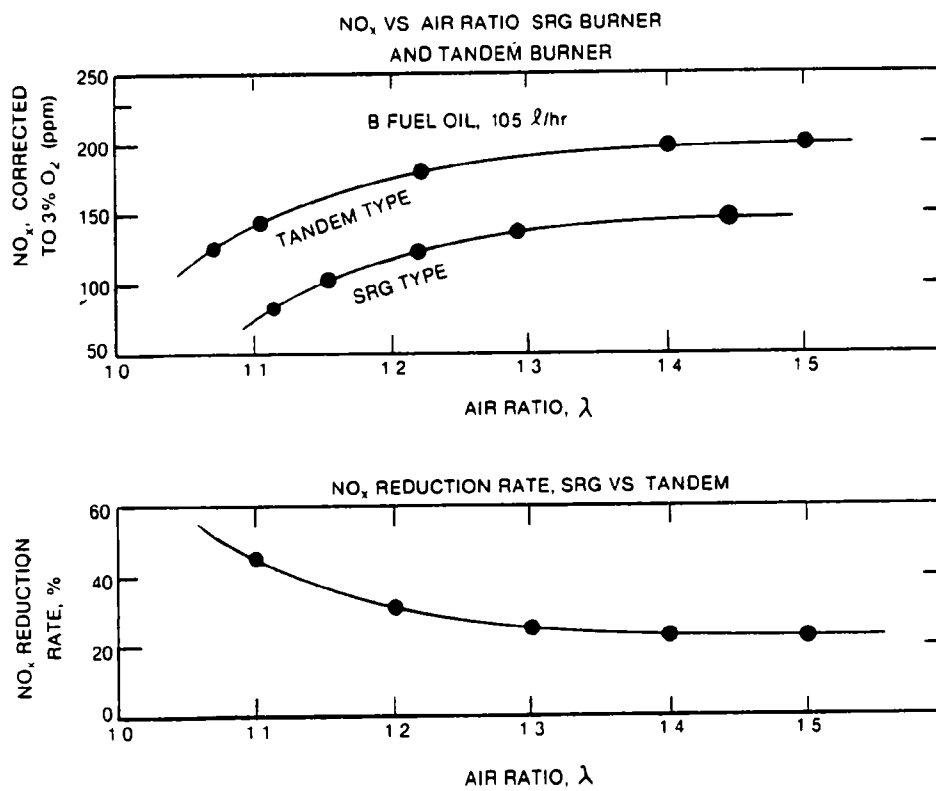


Figure 2-76 Effect of SRG Burner on NO_x Reduction.

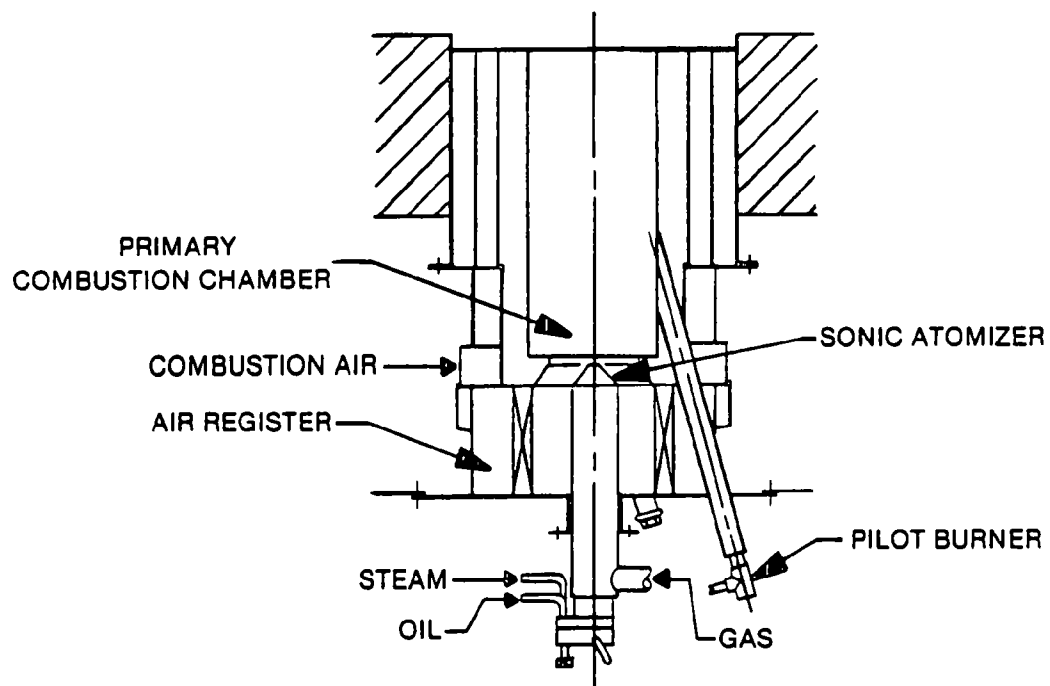


Figure 2-77 Schematic of CVS Voltmetric Burner (Chugairo Kogyo).

Figure 2-78 shows the TCG burner developed by Osaka Gas Co. jointly with Hirakawa Tekko Co. Self recirculation of combustion gas is achieved by the high-velocity secondary fuel, while off-stoichiometric combustion is attained by separate injection of fuels.

The HLN burner developed by Hosoyama Neki Co. is shown in Figure 2-79. The burner applies flue gas recirculation and two-stage combustion. NO_x levels with the burner are shown in Figure 2-80.

2.8 COMBUSTION MODIFICATION FOR SPECIAL NO_x SOURCES AND FUELS

2.8.1 Refuse Incinerators (14)

Flue gas from refuse incinerators usually contains about 150 ppm NO_x (corrected to 12% O_2). A large portion (70-80%) of the NO_x is derived from nitrogen compounds in the refuse. The conversion ratio of fuel nitrogen to NO_x is considered to be 8-12% under normal incineration conditions. In a low excess air incinerator, a conversion ratio of 8% was reported.

NO_x conversion characteristics for refuse incineration are similar to those of oil and coal burning for the following reasons:

- (1) Furnace temperatures do not affect the conversion ratio appreciably.
- (2) Types of nitrogen compounds in the refuse do not greatly influence the conversion ratio.
- (3) Generally, the larger the nitrogen content, the smaller the conversion ratio. The conversion ratio, however, essentially stays constant above a certain nitrogen content.
- (4) The conversion ratio increases with the excess air factor.

Based on these characteristics, staged combustion is considered most effective for abatement of NO_x abatement in incinerator flue gas. Reducing gases such as NH_3 , hydrocarbons, and HCN, formed at the first stage in the

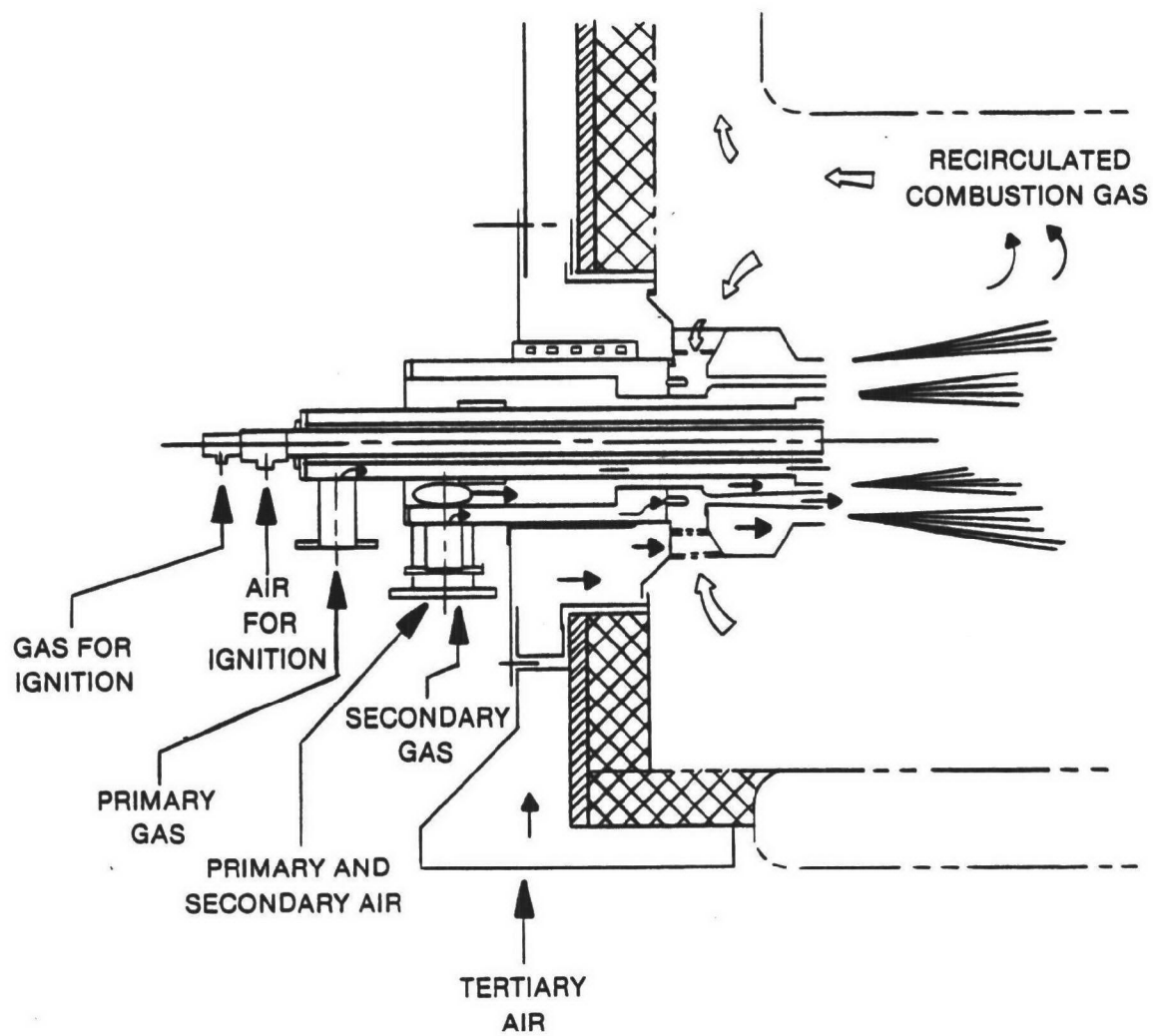


Figure 2-78 Schematic of TCG Burner (Osaka Gas/Hirakawa Tekko).

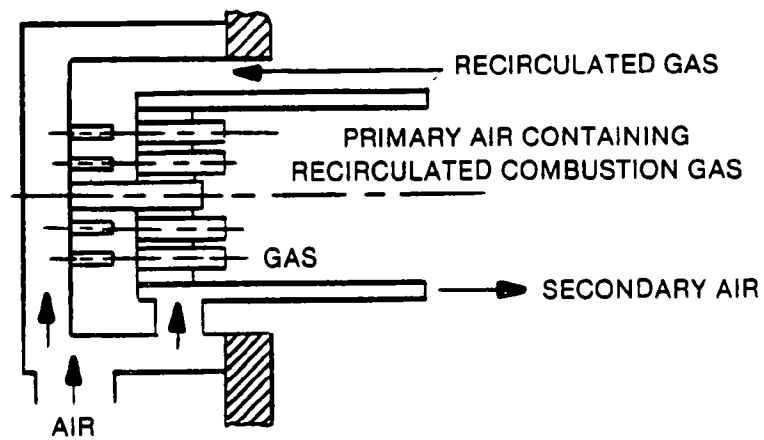
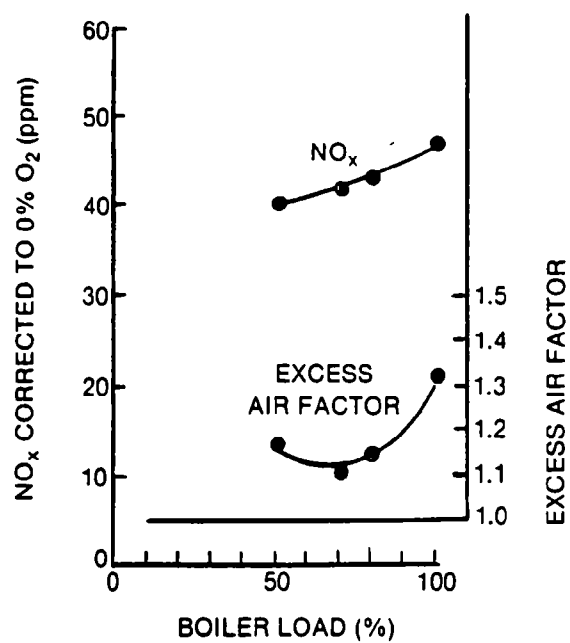


Figure 2-79 Schematic of HLN Burner (Hosoyama Neki).



(Fuel: city gas; calorific value: 5000 kcal/h)

Figure 2-80 NO_x Emission Level with HLN Burner in a Boiler with a Capacity of 1.3 t/hr.

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reducing atmosphere, decompose NO_x and keep the NO_x conversion ratio as low as 5%.

Problems with staged combustion and modifications to remedy them are shown below:

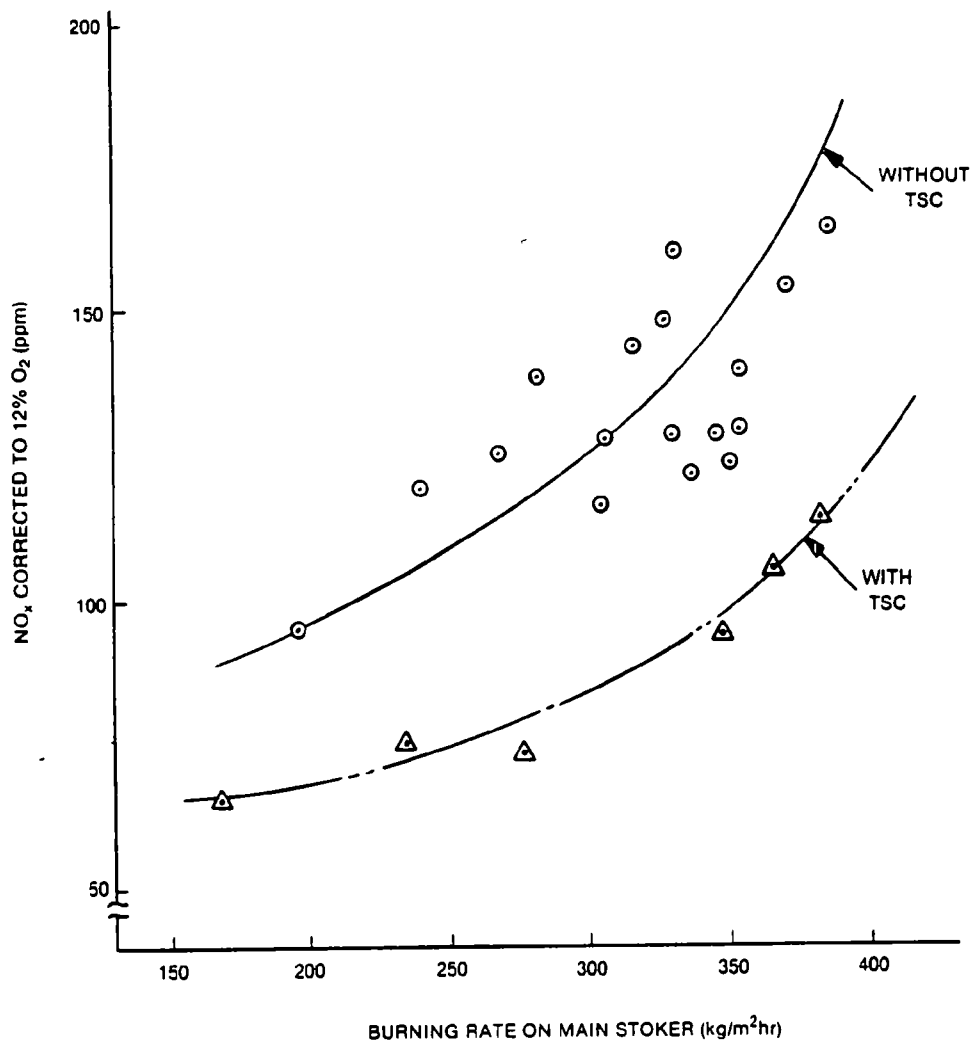
<u>Problems</u>	<u>Modifications</u>
Increase of unburned carbon	Increase of stoker area Application of after-burning system
Control of furnace temperature	Flue gas recirculation Water injection Steam injection

By making these modifications to two-stage combustion, NO_x emissions below 120 ppm (corrected to 12% O_2) are achieved, as shown in Figure 2-81. This emission level more than meets the emission standard of 250 ppm NO_x (corrected to 12% O_2) for a new incinerator.

2.8.2 Cement Kilns (15)

Rotary kilns for cement production usually produce a flue gas containing a high concentration of NO_x —400–1,000 ppm—even with oil firing. This is due to the long retention time of the gas at temperatures of 1000–1550°C and the presence of a large excess of air. A new NSP kiln with suspension preheaters and a gas generator (GG) or a flash furnace (FF) (Figures 2-82 and 2-83) has been developed and used in Japan. It has a high production efficiency and produces NO_x emissions below 200 ppm; the emission standard for new kilns is 250 ppm (corrected to 10% O_2).

A conventional rotary kiln uses all of the fuel from a burner located at one end of the kiln to produce a wide range of high temperatures (1000–1550°C). This assures the decomposition of calcium carbonate and the reaction of lime with clay and other raw materials to form the cement clinker. With the new types of kilns equipped with GG or FF systems, one half of the fuel is injected into the gas generator or flash furnace (calciner). The furnace is installed at the opposite end of the kiln to assure calcination of the feed



(Refuse feed rate 150 t/24hr)

Figure 2-81 NO_x Reduction by Two-Staged Combustion in a Refuse Incinerator.

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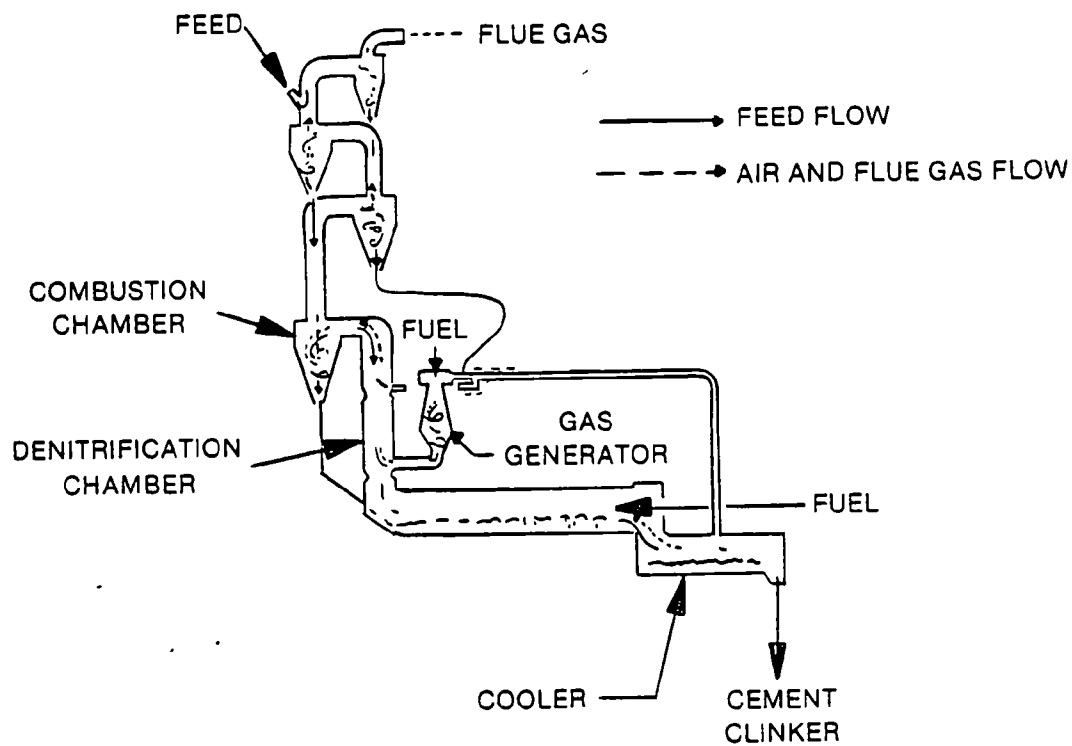


Figure 2-82 Flow Diagram of the GG Process Used in Cement Kilns.

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and decomposition of the calcium carbonate at around 1,000°C. NO_x formation in the kiln is substantially lowered by the reduced heat load. With the GG system, it is possible to use the reducing gas to remove NO_x formed in the denitrification chamber. The reducing gas is burned by the hot air leaving the cement clinker cooler. NO_x concentrations can be reduced below 150 ppm (corrected to 10% O₂), easily meeting the emission standard.

Use of coal instead of oil with the GG system does not cause a substantial increase in NO_x since NO_x can be removed in the denitrification chamber by the reducing gas.

Mitsui Mining Co. has modified the FF system originally developed for oil firing for use with coal, as shown in Figure 2-83. The major modifications are as follows (16):

- (1) A larger calciner (furnace) is used to ensure complete coal combustion.
- (2) A low-pressure-drop suspension preheater is used to deal with the increase in gas volume caused by the use of coal rather than oil.
- (3) The feed is introduced into the calciner from both the bottom and the side to ensure better calcination and the correct combustion temperature for NO_x reduction.

2.8.3 Glass Melting Furnaces

Glass melting furnaces burning gas or oil used to emit high levels of NO_x (above 500 ppm) due to: 1) high furnace temperatures of approximately 1,600°C, 2) relatively long gas-retention times needed to ensure the melting and clarification of the glass, and 3) the high O₂ concentration of the gas. When sodium nitrate is used as a feed to promote clarification, the NO_x concentration in the flue gas commonly exceeds 2,000 ppm. The use of nitrate, however, has almost been eliminated in Japan in order to reduce NO_x emissions.

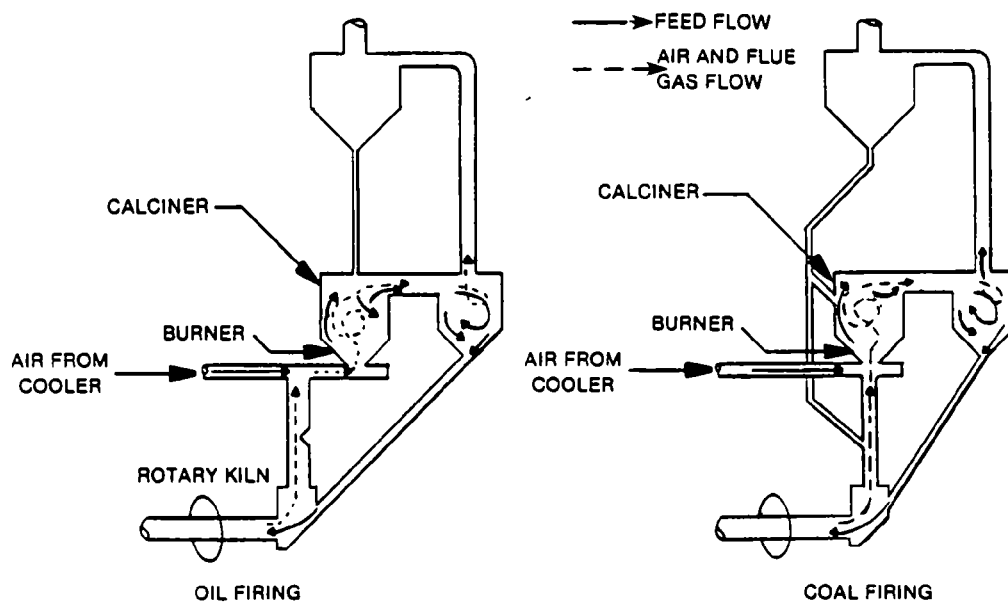


Figure 2-83 The FF System Used in Both Oil and Coal-fired Cement Kilns.

In furnaces not using nitrate, virtually all of the NO_x present in the flue gas is thermal NO_x . Using the following measures, this thermal NO_x is reduced in much the same manner as it is in other oil- or gas-fired industrial furnaces.

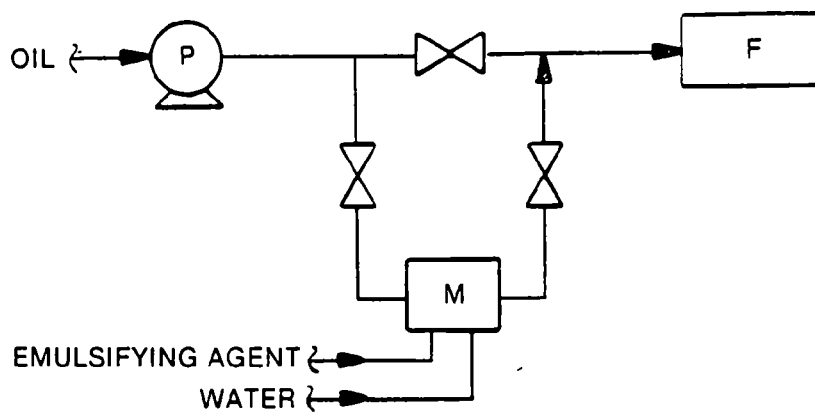
- (1) Suppression of excessively high temperatures
- (2) Prevention of air leakage
- (3) Application of low excess air combustion
- (4) Strict control of O_2 in flue gas using oxygen sensors

A mild flame with a slow reaction is considered an effective method of NO_x abatement for these furnaces. For oil-fired furnaces, the atomizer has been changed from an air to an oil-pressure type. An oil-pressure atomizer that produces a plane flame shape has been developed by the Asahi Glass Company for NO_x abatement purposes (17). The plane flame shape is reduced by the slit in the atomizer tip. With the combination of this atomizer and an adequately shaped port, a 40% NO_x reduction can be achieved.

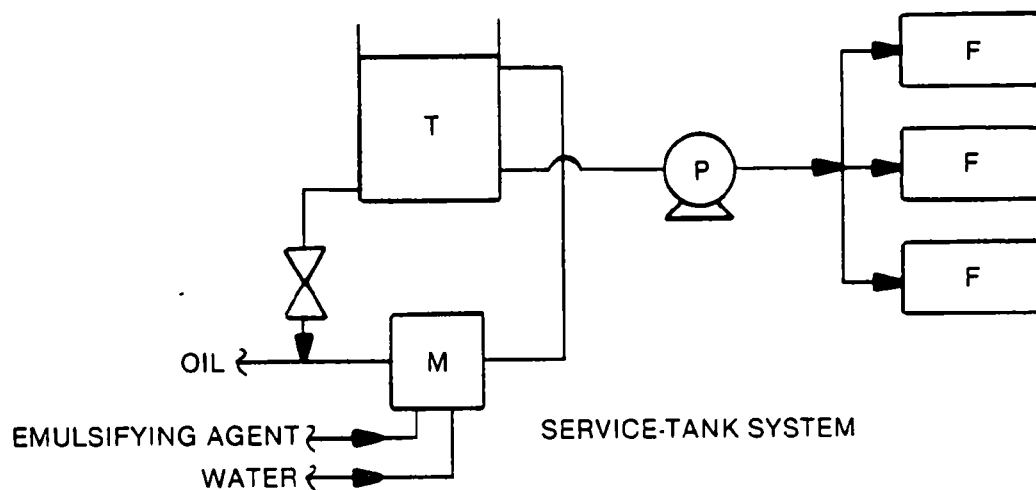
2.8.4 Use of Emulsified Oil for Small Boilers

Emulsified oil (oil-water emulsion) has been used as an efficient method of NO_x abatement for small boilers. In some cases emulsified oil also may be effective for saving energy because it allows a reduction in excess air without causing incomplete combustion.

Many companies have developed systems for producing emulsified oil. These systems may be divided into two categories, as shown in Figure 2-84. The line blending system generally is more advantageous than the service tank system because of its simplicity. On the other hand, the service tank system is compatible with many types of combustion equipment, although pump cavitation may be an operational problem with this system. Different types of emulsifying agents, in concentrations of 0.1 to 0.2%, are used with various types of boiler fuels.



LINE BLENDING SYSTEM



SERVICE-TANK SYSTEM

P· PUMP
M· MIXER
T· TANK
F FURNACE SYSTEMS

Figure 2-84 Emulsified Oil Production Systems.

Upon combustion of the emulsified oil, the atomized oil droplets are separated into very small particles by sudden expansion of the water contained in the emulsion. This increases the contact area for the oil and air, thus increasing the combustion rate, and reducing thermal NO_x formation. Since water and steam can be used to slow the formation of soot as shown in Figure 2-85, excess air can be further reduced as shown in Figure 2-86 (18). Therefore, an increase in thermal efficiency may be expected when using emulsified oil for small boilers. The reducing atmosphere formed by the reaction of the water and fuel promotes the reduction of NO_x . Injection, agitation, and static mixers all have been used to produce emulsified oil.

2.8.5 Special Fuels and Processes

Coal Oil Mixture (COM)

COM is a slurry composed of equal amounts of oil and pulverized coal. In Japan, EPDC and major boiler manufacturers have conducted studies of COM, because the slurry can reduce oil consumption without the handling problems inherent in coal use. The combustion properties of COM compared with those of oil are as follows.

- (1) The ignition characteristics of COM are similar to those of oil, but the atomized particles are often finer.
- (2) With COM the flame becomes longer; oil burns initially, followed by the combustion of volatile matter, and then by the combustion of the fixed carbon of the coal.
- (3) The flame temperature with COM-firing is about equal to that for oil firing.
- (4) The COM burning rate is slower which means that a larger amount of excess air is required. Because of this, the NO_x concentration becomes higher.

Because of COM's higher nitrogen content compared to oil, staged combustion is more effective than flue gas recirculation for NO_x abatement purposes. NO_x concentrations below 200 ppm are achieved by staged combustion.

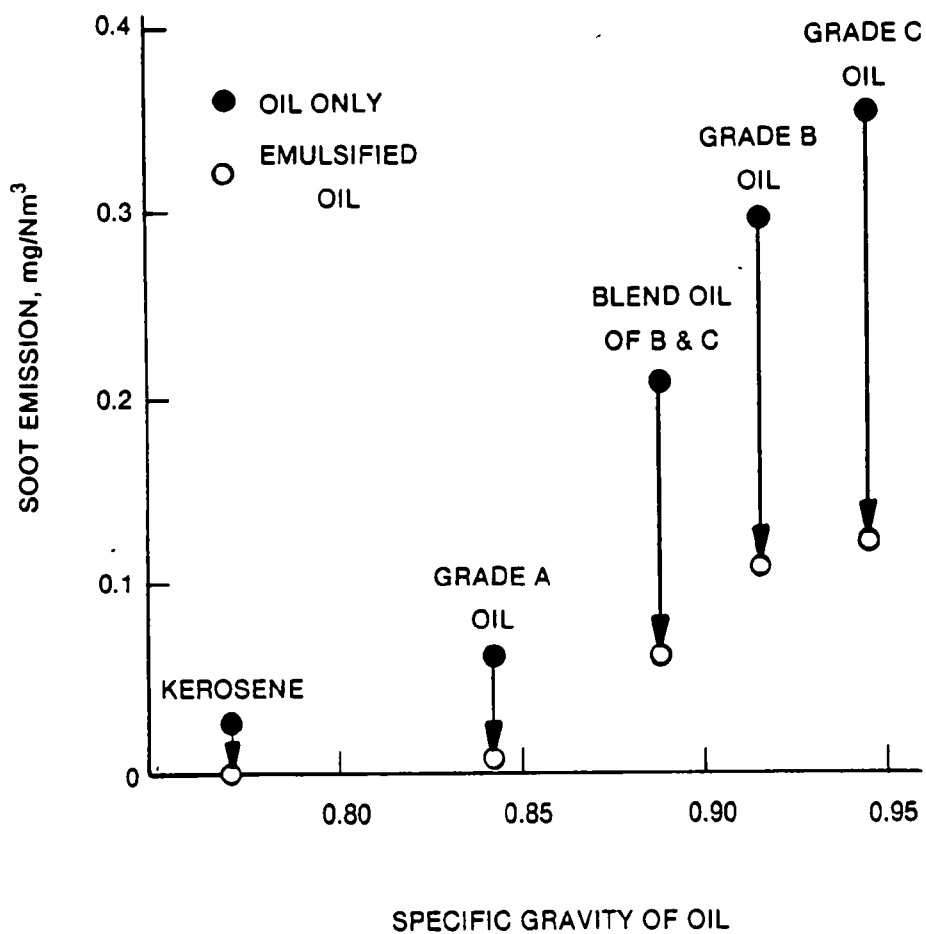
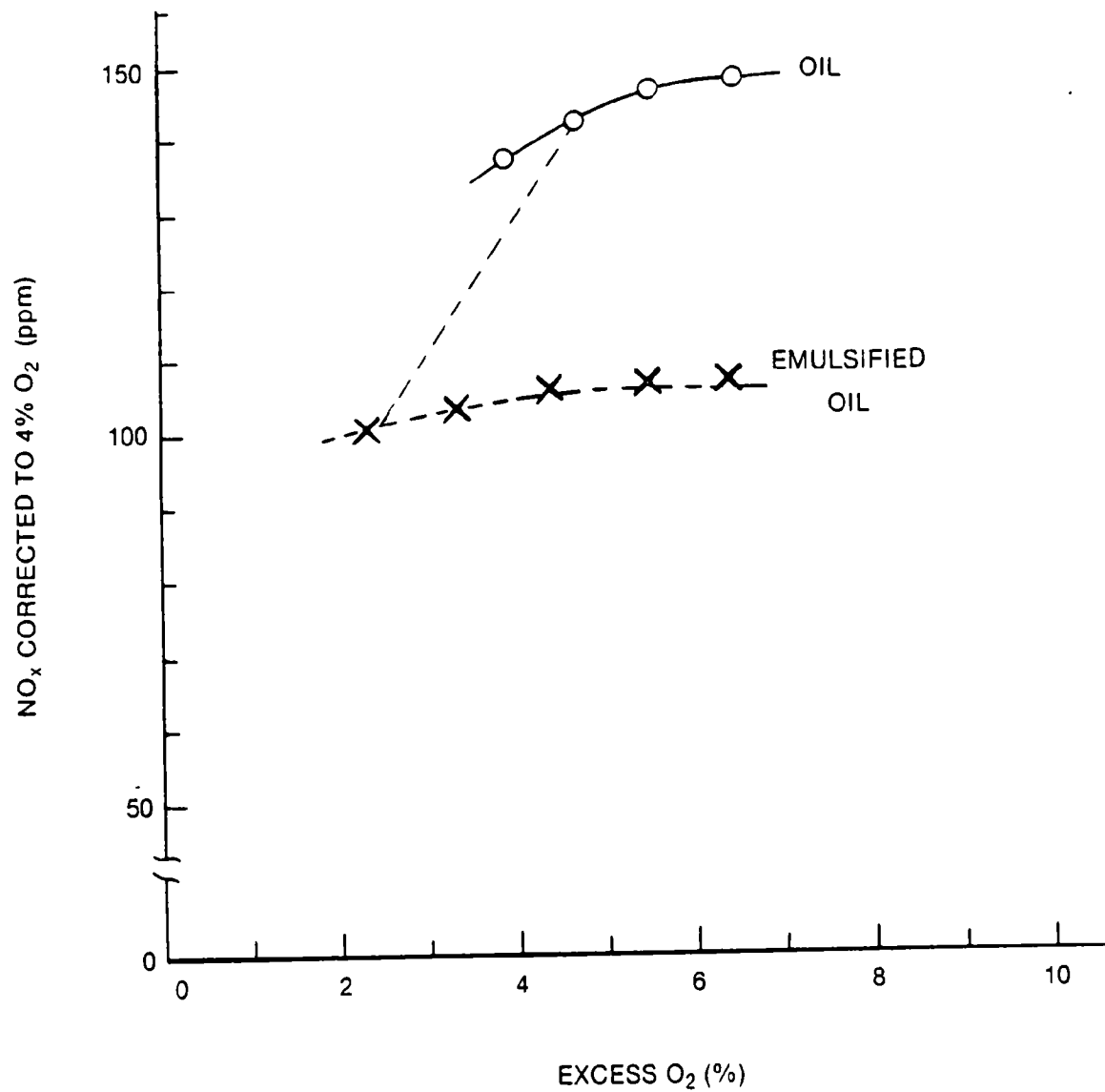


Figure 2-85 Reduction of Soot Emissions by Emulsified Oil.



(Fuel grade C oil, water mixing ratio 30%)

Figure 2-86 NO_x Reduction By Emulsified Oil in a Water Tube Boiler with a Capacity of 12 t/h.

Methanol

A feasibility study on the use of methanol by utility boilers has been conducted (19). Combustion tests using a small test furnace produced NO_x emissions below 30 ppm under normal conditions and of about 20 ppm when flue gas recirculation was applied.

Catalytic Combustion

Basic studies on catalytic combustion of gaseous fuels also have been conducted. Catalytic combustion has the following advantages.

- (1) Low-temperature combustion is possible, resulting in low NO_x concentrations.
- (2) A wide range of excess air factors can be used without affecting the flame stability.
- (3) Uniform temperature and composition of the combustion gas can be obtained thus avoiding local overheating and formation of high NO_x concentrations which occur during conventional combustion.

One test indicated that NO_x levels below 20 ppm were attained even with a combustion temperature of $1,600^\circ\text{C}$ and a catalyst. A large volumetric heat release rate was produced without forming unburned species such as CO and hydrocarbons (20).

One disadvantage of catalytic combustion is that the catalyst can be physically unstable if subjected to repeated temperature variations.

Fluidized Bed Combustion

Fluidized bed combustion (FBC) of coal has the following advantages:

- (1) Low SO_x emissions can be achieved by adding limestone or dolomite in the combustion zone.

- (2) Low NO_x emissions may be achieved because of the low combustion temperature (around $1,000^\circ\text{C}$).
- (3) Smaller boiler sizes are possible due to a higher heat transfer efficiency and a higher heat release rate in the furnace.
- (4) Low-grade as well as high-grade coals may be burned.

The Coal Mining Research Center, jointly with EPDC, KHI, and Babcock Hitachi, constructed a 5 MW equivalent atmospheric FBC pilot plant at EPDC's Wakamatsu Station. The plant began operation in April 1981 (21). Preliminary tests using domestic low-sulfur coal (0.2% S and 0.9% N) and limestone indicated that when staged combustion was applied, NO_x was reduced to 64 ppm. Construction of a 75 MW demonstration plant will begin in 1983; the plant should be operating by 1985.

A small commercial atmospheric FBC plant owned by the Sumitomo Colliery Akabira Company (10 t/hr steam, 2.5MW equivalent) began operation in April 1980 (22). The furnace burns a low-grade coal (3,050 kcal/kg) recovered from coal-wash water and uses silica sand as the fluidizing agent. The plant, constructed by Babcock Hitachi, is a modification of an oil pulverized coal-fired boiler. NO_x concentrations in the flue gas have ranged from 260-350 ppm.

However, fluidized bed combustion has the following disadvantages in Japan:

- (1) There is no land space for disposal of ash containing calcium sulfate, lime, and other materials.
- (2) Although tests have been conducted on a process to separate and regenerate the SO_x absorbent, there are both technical and economic problems associated with the process.
- (3) SO_x and NO_x concentrations in the flue gas may not be low enough to meet the stringent local regulations. In Japan, both FGD and SCR have been applied successfully to coal-fired boilers to reduce SO_x and NO_x to very low levels.

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SECTION 3

SELECTIVE CATALYTIC REDUCTION (SCR) OF NO_x

3.1 REDUCTION OF NO_x BY AMMONIA

3.1.1 Basic Reactions

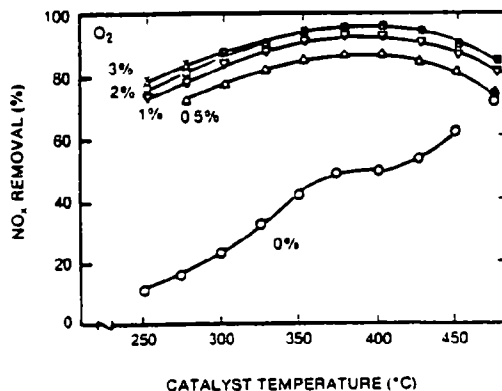
Virtually all of the NO_x in combustion gases is present in the form of NO, while NO_x from non-combustion sources, e.g., nitric acid plant tail gas, consists of both NO₂ and NO. Although NO_x can be reduced to N₂ with the use of reducing gases such as CH₄, H₂, and CO, these gases are also readily consumed by reaction with O₂. NH₃ is a more economical reducing agent for a gas with a high O₂/NO_x ratio, because NH₃ selectively reacts with NO_x.

Since a small amount of O₂ promotes the reaction of NH₃ with NO_x, the reaction is usually expressed by equations 1 and 2.



Combustion gases usually contain at least one percent O₂, which is sufficient for the reaction (Figure 3-1).

The optimum temperature for the reactions without a catalyst is 900-1000°C. Above this temperature, a considerable portion of the NH₃ is converted to NO_x. Below this temperature, the reaction rate is slow. Selective noncatalytic reduction (SNR), the injection of NH₃ into a boiler or furnace at 800-1000°C, has been applied on a commercial scale, but NO_x removal is usually limited to 30-50% at NH₃/NO mole ratios of 1-2 (Section 6.2).



(SV 10 000 hr⁻¹ NO_x 100 ppm NH₃/NO_x 1.0)

Figure 3-1 Effect of Oxygen on NO_x Removal (1)

Selective catalytic reduction (SCR) uses a catalyst at 150–450°C and achieves 80–90% NO_x reduction with an NH₃/NO mole ratio in the range of 0.85–1. Various catalysts are effective in the temperature range of 300–400°C, which is the temperature of utility boiler economizer outlet gas.

3.1.2 Problems with SCR

The serious problems encountered in the early stages of SCR development have largely been solved. Catalyst poisoning by SO_x was solved by substituting base metal catalysts based on TiO₂ for Al₂O₃ or Fe₂O₃. Catalyst plugging problems in dust-laden gases were eliminated with the use of honeycomb, plate, and tube ("parallel flow") catalyst configurations or parallel flow reactors. Soot blowing is also used to remove dust. Ammonium bisulfate formation occurs when NH₃, SO₃, and H₂O react due to temperatures below 300°C caused by reduced boiler loads. Bisulfate deposits lower catalytic activity. Ammonium bisulfate formation has been prevented by maintaining a gas temperature above 300°C, either by adjustments in economizer efficiency or with a hot gas bypass upstream of the economizer. Economizer energy losses are recovered with an air preheater downstream of the SCR. Ammonium bisulfate tends to deposit in the air preheater. The deposits can be prevented or minimized by maintenance of low levels (<5 ppm) of NH₃ in the reactor outlet gas.

Oxidation of SO_2 to SO_3 also occurs with some catalysts, increasing the formation of ammonium bisulfate. Low-oxidation catalysts have been developed to address this problem. Finally, catalyst erosion by fly ash particles has been prevented by maintaining moderate gas velocities, increasing catalyst hardness, and employing the "dummy spacers" described in Section 3.4.

These improvements have increased the reliability and ease of operation of SCR processes, resulting in the construction of over 150 commercial plants. Most have been operated with few problems, although ammonium bisulfate deposition in the air preheater continues to occur at some plants.

Catalyst life in commercial SCR systems varies depending on boiler fuel. For gas- and oil-fired boilers virtually no degradation has been evident after more than 4 years of operation. In July 1982 coal-fired boilers had operated for over 2 years with little catalyst degradation. The actual life of SCR catalysts may be as long as 6-7 years for gas-fired boilers, 5 years for oil-fired boilers, and 3 years for coal-fired boilers.

Disposal of the spent catalysts is considered a potential problem because of the presence of heavy metals. Virtually no catalysts had required replacement at the time this report was written, so there is little experience with spent catalyst disposal. Since catalyst composition is confidential, producers must recycle all of the spent catalysts to recover the heavy metals. For example, titanium producers are expected to recover TiO_2 . The feasibility of these recovery practices for exported catalysts is uncertain.

3.1.3 Major Factors in Catalytic Reaction

Equation 4 shows the relationship between space velocity (SV) and NO_x removal rate:

$$\log(1-x) = -k/\text{SV} \quad (4a)$$

where:

$$k = k_0 S_{ap} \quad (4b)$$

x = Reaction ratio (NO_x removal ratio).

k = Reaction constant.

k_0 = A constant at a given temperature relating to the catalyst property.

S_{ap} = Apparent surface area. The surface area of the catalyst assuming that the catalyst surface is smooth, not porous.

Space velocity is defined as the ratio of the gas volume passing through the catalyst bed per hour to the volume of the catalyst itself.

A smaller SV and a larger k give a larger x . A smaller SV implies that a larger amount of catalyst has been used. The reaction constant, k , is larger with a larger k_0 and S_{ap} . The constant, k_0 , is larger when the catalyst material is more active, while S_{ap} is larger with a more closely spaced catalyst. The latter, however, not only produces a larger pressure drop but makes the catalyst more susceptible to dust plugging (Figure 3-2). Therefore, usually a granular catalyst with a 3-6 mm diameter is used for clean gas while a honeycomb configuration with a 5-8 mm channel diameter and a parallel plate with a 4-7 mm clearance are used for dusty gas.

The inlet NH_3/NO_x mole ratio also influences the NO_x removal efficiency as shown in Figure 3-3. A larger mole ratio produces a higher efficiency and a larger amount of unreacted ammonia leaving the reactor. In practice, a mole ratio between 0.83 and 1.0 is generally used to attain 80-90% NO_x removal and maintain NH_3 emissions below 5 ppm.

For a catalyst with a given SV, NH_3/NO_x mole ratio and temperature, the NO_x removal efficiency as well as ammonia reaction ratio changes little with the inlet NO_x concentration. This indicates that both outlet NO_x and NH_3 concentrations increase with inlet NO_x concentration. Therefore, in order to maintain both NO_x removal efficiency and unreacted NH_3 at a constant level, a large amount of catalyst (smaller SV) is needed with an increase in inlet NO_x (Figure 3-4). The relationship between NO_x removal efficiency and catalyst requirements at a constant inlet NO_x concentration and unreacted NH_3 level is shown in Figure 3-5.

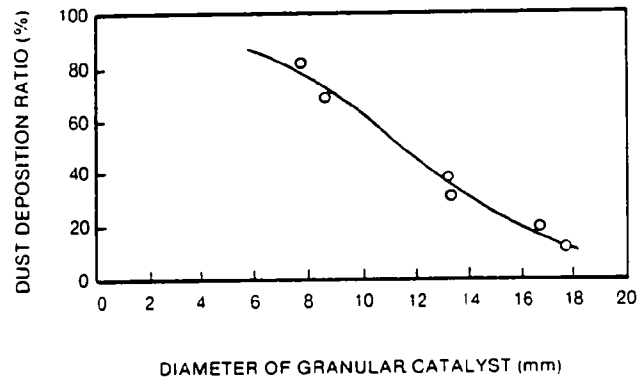
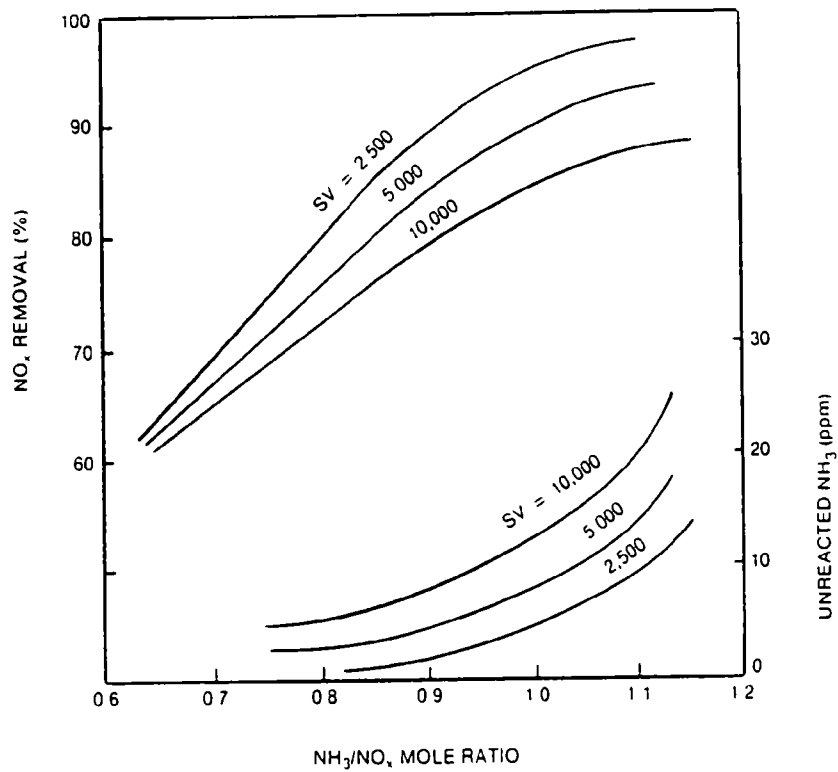


Figure 3-2 Catalyst Size vs Dust Deposition for Oil Fired Dust (Hitachi Ltd)



(Honeycomb Catalyst low sulfur oil inlet NO_x 150 ppm)

Figure 3-3 SCR for Oil Fired Boiler Flue Gas at 350°C

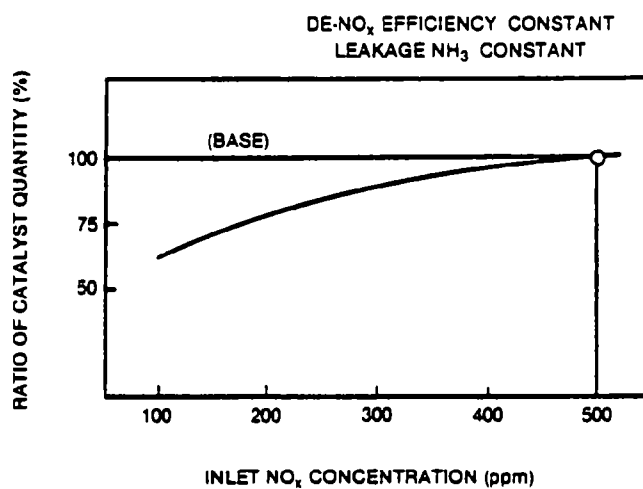


Figure 3-4 NO_x Concentration vs. Catalyst Quantity. (2)

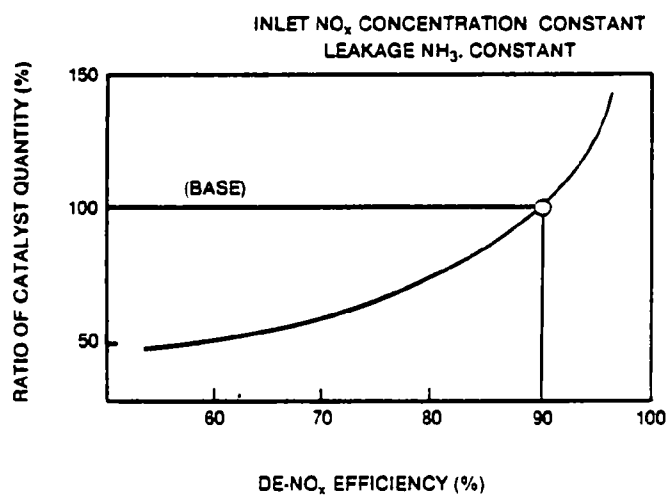


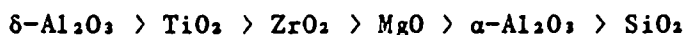
Figure 3-5 De-NO_x Efficiency vs. Catalyst Quantity. (2)

3.2 COMPOSITION AND PROPERTIES OF SCR CATALYSTS

3.2.1 History

SCR catalysts have been produced by many manufacturers. The four major manufacturers are Catalyst and Chemicals, Inc., NGK Insulators Co., Sakai Chemical, and Nihon Shokubai Kagaku which produce various types of ceramic catalysts with honeycomb, ring, tube, and pellet configurations. SCR process developers such as MHI, IHI, KHI, JGC Corp., and Kurabo have conducted their own studies on SCR catalysts and have provided manufacturers with specifications for use in catalyst production. Other process developers produce catalysts themselves; Hitachi Ltd. and Hitachi Zosen make metal-based catalysts while Sumitomo Chemical and Kobe Steel manufacture ceramic ones.

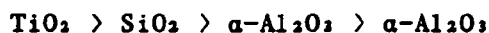
At an early stage in SCR development, catalysts based on alumina carriers were used predominantly. At that time, δ - Al_2O_3 was popular as a heat resistant carrier due to its large surface area and high catalytic activity. The relationships between the surface areas of various carriers are shown below (1):



Catalysts based on ferric oxide also have been used. Ferric oxide is catalytically active and can be obtained both as a natural mineral and as a by-product.

A problem associated with both alumina- and ferric oxide-based catalysts is that they have been found to be poisoned by SO_x in the flue gas. This occurs because of the formation of sulfate which tends to plug the small pores of the catalyst and reduce its surface area and activity. Although the sulfate can be decomposed by heating it to 700–800°C, the treatment requires a substantial amount of energy.

More recently, titania (TiO_2)-based catalysts have become popular for dirty gas treatment because of their high activity and resistance to SO_x . The relative SO_x resistances of the catalyst carriers are shown below (1):



The properties of various catalyst carriers are compared in Table 3-1.

TABLE 3-1. COMPARISON OF CATALYST'S CARRIER CHARACTERISTICS (KAWASAKI HEAVY INDUSTRIES)

Characteristics	Material				
	Alumina	Ferric Oxides	Silicates	Tuff	Titania
SO_x resistivity	C	D	A	B	A
Initial activity for DeNO_x	A	C	C	B	A
Physical strength	B	D	A	A	C
Durability	C	D	C	B	A
Cost of catalyst	C	B	C	A	D

Note: Symbols A - D indicate ratings with A being the best.

Adding V_2O_5 to TiO_2 produces a highly active SCR catalyst. However, a drawback is that vanadium promotes the oxidation of SO_2 to SO_3 which causes ammonium bisulfate deposits in the air preheater. Recent efforts to improve SCR catalysts have concentrated on development of an active catalyst which is not poisoned by SO_x and has little SO_2 oxidation capability.

Low-temperature catalysts active at 150-250°C also have been evaluated for use with low-temperature gases such as those from coke ovens and sintering machines. The greatest problem with the low-temperature catalyst is that ammonium bisulfate deposits on it. In practice, the deposits are removed

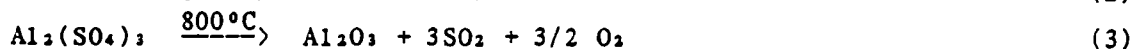
by periodically heating the catalyst above 400°C. This heating process is necessary to restore catalytic activity.

Ammonia decomposition catalysts were studied and used a few years ago but have not been developed. This type of catalyst tends to be poisoned by SO_x and to oxidize a considerable portion of SO₂ to SO₃. In recent practice, unreacted NH₃ has been reduced by using a low NH₃/NO_x mole ratio and an increased amount of SCR catalyst.

3.2.2 Alumina-Based Catalysts

Most alumina carrier catalysts are in the form of δ-Al₂O₃ which has a large surface area and high activity. This type of catalyst has been used with clean gas containing little or no SO_x. The performance of alumina-based catalysts for clean gases is shown in Figure 3-6. A catalyst made of alumina impregnated with Cr₂O₃ shows a high activity around 250°C, while one with Fe₂O₃ shows a high activity around 430°C. A catalyst active at 300-400°C can be obtained by using both Cr₂O₃ and Fe₂O₃ or V₂O₅ and Cr₂O₃.

The alumina in δ form readily reacts with SO₃ to form Al₂(SO₄)₃ with reduced surface area and activity (see Figure 3-7). Even though a gas may contain SO₂ and no SO₃, a portion of SO₂ is oxidized to SO₃ on the catalyst surface and reacts with Al₂O₃. When the poisoned carrier is heated to 800°C, Al₂(SO₄)₃ decomposes to regenerate Al₂O₃ and catalytic activity is restored. These reactions are:



However, the heating requires a considerable amount of energy and is not economical. Heating δ-Al₂O₃ to 1100°C, produces α-Al₂O₃ which is resistant to SO_x. However, α-Al₂O₃ has a much smaller surface area and is less active than δ-Al₂O₃. Since SO_x-resistant catalysts based on TiO₂ have become popular, alumina-based catalysts now are seldom used for gas containing SO_x.

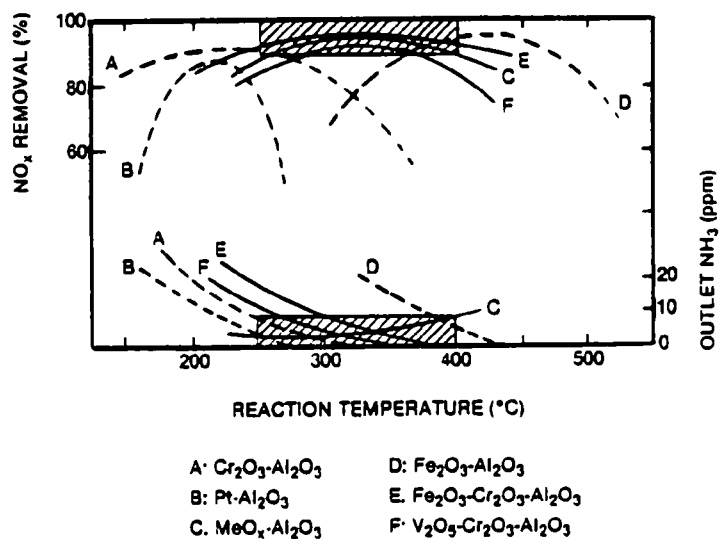


Figure 3-6 Criteria for Catalysts Used with Clean Gas. (1)

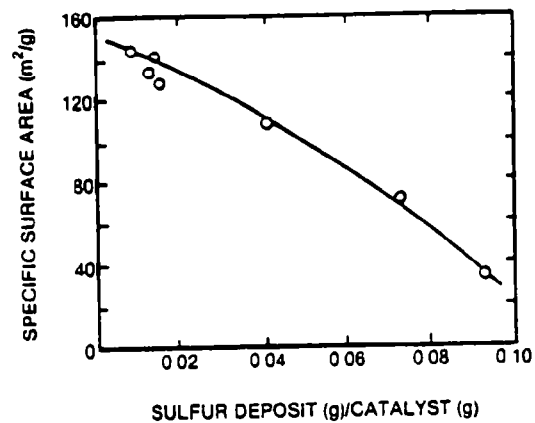


Figure 3-7 Deactivation of Catalyst on γ - Al₂O₃ Carrier by SO_x. (1)

3.2.3 Fe₂O₃-Based Catalysts

Fe₂O₃-based ring-shaped catalysts were used several years ago at a few SCR plants but they were found to be poisoned by SO_x. Nippon Kokan recently began using a special type of iron ore as the SCR catalyst to treat flue gas from an iron sintering machine. Contaminated by SO_x and dust, the catalyst, along with other iron ores, is used for steel production. Catalyst and Chemicals, Inc. recently studied the production of a low-cost Fe₂O₃ catalyst using red mud, a useless by-product of aluminum production, and limonite, a neutral mineral mined in the Aso and Kurohime Mountains (3).

The chemical composition of the red mud and limonite catalyst is shown in Table 3-2. The red mud's major component is highly crystalline α-Fe₂O₃; limonite is composed of α-FeOOH and α-Fe₂O₃ with low crystallinity.

TABLE 3-2. CHEMICAL COMPOSITION OF RED MUD AND LIMONITE CATALYSTS (3)
(%, on dry basis)

	Red Mud	Limonite
Fe ₂ O ₃	52-55	84-85
Al ₂ O ₃	20-27	13
SiO ₂	7-10	13-14
TiO ₂	7-10	Trace
CaO	0-2.5	0.1
MgO	-	0.15
Na ₂ O	3-5	0.3
K ₂ O	Trace	0.3
SO ₄	0.3	0.3
MnO	Trace	0.4
(H ₂ O)	About 80	30-40

During the first stage of catalyst production, the red mud is washed with sulfuric acid and water to remove sodium. The red mud and limonite then are combined with water, kneaded, shaped and calcined to produce pellets 3 mm in diameter. The catalyst pellets (25 ml) are placed in a reactor tube. Then a synthetic gas containing 500 ppm NO, 500 ppm SO₂, 3% O₂, 10 - 15% H₂O, with

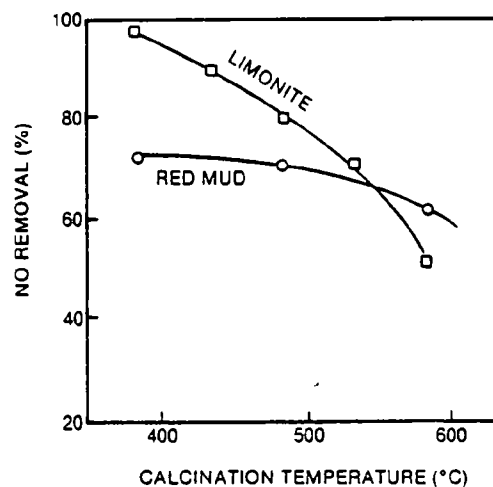
600 or 750 ppm NH_3 is passed through the catalyst bed at 200–380°C with an SV of 10,000 or 6,000 hr^{-1} .

Figure 3-8 shows the effect of the catalyst's calcination temperature on its initial activity (before SO_x poisoning). The limonite was highly active when calcined at 400°C and became much less so when calcination took place at higher temperatures. Since SCR usually takes place at 300–400°C, calcination of the catalyst at 400–500°C may be adequate to produce good activity and sufficient physical strength. The red mud catalyst was not very active when calcined at 400°C.

The effects of adding various compounds to the catalysts are shown in Figure 3-9. Red mud's activity was increased by the addition of V_2O_5 and CuO but decreased when SnO_2 was added. The optimum amount of V_2O_5 was 5–10% of the amount of the red mud. TiO_2 increased the activity of limonite.

Figure 3-10 shows the increase in SO_4 and decrease in NO_x removal efficiency which resulted when three types of catalysts were exposed to flue gas from an oil-fired boiler. After varying exposure periods up to 1,200 hours, the catalysts were subjected to both an SO_4 analysis and an NO_x removal test. Limonite with TiO_2 calcined at 500°C showed a high initial efficiency which decreased rapidly during exposure (with the concurrent increase in SO_4). Virtually all of the Fe_2O_3 was converted to $\text{Fe}_2(\text{SO}_4)_3$ after 200 hours exposure. Limonite calcined at 700°C with TiO_2 was inactive although it became more active with an exposure of 200 to 600 hours. Red mud calcined at 500°C was moderately active and remained that way during a period of 1,200 hours.

Figure 3-11 shows the results of the exposure tests on red mud catalysts which contained additives of TiO_2 or TiO_2 and V_2O_5 . The improved red mud catalysts maintained fairly good activity even after 3,000 hours of exposure. This indicates that it may be possible to produce a relatively inexpensive SO_x -resistant catalyst using red mud.



(350°C, SV 6,000 hr⁻¹, NO 500 ppm, NH₃ 700 ppm)

Figure 3-8 Calcination Temperature vs Initial Activity. (3)

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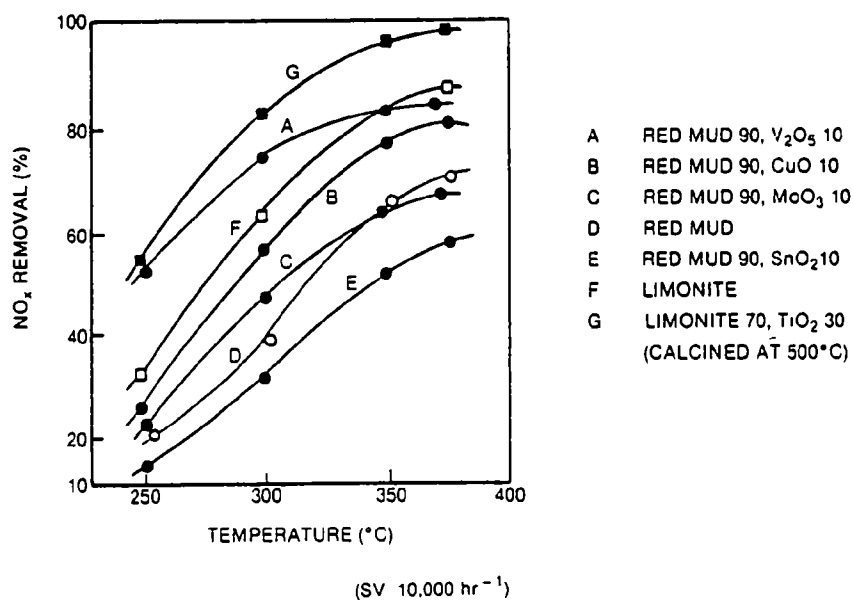


Figure 3-9 Effect of Additives on NO_x Removal.

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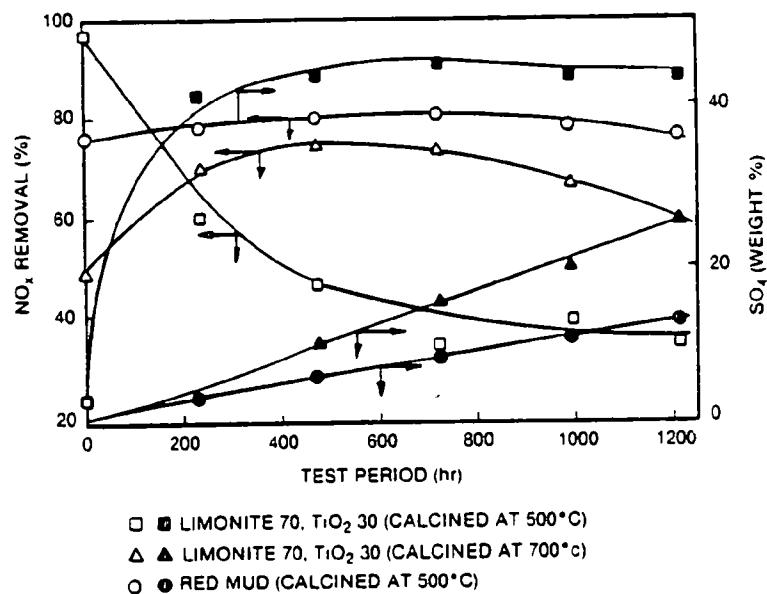


Figure 3-10 Catalyst Tests with Oil-Fired Boiler Flue Gas. (3)

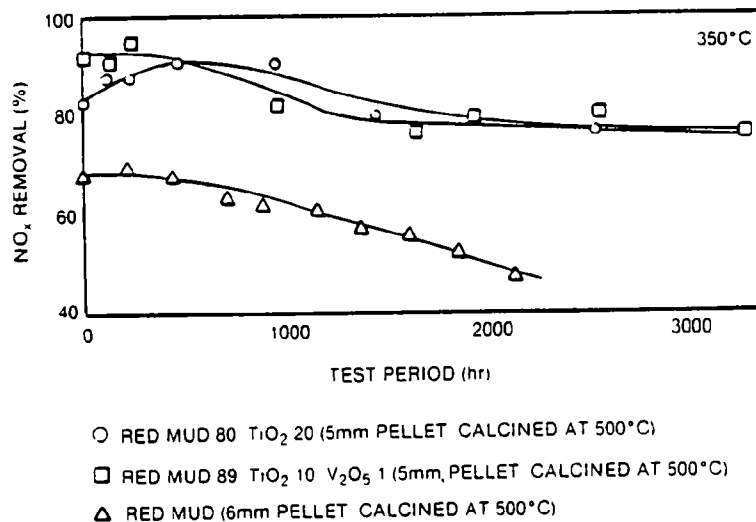


Figure 3-11 Additional Catalyst Tests with Oil-Fired Boiler Flue Gas (3)

3.2.4 TiO₂-Based Catalysts

Titania (TiO₂), in the form of anathase, is catalytically active and has a good resistance to SO_x. Its activity can be increased by adding base metal oxides. As shown in Figures 3-12 and 3-13, Vanadium (V) is a most effective additive for this purpose. For this reason, a TiO₂-based catalyst containing 1-5% V₂O₅ has been most popular for gas containing SO_x. However, a common problem associated with this catalyst is the oxidation of a portion of the SO₂ to SO₃. During cooling, the SO₃ combines with NH₃ and H₂O to form NH₄HSO₄ which results in the plugging of the air preheater elements. The oxidation ratio is larger with a lower SV and a smaller NH₃/NO_x mole ratio; NH₃ works as a reducing agent to lower the oxidation ratio (Figure 3-14).

When Cu, Co, and Ce are used as additives to the TiO₂-based catalyst, a substantial amount of oxidation occurs; when V is used with Mo and W only a slight amount of oxidation occurs.

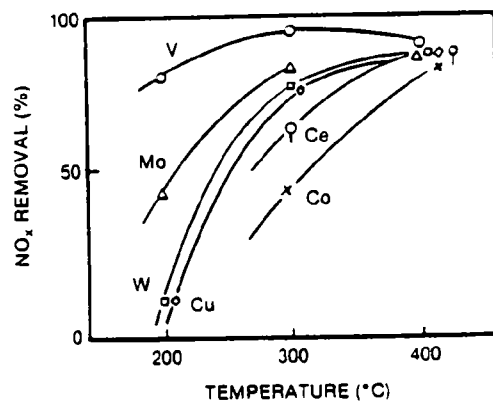
Catalyst producers are making efforts to lower the oxidation ratio. A common method is to replace a considerable portion of V with other metals such as Mo or W (Figure 3-15). With the replacement, the NO_x removal efficiency is slightly lowered while the oxidation ratio is lowered to a much greater extent. Table 3-3 shows the TiO₂-V₂O₅ catalyst (108-H) and improved catalysts (109 H - 111 HC).

The TiO₂-V₂O₅ catalyst is poisoned by alkali compounds, particularly by potassium at low temperatures (Figure 3-16). Figure 3-17 shows that a catalyst using two kinds of selected base metals is poisoned to a lesser degree.

3.3 LOW-TEMPERATURE CATALYSTS

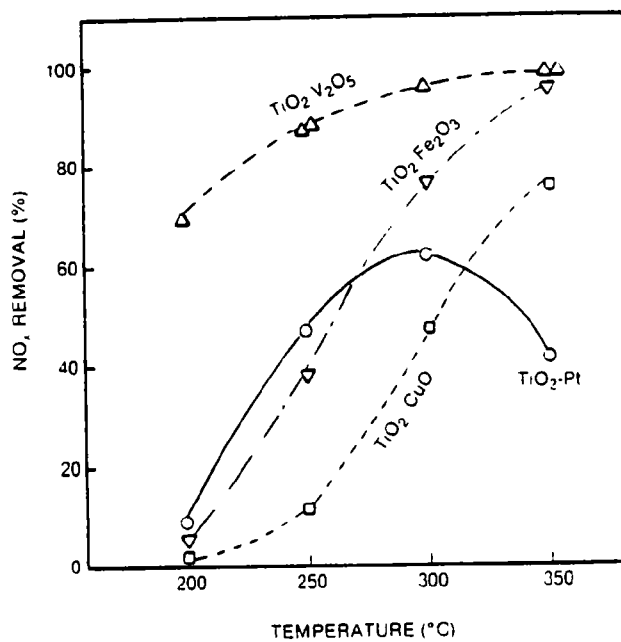
3.3.1 Introduction

For some gas sources, such as coke ovens and iron-ore sintering machines, the temperature of the gas stream requiring NO_x removal is low (150-250°C). Since heating the gas to 300-400°C requires a large amount of energy, low-



(metal oxide $\text{TiO}_2 = 5.100, 3.3\text{mm}$ pellet
 $\text{NO} = 200\text{ ppm}$, $\text{NH}_3 = 200\text{ ppm}$, $\text{SO}_2 = 500\text{ ppm}$
 $\text{O}_2 = 1.5\%$, $\text{H}_2\text{O} = 10\%$, $\text{SV} = 10,000\text{ hr}^{-1}$)

Figure 3-12 Additives' Effect on TiO -Based Catalyst (4)



(3mm pellets $\text{SV} = 15,000\text{ hr}^{-1}$, $\text{NO} = 150\text{ ppm}$
 $\text{NH}_3 = 180\text{ ppm}$, $\text{O}_2 = 4\%$, $\text{H}_2\text{O} = 10\%$, $\text{SO}_2 = 1,000\text{ ppm}$)

Figure 3-13 Activity of TiO Based Catalyst (5)

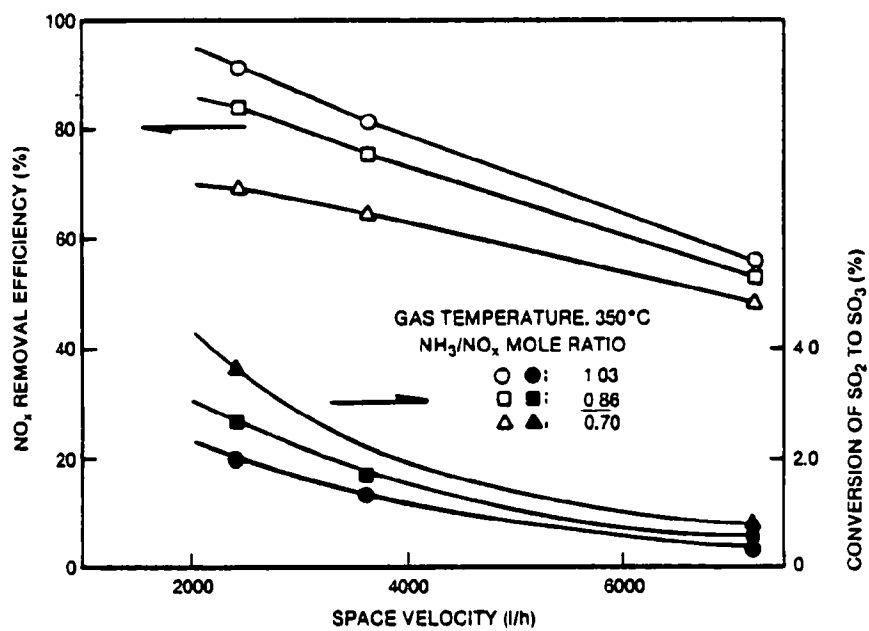


Figure 3-14 NO_x Removal and SO₂ Oxidation. (6)

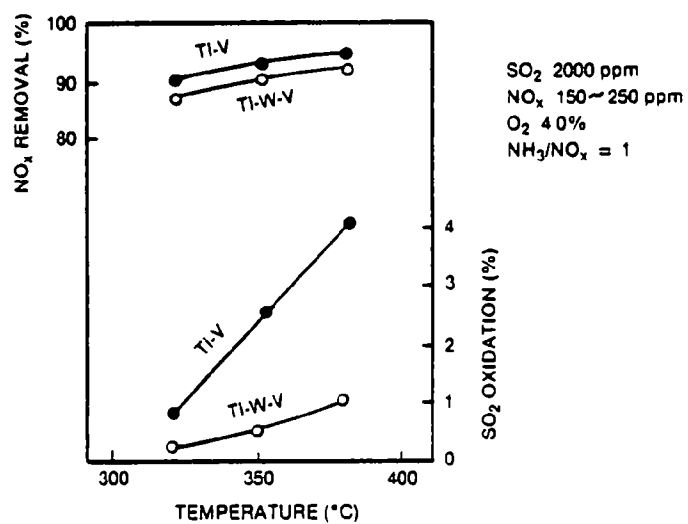


Figure 3-15 Performance of Ti-V and Ti-W-V Catalysts.
(Kawasaki Heavy Industries)

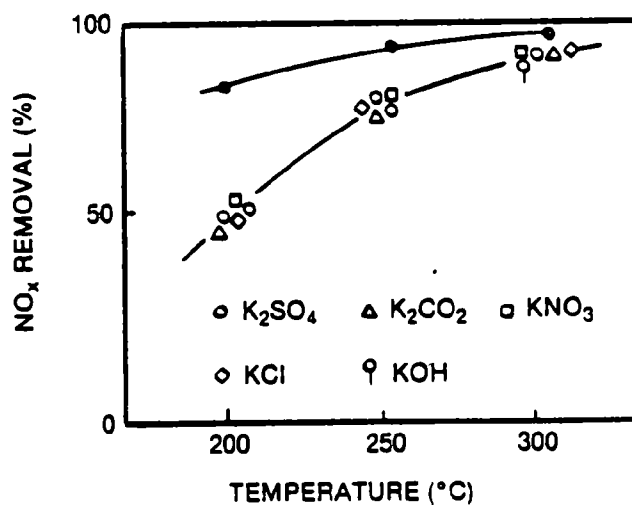


Figure 3-16 Effect of Potassium on $\text{TiO}_2\text{-V}_2\text{O}_5$ Catalyst. (4)

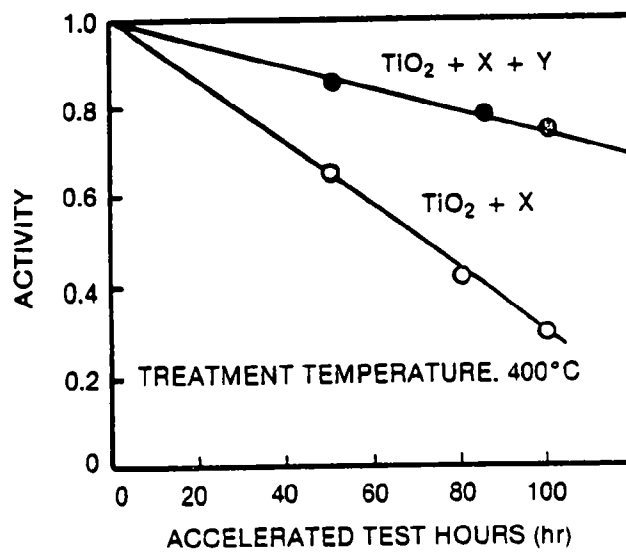


Figure 3-17 Test Results of Accelerated Deterioration Test with Alkali metal Sulfate. (7)

TABLE 3-3. PERFORMANCE OF HONEYCOMB CATALYSTS (NIHON SHOKUBAI KAGAKU)
 (Gas Composition: NO_x 180-200 ppm, SO_x 150-200 ppm), CO₂
 7-10%, H₂O 7-10%, O₂ 7-10%, NH₃/NO_x mole ratio: 1.0, Area
 Velocity 1.0 m/hr)

Catalyst No.	SV ₁ (hr ⁻¹)	NO _x Removal (%) at			SO ₂ oxidation (%) at	
		300°C	350°C	380°C	350°C	380°C
108 H ^a	4,830	92	96	97	2.1	4.0
109 H ^a	4,830	87	94	95	0.5	1.0
110 H ^a	4,830	77	85	89	0.05	0.1
111 H ^a	4,830	84	92	94	0.2	0.4
109 HC ^b	3,710	79	87	90	0.5	1.1
111 HC ^b	3,710	76	84	88	0.2	0.4

^aHoneycomb for oil-fired flue gas: channel diameter 6 mm, wall thickness 1.4 mm.

^bHoneycomb for coal-fired flue gas: channel diameter 8 mm, wall thickness 1.8 mm.

temperature catalysts active at 150–250°C, have been developed. However, the following problems have occurred with this type of catalyst: (1) the reaction rate is generally slow; (2) ammonium bisulfate deposits on the catalyst below 300°C; and (3) poisoning by potassium compounds occurs more seriously at lower temperatures (Figure 3-16).

Kureha Chemical has developed a catalyst which is active at 150°C (8). However, this catalyst, is seriously poisoned by SO_x in the gas stream and therefore has not been used commercially. SO_x -resistant catalysts active at 200–250°C also have been developed by several manufacturers. Even with an SO_x -resistant catalyst, ammonium bisulfate deposits form, thereby lowering catalytic activity. To increase its activity, the catalyst occasionally must be heated above 400°C. This heating can be achieved either by mixing a hot gas with the low-temperature gas or by removing the catalyst from the reactor (moving bed) for thermal treatment.

Many of the early low-temperature catalysts were based on zeolite combined with various metals, as shown in Figures 3-18 (5) and 3-19 (11). They generally consumed less than 1 mol NH_3 to 1 mol NO , but were no more efficient than the TiO_2 - V_2O_5 catalyst, except for those containing Pt and Pd (which are readily poisoned by SO_x). Most of the recently developed low-temperature catalysts are based on TiO_2 , except for those developed by Kobe Steel which are alumina-based. (Section 5.6).

3.3.2 Catalytic Activity Decrease Caused by Ammonium Bisulfate Deposit

Figure 3-20 illustrates the decreased catalytic activity of TiO_2 -based metal catalysts during a 100 hour period at 250°C. The decrease is due to ammonium bisulfate deposition. The gas used for the test contained 1,000 ppm SO_2 without SO_3 . It is obvious that a portion of SO_2 is oxidized on the catalyst surface to form the bisulfate. The decrease in catalytic activity was substantial with the Ce catalyst, slightly less severe with the Cu, V, and Co catalysts, and only slight with the Mo and W. Although the catalysts with Mo and W additives were barely affected by the bisulfate, the initial activity of these catalysts was much lower than that of the vanadium catalyst.

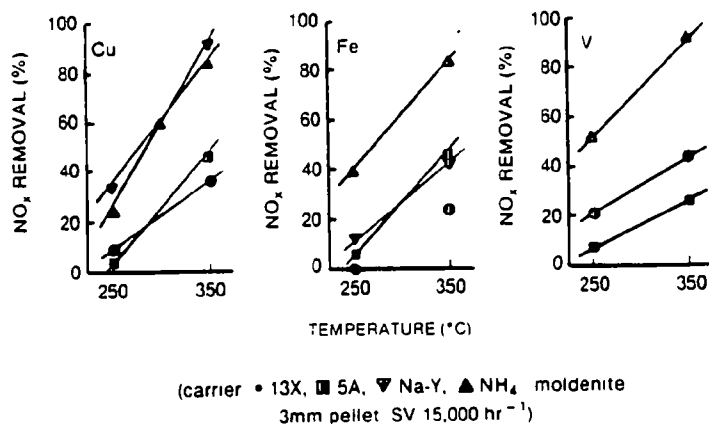
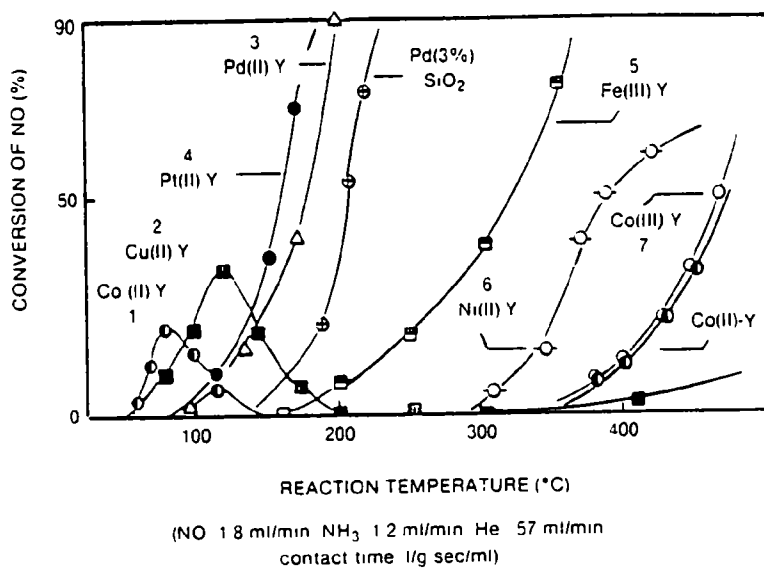
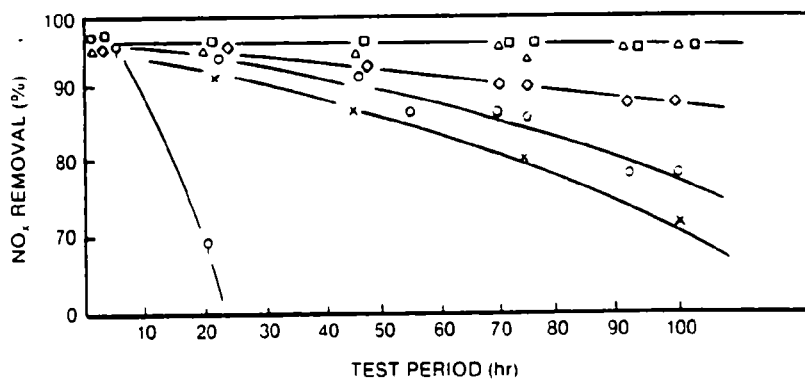


Figure 3-18 Low-Temperature Catalyst with Zeolite Carrier (5)



NOTE The degree of ion exchange is as follows: 1) Co(II) Y 70%
2) Cu(II) Y 68% 3) Pd(II) Y 48% 4) Pt(II) Y 52%
5) Fe(III) Y 75% 6) Ni(II) Y 80% 7) Co(III)-Y 95%

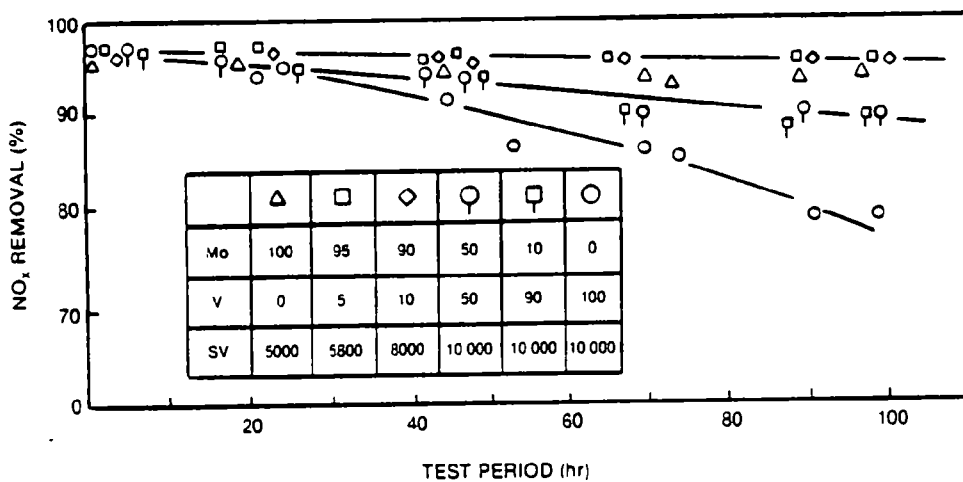
Figure 3-19 Catalytic Activity of Various Transition Metal Ion Exchanged Y Type Zeolites for the NO NH₃ Reaction



○ V SV = 10,000 △ Mo SV = 5000 □ W SV = 1700
 ◇ Cu SV = 1700 ◊ Ce SV = 1500 × Co SV = 1000

(NO 200 ppm NH₃ 300 ppm SO₂ 1000 ppm
 O₂ 1.5% H₂O 10% 3mm pellet)

Figure 3-20 Decrease in Catalytic Activity of TiO₂-Metal Oxide Catalysts at 250°C. (4)



(NO 200 ppm NH₃ 300 ppm SO₂ 1000 ppm O₂ 1.5% H₂O 10% 3mm pellet)

Figure 3-21 Decrease in Activity of TiO₂-MoO-V₂O₅ Catalyst at 250°C. (4)

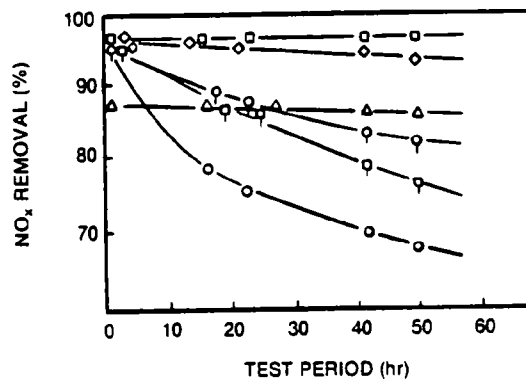
Figures 3-21 and 3-22 show the results of tests performed on the $\text{TiO}_2\text{-MoO}_3\text{-V}_2\text{O}_5$ catalysts at 250° and 200°C, respectively. A more noticeable decrease in catalytic activity occurred at 200°C than at 250°C. A catalyst with an Mo:V ratio of 95:5 exhibited only a slight decrease in activity during a 50 hour test period at 200°C, as well as during 100 hours at 250°C.

Figure 3-23 shows the decrease in catalytic activity which occurs when the catalyst is used with a gas containing 200 ppm SO_2 and 50 ppm SO_3 . This decrease was considerably smaller than that with gas containing 1000 ppm SO_2 without SO_3 , as shown in Figure 3-21. These results indicate that a considerable portion of SO_2 is converted to SO_3 on the catalyst surface.

Table 3-4 shows the properties and chemical composition of $\text{TiO}_2\text{-V}_2\text{O}_5\text{-MoO}_3$ catalysts before and after use at 250°C for 100 hours and 200°C for 50 hours. With use, NH_4 and SO_4 deposited on the catalysts, lowering the surface area and decreasing the pore volume. Both the deposition and the lowered activity occurred to a greater degree with the catalyst that contained more vanadium. The NH_4/SO_4 weight ratio ranged from 0.12 to 0.25 and the NH_4/SO_4 mole ratio from 0.6 to 1.33, indicating that the deposits were mostly ammonium bisulfate (NH_4HSO_4).

3.3.3 Use of Heating to Recover Catalytic Activity

The activity of TiO_2 -based catalysts can be restored by heating them to 400-450°C. In one series of tests, a catalyst contaminated with ammonium bisulfate was heated for three hours at 400°, 430°, 450° and 470°C and then again used for SCR at 200°, 250° and 300°C (Figure 3-24). The activity of the catalyst heated at 450° and 470°C was almost equal to that of the fresh catalyst. Figure 3-25 shows that by heating the catalyst at 450°C for three hours, virtually all of the NH_4 and SO_4 were removed and the catalytic activity was restored. Table 3-5 shows that when the used catalyst is heated at 450°C for three hours, both surface area and pore volume increased to approach those of the fresh catalyst.

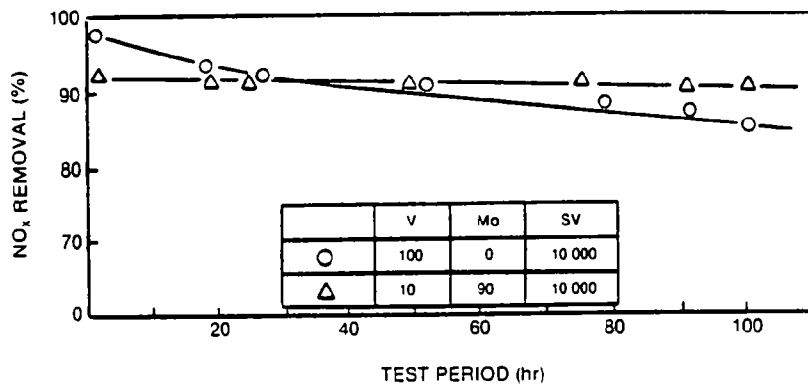


	△	□	◇	○	◻	○
Mo	100	95	90	50	10	0
V	0	5	10	50	90	100
SV	3000	3000	4000	6000	6000	6000

(NO 200 ppm, NH₃ 300 ppm, SO₂ 1000 ppm,
O₂ 1.5%, H₂O 10%, 3mm pellet)

Figure 3-22 Decrease in Activity of TiO₂-MoO-V₂O₅ Catalyst at 200°C. (4)

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(NO_x 200 ppm, NH₃ 300 ppm, SO₂ 200 ppm, SO₃ 50 ppm,
O₂ 1.5%, H₂O 10%, 3mm pellet)

Figure 3-23 Decrease in Activity of TiO₂-MoO-V₂O₅ Catalyst at 250°C. (Gas contains SO₃) (4)

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TABLE 3-4. PROPERTIES AND COMPOSITIONS OF CATALYSTS (FRESH AND USED)

Ratio V:Mo	Reaction Temp. (°C)	Surface Area (m ² /g)	Pore Volume (ml/g)	Chemical Composition		
				NH ₄ (%)	SO ₄ (%)	NH ₄ /SO ₄
100:0	f ^a	31	0.27	-	-	-
	250 ^b	17	0.18	1.3	10.9	0.12
	200 ^c	17	0.19	1.6	10.2	0.16
0:100	f	34	0.25	-	-	-
	250	31	0.25	0.1	0.5	0.20
	200	32	0.26	0.2	0.8	0.25
90:10	f	34	0.28	-	-	-
	250	17	0.23	1.0	7.1	0.14
	200	16	0.20	1.6	8.3	0.19
50:50	f	33	0.29	-	-	-
	250	17	0.25	0.8	4.7	0.17
	200	20	0.23	1.3	5.7	0.23
10:90	f	35	0.30	-	-	-
	250	26	0.29	0.2	1.2	0.17
	200	28	0.28	0.3	1.3	0.23
5:95	f	35	0.30	-	-	-
	250	31	0.29	0.2	0.9	0.22
	200	29	0.27	0.2	0.8	0.25

^aFresh (before use)^bAfter used at 250°C for 100 hours^cAfter used at 200°C for 50 hours

TABLE 3-5. PROPERTIES AND COMPOSITIONS OF CATALYSTS (FRESH, USED, AND HEATED AT 450°C FOR THREE HOURS)

Ratio V:Mo	Type	Surface Area (m ² /g)	Pore Volume (ml/g)	Chemical Composition		
				NH ₄ (%)	SO ₄ (%)	NH ₄ /SO ₄
90:10	Fresh	34	0.28	-	-	-
	Used	20	0.23	0.9	4.3	0.21
	Heated	27	0.30	-	-	-
50:50	Fresh	33	0.29	-	-	-
	Used	20	0.24	0.7	3.2	0.22
	Heated	30	0.30	-	-	-

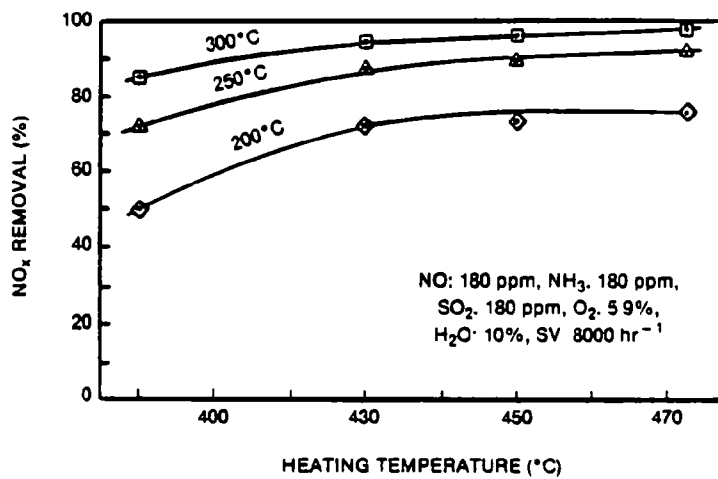


Figure 3-24 Recovery in Activity of Contaminated Catalyst During Three-Hour Heating Period. (9)

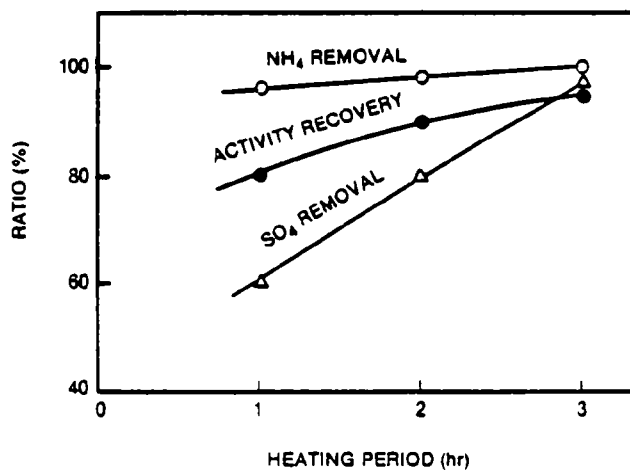


Figure 3-25 Effects of 450°C Thermal Treatment on Catalyst Contaminated with Ammonium Bisulfate. (9)

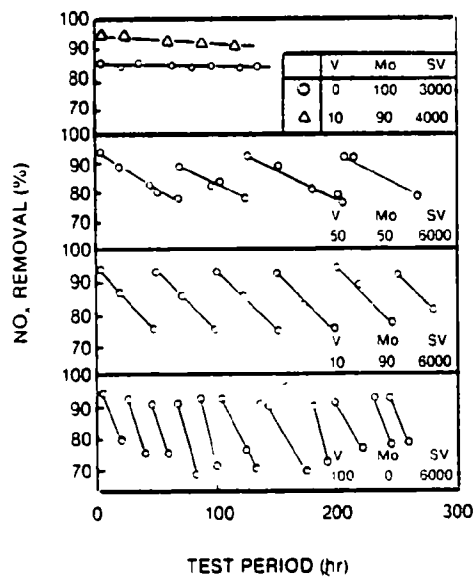
Figure 3-26 shows that the vanadium-rich catalyst is very active initially, but requires frequent heating because of rapid bisulfate deposition. The TiO_2 -Mo catalyst has a low initial activity which did not decrease during 100 hours of use; a catalyst with an Mo:V ratio of 90:10 has a fairly high initial activity which decreased slightly with 100 hours of use.

3.3.4 Alkali Poisoning and Poisoning Countermeasures

When alkali is added to the TiO_2 - V_2O_5 catalyst, the catalyst becomes less active (Figure 3-27). Potassium proved to be even more poisonous to this catalyst than sodium. Figure 3-28 compares the poisoning of various TiO_2 -metal oxide catalysts. Mo and W catalysts showed a considerable amount of poisoning. Figure 3-29 shows the poisoning of TiO_2 -MoO- V_2O_5 catalysts; poisoning was more extensive with a larger Mo:V ratio.

Tests have indicated that alkali compounds present in the contaminated catalysts can be removed with a hot water wash or with aqueous solutions of H_2O_2 and H_2SO_4 . Figure 3-30 shows how washing restores catalytic activity. The TiO_2 - V_2O_5 catalyst's activity is partially restored by a hot water wash and almost completely restored after a wash with aqueous solutions of H_2O_2 and H_2SO_4 . During the same test, the activity of the TiO_2 -MoO catalyst was not restored by the wash. The activity of the TiO_2 - V_2O_5 -MoO catalyst (V:Mo=10:90) recovered well after a wash with a mixed solution of H_2O_2 and H_2SO_4 .

Table 3-6 shows the change in the TiO_2 - V_2O_5 catalyst caused by alkali poisoning and the subsequent washing of the poisoned catalyst with hot water and a mixture of H_2O_2 and H_2SO_4 . After the wash, most of potassium was removed and the pore volume was restored. The V_2O_5 decreased during washing because it is slightly soluble in water and the H_2O_2 and H_2SO_4 solution. For this reason, it may be necessary to add V_2O_5 to the catalyst after it has been washed several times.



(NO_x 200 ppm NH₃ 300 ppm SO₂ 1000 ppm
O₂ 15% H₂O 10% 200°C 3mm pellet)

Figure 3-26 Effect of Thermal Decomposition at 450°C. (4)

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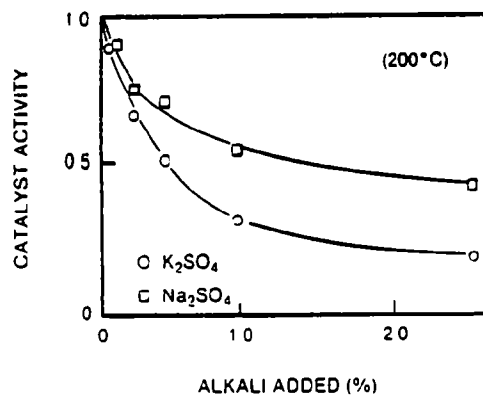


Figure 3-27 Effect of Alkali on TiO₂-V₂O₅ Catalyst (4)

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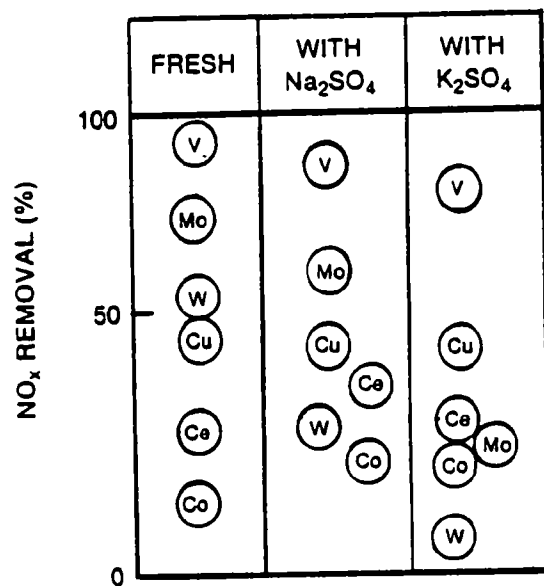


Figure 3-28 Effect of Alkali on TiO₂-Metal Oxide Catalysts.

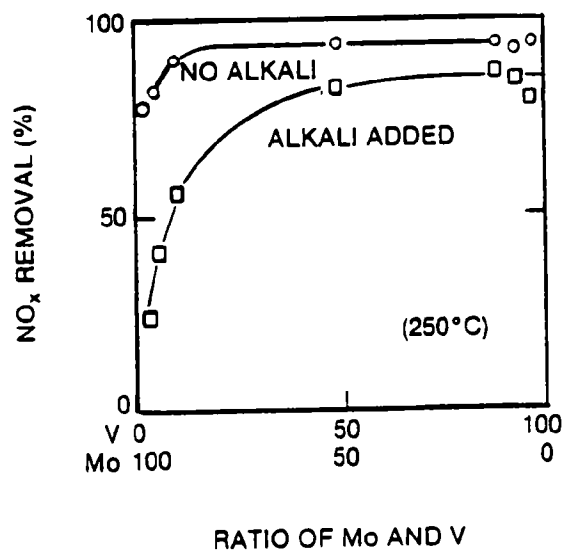


Figure 3-29 Effect of Alkali on TiO₂-MoO-V₂O₅ Catalyst. (4)

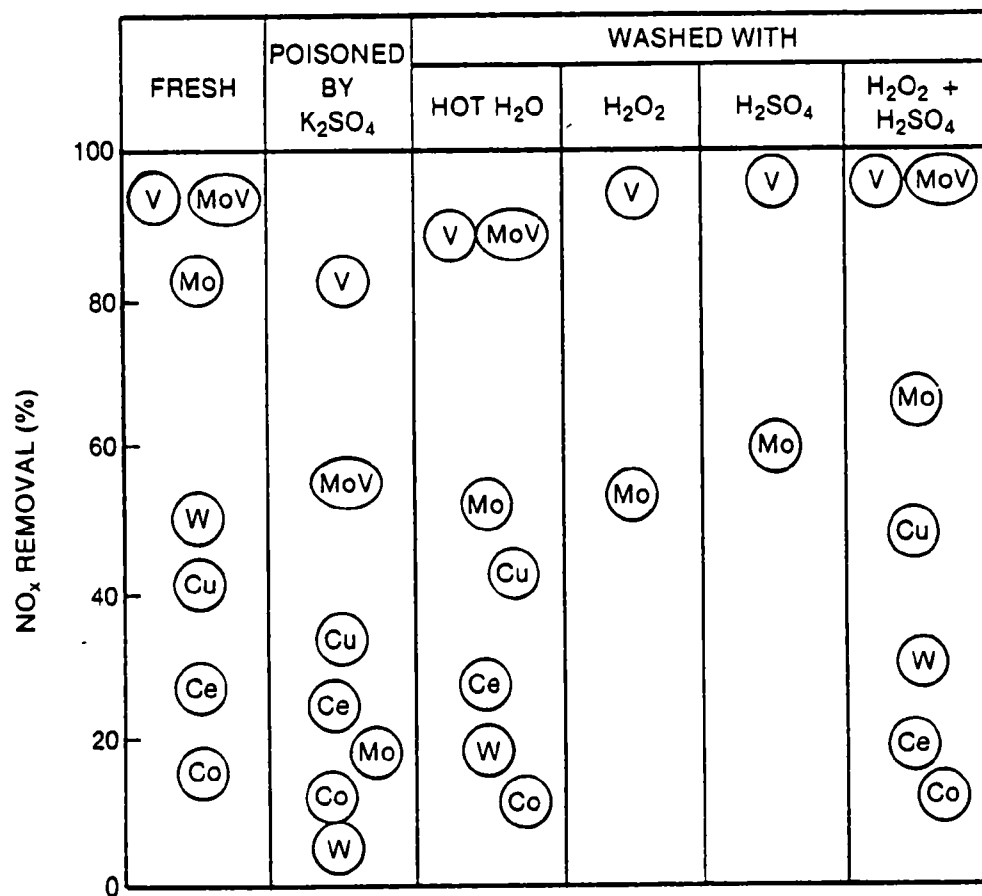


Figure 3-30 K₂SO₄ Poisoning and Recovery of the TiO₂-Based Catalyst.
(MoV indicates Mo:V = 90:10) (4)

70A2721

TABLE 3-6. CHANGES IN THE $\text{TiO}_2\text{-V}_2\text{O}_5$ CATALYST CAUSED BY ALKALI ADDITION AND BY WASHING

	Surface Area (m^2/g)	Pore Volume (ml/g)	V_2O_5 (%)	K_2O (%)
(A) Fresh	31	0.27	4.7	0.03
(B) Alkali added	31	0.25	4.5	0.60
(C) B was washed by hot water	31	0.28	4.1	0.17
(D) B was washed by $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$	30	0.27	4.0	0.10

3.3.5 Summary

The $\text{TiO}_2\text{-V}_2\text{O}_5$ catalyst is active even at low temperatures of 200-250°C. However, ammonium bisulfate readily deposits on the catalyst at these temperatures and reduces catalytic activity due to the oxidation of SO_2 to SO_3 . Frequent heating of the catalyst to 450°C is needed to remove the bisulfate and restore activity. A $\text{TiO}_2\text{-MoO}_3$ catalyst does not have as much of a problem with ammonium bisulfate deposition but is not very active. TiO_2 -based catalysts with MoO_3 and V_2O_5 in a ratio of (90-95):(10-5) may be suitable for low-temperature applications because they are catalytically active and have no problem with bisulfate deposition.

Alkali compounds, particularly those containing potassium, poison the catalysts. This poisoning occurs most seriously at low temperatures. Although the alkali contained in the catalyst can be removed by washing with hot water or aqueous solutions, some V_2O_5 is lost in the wash. This means that more V_2O_5 must be added and the wash liquor must be treated. For these reasons, it may not be appropriate to treat alkali-rich gas with a low-temperature catalyst.

For boilers, the application of SCR to 300-400°C economizer outlet gas may be preferable to using a low-temperature catalyst for the 150-200°C air-

preheater outlet gas. This is true despite the fact that an existing boiler requires considerable modification for application of SCR to the economizer outlet.

For low-temperature gas such as that from coke ovens (200-250°), the use of a low-temperature catalyst is preferable to using a conventional catalyst combined with gas heating to 300-350°C. Although the low-temperature catalyst requires occasional heating up to 400°C, it can save a considerable amount of energy compared with continuous gas heating to 300-350°C.

3.4 CATALYST SHAPE AND REACTOR TYPE

3.4.1 Introduction

Various types of catalysts and reactors have been in commercial use in Japan, as shown in Table 3-7.

Both spherical- and cylindrical-shaped granular catalysts (3-6 mm diameter) have been used with clean gas. Since only the 0.3mm-thick surface layer of the catalyst is effective for catalytic action, smaller catalysts are more efficient. However, since small catalysts are susceptible to dust plugging, ring or ring-tube catalysts, 10-30 mm in diameter, have been used with gas containing a small amount of dust such as 20 mg/m³ or less.

A rough calculation indicates that when a gas containing 20 mg/m³ of dust is sent through a catalyst bed for ten hours at an SV of 5,000 hr⁻¹, the volume of the dust in the gas is approximately equal to the volume in the catalyst.

TABLE 3-7. SCR CATALYSTS AND REACTORS SUITABLE FOR VARIOUS GASES

Gas Type	Fuel (Gas Source)	Dust (g/Nm ³)	Catalyst Shape	Reactor Type
Clean	Natural gas Kerosene Naphtha	Below 0.02	Granule, Ring	Fixed bed
Semi- Dirty	Heavy oil Coal with hot ESP ^b	0.02-0.2	Granule, Ring Honeycomb, Plate	Moving bed Fixed bed ^a
Dirty (dusty)	Coal	15-25	Granule (in elements) Tube, Plate, Honeycomb	Parallel passage ^a Fixed bed ^a
Very dirty ^c	Glass furnace, cement kiln sintering machine		Granule	Moving bed

^aParallel flow type.

^bElectrostatic precipitator.

^cContaining vapor of alkaline compounds which deposit on the catalyst.

Dusty gas can be treated either with a moving bed or a parallel flow reactor. Moving bed reactors have been developed by several vendors. The parallel passage reactor was originally developed by Shell for FGD and later modified by JGC Corp. for SCR. These reactors were first applied commercially several years ago. More recently, parallel flow reactors using parallel flow catalysts with honeycomb, plate and tube configuration have become quite popular. Among the parallel flow catalysts, the honeycomb and plate types have been used most widely.

3.4.2 Moving Bed Reactor

A basic sketch of a moving bed reactor is presented in Figure 3-31. The granular catalyst is charged from the top of the reactor and moves down either intermittently or continuously while the gas is sent through the catalyst

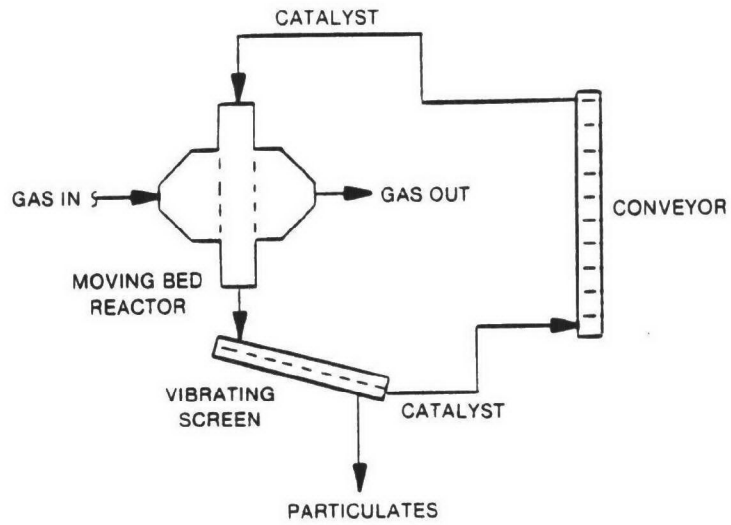


Figure 3-31 Schematic of a Moving Bed Reactor.

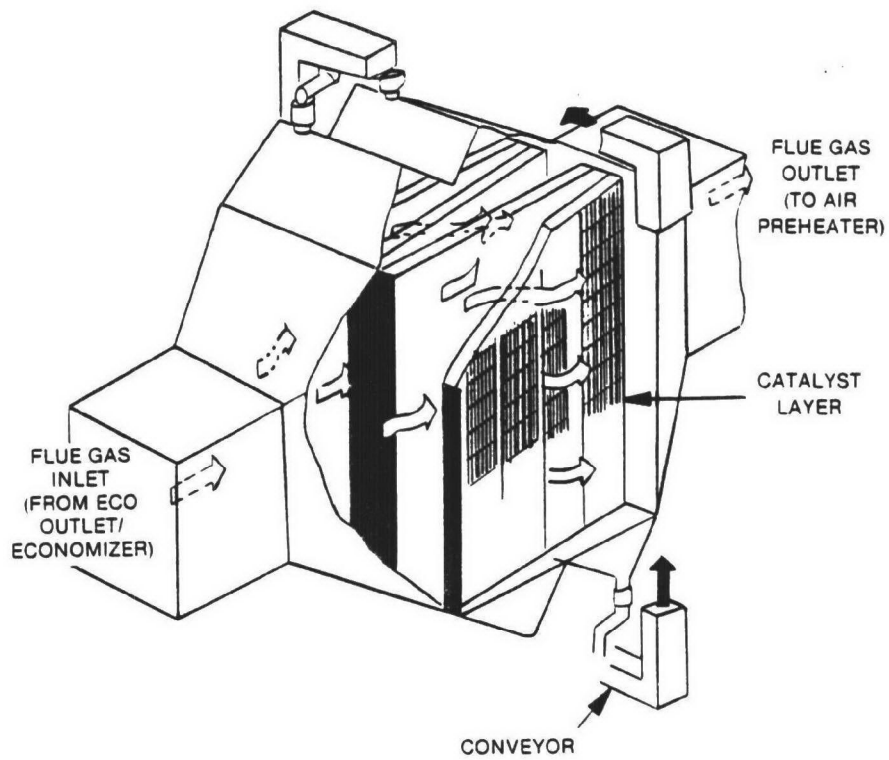


Figure 3-32 Moving Bed Reactor for a Large Amount of Gas. (IHI)

layer in a cross flow (Figure 3-31). The catalyst discharged from the bottom of the reactor is screened to remove dust and returned to the reactor. A larger amount of dust in the gas being heated requires more frequent screening and recycling to keep the pressure drop below a certain level. This results in an increase in power consumption as well as catalyst loss. For practical purposes the dust content of the gas being heated by a moving bed reactor should be no more than 200 mg/Nm³.

Moving bed reactors are best suited to dirty gas, such as that from glass melting furnaces, which contains sodium sulfate vapor. The vapor deposits on the catalyst. These reactors are also appropriate for low temperature gas in which ammonium bisulfate deposits on the catalyst. The contaminated catalyst can be withdrawn from the reactor, cleaned by water washing or heating, and returned to the reactor without interrupting plant operation.

Moving bed reactors have a number of advantages over parallel flow reactors:

- (1) The catalyst can be changed without stopping the operation of the system.
- (2) The catalyst is usually granular and is considerably cheaper than parallel flow catalysts. It also can be packed easily in the reactor.
- (3) The moving bed can remove up to about 70% of the dust in the gas and may be well suited to gases for which 70% dust removal is sufficient to meet regulatory requirements. These gases include those from coke ovens and relatively small oil-fired boilers not equipped with dust removal facilities.
- (4) Moving bed reactors may be suitable for low temperature gas or dirty gas which causes deposition on the catalyst.

On the other hand, moving bed reactors have the following disadvantages:

- (1) The operation of a moving bed reactor is more costly and troublesome than that of a fixed bed reactor. The latter has no moving parts and usually does not require an operator.
- (2) A low gas velocity (0.5-1.5 m/sec) is used to maintain a small pressure drop in the reactor. Therefore, when a large amount of gas is being treated, a special reactor design is needed to obtain a large gas flow area and to maintain uniform gas flow and movement of the catalyst (Figure 3-32).
- (3) The reactor cannot easily treat gases containing more than 200 mg/Nm³ of particulates.
- (4) Attrition of the catalyst tends to occur.

Moving bed reactors have been used in many pilot plants and commercially as well. They also have been used at prototype plants to treat dirty gas from glass melting furnaces and low temperature gas from coke ovens (Table 3-8). For oil- and coal-fired boilers, parallel flow reactors have become more popular since they now have a longer life cycle.

3.4.3 Parallel Flow Reactors

Various parallel flow catalysts, including honeycomb, plate, and tube types, have been developed (Figure 3-33). These 50-100 centimeter-long catalysts are placed in containers, transported to the reactor site, and installed as shown in Figure 3-34.

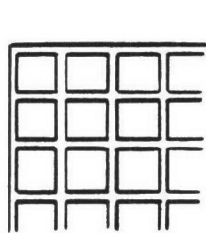
For parallel flow catalysts, "area velocity" (AV) is often used in place of SV (space velocity). It is defined as:

$$AV = \frac{\text{Volume of gas treated (Nm}^3\text{/hr)}}{\text{Apparent surface area of catalyst (m}^2\text{)}}$$

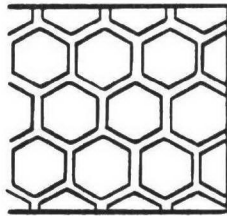
TABLE 3-8. SCR PLANTS USING A MOVING BED REACTOR

Process Developer	User	Plant Site	Gas Source	Fuel	Capacity (Nm ³ /hr)	Completion
Kurabo	Kurabo	Hirakata	Boiler	HO ^a	30,000	1975
Asahi Glass	Asahi Glass	Keihin	Furnace	HO	70,000	1976
J.G.C. Corp.	Catalyst & Chemicals	Wakamatsu	Furnace	HO	10,000	1976
Mitsubishi H.I.	Sumitomo Chemical	Sodegaura	Boiler	HO	350,000	1976
Hitachi Ltd.	Kawatetsu Chemical	Chiba	Coke Oven	COG ^b	500,000	1976
Hitachi Ltd.	Chiyoda Kenzai	Kaizuka	Boiler	HO	15,000	1977
Hitachi Ltd.	Nisshin Steel	Amagasaki	Boiler	HO	19,000	1977
Hitachi Ltd.	Nippon Oil & Fats	Amagasaki	Boiler	HO	20,000	1978
Kobe Steel	Kansai N.K.	Amagasaki	Coke Oven	COG	104,000	1977

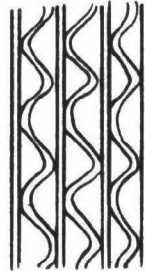
^aHeavy oil^bCoke oven gas



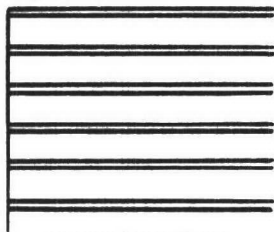
A: HONEYCOMB
(CERAMIC)
(SQUARE)



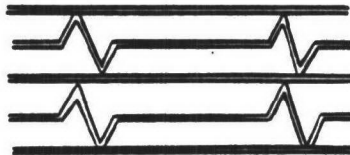
B: HONEYCOMB
(CERAMIC)
(HEXAGONAL)



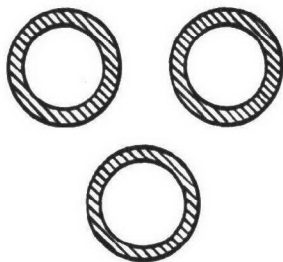
C: HONEYCOMB
(METAL)
(WAVE TYPE)



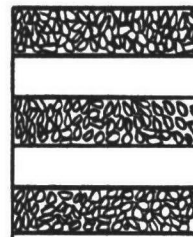
D: PLATE (METAL)



E: MODIFIED PLATE (METAL)



F: TUBE (CERAMIC)



G: PARALLEL PASSAGE

Figure 3-33 Cross-Sections of Parallel Flow Catalysts. (actual size)

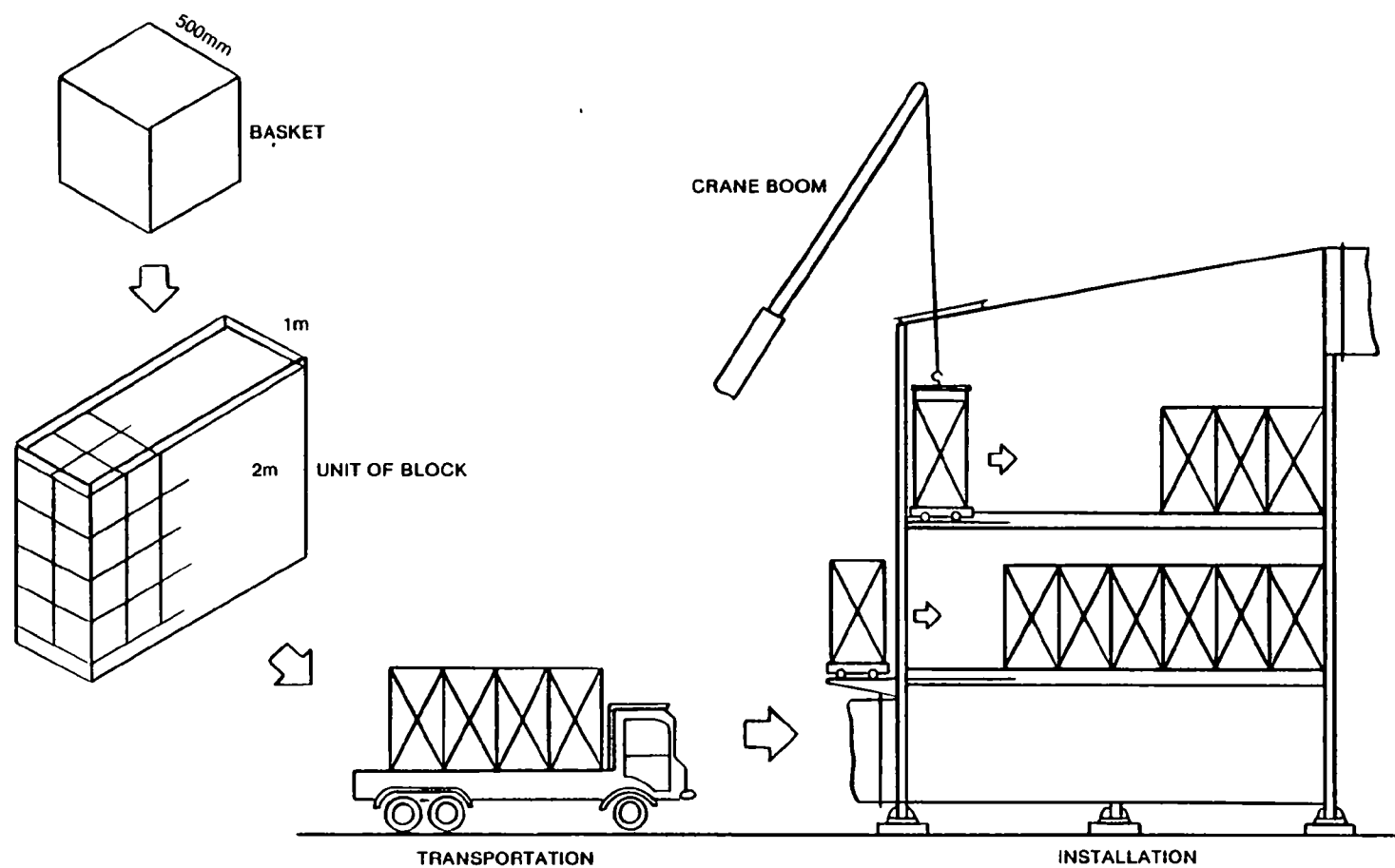


Figure 3-34 Installation of the Catalyst (Hitachi Ltd)

Apparent surface area is the surface area assuming that the catalyst surface is smooth, without pores. Examples of the relationship between AV and SV for a square honeycomb catalyst are shown in Table 3-9.


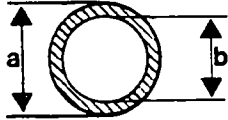
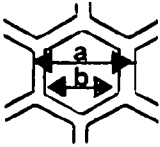
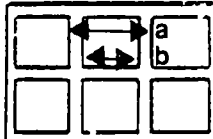
TABLE 3-9. AV AND SV OF SQUARE HONEYCOMB CATALYST

Channel Diameter (mm)	Wall Thickness (mm)	AV (m/hr)	SV (hr ⁻¹)
5	1	5	2,800
		10	5,600
7	1.5	5	1,900
		10	3,800
10	2	5	1,400
		10	2,800

Since the catalytic action occurs on a thin surface layer of the catalyst, a thinner catalyst is more efficient than a thicker one (Table 3-10). Recent technology improvements have made it possible to produce honeycomb and plate catalysts with a thin wall, 0.6-1 mm thick (10). This has resulted in the widespread use of these catalysts, especially for utility boilers (Table 4-1). By comparison, a tube catalyst (Figure 3-33, F) with a length of 100 cm must be more than 2.5 mm thick to have sufficient mechanical strength; it is also a less efficient catalyst. Tube catalysts have been tested with gas containing a large amount of dust, such as the gas from a coal-fired boiler which tends to erode the catalyst.

Another type of parallel flow reactor originally developed by Shell is the parallel passage reactor (Figure 3-33, G). This reactor uses a small catalyst, about 1 mm in diameter and 2-3 mm in length, packed in a 7-8 mm-thick envelope made of steel gauze. The envelopes are placed in parallel in a container with a clearance of 7-9 mm. The catalyst does not need much mechanical strength and thus a very active catalyst can be used. However, inside the envelope, the catalyst may not work as efficiently as it would on the outside surface.

TABLE 3-10. SPECIFIC SURFACE AREA OF CATALYSTS

Dimension (mm)		Specific Surface Area (m^2/m^3)	
		Surface Area ^a Catalyst Volume ^b	Surface Area Packed Volume
Granule (Sphere)			
	Diameter		
	4	1500	1100
	6	1000	740
	8	750	555
	10	600	444
Tube ^c			
	<u>a</u> <u>b</u>		
	10 7	1350	405
	15 10.5	900	270
	20 14	677	203
	25 17.5	543	163
	33 23.1	410	124
Honeycomb			
	<u>a</u> <u>b</u>		
	9 7	1866	437
	10 7	1204	387
	14 10	908	278
	20 14	602	193
	<u>a</u> <u>b</u>		
	7 5	1819	556
	10 7	1204	388
	14 10	909	277
	20 14	601	194
Parallel Plate			
	Thickness Clearance		
	1 5	2000	320
	1 8	2000	220
	8 8	250	125
	10 12	200	91

^a Apparent surface area.^b True volume of catalyst assuming that it has no pores.^c Optimum separate packing.

3.4.4 Honeycomb and Plate Catalysts

The composition, production methods, and characteristics of honeycomb and plate catalysts are compared in Table 3-11. The most popular of these catalysts is the solid or molded (C-S) ceramic honeycomb which is produced by kneading, extruding, drying, and calcinating catalyst material such as TiO_2 and V_2O_5 . The production process is simple but requires a large amount of material for the honeycomb's relatively thick walls. The thick walls are needed to maintain sufficient mechanical strength.

TABLE 3-11. HONEYCOMB AND PLATE CATALYSTS

Type	Production Method	Simpliary of Production	Mechanical Strength	Variety of Composition
Ceramic Honeycomb				
C-S	Solid (or molded) type	A	C	A
C-C	Ceramic carrier, coated	B	B	A
C-I	Ceramic carrier, impregnated	B	B	B
Metal Based				
M-C	Metal plate, coated	C	A	A
MG-C	Metal gauze, coated	B	B	A
M-E	Metal plate, etched	B	A	C
A = Superior B = Medium C = Inferior				

The coated ceramic honeycomb (C-C) catalyst has thin walls (0.6-1.2 mm in diameter). To produce the catalyst, a honeycomb substrate (support) with walls 0.3-0.9 mm is formed. The substrate which consists of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) or cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) is then coated with 0.15 mm of catalyst material, dried and calcined again. This coated honeycomb has been produced chiefly by NGK Insulators Co., and Kobe Steel. Compared with solid honeycomb, the coated type uses less catalyst material but has greater mechanical strength and a larger surface area, as shown in Figure 3-35.

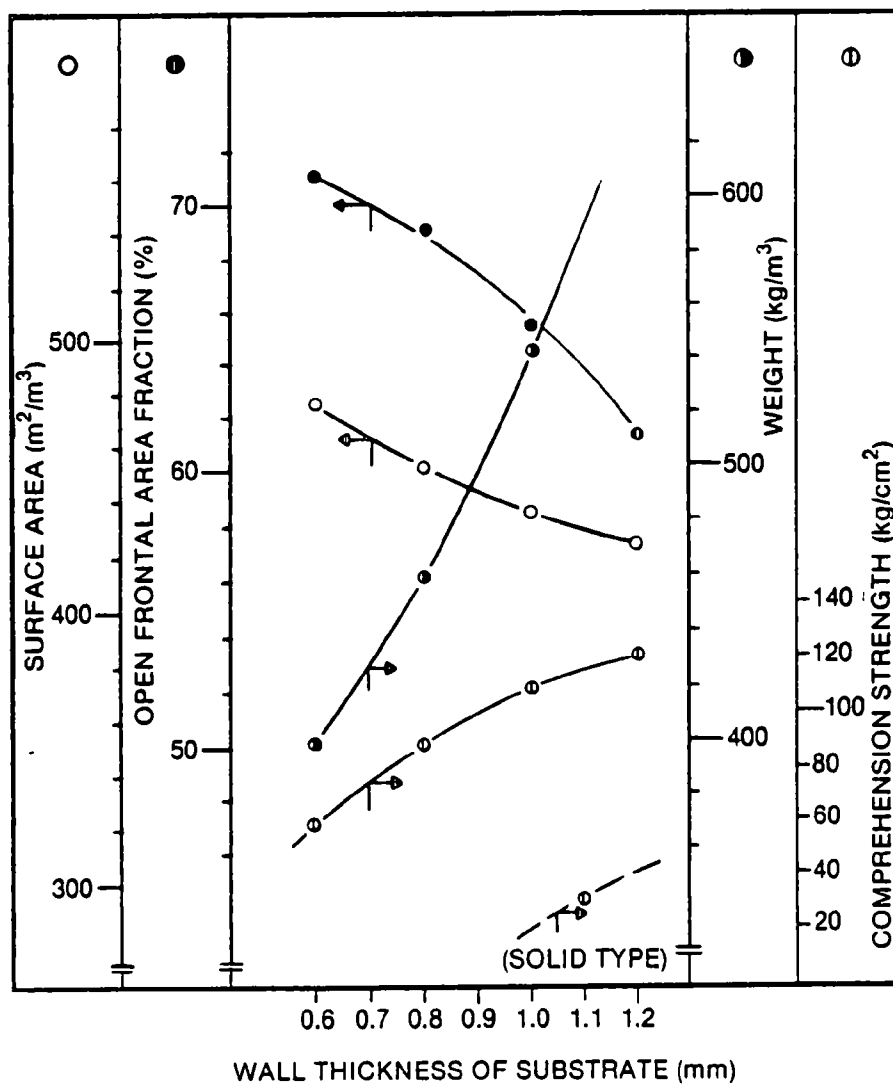


Figure 3-35 Characteristics of Coated Honeycomb Substrate.
(NGK Insulator Co.)

A third type of ceramic honeycomb is produced by impregnating the ceramic substrate with catalyst material. This type is not popular as an SCR catalyst although it has been widely used for automobile exhaust treatment.

There are also plate or honeycomb catalysts which are produced by coating thin metal plates (M-C) or metal gauze (MG-C) with catalyst material. The thickness of the coating and the metal plate (or gauze) is 0.1-0.2 and 0.3-0.5 mm, respectively. The M-E catalyst is made by etching a special type of stainless steel plate (about 1 mm thick) to produce a reactive 0.15 mm thick surface layer. Honeycomb catalysts made with metal plate (M-C and M-E) may have greater mechanical strength than metal gauze-based and ceramic ones. On the other hand, M-C catalysts need a special cementing material to prevent their coating from coming off during thermal and mechanical shocks; M-E is limited by its chemical composition.

The M-C plate has been produced mainly by Hitachi Ltd., which recently also began manufacturing modified plate catalysts as shown in Figure 3-33, E. To make the modified plate, a stainless steel plate is processed to form wire netting. The netting is treated chemically to prevent SO₂ corrosion, coated for flexibility and formed in the shape of the air preheater element. The M-E catalyst is produced by Hitachi Zosen, which recently began producing the MG-C catalysts as well.

Figure 3-36 shows the gas velocity distribution in each section of a channel of plate and honeycomb type catalysts. The velocity is higher at the center and lower near the wall; it is particularly low in the small-angled corners which are susceptible to dust plugging. Since the honeycomb catalyst has many corners, its efficiency is not substantially higher than that of a plate catalyst although honeycomb does have a larger surface area.

Among the types of honeycomb catalysts, the hexagonal variety is superior to the square or wave types because of its larger corner angles (Figure 3-33). However, the mechanical strength of the hexagonal type is less than that of the square.

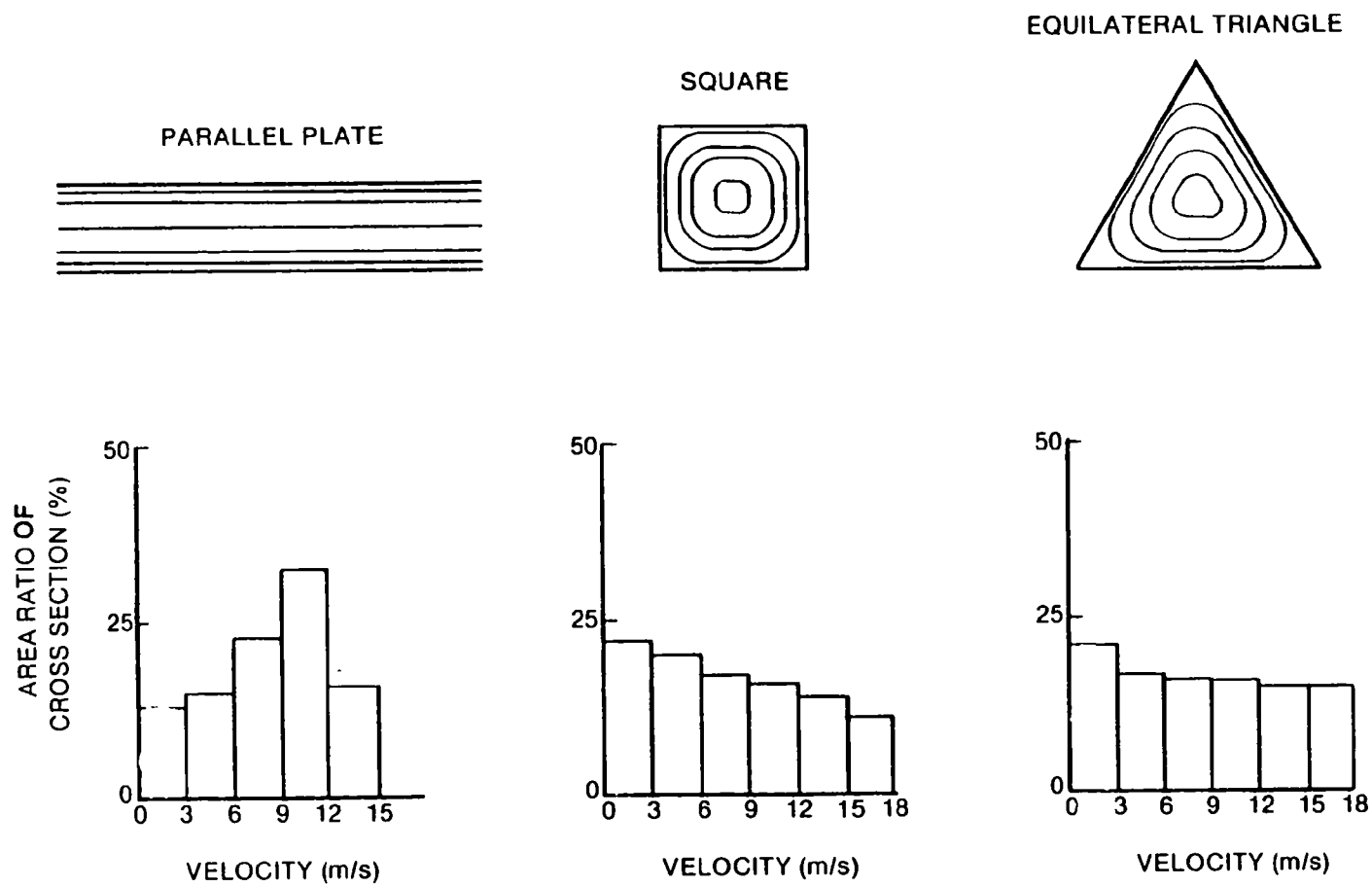


Figure 3-36 Velocity Distribution In Each Section of a Channel of Plate and Honeycomb Catalysts. (Hitachi Ltd.)

3.4.5 Comparison of Catalysts and Reactors

The operation parameters and performance of catalysts and reactors are compared in Tables 3-12 and 3-13. A moving bed reactor has a thin catalyst bed through which a low velocity gas passes in order to minimize pressure drop. Parallel flow reactors have much deeper beds and much higher gas velocities. With parallel flow catalysts, especially those with large channel diameters, a low gas velocity produces a low NO_x removal efficiency due to the laminar flow of the gas. Moreover, particulates tend to adhere to the catalyst at a low gas velocity thereby reducing catalytic activity (Figure 3-37). A high gas velocity causes a turbulent flow, reduces particulate adhesion and increases NO_x removal efficiency (Figure 3-37, B). On the other hand, a high velocity also increases the pressure drop and the catalytic erosion caused by particulates. Therefore, it is best to use a moderate gas velocity with an appropriate channel diameter and bed depth suited to the NO_x removal efficiency required, dust content of the gas, fan capacity, etc.

As shown in Tables 3-12 and 3-13, a moving bed reactor can have a larger SV than a parallel flow reactor. The moving bed reactors have not been widely used because of their higher pressure drop and the possibility of mechanical problems including catalyst attrition. Parallel flow reactors have no moving parts and this allows unattended operation. Both honeycomb and plate catalysts with thin walls are most commonly used because of their high efficiency and low pressure drop.

A particular catalyst and reactor should be chosen according to the composition of the gas to be cleaned, nature of the dust, desired NO_x removal efficiency, catalyst life, and other factors.

TABLE 3-12. COMPARISON OF CATALYSTS AND REACTORS^a

	Moving bed	Ceramic Molded	Honeycomb Coated	Honeycomb or Plate Metal Base	Tube	Parallel Passage
Catalyst size (mm)						
Diameter	5-7					
Wall thickness		1-2	0.6-1.2	0.5-1	3-5	7-9 ^e
Channel diameter		5-8	4-8	4-8	15-30	7-9
Gas Velocity (m/sec) ^b	0.5-1.5	3-7	3-7	3-7	5-10	5-10
Bed depth (m)	0.3-0.6	1.5-3.5	1.2-3	1.2-3	3-5	3-5
SV (1000 hr ⁻¹) ^c	5-8	3-6	3.5-7	3.5-7	2-4	2.5-5
Pressure drop (mm H ₂ O) ^d	50-90	20-60	15-50	15-40	50-90	50-90

^a80-85% NO_x removal with an NH₃/NO_x mole ratio of 0.85-0.9 at 350-400°C for dirty gas. (SO_x: 200-2000 ppm. Particulates: 0.02-0.2 g/Nm³ for moving bed and 0.02-20 g/Nm³ for others.)

^bVelocity at 350-400°C in open column (superficial velocity)

^cGas volume (Nm³/hr)/catalyst volume (m³)

^dBy catalyst bed

^eThickness of envelope

TABLE 3-13. TYPICAL EXAMPLES OF SCR FOR BOILER FLUE GASES (350°C, Leak NH₃ 5-10 ppm)

Fuel	Dust (g/Nm ³)	Inlet NO _x (ppm)	NO _x Removal (%)	NH ₃ /NO _x mole ^x Ratio	Granular Catalyst			Honeycomb Catalyst ^d			
					Diameter (mm)	SV (hr ⁻¹)	Pressure Drop (mm H ₂ O) ^e	Channel Diameter (mm)	Wall Thickness (mm)	SV (hr ⁻¹)	Pressure Drop (mm H ₂ O) ^f
Gas	0-0.01	100	80	0.90	5 ^d	18,000	50	5	1.2	9,500	30
			90	1.00	5 ^d	13,500	65	5	1.2	7,000	40
Oil (lows)	0.01-0.05	100	80	0.90	5 ^e	11,000	70	6	1.4	5,300	40
			90	1.00	5 ^e	8,000	85	6	1.4	3,800	50
		200	80	0.86	5 ^e	9,000	80	6	1.4	4,700	45
			90	0.96	5 ^e	6,500	95	6	1.4	3,300	55
Oil (highs)	0.05-0.2	200	80	0.86	5 ^f	7,000	90	7	1.6	3,600	50
			90	0.96	5 ^f	5,000	105	7	1.6	2,500	60
Coal ^a	0.05-0.2	300	80	0.85	5 ^f	6,500	95	7	1.6	3,300	50
			90	0.95	5 ^f	4,500	110	7	1.6	2,200	60
Coal ^a	15-25	300	80	0.85	Not feasible			8	1.8	2,700	55
			90	0.95				8	1.8	1,800	80

^a Flue gas is passed through a hot-side ESP prior to SCR.^b Flue gas with full dust load is treated by SCR.^c Pressure drop through catalyst bed^d Fixed bed^e Intermittent moving bed^f Continuous moving bed

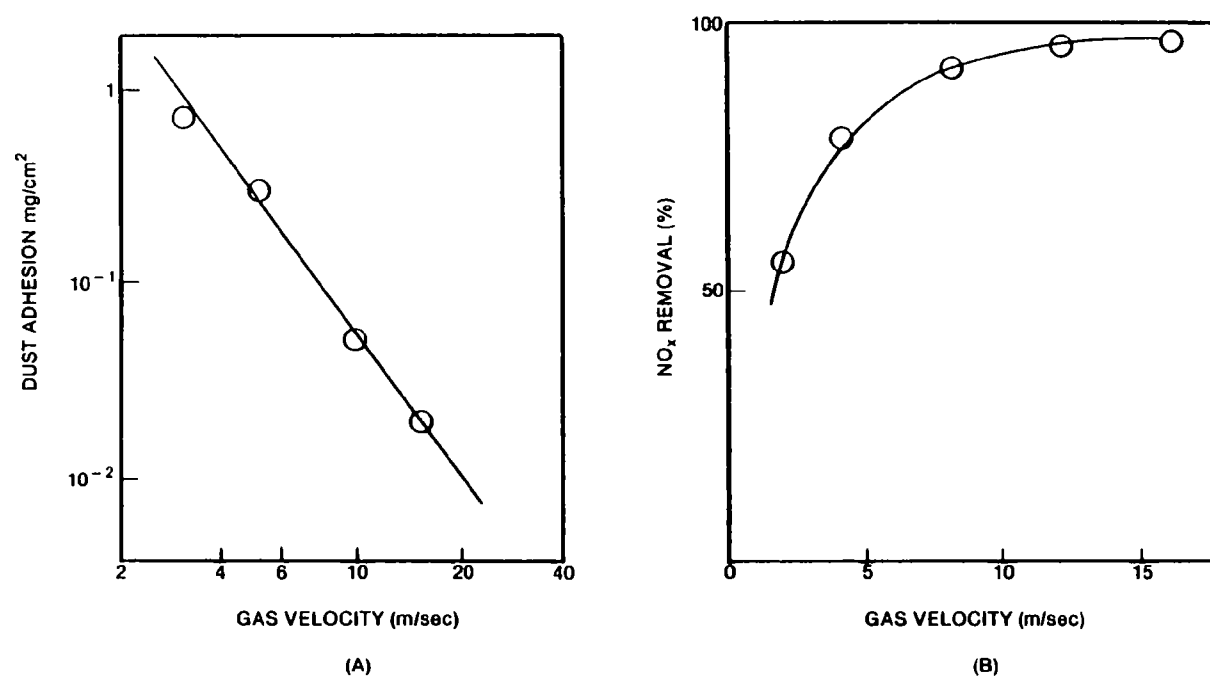


Figure 3-37 Results of a Test Using a Honeycomb Catalyst with Flue Gas Containing 380 mg/Nm³ of Fly Ash.

3.5 PROBLEMS WITH SCR FOR COAL-FIRED BOILERS

3.5.1 Introduction

The application of SCR to flue gas from coal-fired boilers has become more and more important in Japan because of the increase in the number of coal-fired boilers and the relatively high NO_x concentration in their flue gas --- 200-400 ppm (depending on coal and furnace types) even with advanced combustion modification. Table 3-14 lists commercial SCR plants for coal-fired boilers.

SCR for coal-fired boiler flue gas has had the following problems:

- (1) When coal-fired utility boilers use pulverized coal, the flue gas contains 15-25 g/ Nm^3 of fly ash. This fly ash is made up of hard spherical particles (1-30 microns in diameter) which erode the catalysts.
- (2) Adhesion of the fly ash to the catalyst causes a decrease in catalytic activity as well as plugging of the catalyst.
- (3) A low-oxidation catalyst may be needed because the flue gas is usually rich in SO_2 .
- (4) The fly ash may become contaminated by ammonium compounds which may present problems with the utilization and disposal of the ash (Section 3.7.2).

There are two SCR systems available for the treatment of flue gas--- high-dust and low-dust, as shown in Figure 3-38. In the high-dust system, economizer outlet gas with a full dust load is passed through an SCR reactor, air preheater, and then a cold-side electrostatic precipitator (cold ESP) or baghouse. In the low-dust system, the economizer outlet gas is first treated with a hot-side ESP (hot ESP) to reduce the dust content to 50-200 mg/ Nm^3

TABLE 3-14. COMMERCIAL SCR PLANTS FOR COAL-FIRED BOILERS IN JAPAN

Power Company	Power Station	Capacity (Nw)	N/R	Manufac-turer	Catalyst	Year of Completion	High Dust or Low Dust	NO _x Removal % (Design)
Chugoku Electric	Shimonoseki	175	R ^a	MHI ^c	II ^g	1980	High	55 ^k
"	Shin Ube	75	R	MHI	II	1982	High	65 ^k
"	Shin Ube	75	R	MHI	II	1982	High	65 ^k
"	Shin Ube	156	R	MHI	II ^h	1982	High	65 ^k
"	Nizushima	125	R	BHI	P ^h	1984	High	65 ^k
"	Nizushima	156	R	BHI	P	1984	High	65 ^k
Electric Power D.C.	Takehara	250 x 1/2	R	BHI	P	1981	Low	80
"	Takehara	250 x 1/2	R ^b	KHI ^c	T ¹	1981	Low	80
"	Takehara	700	N ^d	BHI	P	1983	Low	80
Hokkaido Electric	Tomato	350 x 1/4	N	BHI	P	1980	Low	80
Joban Kyodo Electric	Nakoso	600	N	MHI ^f	II	1982	High	80
"	"	600	N	MHI	II	1983	High	80
Kyushu Electric	Minato	156	R	MHI	II	1983	High	50 ^k
Tohoku Electric	Sendai	175	R	BHI	P	1982	High	56 ^k
Tohoku Electric	Sendai	175	R	BHI	P	1982	High	56 ^k

^a Retrofit^b New^c Mitsubishi Heavy Industries^d Babcock Hitachi^e Kawasaki Heavy Industries^f Ishikawajima-Harima Heavy Industries^g Honeycomb^h Plateⁱ Tube^k Reactor is designed for 80% removal, which is attained by increasing the amount of catalyst

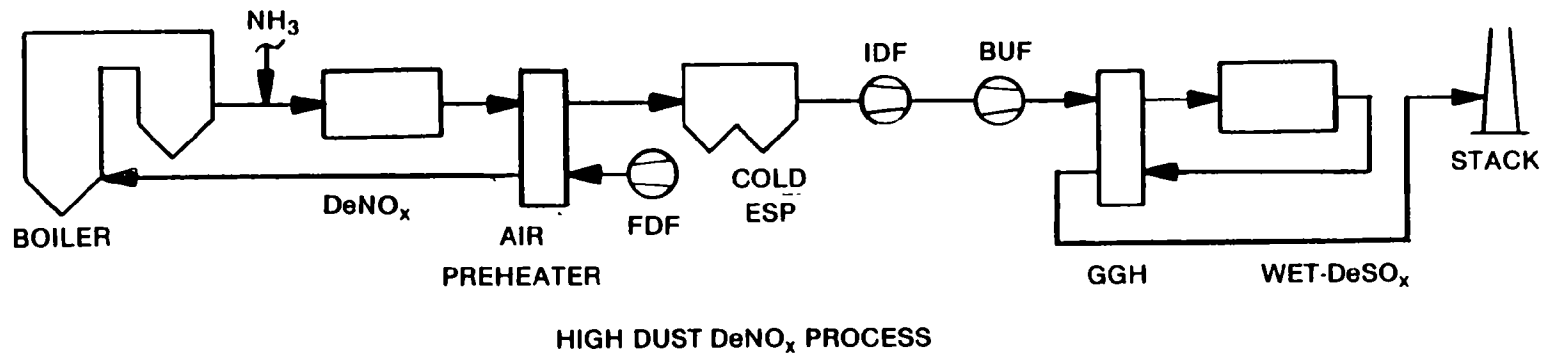
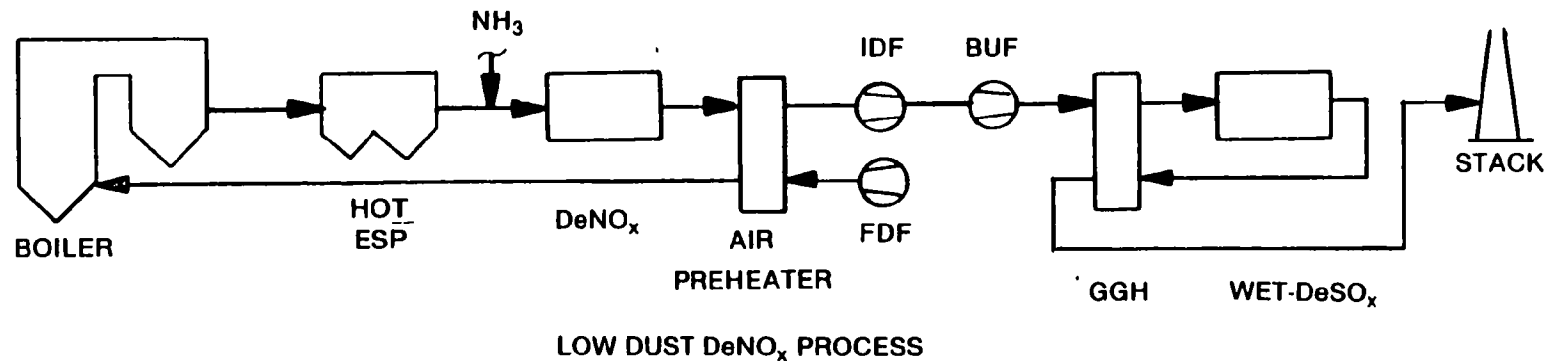


Figure 3-38 Total Flue Gas Treatment Process for Coal-Fired Boilers.

(over 99% removal) and then passed through an SCR reactor and an air preheater.

The advantages and disadvantages of the high-dust and low-dust systems are compared in Table 3-15.

TABLE 3-15. COMPARISON OF HIGH-DUST AND LOW-DUST SCR SYSTEMS FOR COAL

	High-Dust System	Low-Dust System
Catalyst erosion by dust	More	Less
Dust adhesion to catalyst	Less	More
Ammonium bisulfate deposition in air preheater	Less	More
Contamination of fly ash by ammonium compounds	Can be prevented by reducing unreacted NH_3	None
Cost of ESP	Less	More
Nature of ESP	Suitable to medium and high sulfur coals	Suitable to low sulfur coal

With the low-dust system, catalyst erosion does not occur but the dust leaving the hot ESP consists of fine, relatively alkaline ash which tends to adhere to the surface of the catalyst. In addition, ammonium bisulfate deposits tend to form in the air preheater. With the high-dust system the large amount of dust prevents the deposit of bisulfate. On the other hand, fly ash caught by the cold ESP may contain a noticeable amount of ammonium compounds, which can cause problems in utilizing or disposing of the ash. Both high-dust and low-dust systems have been used commercially in Japan (Table 3-15). The high-dust system may prove to have more advantages than the low-dust system if the problem of ammonia contamination of the fly ash can be solved (Section 3.7).

3.5.2 Fly Ash Erosion of the Catalyst

With a parallel flow catalyst, erosion occurs mainly at the gas inlet and, to a lesser degree, on the inside surfaces. Figure 3-39 compares the

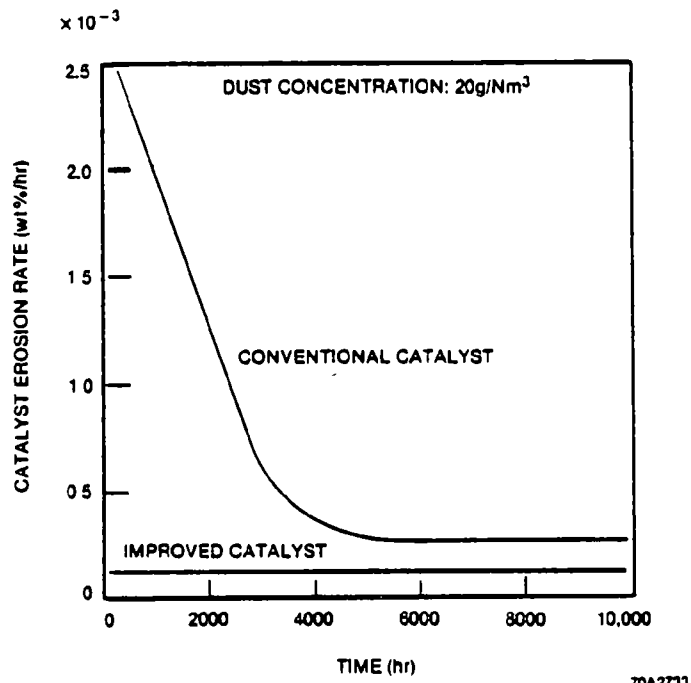


Figure 3-39 Change in Catalyst Erosion Rate with Time. (8)

EXPERIMENTAL EQUATION
 $W = K \cdot V^{2.9} \cdot C^{1.7} \cdot T^{0.84}$

W WEIGHT LOSS OF CATALYST (wt%)
 K CONSTANT
 V GAS VELOCITY (m/s)
 C DUST CONCENTRATION (g/Nm³)
 T OPERATING TIME (hr)

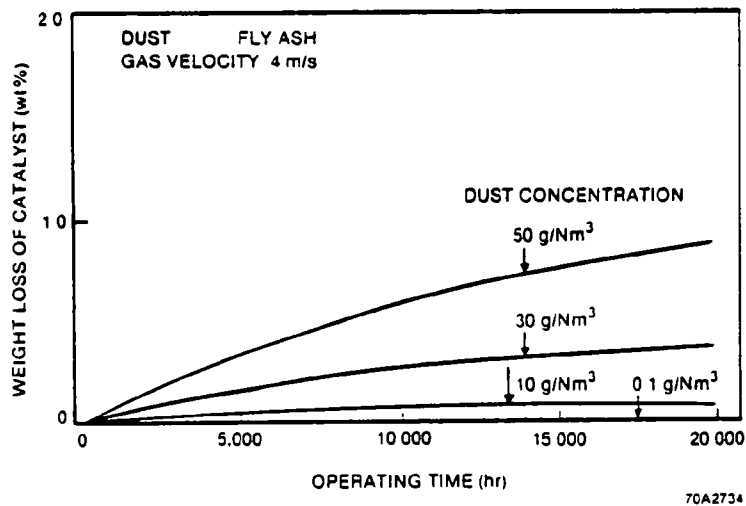


Figure 3-40 Anticipated Weight Loss of Plate Catalyst vs. Operating Time. (2)

erosion rates of conventional and improved tube catalysts (6). With the conventional molded catalyst a substantial amount of erosion occurs at the beginning of operation and then continues slowly. The erosion can be significantly reduced by hardening as much as 1/100 to 1/50 of the length of the inlet portion of the catalyst by impregnation with a certain material (6).

Figure 3-40 shows the weight loss in a metal-based plate catalyst that is caused by fly ash erosion (2). The figure indicates that as far as erosion is concerned, the catalyst may be useful for over 2 years; the weight loss in 20,000 hours is about 0.3% with flue gas containing 30 g/Nm³ of dust at a velocity of 4 m/sec. The figure also shows an empirical equation which explains the relationship between the weight loss and the gas velocity, dust concentration, and operation time. The equation indicates that the weight loss associated with a flue gas (velocity: 6 m/sec) containing 20 g/Nm³ of dust is about 0.5% in 20,000 hours.

Figure 3-41 compares the erosion ratio of different types of honeycomb catalysts (7). A conventional molded catalyst D is most susceptible to erosion, while catalyst C, which contains an impregnated catalyst carrier, undergoes less erosion because of the hardness of the carrier. Catalyst B, which contains erosion-resistant material, undergoes even less erosion. In the case of the improved catalyst B (B and dummy), erosion was eliminated altogether by using a dummy layer which has the same cross section as the catalyst and is placed upstream of it to absorb the impact and act as a flow straightener.

3.5.3 Dust Adhesion and Plugging

Fly ash from pulverized coal usually consists of spherical particles of a hard glassy substance. The particles are generally 1-30 microns in diameter and have fairly smooth surfaces as shown in Figure 3-42. Therefore, the dust adhesion and plugging problem can be eliminated when a flue gas with full dust load is sent down through parallel flow catalysts with a sufficient channel diameter. An excessively high gas velocity can cause the catalyst to erode and a large channel diameter makes the process less efficient. A gas velocity

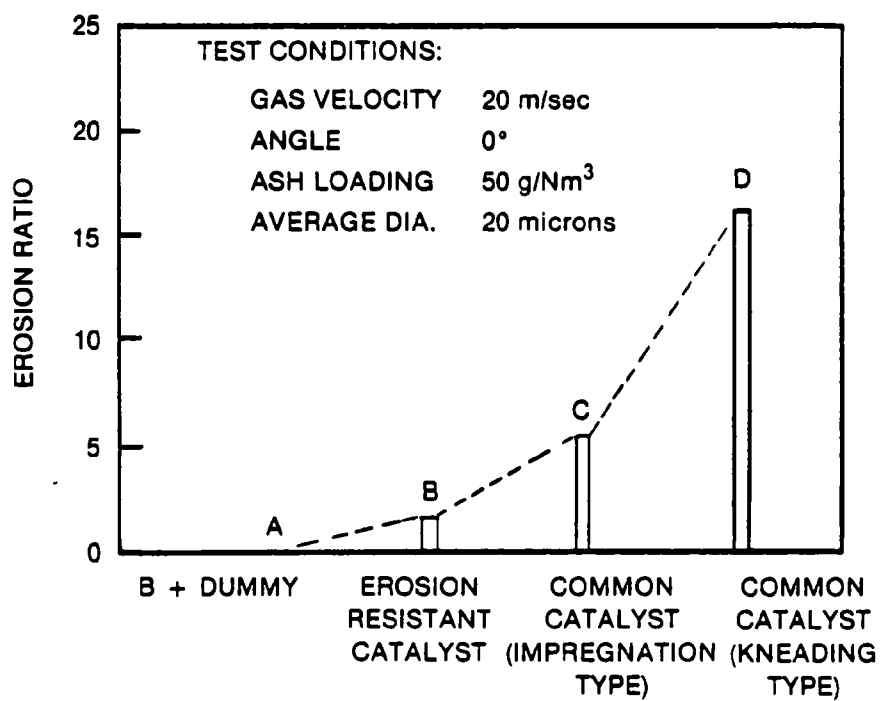
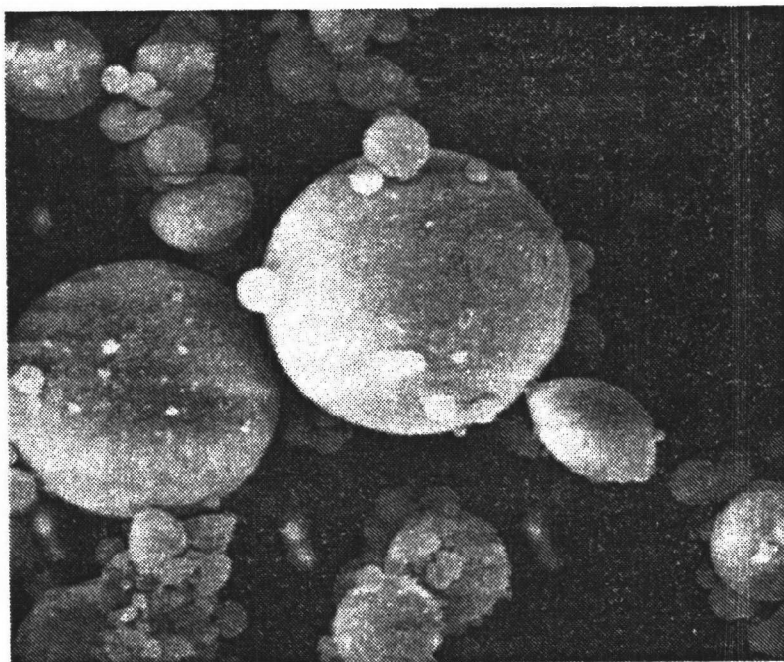
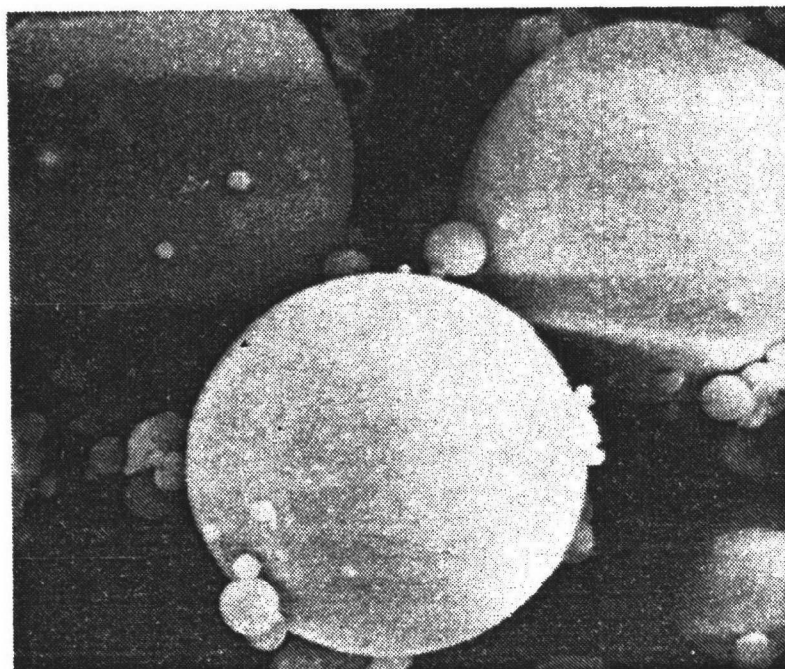


Figure 3-41 Results of Accelerated Erosion Test. (7)



(A) TAKASAGO (MEDIUM-SULFUR COAL)



(B) ISOGO (LOW-SULFUR COAL)

**Figure 3-42 Fly Ash From Coal-Fired Boilers In Japan
(Japanese Coals) (x3000)**



around 5 m/sec and a channel diameter of 5-8 mm for honeycomb, or clearance of 4-7 mm for the plate catalyst, are usually used to eliminate these problems.

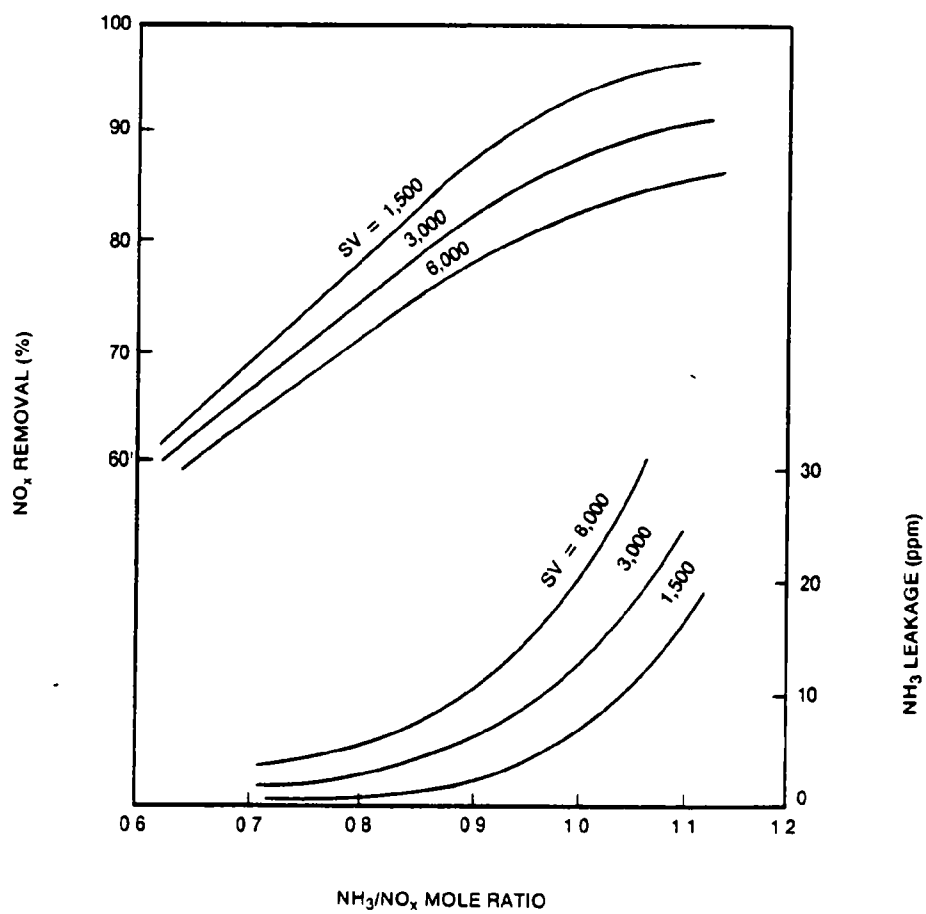
On the other hand, the fly ash leaving a hot ESP consists mainly of smaller particles which are often rich in alkaline components and have a tendency to adhere to the catalyst surface, especially at the gas inlet. Since the amount of ash leaving the hot ESP is not large, the dust adhesion and plugging problem can be eliminated by occasional soot blowing.

The design and operation of SCR plants for coal-fired boilers in Japan have been improved significantly so that there is generally no dust clogging problem with the catalyst, even without soot blowing. The U.S. Environmental Protection Agency (EPA) conducted SCR demonstration tests with Hitachi Zosen's honeycomb catalyst at Georgia Power's Mitchell Pilot Plant. Results of this test showed that the fly ash adhered considerably on the catalyst surface even with soot blowing, resulting in a decrease in NO_x removal efficiency and/or an increase in the pressure drop. Although the adhesibility might be caused by a unique condition at the pilot plant (Section 4.10.3) further studies are needed on the adhesive properties of fly ash with different compositions.

It may not be feasible to use SCR on plants fired with coal if a considerable portion of the alkali compounds are volatilized by combustion. The alkali components may condense on the catalyst and poison it to some extent.

3.5.4 NO_x Removal Efficiency for Flue Gas from Coal

An example of SCR for coal-fired boiler flue gas using a honeycomb catalyst is shown in Figure 3-43. Generally speaking, the amount of catalyst needed for coal-fired boilers is about twice the amount needed for low-sulfur oil-fired boilers with equal power generation capacities. This is true for the following reasons: 1) Flue gas volume is nearly 20% more for coal than for oil given an equal power generation capacity. 2) Because of a higher SO_2 concentration in the coal flue gas, a less active low-oxidation catalyst is needed. 3) Since a large amount of fly ash in coal flue gas tends to cause erosion, the catalyst has to be harder and less active. 4) In order to



(channel diameter 8mm, wall thickness 1.8mm, inlet NO_x 300 ppm,
full dust load, pilot plant test)

Figure 3-43 SCR for Coal-Fired Boiler Flue Gas at 350°C Using Honeycomb Catalyst.

prevent dust plugging, a larger channel diameter is needed (Table 3-13). 5) Higher inlet NO_x concentrations require a larger amount of the catalyst for a given NO_x removal ratio with a given concentration of unreacted NH_3 (Figure 3-4).

In order to prevent the plugging of the air preheater with ammonium bisulfate (Section 3.6), it is necessary to keep unreacted NH_3 below 10 ppm for the high-dust system and below 5 ppm for the low-dust system. For the high-dust system, it may be necessary to maintain the unreacted NH_3 level below 5 ppm in order to eliminate the contamination of fly ash by ammonium compounds.

Figure 3-43 indicates that a 90 percent NO_x removal efficiency with an unreacted NH_3 level below 5 ppm may be attained with the NH_3/NO_x mole ratio of 0.93 and an SV of $1,500 \text{ hr}^{-1}$. When treating a large amount of flue gas from a utility boiler, it may be difficult to attain 90 percent removal with 5 ppm unreacted NH_3 for two reasons. First, the flue gas velocity as well as NO_x concentration is not uniform in each portion of the large inlet duct and reactor, and second, boiler load often fluctuates, resulting in the fluctuation of the gas volume and NO_x concentration. In order to maintain unreacted NH_3 below 5 ppm, an 80-85 percent NO_x removal efficiency may be a practical limit for a large coal-fired boiler.

3.6 AMMONIUM BISULFATE DEPOSITION IN THE AIR PREHEATER

3.6.1 Formation and Behavior of Ammonium Bisulfate

While most problems with SCR already have been solved, the greatest remaining problem is the deposit of ammonium bisulfate in the air preheater or heat exchanger causing plugging and corrosion (Figure 3-44). The problem is significant, not only for SCR but also for selective noncatalytic reduction (SNR or Thermal DeNO_x) as well.

SO_3 , NH_3 , and H_2O present in hot gas combine to form ammonium bisulfate (NH_4HSO_4), on cooling:

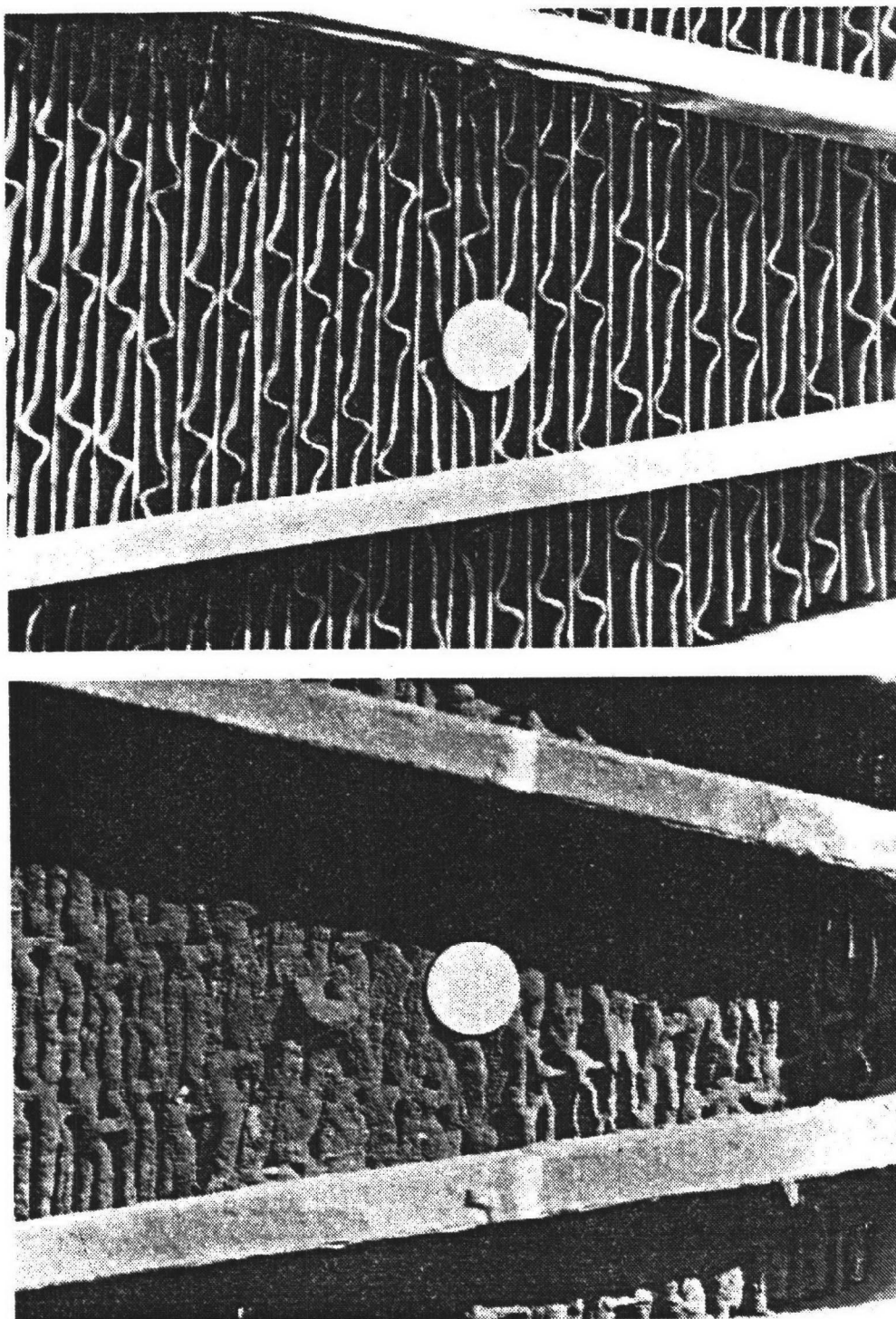
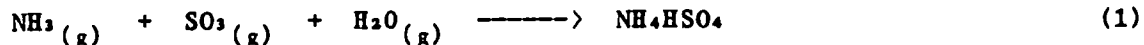


Figure 3-44 **Air Preheater Elements: Clean (Above)**
Plugged (Below)

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The formation temperature is shown in Figure 3-45. Bisulfate will form below approximately 230° C in a gas containing about 10 ppm of both NH₃ and SO₃.

Ammonium bisulfate has a melting point of 147°C (Figure 3-46). Between the formation temperature and the melting point, bisulfate exists as a corrosive melt. Below the melting point, it exists as a very hygroscopic solid. A simple calculation shows that 10 ppm each of SO₃ and NH₃ in gas from a 500 MW boiler could account for the formation of 2 tons/day of bisulfate. This amount is sufficient to cause problems such as plugging and corrosion in an air preheater or heat exchanger. Many problems of this nature have been encountered in a few SCR facilities in Japan. The problem has not been as serious for small boilers and furnaces that discharge flue gas at a temperature above about 230°C. However, for larger boilers and furnaces which require sufficient heat recovery from the flue gas, countermeasures must be taken to eliminate the bisulfate problem.

There is some question about the composition of the substance which first forms. Based on thermodynamic data, it appears that ammonium sulfate, (NH₄)₂SO₄, deposits from NH₃-rich gas. However, the sulfate may not be stable at a high temperature. This author's study indicates that (NH₄)₂H(SO₄)₃, a double salt of (NH₄)₂SO₄ and NH₄HSO₄, forms at a high temperature under the presence of excessive NH₃ (16).

Other studies indicate that when gas containing equal amounts of SO₃ and NH₃, is cooled, mists of sulfuric acid H₂SO₄ form prior to the formation of bisulfate (13). Even though the mists form, they must absorb ammonia immediately, according to the NH₃ concentration. When a hot gas cools, the result may be the formation of mists with varying compositions based on the gas composition. The mists solidify either partly or entirely on further cooling to form a mixture of sulfuric acid and ammonium bisulfate, bisulfate and double salt, or double salt and ammonium sulfate as will be shown in Section 3.6.3.

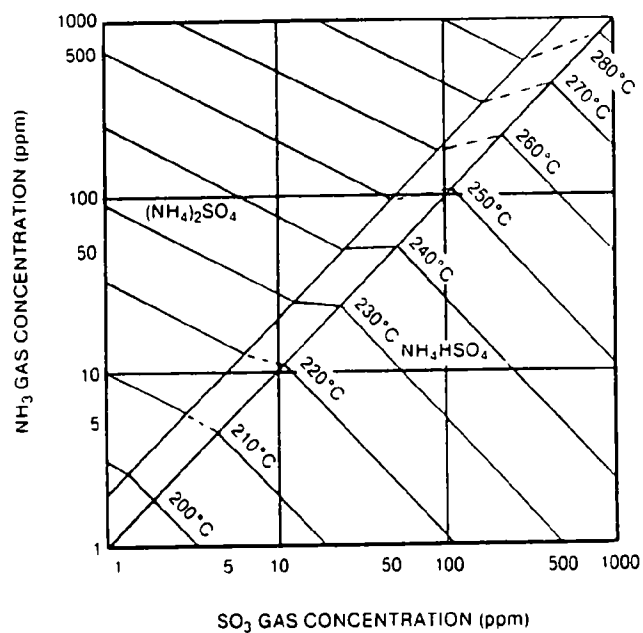


Figure 3 45 Formation Temperature of Ammonium Sulfate and Bisulfate (12)

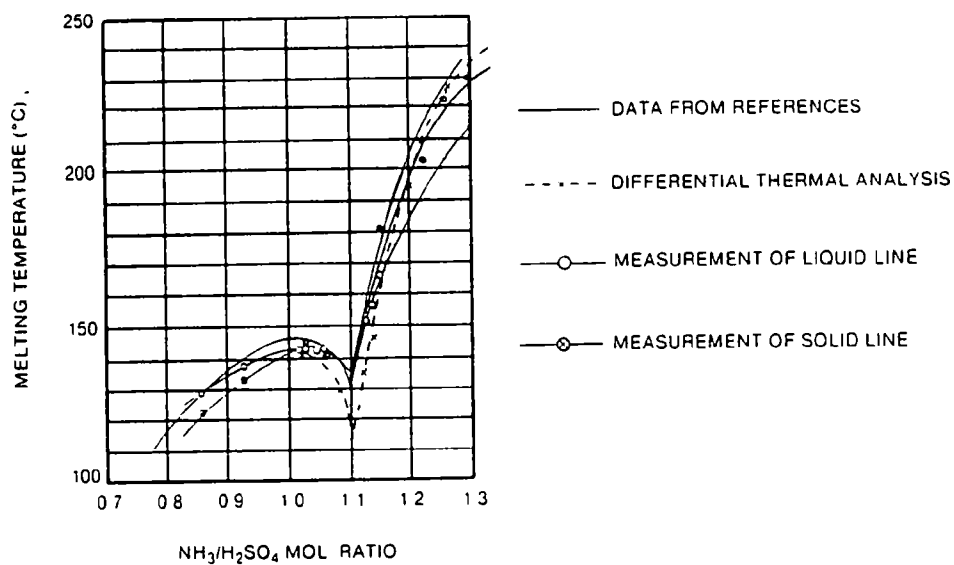


Figure 3 46 Melting Point of NH_3 - H_2SO_4 System (12)

Bisulfate, particularly when combined with sulfuric acid, is highly corrosive and readily reacts with air preheater material and fly ash to form various solid compounds (Sections 3.6.6 and 3.6.7). The reaction products also cause plugging of the air preheater.

It should be noted that although the formation of compounds causes problems, at the same time it helps to reduce SO_3 emissions. Sulfuric acid mists are far more hazardous than SO_2 and yet are not well captured with FGD. Ammonium promotes deposit formation and prevents the emission of SO_3 or sulfuric acid mists.

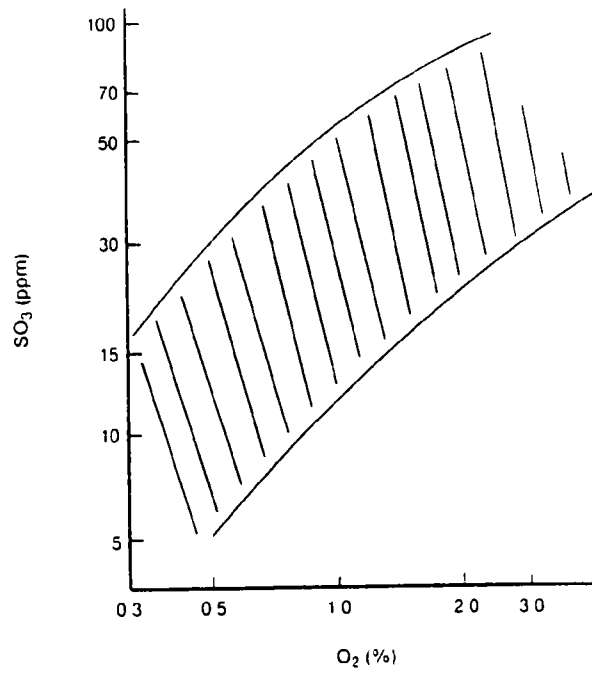
3.6.2 Formation of SO_3

The relationship of SO_3 and O_2 concentrations in flue gas from the combustion of heavy oil is shown in Figure 3-47. The figure indicates that SO_3 increases with an increase in the O_2 concentration in the gas. Therefore, low-oxygen combustion to reduce NO_x also helps to reduce SO_3 . The use of less oxygen, however, tends to increase the particulate content; particulates increase as SO_3 decreases, as shown in Figure 3-48. Usually 1-3 percent of the total SO_x in flue gas from heavy oil is present as SO_3 under good combustion conditions. It has been shown that the SO_3 concentration in gas from coal is lower than that in gas from heavy oil. This is because coal fly ash is a better adsorbent of SO_3 .

The catalyst for selective catalytic reduction of NO_x oxidizes a small portion of SO_2 to SO_3 . The actual oxidation ratio differs with catalyst composition, temperature, and O_2 and NH_3 concentrations (Section 3.2.4). Although catalysts with a low oxidation ratio (below 1%) can be used, a considerable amount of SO_3 still may form in SO_2 -rich gas.

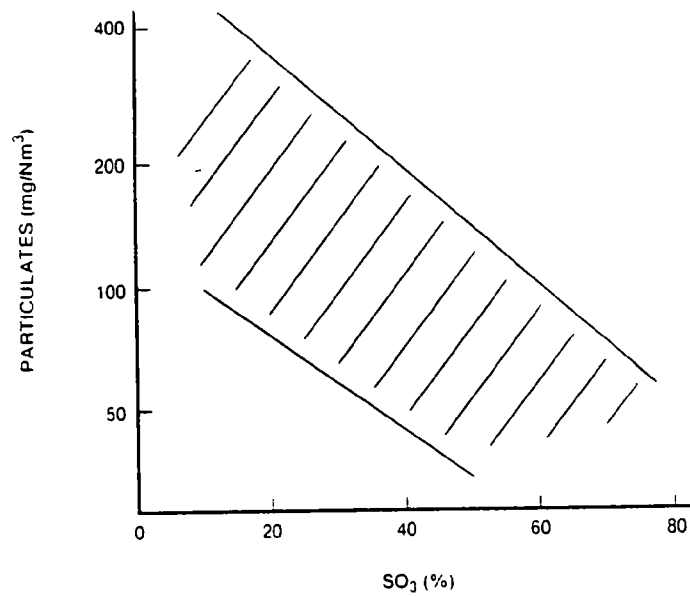
3.6.3 Laboratory Tests on Bisulfate Deposition (12)

Figures 3-49 and 3-50 show an apparatus used to test ammonium bisulfate deposition. Gases containing NH_3 , SO_3 , and H_2O , are preheated and mixed at 400°C , and then sent through connected pyrex glass tubes 9.5 mm in inner



(heavy oil S 1.3%) (14)

Figure 3 47 Relationship of O_2 and SO_3 Concentrations



(heavy oil S 1.3%, O_2 in gas 0.33%) (14)

Figure 3 48 Relationship of SO_3 Concentration to Particulate Content

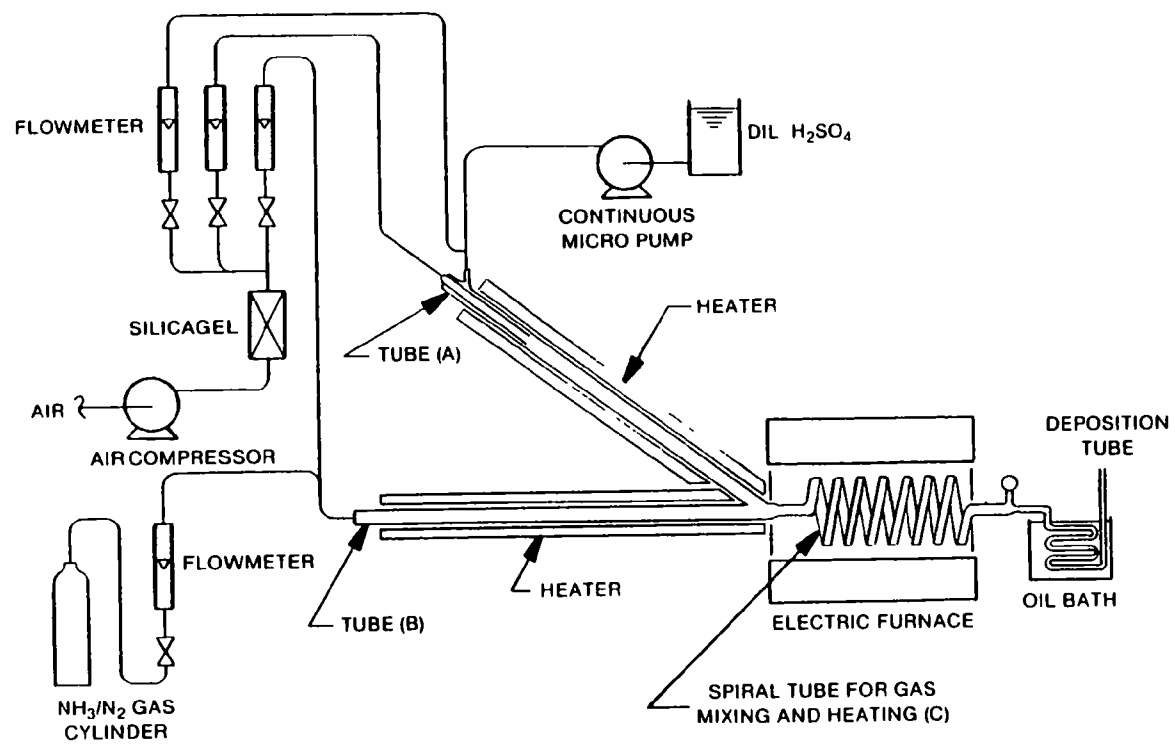


Figure 3-49 Apparatus for Ammonium Bisulfate Deposition Test

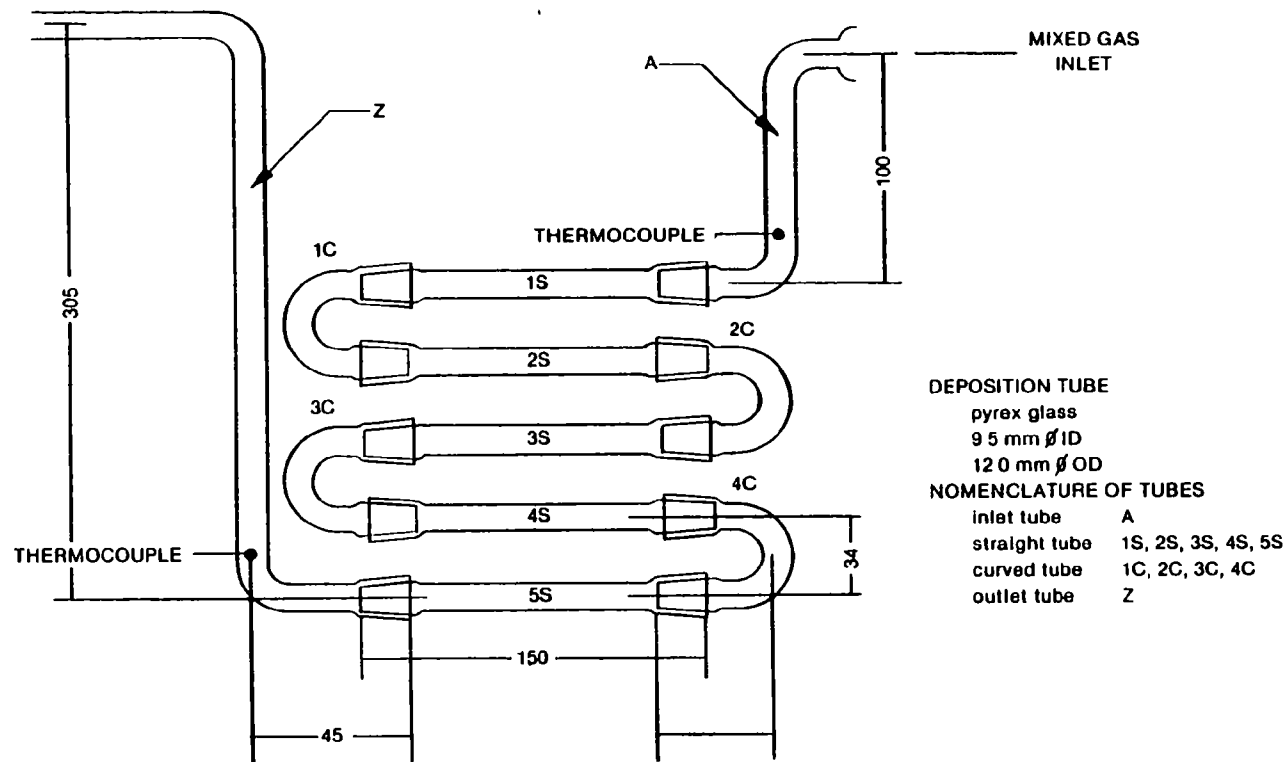


Figure 3-50 Tube Used for Ammonium Bisulfate Deposition Test.

diameter and 1.2 m long. At the end of the test cycle these tubes are submerged in an oil bath kept at different temperatures ranging from 120 to 280°C. After the gas has passed through them for a certain period of time, the tubes are analysed for deposits.

Figure 3-51 shows the deposit ratio of SO₃ and NH₃ when a gas containing 200 ppm each of SO₃ and NH₃ with 10 percent H₂O was sent through the apparatus. A maximum deposit ratio (nearly 100 percent) was obtained at a temperature of 200°C and a velocity of 10 m/sec. It appears that the high gas velocity caused gas turbulence which in turn promoted deposit formation. The deposits were mainly NH₄HSO₄ with a small amount of (NH₄)₂H(SO₄)₂; the NH₃/SO₄ mole ratio was almost 1.1.

Measurement of the deposits formed in each section of the tube at a gas velocity of 6 m/sec revealed that nearly all of the deposits formed within 60 cm of the inlet. This indicates that most of the deposits formed within 0.1 second after being introduced into the glass tube at 120-240°C.

Figure 3-52 shows the NH₃/SO₄ mole ratios of the deposits formed in each section of the tube when gases with different mole ratios were passed through the tube at a temperature of 160°C. Despite differing inlet gas compositions the deposits formed at the inlet of the tube had ratios of about 1.1; the ratios of deposits formed downstream were closer to that of the inlet gas. Figure 3-53 indicates that the deposit ratio was the highest when the NH₃/SO₃ mole ratio of the gas was around 1.1. The low melting point at the 1:1 ratio (Figure 3-46) may favor deposit formation. Figure 3-54 shows that the deposit ratio was nearly 100%, even with low NH₃ and SO₃ (10 ppm each) concentrations in the gas, although the tests using these low concentrations may contain experimental errors.

The tests described above show that deposits form very rapidly when the gas is cooled to the critical temperature, and that the deposit ratio of SO₃ is usually slightly smaller than that of NH₃. A portion of the SO₃ may form fine mists of H₂SO₄ which have a tendency to pass through the tube along with

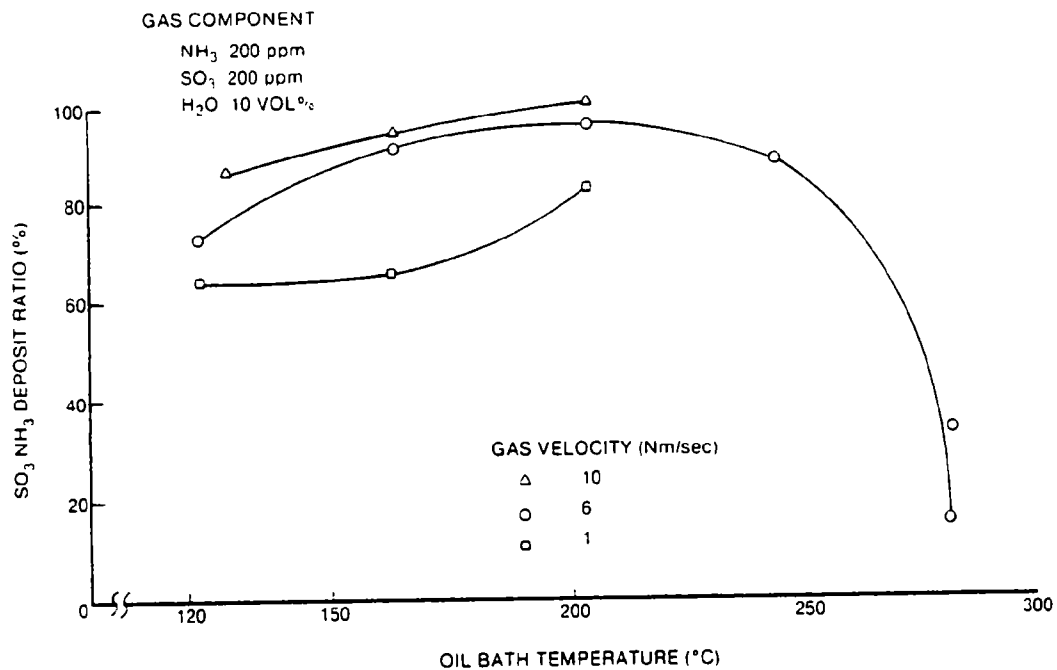


Figure 3-51 Gas Velocity and Deposition Ratio

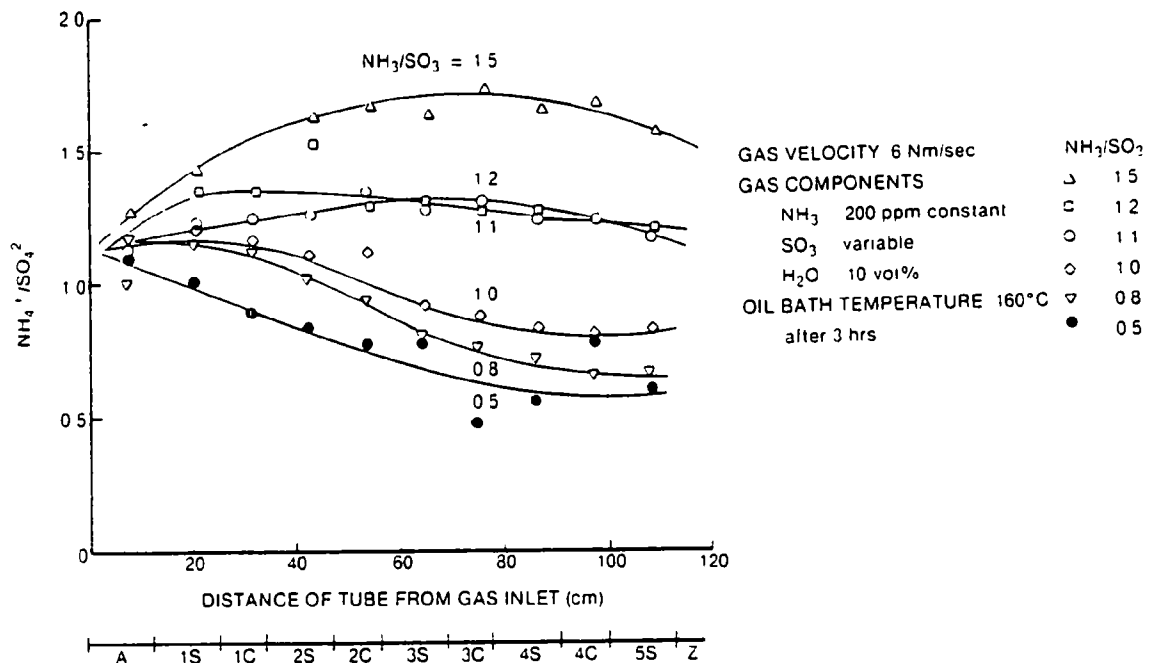


Figure 3-52 NH_4/SO_4 Ratio of Deposits Formed from Gases of Varying Compositions in Different Tube Sections

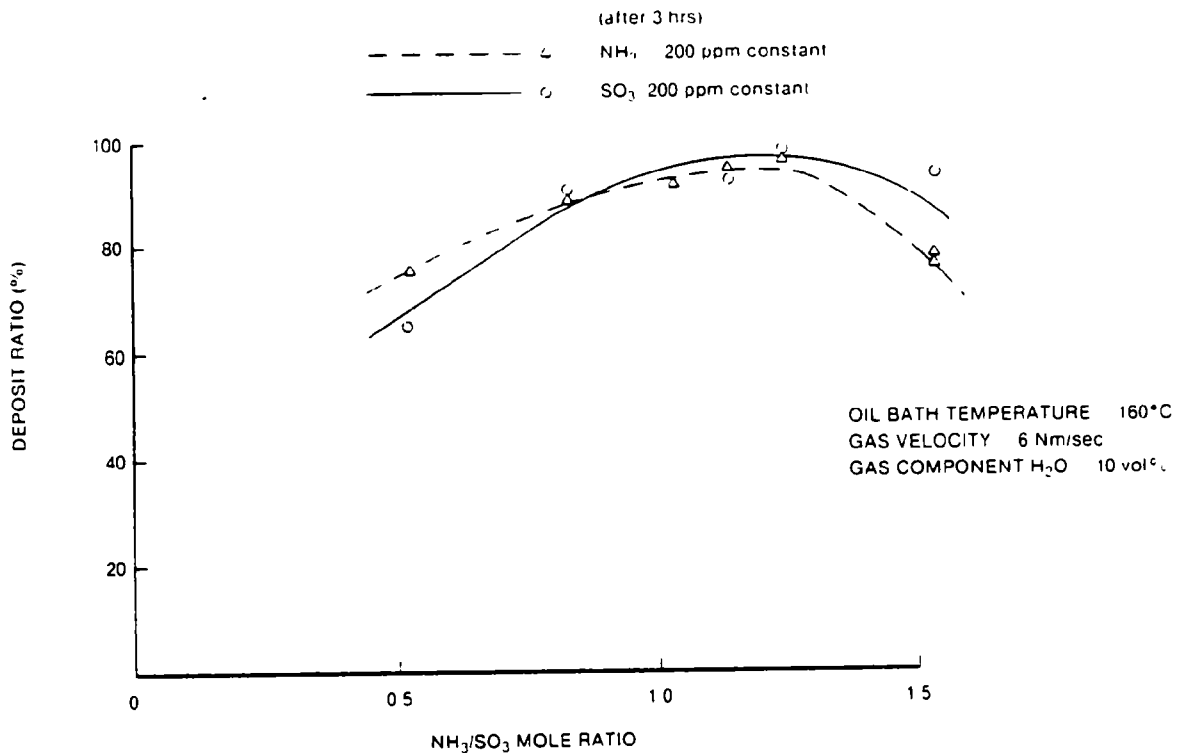


Figure 3-53 NH_3/SO_3 Mole Ratio vs. Deposit Ratio

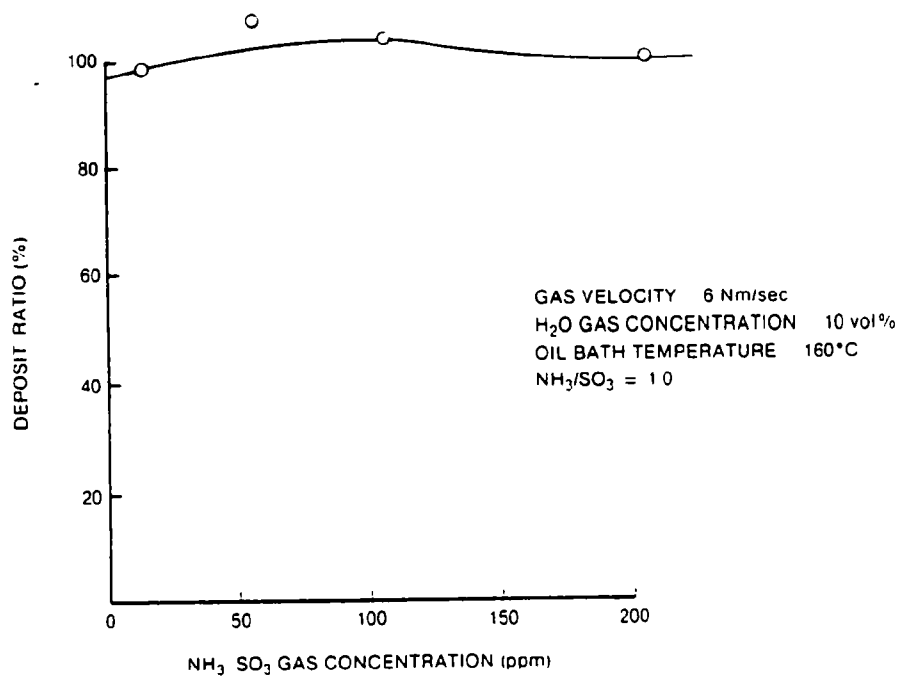


Figure 3-54 Inlet SO_3 and NH_3 Concentration vs. Deposit Ratio

the gas. The NH_3 in the gas is immediately absorbed by the deposits, particularly by those in the liquid phase.

Because the deposits are very hygroscopic, a considerable amount of liquid may be present even at temperatures between the melting point and 100°C . The liquid phase may be the most corrosive.

3.6.4 Air Preheaters (Heat Exchangers)

There are two types of air preheaters or heat exchangers used to heat flue gases. These are shown in Table 3-16.

TABLE 3-16. TYPES OF AIR PREHEATERS (HEAT EXCHANGERS)

-
- | |
|--|
| 1. Rotating |
| a. Ljungstrom (with rotating elements) |
| b. Rothemuehle (with rotating hoods) |
| 2. Multi-tube (no moving parts) |
-

Rotating preheaters have a better heat transfer efficiency and have been used mainly for treating a large amount of gas while multi-tube preheaters are simpler and have been used mainly for smaller gas sources.

For large boilers, Ljungstrom preheaters have been widely used. This type of preheater has rotating elements as shown in Figure 3-55. Flue gas leaves the boiler economizer (or SCR reactor) at $300\text{--}400^\circ\text{C}$ and then passes through one side of the elements and is cooled to $150\text{--}160^\circ\text{C}$, while air or cold gas passes through the other side of the elements and is heated to $250\text{--}300^\circ\text{C}$. Figure 3-56 shows the temperatures of the gas, air, and heating elements. These temperatures usually fall into three zones: high-, intermediate-, and low-temperature. The temperatures of the elements are between those of the gas and air and fluctuate within a certain range as the elements rotate between the gas and air. For example, Figure 3-56 shows that at the boundary of the intermediate- and low-temperature zones, the temperatures of the gas and

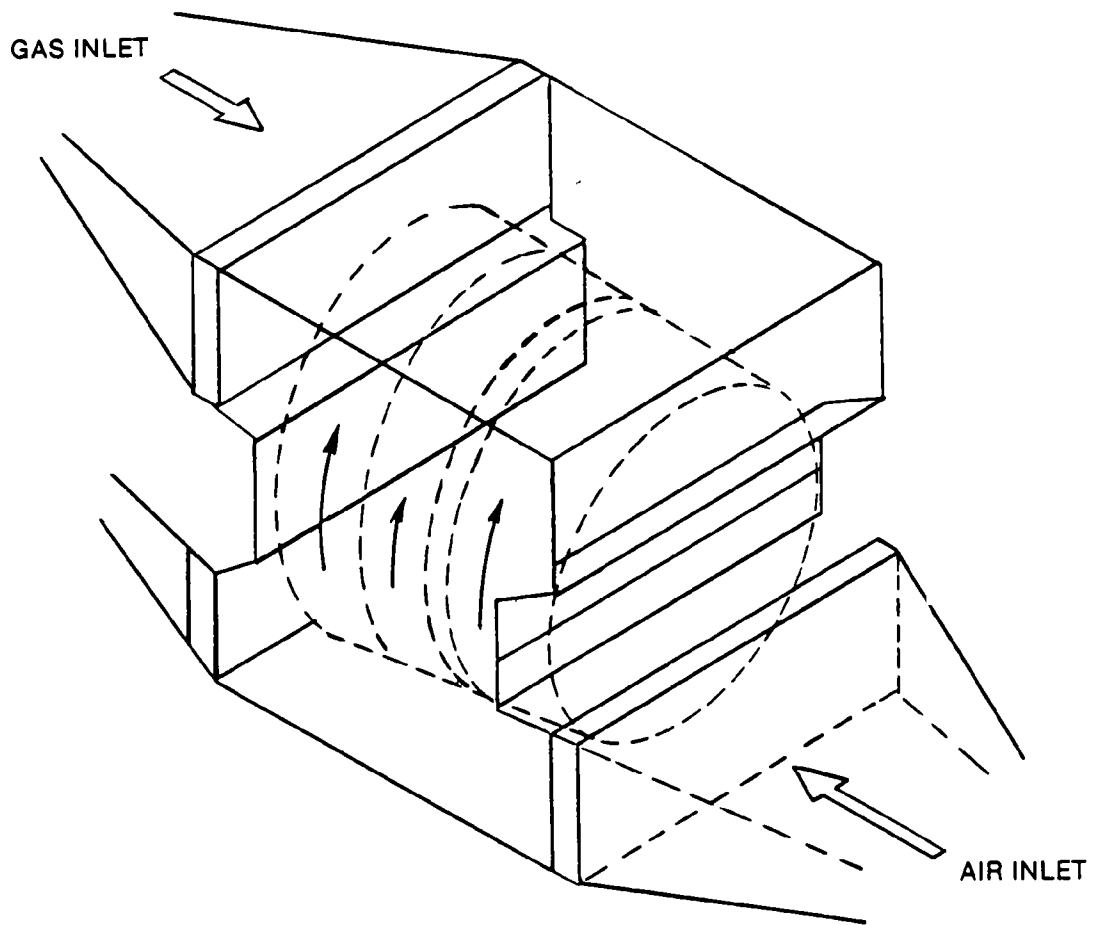


Figure 3-55 **Schematic of Ljungstrom Air Preheater.**

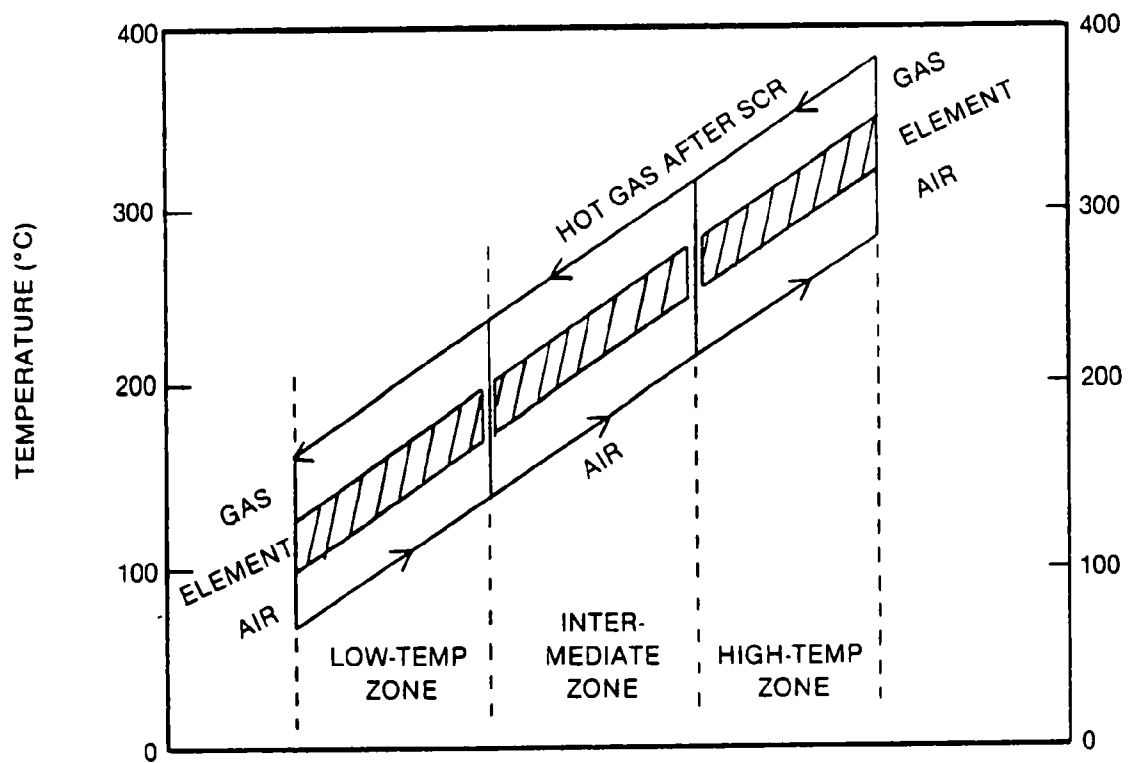


Figure 3-56 Temperatures of Gas, Air and Heating Element in a Ljungstrom Air Preheater.

air are 230°C and 140°C respectively. At the same time the temperature of the elements fluctuates between 200 and 170°C. These are the most favorable temperatures for the formation of deposits.

The gas velocity through the heating elements is normally about 3 m/sec. The retention time for the gas in the preheater is approximately 1 second at a temperature below 230°C. During this time most of the SO₃ or NH₃ in the gas (whichever is present in a lower concentration) may precipitate to form ammonium bisulfate and related compounds while the rest of the SO₃ and NH₃ is released from the preheater.

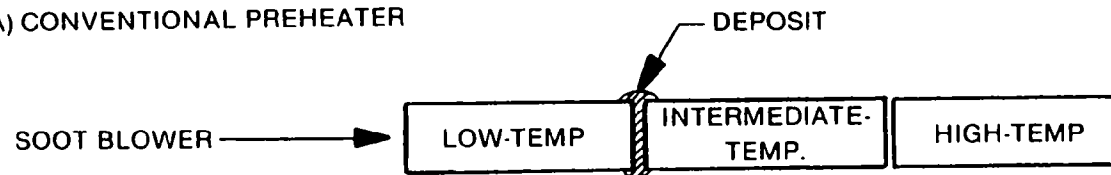
An air preheater or heat exchanger usually has a soot blowing system on the cold side of the elements (Figure 3-57A). However, this system cannot effectively remove the deposits, particularly those formed between the elements in low-temperature and intermediate zones (Figure 3-57).

Recently an improved type of air preheater (Figure 3-57,B) has been used commercially. This preheater has two elements, with hot- and intermediate-, and low-temperature zones and a soot blowing system applied to both the cold and hot sides of the heater. This preheater is considerably more costly than conventional preheaters and is used with the low-dust SCR system to treat flue gas from coal. (Section 3.5.1)

Figure 3-58 shows two of the most popular kinds of heating elements. Tests have proven that the notched-flat type (Figure 3-58, A and Figure 3-44) is easier to clean with soot blowing than the notched-undulated type (Figure 3-60,B). Further studies are being conducted to develop heating elements which minimize the bisulfate problem.

Another rotating air preheater, the Rothemuehle type, is shown in Figure 3-59. It has stationary elements with a rotating hood for hot gas. Ammonium bisulfate deposits form in this preheater in the same way that they form in a Ljungstrom preheater.

(A) CONVENTIONAL PREHEATER



(B) IMPROVED PREHEATER



Figure 3-57 Heating Element Configurations in Conventional and Modified Ljungstrom Air Preheaters.

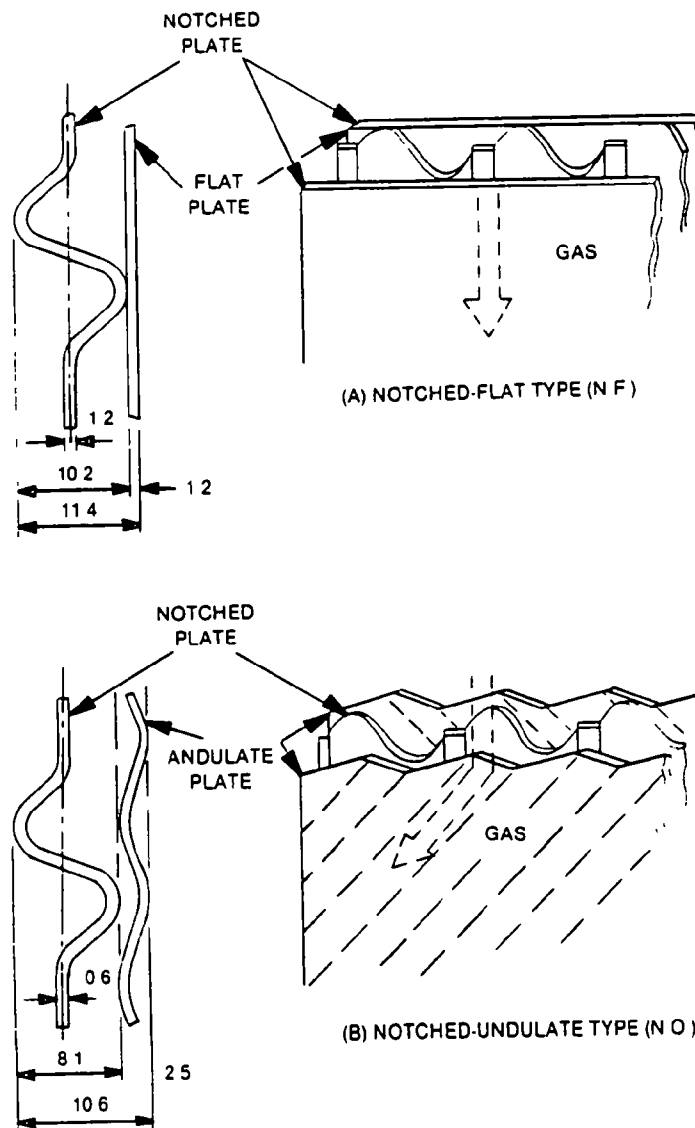


Figure 3-58 Two Types of Heating Elements.

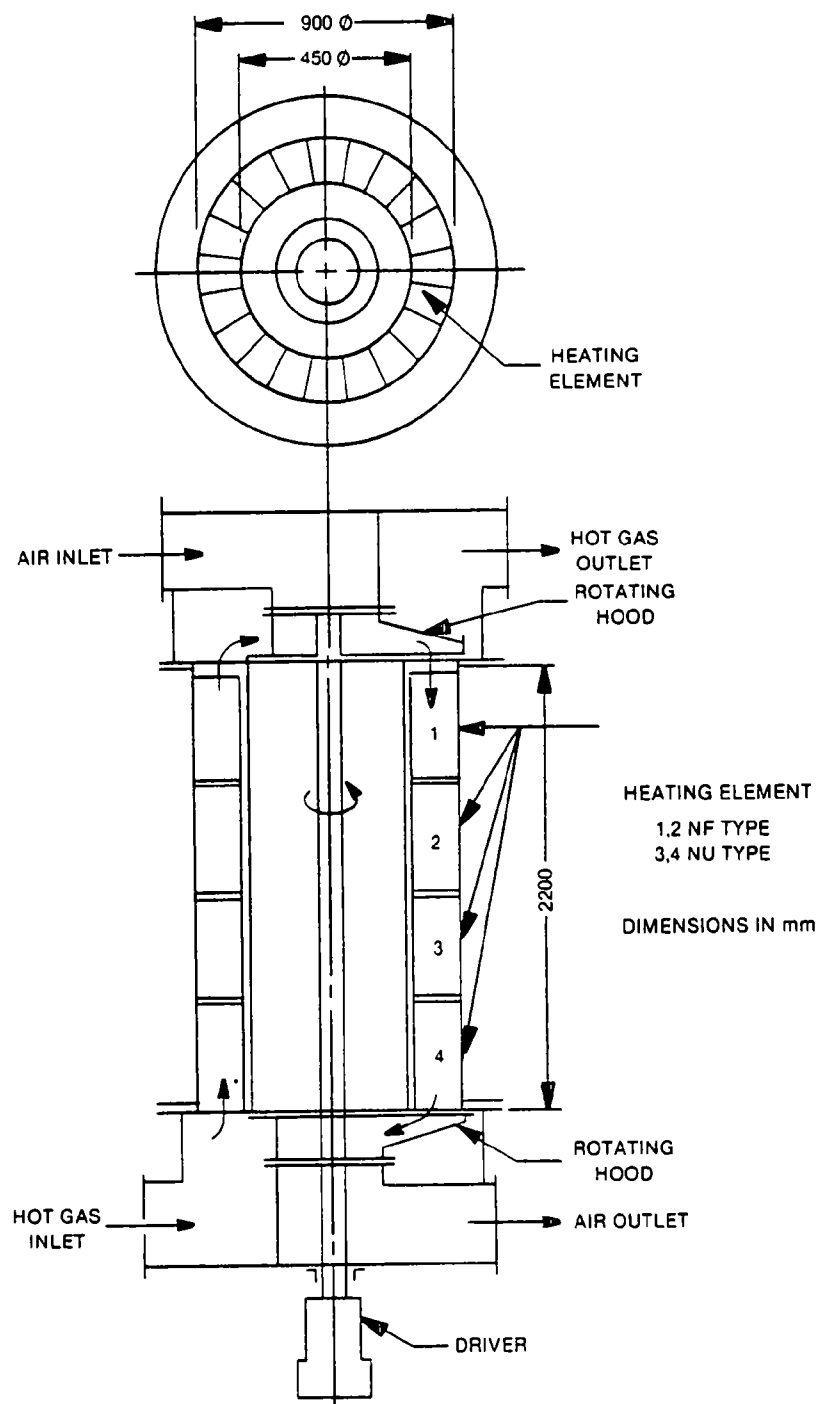


Figure 3-59 Rothemuehle Air Preheater Used in a Pilot Test Plant.

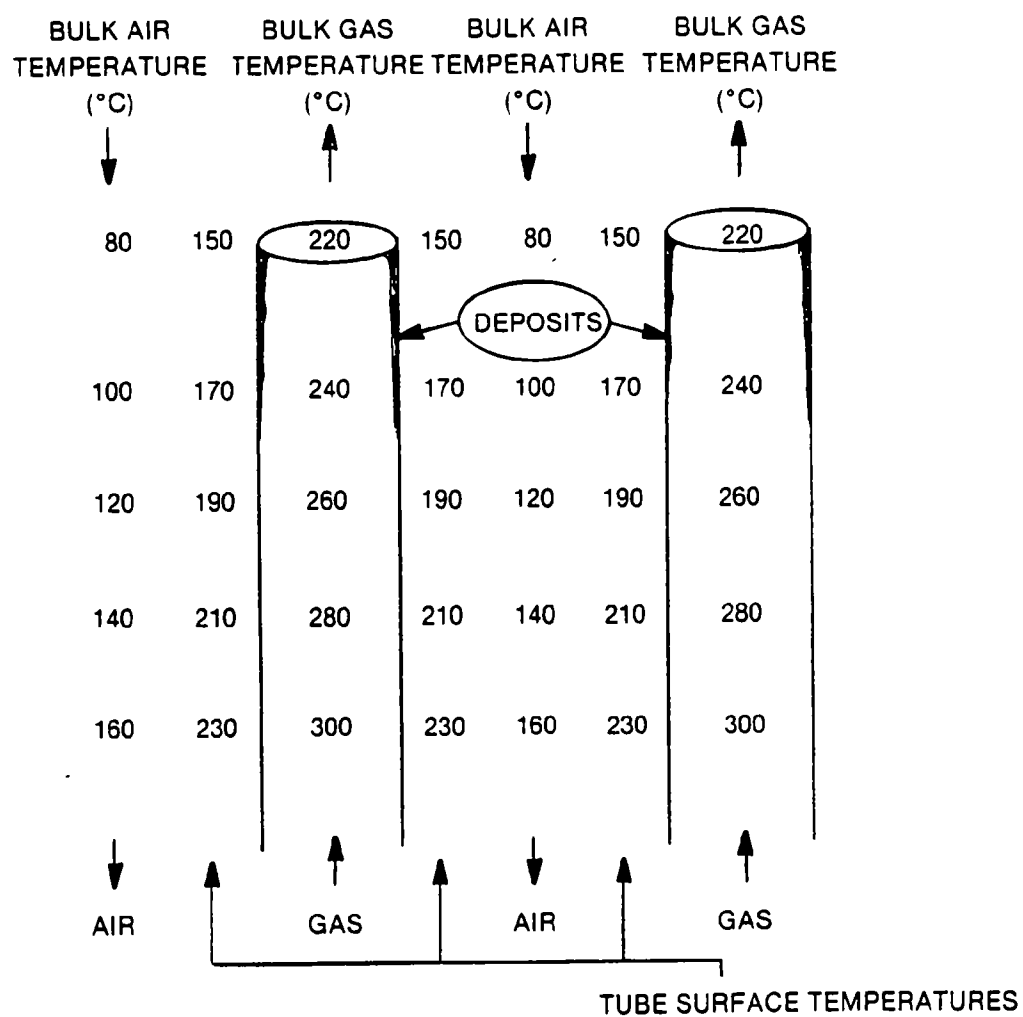


Figure 3-60 Deposits in Air Preheater Tubes.

Figure 3-60 shows the temperatures of the gas, air, and tubes as well as the deposits formed in a typical multi-tube air preheater. The preheater has been used with a 10 MW equivalent oil-fired industrial boiler with an SCR system. The 350°C gas leaves the SCR reactor and passes through the tubes with a velocity of 10 m/sec. The gas is then cooled to 220°C while air preheated to 80°C is passed outside the tubes and heated to 160°C. The deposits which formed inside the tube at temperatures below 200°C, were found to be the reaction product of ammonium bisulfate and the tube material.

3.6.5 Laboratory Corrosion Tests (15)

Corrosion tests have been conducted using four different steel samples. The chemical composition of the steels are shown in Table 3-17. Each sample was dipped into melted ammonium bisulfate at 200°C. As shown in Figure 3-61, low-alloy steel and SS 41 steel corroded slowly at the beginning and then fairly rapidly while stainless steels corroded rapidly at the onset and then more slowly after that. The corrosion rates of the stainless steels and aluminum are shown in Figure 3-62. The figure indicates that aluminum underwent little corrosion because it formed a protective coating.

Figures 3-63 and 3-64 illustrate that addition of ammonium sulfate reduces corrosion; the strong acidity of the bisulfate is weakened by the sulfate. On the other hand, corrosion is substantially increased by the addition of sulfuric acid as shown in Figure 3-65. Most of the liquid in the tube reacted with the steel in about 60 hours and the corrosion (as shown by the dotted line) almost stopped after that. The broken line of the figure shows the maximum amount of corrosion possible when a sufficient amount of the liquid is present.

Figure 3-66 shows that potassium chloride (KCl) promotes the corrosion process. The effects of various additives on corrosion are shown in Table 3-18. CaO, MgO, and Fe₂O₃ reduced the corrosion because they neutralized the acidity of the liquid. Al₂O₃ and SiO₂ had little effect. Corrosion was increased substantially by NH₄Cl, KCl, and Fe₂(SO₄)₃. This was due presumably to the following reactions:

TABLE 3-17. CHEMICAL COMPOSITION OF STEELS (%)

	C	Si	Mn	P	S	Cr	Ni	Cu	Mo
SS 41 Mild Steel	--	--	--	<0.05	<0.05	--	--	--	--
Low-Alloy Steel	0.07	0.27	0.36	0.075	0.017	0.36	0.10	0.28	--
304 Stainless Steel	0.05	0.60	0.92	0.026	0.005	18.32	9.15	--	--
316 Stainless Steel	0.06	0.59	1.06	0.031	0.004	16.90	12.50	0.29	2.29

TABLE 3-18. EFFECT OF ADDITIVES ON CORROSION OF LOW-ALLOY STEEL BY AMMONIUM BISULFATE AT 200° FOR 75 HOURS.

	Additive	None	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	KCl	NH ₄ Cl	Fe ₂ (SO ₄) ₃
236	Amount of Additive (%)	0	18.3	20.0	16.7	20.6	37.5	25.9	27.5	27.0
	Corrosion (g/m ²)	22.50	15.48	7.68	24.37	14.39	27.64	254.8	58.72	344.7
			11.87	6.36	19.90	10.44	26.83	267.6	170.8	421.2
	Corrosion rate (g/m ² /hr)	0.30	0.21	0.10	0.32	0.19	0.37	3.40	0.78	4.60
			0.16	0.08	0.27	0.14	0.36	3.53	2.28	5.62

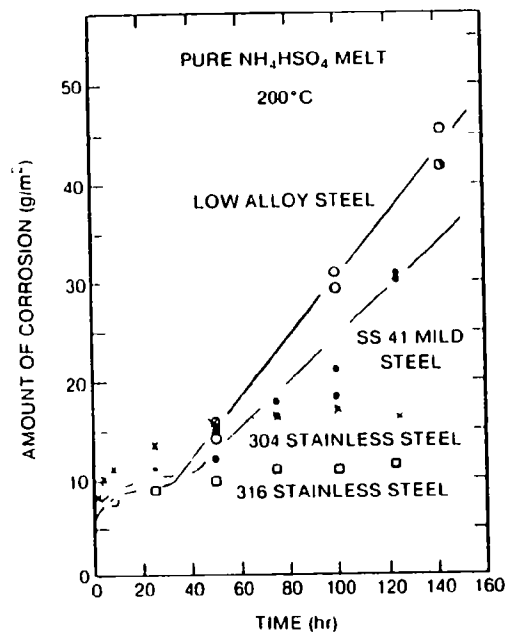


Figure 3 61 Corrosion of Steel by Ammonium Bisulfate

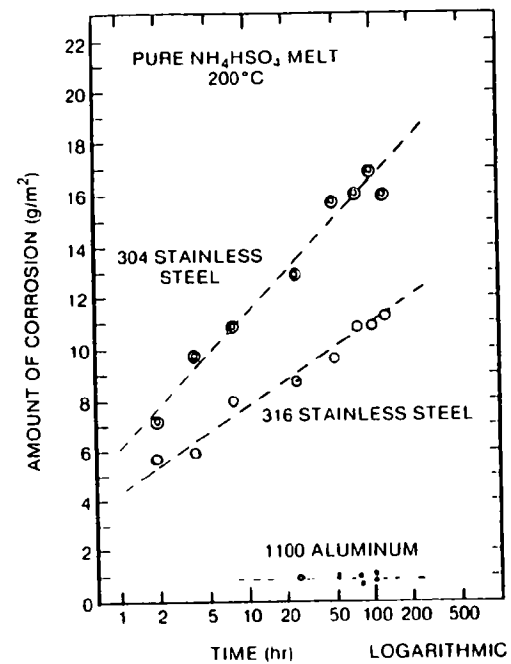


Figure 3 62 Ammonium Bisulfate Corrosion Rate of Stainless Steel and Aluminium

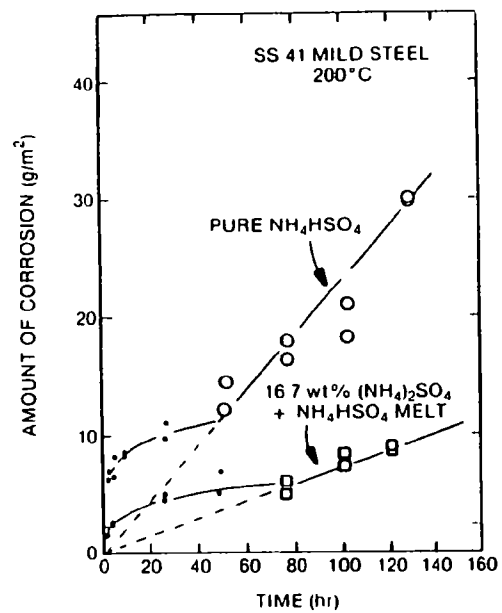


Figure 3 63 Corrosion of Mild Steel by Ammonium Bisulfate Showing the Effect of Ammonium Sulfate

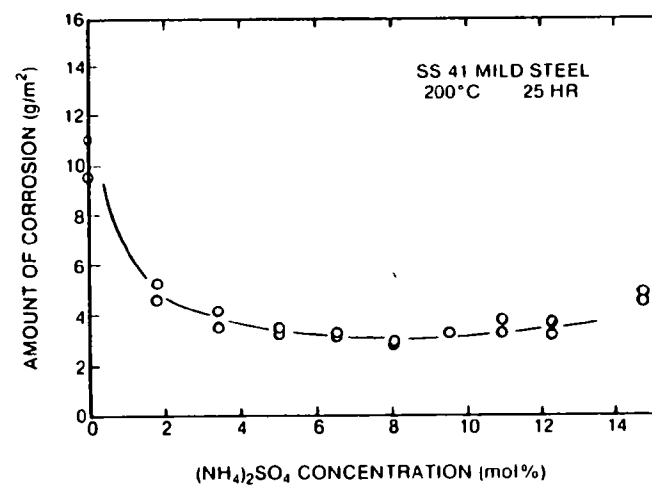


Figure 3 64 Effect of $(\text{NH}_4)_2\text{SO}_4$ on Corrosion of Mild Steel by Ammonium Bisulfate

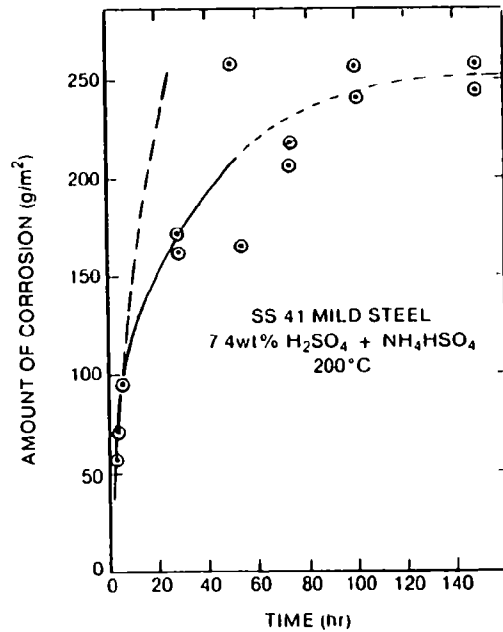


Figure 3 65 Corrosion of Mild Steel by Sulfuric Acid Containing Ammonium Bisulfate

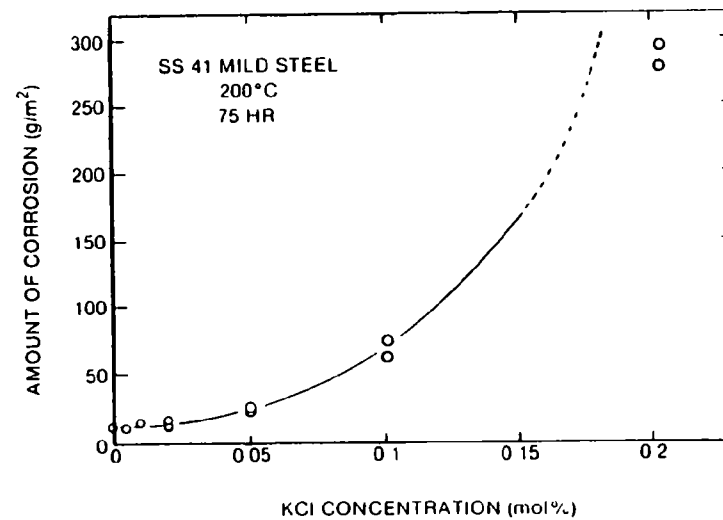
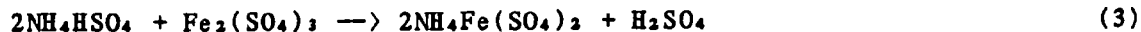
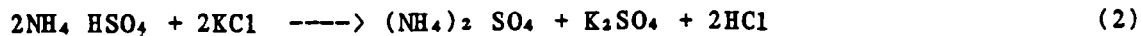
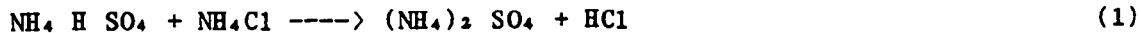
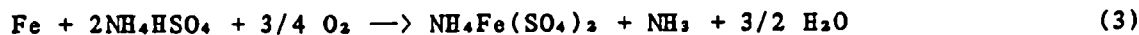
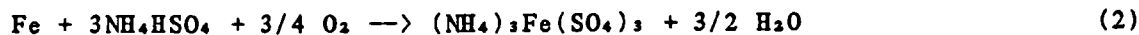
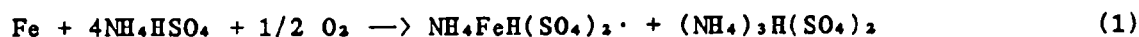


Figure 3 66 Effect of Potassium Chloride on Corrosion of Mild Steel by Ammonium Bisulfate



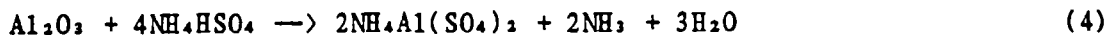
3.6.6 Ammonium Bisulfate/Iron and Fly Ash Reaction Products (16)

The author has studied the reactions of ammonium bisulfate with iron and fly ash at temperatures ranging from 150° - 300°C. When ammonium bisulfate reacted with iron the major products were $\text{NH}_4\text{FeH}(\text{SO}_4) \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$, and $\text{NH}_4\text{Fe}(\text{SO}_4)_2$. These products indicate that the following reactions occurred:



The first reaction (1) occurred readily at the low temperatures (150°-200°) while the third reaction (3) occurred readily at the higher temperatures of 250°C or above. The intermediate temperatures promoted the second reaction (2).

Upon heating, the aluminum and calcium in the fly ash reacted with ammonium bisulfate to form $\text{NH}_4\text{Al}(\text{SO}_4)_3$ and CaSO_4 by the following reactions:



These reaction products are the major compounds which comprise the deposits found in air preheaters and heat exchangers.

3.6.7 Compounds in Air Preheater and Heat Exchanger Deposits (13,16)

This author also used X-ray diffraction to determine the composition of

the deposits found in a heat exchanger and two air preheaters. Table 3-19 lists the samples. Two of the deposit samples (A-1 and A-2) were obtained from a commercial heat exchanger for flue gas from an oil-fired industrial boiler. In this system the 60°C gas leaves the FGD system while the hot gas leaves the SCR reactor at 400°C. Samples B-1 and B-2 were obtained from an air preheater at a SCR pilot plant which treats coal-fired boiler flue gas. Samples C-1 and C-7 were obtained from seven different temperature zones of a commercial air preheater. The preheater was used with a flue gas from an oil-fired utility boiler (low-sulfur oil) subjected to SNR (Thermal DeNO_x).

The results of the analysis of these samples are shown in Table 3-20. Samples A-1 and A-2 were composed of $\text{NH}_4\text{FeH}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. This compound is formed by reaction (1) described in Section 3.6.6. A-1 also contained $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ which did not form by the reaction of NH_4HSO_4 and Fe. This indicates that sulfuric acid condensed and reacted with Fe to form the compound; the flue gas is rich in SO_3 and lean in NH_3 . Samples B-1 and B-2 contained $\text{NH}_4\text{Al}(\text{SO}_4)_2$ and CaSO_4 in addition to fly ash and $\text{NH}_4\text{Fe}(\text{SO}_4)_2$. The aluminum and calcium compounds were formed by the reaction of NH_4HSO_4 with fly ash from coal (Section 3.6.6).

Sample deposits C-1 through C-7 formed in a gas which was rich in NH_3 and lean in SO_3 . $(\text{NH}_4)_2\text{SO}_4$ was present in the deposits in the low-temperature zones (C-1 through C-3), while $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ was present in the deposits in the intermediate zones (C-2 through C-4). Reaction products of NH_4HSO_4 with Fe were present in C-4 through C-7, indicating that corrosion occurred in the high temperature zones. All of the deposits contained a large amount of unburned carbon, which indicated that carbon seemed to increase the amount of deposition and promoted plugging.

Tests on the three sets of samples also revealed that almost no NH_4HSO_4 was present in the deposits. NH_4HSO_4 is very corrosive and had reacted with Fe and fly ash to form various compounds.

TABLE 3-19. DEPOSITS AND GAS COMPOSITIONS

System	Sample No.	Location	Boiler Fuel	SO ₂ (ppm)	NH ₃ (ppm)
A	A-1, A-2	Shindaikoywa Petrochemical's Yokkaichi Plant	High-Sulfur Oil	30-40	10
B	B-1, B-2	EPDC's Test Facility	Medium-Sulfur Coal	3-15	10-20
C	C-1 - C-7	Chuba Electric's Chita Plant	Low-Sulfur Oil	2-3	20-30

3.6.8 Deposit Formation Reduction

Ammonium bisulfate deposition may be reduced in 5 main ways: 1) reduction of unreacted NH₃; 2) reduction of SO₂; 3) combustion control to reduce soot in oil-fired burners; 4) use of coal fly ash for cleansing; and 5) selection of appropriate air preheater elements/soot blowing systems. Reducing unreacted NH₃ is the most commonly used method of decreasing bisulfate formation. This can be accomplished by lowering the inlet NH₃/NO_x mole ratio to less than 1.0 and simultaneously using a large amount of catalyst. Keeping unreacted NH₃ below 5 ppm will substantially reduce deposition but may not solve the problem entirely. Some of the SCR plants maintain an unreacted NH₃ concentration of less than 2 ppm to minimize deposit formation. (Sections 4.4 and 5.2). On the other hand, with a low unreacted NH₃ concentration, acidic deposits with NH₃/SO₂ mole ratios below 1.0 may form, causing corrosion.

SO₂ can be reduced in 3 ways: 1) by using low-sulfur fuel; 2) by combustion control in order to use a minimum amount of excess air; and 3) by using a low-oxidation SCR catalyst. When the gas is lean in SO₂ and rich in NH₃, (NH₄)₂H(SO₄)₂ will be formed at higher temperatures and (NH₄)₂SO₄ will form at lower temperatures. Both of these compounds are less corrosive than NH₄HSO₄. The deposits may be removed quite easily with the soot blower.

For oil-fired boilers, combustion control to reduce soot (unburned carbon) is a good way to decrease deposits. Soot tends to form deposits along with the NH_3 and SO_3 compounds, thereby causing an increase in plugging. The cleansing effect of coal fly ash can be observed in a boiler burning pulverized coal with a full dust load. At an adequate gas velocity there will be little or no bisulfate problem primarily because the bisulfate deposits on the ash. In this case, however, the unreacted NH_3 concentration in the flue gas must be kept low in order to reduce the contamination of the ash by the ammonium compounds. Selecting the appropriate air preheater elements and using an effective soot blowing system also will minimize ammonium bisulfate deposition. If these measures are used, the air preheater may be operated continuously for over a year without bisulfate problems.

However, considerable deposition may still occur in some of the SCR plants which use high sulfur oil or a low-dust system for coal. The deposits usually do not hinder the heat transfer efficiency to any great extent, but do increase the pressure drop of the gas in the preheater. When the pressure drop exceeds a certain level, it is necessary to interrupt the operation of the preheater for a water wash. Usually about one day is needed for the wash, which includes the cooling of the preheater, water washing, and drying. Since the wash water becomes acidic when it mixes with the bisulfate and related compounds (Table 3-20), wastewater treatment may be needed for neutralization and also to remove ammonia.

Recently, Chugoku Electric developed a new method of removing deposits called thermal cleaning which may be superior to water washing. (Section 4.3.4).

3.7 OTHER PROBLEMS WITH AMMONIA

3.7.1 Introduction

In addition to the bisulfate problem described in the previous section, ammonia also has the following effects on flue gas treatment systems:

TABLE 3-20. COMPOUNDS IN DEPOSITS IN HEAT EXCHANGER AND AIR PREHEATER (16)

Sample Number	Temperature Zone	Estimated temp. (°C)	Major	Medium	Minor	ph ^b
A-1	Low (cold)	90-110	$\text{NH}_4\text{FeH}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	NH_4HSO_4	1
A-2	Low (Int. ^a)	110-130	$\text{NH}_4\text{FeH}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	1
B-1	Int.	About 200	Fly Ash	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	$\text{NH}_4\text{Al}(\text{SO}_4)_2, \text{CaSO}_4$	1
B-2	Int.	About 200	Fly Ash	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	$\text{NH}_4\text{Al}(\text{SO}_4)_2, \text{CaSO}_4$	1
C-1	Low (cold)	About 120	Carbon	$(\text{NH}_4)_2\text{SO}_4$		3
C-2	Low (hot)	>120	Carbon	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$	1
C-3	Int. (cold)	About 160	Carbon	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$	1
C-4	Int. (Int.)	>160	Carbon	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$	1
C-5	Int. (hot)	About 200	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	1
C-6	High (cold)	>200	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	1
C-7	High (hot)	About 250	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$		1

^aIntermediate^bMeasured roughly with 15 percent aqueous solution.

- (1) Dust removal improvement (with ESP's).
- (2) Ammonium bisulfate deposition on the catalyst.
- (3) Fly ash contamination.
- (4) Plume formation.
- (5) Effects on FGD system.

3.7.2 Dust Removal Improvement

In Japan, ammonia injection is often used to improve ESP dust removal. Ammonia is injected into oil-fired utility boiler flue gas as it leaves the air preheater. This is done in order to improve the soot removal efficiency of the ESP and to prevent corrosion of the ESP by sulfuric acid mists in the gas.

For flue gas from coal, the dust removal efficiency may be increased by using a small amount of ammonia--up to 50 ppm for high sulfur coal, 20 ppm for low sulfur coal. Larger amounts of ammonia may cause excessive adhesion of fly ash to ESP collector plates (17). With baghouses, ammonia leakage from SCR systems could potentially require more frequent cleaning and bag replacement (17). These effects, however, have not really been demonstrated in Japan because of the low ammonia emissions, normally below 5 ppm.

3.7.3 Ammonium Bisulfate Deposition on SCR Catalysts

Ammonium bisulfate and related compounds tend to deposit on SCR catalysts even at temperatures above 300°C; they deposit in air preheaters at a temperature usually below 250°C. Deposition at the higher temperature may be caused by the high SO₃ concentration on the catalyst surface due to the oxidation of SO₂, as well as to the high NH₃ concentration in the reactor. The critical temperature for deposition may be as high as 350°C with an SO_x-rich gas and a high-oxidation catalyst.

The bisulfate essentially lowers catalytic activity by coating the catalyst surface and may even poison some types of catalysts. Most catalysts used for SO_x-containing gases are not poisoned, however, and their activity can

be recovered when they are heated to 400-450°C and the bisulfate is volatilized. With low-temperature catalysts used at 200-250°C, deposit formation is a serious problem and necessitates occasional heating (Section 3.3).

In utility boilers, the economizer outlet gas temperature usually ranges from 350° - 400°C but may drop to 300-330°C when the boiler load is lowered at midnight, for example. A small amount of the bisulfate may deposit on the catalyst but is volatilized as the temperature increases with an increased load, thus causing no problem for SO_x-lean gas. With SO_x-rich gas, however, the NO_x removal efficiency may be noticeably lowered when the gas temperature is kept below the critical temperature for several hours.

In order to maintain the temperature above the critical level, an economizer by-pass system has been used with some coal-fired utility boilers. Oil-firing has been used for the same purpose at smaller gas sources. A moving-bed reactor is used for treating a low-temperature gas of 200-250°C; the contaminated catalyst is removed from the reactor and heated.

3.7.4 Contamination of Fly Ash by Ammonia

Ammonium bisulfate may deposit on fly ash in the gas stream (unreacted NH₃) at temperatures below 250°C. Figure 3-67 shows the relationship between unreacted ammonia (NH₃ leakage) and the ammonia content of fly ash caught by a cold ESP downstream of an air preheater. The ammonia content increased almost linearly until it reached about 800 mg/kg at about 20 ppm of unreacted NH₃ in the gas. It did not increase significantly after that, presumably because of the limited SO₃ content of the gas which combines with NH₃ to form the deposits. Figure 3-67 indicates that the ammonia content of the ash was nearly 200 mg/kg (0.02%) with 5 ppm unreacted NH₃ and around 600 mg/kg with about 15 ppm unreacted NH₃.

When used in concrete or landfill materials, an NH₃-rich ash may produce an ammonia odor. This occurs when the alkaline component of the ash reacts with water. This reaction can be expressed as:

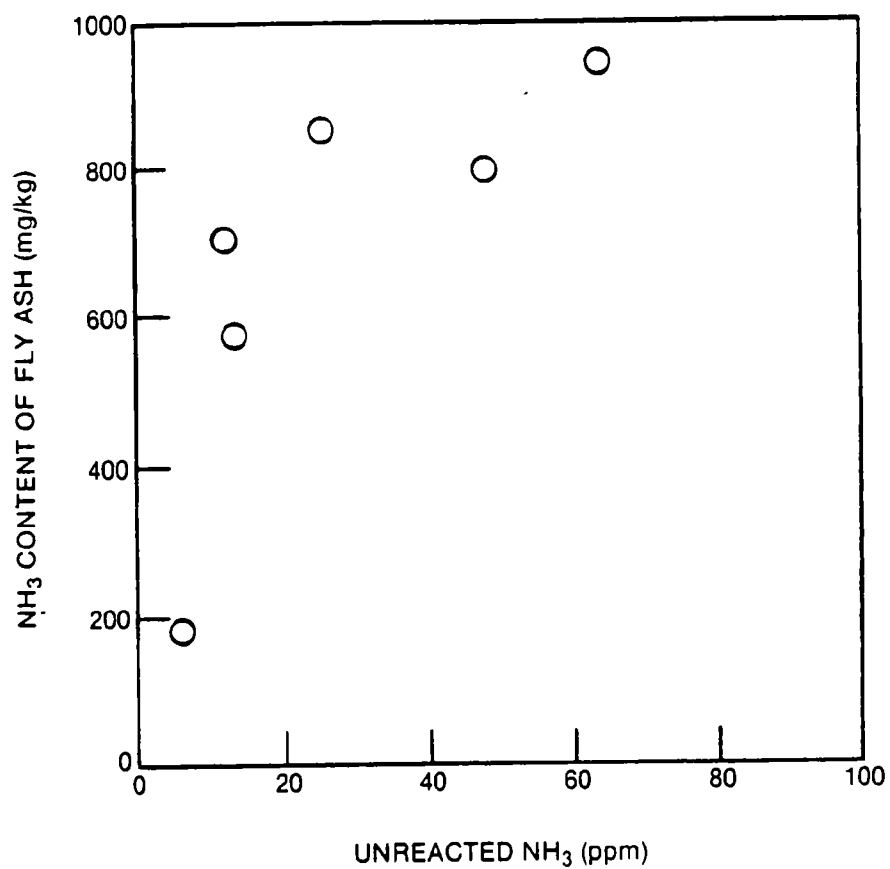


Figure 3-67 Adsorption of Unreacted NH_3 on Fly Ash. (6)



When NH_3 is present in the ash, it also may cause water pollution problems. For these reasons it is best to maintain an acceptable level of NH_3 in the ash. It has been found that an NH_3 content below 0.02% works well. When SCR reactor outlet gas contains 5 ppm NH_3 and 90% of the NH_3 is caught by the ash present in 20 grams/ Nm^3 in flue gas (20 gm/ Nm^3) the NH_3 content of the fly ash is 0.14%.

Chugoku Electric's Shimonoseki Power Station (Section 4.4) maintains unreacted NH_3 below 2 ppm and has produced fly ash which can be used without problems for cement or concrete, or for landfill material.

If necessary, NH_3 may be removed from the fly ash at the power plant by mixing it with a small amount of moisture. This causes reaction (1) to occur and release NH_3 ; the released NH_3 can be emitted from the stack without any trouble. Moistening the ash also can help prevent dust formation during ash handling.

3.7.5 Plume Formation

Plume problems caused by ammonia in flue gas have been known to occur when the gas from an ammonia-scrubbing FGD plant contains more than 10 ppm NH_3 . On the other hand, there is no plume problem associated with flue gas which has undergone SCR. This is true even when the gas has been cooled to 140°C and contains 20 ppm NH_3 . A plume has been observed during the winter with flue gas containing 50 ppm NH_3 after selective noncatalytic reduction (thermal De- NO_x) (Section 6.2).

The difference in the plume formation associated with wet FGD and dry De- NO_x systems is due to differences in moisture content and temperature as well as in the amount and particle size of ammonium compounds in the flue gases. With wet FGD, the 55°C moisture-saturated gas contains a large amount of SO_2 and a considerable amount of SO_3 before it is heated to 70-120°C. In the dry De- NO_x system, flue gas containing a smaller amount of moisture is

cooled from about 400°C to 150°C in an air preheater. In the preheater nearly all of the SO₂ combines with NH₃ to precipitate out as long as NH₃ is present in excess.

Plume problems may occur when flue gas containing a considerable amount of NH₃ after dry DeNO_x is introduced into a wet FGD system. This is described in the following section.

3.7.6 Effect of Ammonia on Flue Gas Desulfurization

The effect of ammonia on flue gas desulfurization varies with the FGD system being used. Three types of wet process FGD systems popular in Japan are shown in Figure 3-68. No. 1 shows limestone scrubbing with a prescrubber in which over 90% of the ammonia in the gas is caught in the prescrubber by an acidic liquor with a pH of about 1. A typical FGD system for a 175 MW coal-fired boiler releases 5/hr of wastewater from the prescrubber. The ammonia content of the wastewater is calculated at roughly 200 ppm, assuming an inlet gas ammonia concentration of 3 ppm. The liquor is sent to a wastewater treatment system where ammonia may be removed either by a conventional activated sludge process or an ammonia stripping process, if necessary. Ammonia stripping has been applied at Chubu Electric's Owase Plant (18); the activated sludge process will be applied at the EPDC's Takehara Plant. The prescrubber outlet gas contains only a small amount of ammonia (below 1 ppm), most of which is caught by the scrubber but does not affect the scrubber system.

No. 2 shows a two-stage limestone scrubbing system. The first scrubber catches 60-70% of the ammonia in the flue gas while the second scrubber removes another 10-20% of the ammonia, which adds up to a total removal efficiency of 70-90%. The ammonia in the scrubber liquor may increase SO₂ removal efficiency and may not produce any adverse effects on the scrubber system (17). The by-product sludge, however, may cause environmental problems.

In Japan, sludge is oxidized to produce gypsum which is subsequently centrifuged and washed with water for use as cement, wallboard, and other

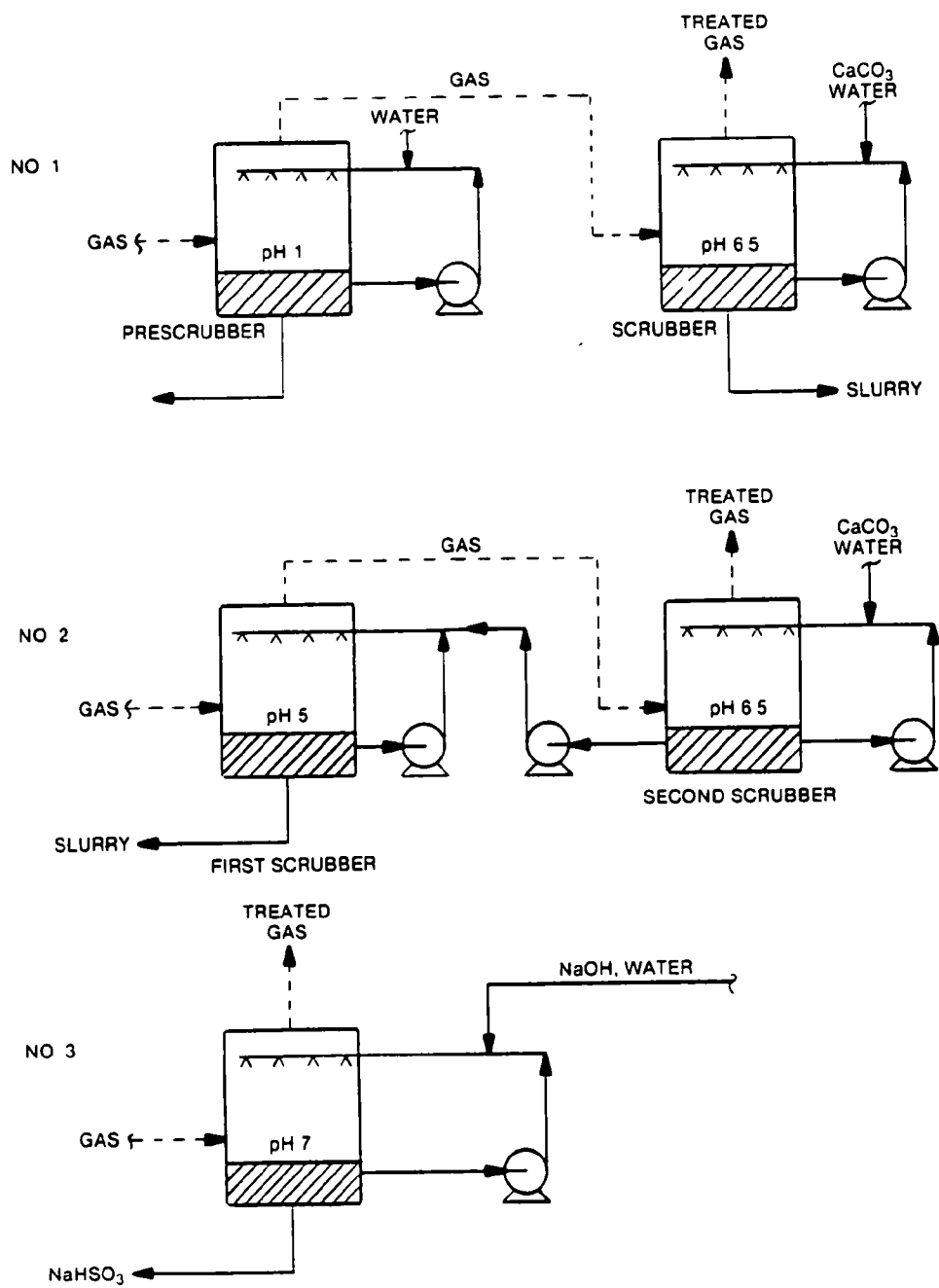


Figure 3-68 Three Most Popular Wet Process FGD Systems Used in Japan

materials. Both the filtrate and the wash liquor are recycled in the scrubber system and a portion of the scrubber liquor is sent to the wastewater treatment system. If necessary, ammonia may be removed from the liquor to prevent environmental problems.

In FGD systems No. 1 and No. 2, flue gas leaving the scrubber contains little ammonia and will not cause a plume problem except in cases when inlet gas containing over 20 ppm NH_3 enters System No. 2.

No. 3 shows simple sodium scrubbing which produces throw-away sodium sulfite or sulfate liquor. Approximately one-half of the NH_3 in the flue gas is caught by the scrubber liquor. Removal of ammonia from the waste liquor may be necessary under certain circumstances. (A plume can be observed at the scrubber outlet of this system when the inlet flue gas contains more than about 20 ppm NH_3 .)

3.7.7 Measurement of Ammonia in Flue Gas

The measurement of unreacted NH_3 in flue gas is important both for control of NO_x removal efficiency and prevention of the problems described above. However, this measurement can be difficult for the following reasons:

- (1) Ammonia is usually present in a small concentration, below 10 ppm.
- (2) The presence of NO_x , SO_x , etc. interferes with the measurement of ammonia.
- (3) At a large plant, the ammonia concentration may be different in each part of the large duct, causing sampling problems.

The major analytical methods used to measure NH_3 in Japan are shown in Table 3-21 and Figure 3-69, I and II. Method I is used to measure the concentrations of NO_x and a total of NO_x and NH_3 , after NH_3 is converted to NO ; the NH_3 concentration equals the difference between these two concentrations.

TABLE 3-21. TWO MAJOR METHODS USED IN JAPAN FOR CONTINUOUS ANALYSIS OF NH₃ IN FLUE GAS

Method No.	I	II
Principle	Oxidation of NH ₃ to NO, followed by Chemiluminescence	Ultraviolet ray absorption by NH ₃
Major Manufacturer	Shimazu Seisakujo Fuji Electric ¹⁹	Anritsu Electric
Example of User	Chugoku Electric's Kudamatsu Power Station (Commercial SCR plant) Electric Power Development Co.'s Isogo Power Station (IHI SCR pilot plant)	Electric Power Development Co.'s Isogo Power Station Hitachi Zosen process SCR pilot plant Mitsubishi Heavy Industries, Takasago Research Station
Problems	Catalytic converter of NH ₃ to NO is needed. Since a small portion of NH ₃ is converted to NO ₂ , catalytic convertor of NO ₂ to NO is also needed. For a gas rich in NO _x , the analytical error may be large.	Interfered with SO ₂ in the gas, although it may be possible to correct the analytical value by also measuring SO ₂ . The gas sampling tube should be kept above 300°C to prevent the condensation of NH ₄ HSO ₄ in the tube.
Maintenance	Not simple	Simple
Price of the Analyzer	5.5 million yen including converter	4.9 million yen for NH ₃ analyzer 5.5 million yen for NH ₃ and SO ₂ analyzer

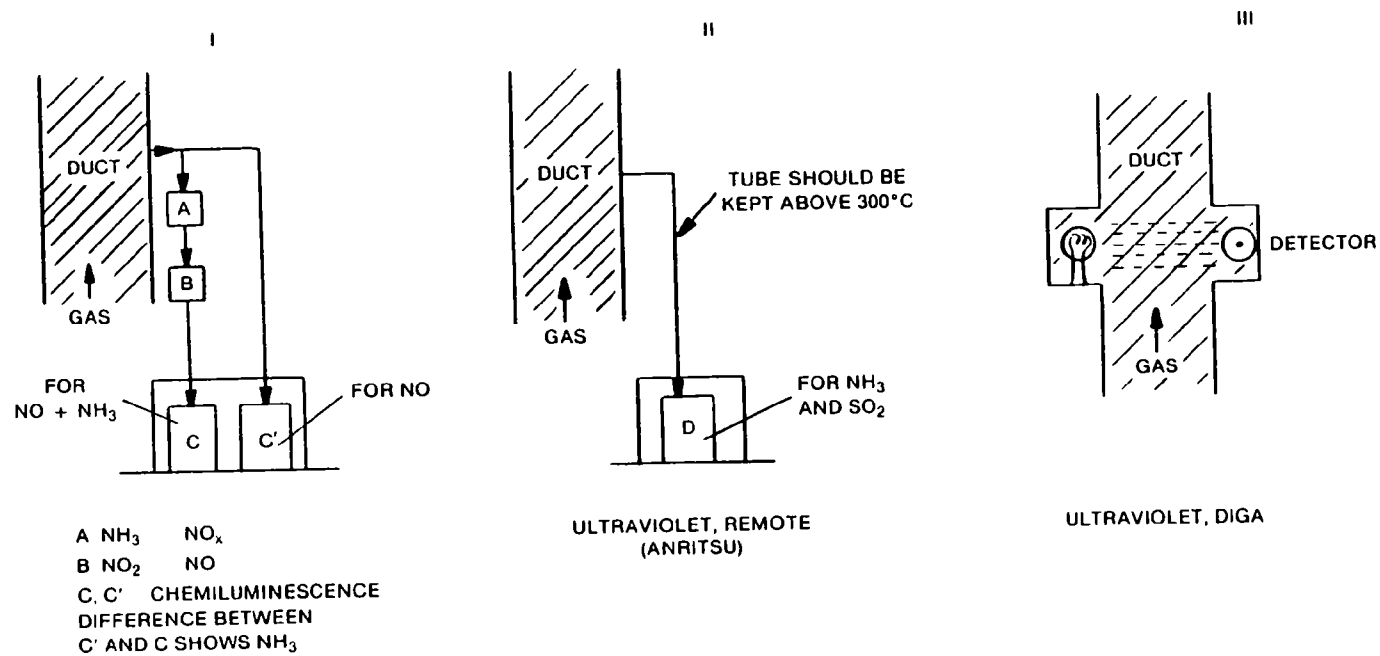


Figure 3 69 Comparison of NH₃ Analysis Methods

With this method there may be a large analytical error when the NO_x concentration is much higher than the NH_3 concentration, as is often the case with flue gases after SCR. A modified method for the determination of a low concentration of NH_3 has been developed, and will be described in Section 4.4.3.

Method II is used for direct analysis of NH_3 . However, any SO_x present in the gas interferes with the measurement, requiring a special calibration in order to take the interference into account. When using this method, the analytical error may be large if the gas contains a large amount of SO_x and a smaller amount of NH_3 . The gas sampling tube also must be kept above 300°C to prevent ammonium bisulfate deposition which can cause additional analytical errors.

Although the analysis itself is fairly accurate when Methods I and II are used properly, gas sampling may cause errors since gas composition may not be homogeneous throughout a large duct. The Direct In-Gas Analysis (DIGA) method developed in the U.S. (Figure 3-69, III) may be superior from this point of view. With the DIGA method a light source is placed on one side of the duct and a detector on the other. Light passes through a pipe across the duct which is slotted to allow gas flow. This method allows quick response which eliminates sampling error. However, the accuracy of the NH_3 measurement is affected by the presence not only of SO_2 , but also of particulates, requiring calibrations according to their concentrations.

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SECTION 4

SCR FOR FLUE GAS FROM UTILITY BOILERS

4.1 DESIGN AND PERFORMANCE OF SCR PLANTS

4.1.1 Development of SCR for Utility Boilers

Following numerous pilot plant tests, the first prototype SCR plant was constructed in 1977 at Kansai Electric's Kainan Station. It was designed to treat one-fourth of the flue gas from an existing 450 MW oil-fired boiler by reducing NO_x from 120 ppm to about 20 ppm. The plant uses a ring-type catalyst in a fixed bed. The first commercial SCR plant for utility boilers began operation in 1978 at Chubu Electric's Chita Station. Using a pellet catalyst, the plant reduces NO_x in the flue gas of two 700 MW gas-fired boilers from 50 ppm to 10 ppm.

Since 1978, parallel flow SCR catalysts, especially the honeycomb and plate types, have significantly improved in quality and decreased in cost. In 1979 the first full scale SCR plant using a honeycomb catalyst began operation at Chugoku Electric's Endamatsu Station. It reduced NO_x in the flue gas of an existing 375 MW oil-fired boiler from 130 to 20 ppm. All of the commercial SCR plants constructed in 1979 for utility boilers use honeycomb or plate catalysts, except for one plant which uses a tubular catalyst. Even for clean gas containing little dust, the parallel flow catalyst with a thin wall is superior to the pellet catalyst because of the lower gas pressure drop it causes.

Full-scale plants for testing a combined system of selective noncatalytic reduction (SNR) and SCR applied to existing oil-fired boilers were constructed in 1978 by Tokyo Electric and Kansai Electric. The tests were subsequently discontinued and the SNR system was removed leaving the SCR system (Section 6.3).

For coal-fired boilers, the first full scale SCR plant began operation in 1980 at Chugoku Electric's Shimonoseki Station. The station treats flue gas from an existing 175 MW boiler using a honeycomb catalyst. In 1980, another SCR plant began operation at Hokkaido Electric's Tomato-Atsuma Station. It uses a plate catalyst to treat one-fourth of the gas from a new 350 MW boiler. Seven SCR plants for coal-fired boilers began operation in 1981 and 1982.

By the end of 1982, the total SCR capacity for utility boilers will exceed 21,000 MW, including about 3,300 MW for coal-fired boilers. SCR plants with a capacity of treating more than 250,000/Nm³/hr of flue gas (75 MW equivalent) from utility boilers are listed in Table 4-1. Almost all of the coal-fired boilers which will begin operation after 1982 will need SCR, although NO_x can be reduced to 160-200 ppm using combustion modification alone.

Most of the SCR plants in Japan are designed for 80-85 percent NO_x removal with unreacted NH₃ below about 5 ppm. Although it may be possible to remove 90 percent or more of the NO_x, 80-85 percent removal has been found to be the optimum level because of the smaller pressure drop, smaller amount of unreacted NH₃, and lower SO₂/SO₃ oxidation rate associated with it. Some of the SCR plants initially are using a small amount of the catalyst to remove 50-60 percent of NO_x and will increase the amount of catalyst to remove 80-85 percent when needed in the future.

All of the SCR plants for utility boilers have been or will be constructed by boiler manufacturers: MHI, BHK, IHI, and KHI. MHI, the largest boiler manufacturer in Japan, builds the largest share of the SCRs; normally the SCR plant is constructed by the boiler manufacturer.

TABLE 4-1. SCR PLANTS FOR UTILITY BOILERS IN JAPAN AND THE UNITED STATES (By 1984)

Power Company	Station Name	Boiler No.	Fuel	Capacity		N/R	Vendor	Catalyst	Start Up
				MW	1000 Nm ³ /hr				
Chubu Electric	Chita	4	Oil, gas	700	2,000	R ^a	MHI ^c	H ^g	1979
"	"	5	Gas	700	1,910	N ^b	BHK ^d	G ^h	1978
"	"	6	Gas	700	1,910	N	BHK	G	1978
"	"	1	Oil	375	1,100	N			1983
"	Nishinagoya	6	Oil	500	1,320	R	IMI ^e	H	1980
"	"	4	Oil	375	1,100	R	BHK ^d	P ⁱ	1981
"	"	3	Oil	375	1,100	R	BHK	P	1982
"	Shinnagoya	3	Oil	220	650	R	MHI	H	1980
"	"	2	Oil	220	650	R	MHI	H	1981
"	"	5	Oil	220	650	R	MHI	H	1981
"	"	6	Oil	220	650	R	MHI	H	1981
"	Atsumi	3	Oil	700	1,870	N	MHI	H	1980
"	"	4	Oil	700	1,870	N	MHI	H	1981
"	Chita No. 2	1	Gas	700	1,910	N	BHK	P	1983
"	"	2	Gas	700	1,910	N	IMI	H	1983
Chugoku Electric	Kudamatsu	2	Oil	375	1,125	R	IMI	H	1979
"	"	3	Oil	700	2,000	N	IMI	H	1979
"	Iwakuni	2	Oil	350	1,000	R	MHI	H	1980
"	"	2	Oil	500	1,450	N	MHI	H	1980
"	Shimonoseki	1	Coal	175	580	R	MHI	H	1980
"	Shin-Ube	1	Coal	75	250	R	MHI	H	1982
"	"	2	Coal	75	250	R	MHI	H	1982
"	"	3	Coal	156	500	R	MHI	H	1982
"	Mizushima	1	Coal	125	400	R	BHK	P ⁱ	1984
"	"	2	Coal	156	500	R	BHK	P	1984

(Continued)

^a Retrofit^b New^c Mitsubishi Heavy Industries^d Babcock Hitachi^e Ishikawajima Harima Heavy Industries^f Kawasaki Heavy Industries^g Honeycomb^h Granuleⁱ Plate^j Tube

TABLE 4-1 SCR PLANTS FOR UTILITY BOILERS IN JAPAN AND THE UNITED STATES (By 1984) (Continued)

Power Company	Station Name	Boiler No.	Fuel	Capacity		N/R	Vendor	Catalyst	Start Up
				MW	1000 Nm ³ /hr				
Electric Power D C	Takeshara	1	Coal	250x1/2	400	R	BHK	P	1981
"	"	3	Coal	250x1/2	400	R	KHI ^f	T ^j	1981
"	"	3	Coal	700	2,340	N	BHK	P	1983
Hokkaido Electric	Tomato-Atsumai	1	Coal	350x1/4	280	N	BHK	P	1980
Hokuriku Electric	Toyama	2	Oil	500	1,470	N	IHI	H	1980
Joban Electric	Nakoso	8	Oil, Coal	600	1,810	N ^b	MHI ^c	H ^d	1982
"	"	9	Oil, Coal	600	1,810	N	IHI	H	1983
Kansai Electric	Osaka	1	Oil	156	500	R ^a	MHI	H	1978
"	"	2	Oil	156	500	R	MHI	H	1981
"	"	3	Oil	156	500	R	MHI	H	1980
"	"	4	Oil	156	500	R	MHI	H	1980
"	Kaigan	1	Oil	450x1/4	300	R ^d	BHK	P ⁱ	1979
"	"	3	Oil	600	1,640	R	MHI	H	1982
"	"	4	Oil	600	1,640	R	BHK	P	1981
"	Himeji I	4	Oil	156	500 ^k	R	IHI ^e	H	1978
"	Himeji II	6	Gas, oil	600	1,640	R	IHI	H	1981
"	Amagasaki-	1	Oil	156	470	R	BHK	P	1978
"	higashi	2	Oil	156	470	R	BHK	P	1980
"	Amagasaki-	1	Oil	156	470	R	BHK	P	1981
"	No. 3	2	Oil	156	470	R	BHK	P	1980
"	"	3	Oil	156	470	R	BHK	P	1980
"	Sakaiko	1	Gas, oil	250	800	R	MHI	H	1980
"	"	2	Gas, oil	250	800	R	MHI	H	1981
"	"	4	Gas, oil	250	800	R	MHI	H	1981

(Continued)

^aRetrofit^bNew^cMitsubishi Heavy Industries^dBabcock Hitachi^eIshikawajima Harima Heavy Industries^fKawasaki Heavy Industries^gHoneycomb^hGranuleⁱPlate^jTube^kCombination with SNR was tested.

TABLE 4-1 SCR PLANTS FOR UTILITY BOILERS IN JAPAN AND THE UNITED STATES (By 1984) (Continued)

Power Company	Station Name	Boiler No.	Fuel	Capacity 1000		N/R	Vendor	Catalyst	Start Up
				MW	Nm ³ /hr				
Kansai Electric	Sakaiko	5	Gas, oil	250	800	R	BHK	P	1980
"	"	6	Gas, oil	250	800	R	MHI	H	1979
"	"	7	Gas, oil	250	800	R	MHI	H	1981
"	Tanagawa	3	Oil	156	500	R	MHI	H	1981
"	"	4	Oil	156	500	R	MHI	H	1981
"	Tanagawa II	2	Oil	600	1,320	R	BHK	P	1981
"	Kasugade	1	Oil	156	470	R	IHI	H	1980
"	"	2	Oil	156	470	R	IHI	H	1981
"	Aioi	1	Oil	375	1,030	N ^b	IHI ^a	H ^a	1982
"	"	2	Oil	375	1,030	N	IHI	H	1982
"	"	3	Oil	375	1,030	N	IHI	H	1982
"	Gobou	1	Oil	600	1,600	N	MHI ^c	H	1984
"	"	2	Oil	600	1,600	N	BHK ^d	P ⁱ	1984
"	"	3	Oil	600	1,600	N	MHI	H	1984
Kyushu Electric	Shinkokuya	3	Gas	600	1,640	N	MHI	G	1978
"	"	4	Gas	600	1,640	N	MHI	G	1978
"	"	5	Gas	600	1,640	N	MHI	G	1982
"	Omura	2	Coal	156	500	R ^a	MHI	H	1982
"	Minato	1	Coal	156	500	R	MHI	H	1983
Tokoku Electric	H.Niigata	2	Oil	600	1,640	N	IHI	H	1981
"	Sendai	3	Coal	175	580	R	BHK	P	1982
Tokyo Electric	Yokosuka	4	Oil	350	1,060 ^k	R	MHI	H	1978
Tokyo Electric	Yokosuka	1	CO ₂ ^l	265	850	R	MHI	H	1984
Tokyo Electric	Yokosuka	2	CO ₂ ^l	265	850	R	MHI	H	1984
"	Ohl	2	Oil	350	1,060 ^k	R	IHI	H	1978
"	Yokohama	1	Oil	156	500 ^k	R	BHK	P	1978
S. Calif. Edison	Huntington Beach	2	Oil	215x1/2	350	R	MHI	H	1981

^aRetrofit^bNew^cMitsubishi Heavy Industries^dBabcock Hitachi^eIshikawajima Harima Heavy Industries^fKawasaki Heavy Industries^gHoneycomb^hGranuleⁱPlate^jTube^kCombination with SNR was tested^lCoal-Oil Mixture

For oil- and coal-fired boilers, MHI and IHI use a honeycomb catalyst while BHK uses a plate catalyst (Figure 3-33). KHI has constructed an SCR plant for a coal-fired boiler at EPDC's Takehara Station which uses a tubular catalyst. However, KHI probably will use honeycomb catalysts for future plants.

Compared with FGD, SCR is much simpler and costs about one-third to one-fourth less. An SCR unit is also much easier to operate and does not require an operator. When applied to oil-fired boilers, SCR plants have experienced almost no problems except for ammonium bisulfate deposition in air preheaters (Section 3.6).

4.1.2 Design of SCR Plants

A typical design of an SCR plant for an oil-fired utility boiler is shown in Figures 4-1 and 4-2. Flue gas leaving the boiler economizer outlet at 300-400°C is mixed with ammonia and sent into an SCR reactor. Although one reactor may be adequate to treat flue gas from a 700 MW boiler, two reactors in parallel also may be used with a boiler larger than 400 MW. The flue gas leaving the reactor is passed through an air preheater, an ESP, and then a scrubber, if necessary. The flue gas from an oil-fired boiler may be passed horizontally or up through the reactor while that from a coal-fired boiler must pass downward to eliminate dust plugging.

Figure 4-3 shows an example of an ammonia injection system. Generally, the ammonia flow rate is controlled by the flue gas flow rate and the incoming NO_x concentration. In a large boiler it is difficult to precisely measure the flue gas flow rate. The steam flow rate to the turbine is used as a measure of the amount of fuel being burned and the combustion gas produced. This control method can be finely tuned using the outlet NO_x level as a feedback signal.

When a boiler is operated at a low load, a low-temperature economizer outlet gas is produced. When this happens ammonium bisulfate deposits may

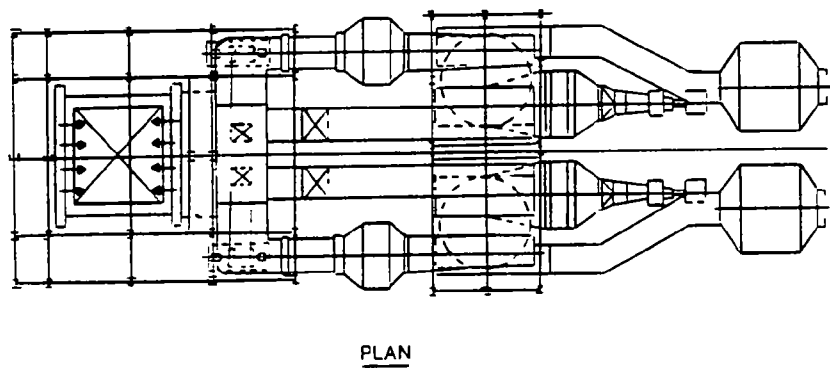
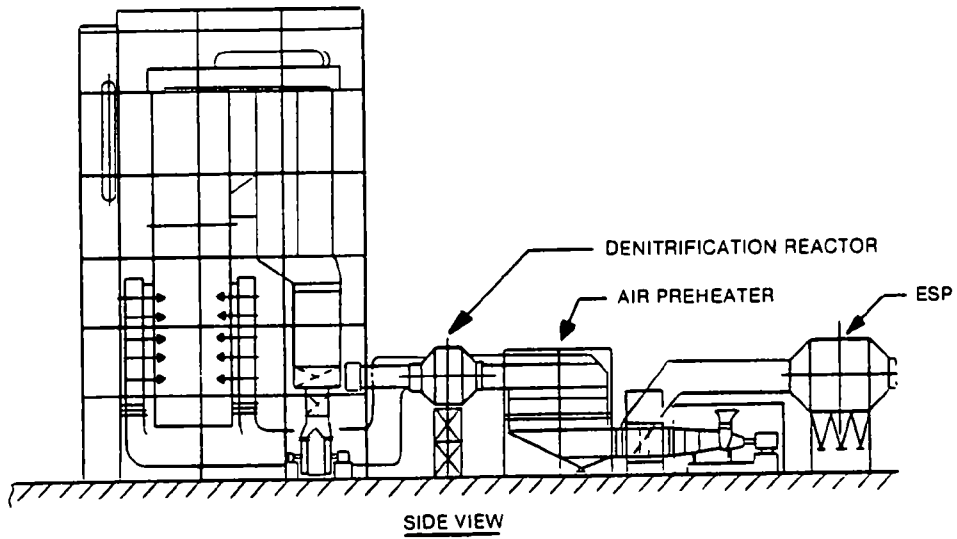


Figure 4-1 SCR Plant Layout (IHI)

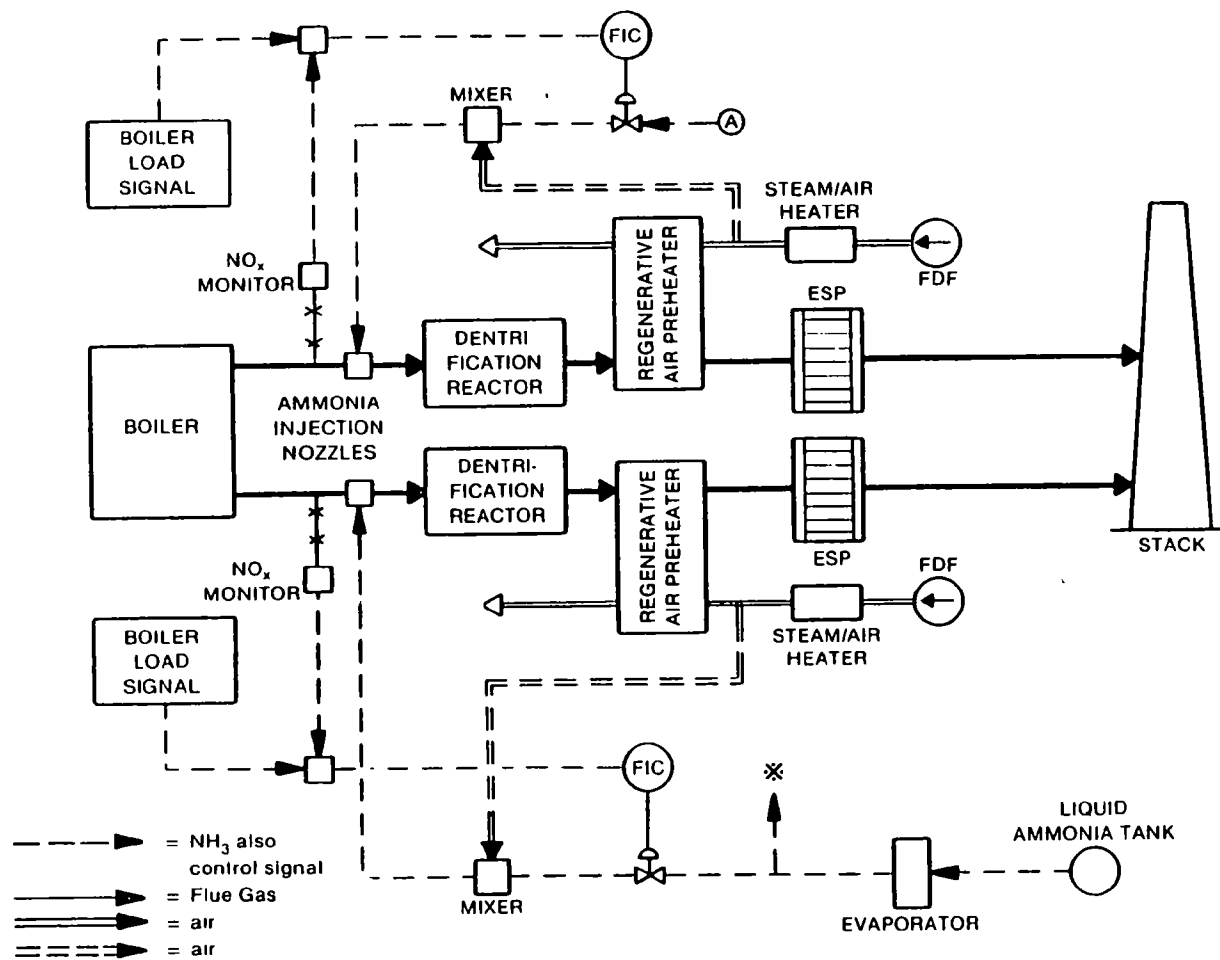


Figure 4 2 Flowsheet for Standard Boiler Denitrification Equipment Used with Heavy Oil Combustion Gas (IH1)

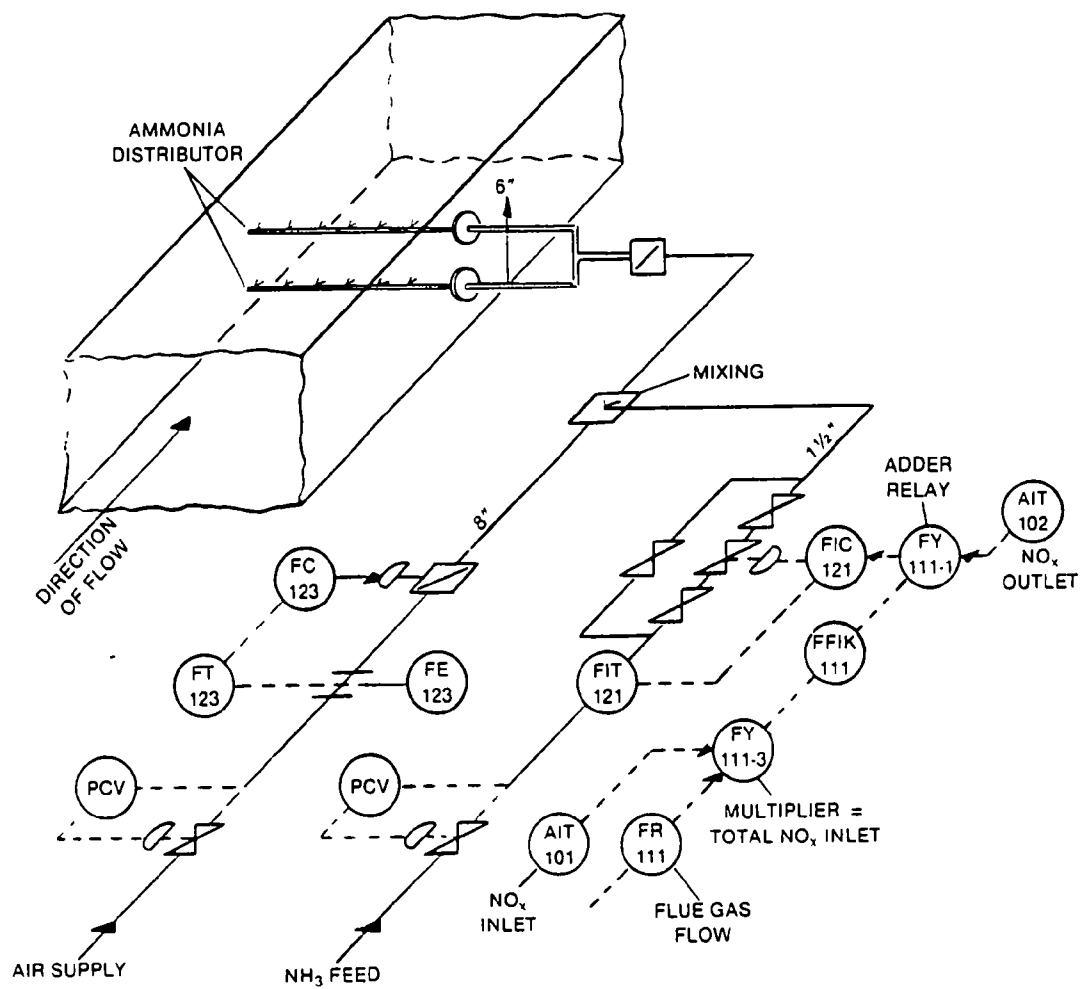


Figure 4-3 Ammonia Injection System (1)

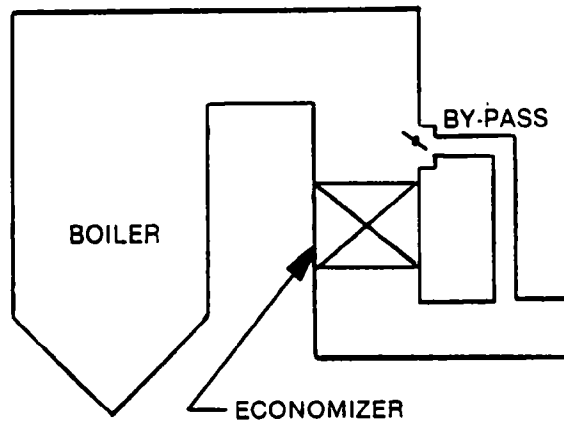
decrease the SCR catalyst's activity (Section 3.7.2). To eliminate the problem, a gas heating device can be installed on some boilers. The gas is heated either by an economizer by-pass as shown in Figure 4-4A or by modifying the economizer as shown in Figure 4-4B. The modified economizer has two heat transfer compartments, one with high efficiency and the other with low efficiency. Most of the gas is passed through the low-efficiency compartment at the low load to maintain the gas temperature above a desired level. Using such a device lowers the heat recovery efficiency at the economizer but allows the heat to be recovered by the air preheater downstream of the SCR reactor, thus avoiding a loss of energy.

The SCR reactor usually has a soot blowing system which cleans the catalyst using hot air or steam. An example of a soot blowing system is shown in Figure 4-5. However, a soot blower has not been used with most of the reactors which utilize parallel flow catalysts.

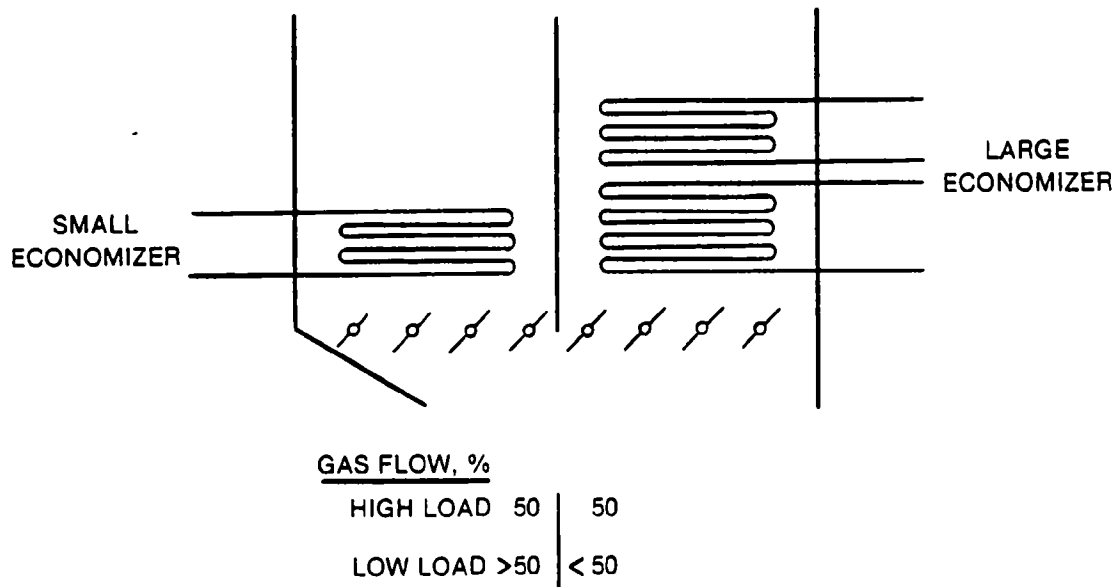
4.1.3 SCR Performance

The typical performance of an SCR unit used with a utility boiler is shown in Figure 4-6. When the boiler load is reduced, the gas temperature is substantially lowered and the NO_x removal efficiency remains almost the same. In this situation, the reduced flue gas volume results in a smaller SV, or longer reaction time. The SO_2 oxidation ratio also remains essentially the same despite a decrease in the boiler load. However, both unreacted NH_3 and pressure drop are lowered with the load.

Below a certain temperature, ammonium bisulfate (or related compounds) deposits on the catalyst and lowers catalytic activity. The critical temperature depends upon the inlet concentrations of SO_x and NH_3 and on the degree of SO_2 oxidation by the catalyst. For a flue gas from a low-sulfur oil, the critical temperature is typically around 300°C ; for flue gases from coal and high-sulfur oil, it is 20 – 40°C higher. If the gas temperature remains below the critical temperature for a few hours a day (for example during the low boiler load at midnight) and is kept around 400°C for the remainder of the



A: ECONOMIZER BY-PASS



B: SPLIT ECONOMIZER ARRANGEMENT (3)

Figure 4-4 Economizer Outlet Temperature Adjustments.

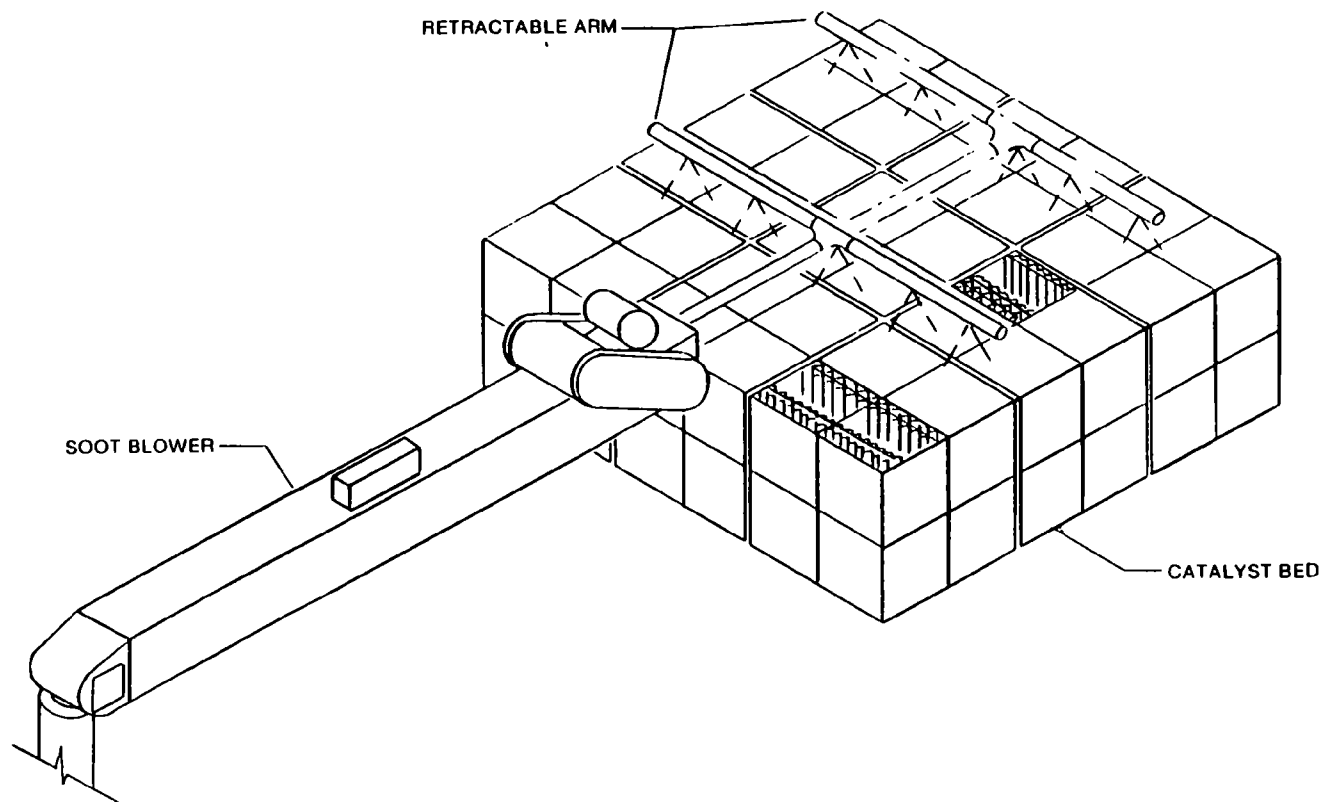


Figure 4 5 Soot Blower Used with an SCR Reactor (1)

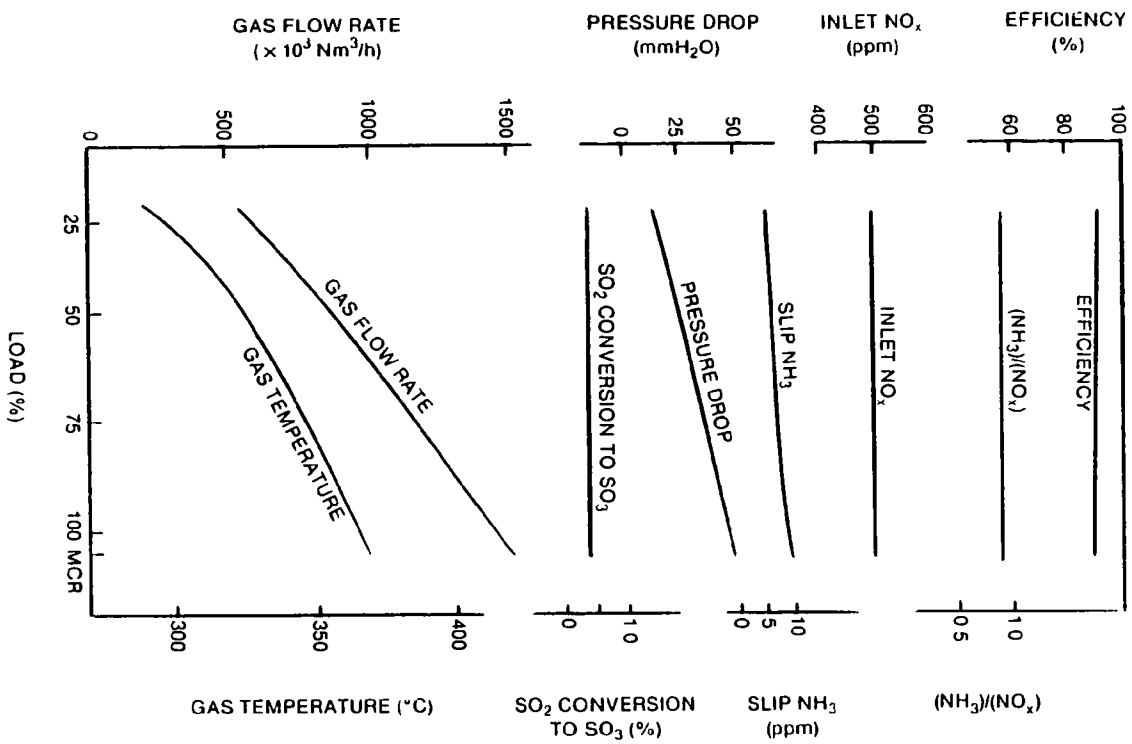


Figure 4-6 Expected Performance of an SCR Unit for a Utility Boiler (2)

day, the small amount of bisulfate formed on the catalyst at the low temperature will be removed at around 400°C. Thus, there will not be much of an adverse effect on the overall NO_x removal efficiency. If the gas temperature is maintained below the critical temperature for a longer period, the bisulfate deposition may become pronounced. To eliminate this problem the gas temperature should be maintained above a certain level, as previously described in Section 4.1.2.

For most utility boiler SCR plants, an NH₃/NO_x mole ratio of 0.83-0.90 has been used to remove 80-85 percent of NO_x while maintaining unreacted NH₃ below 10 ppm. Soot blowing is seldom used and thus no operator is needed for routine operation.

The remaining problem associated with SCR is ammonium bisulfate deposition in the air preheater. In most of the SCR plants the problem has been solved by maintaining unreacted NH₃ below 5 ppm, and using combustion control to reduce SO₂, and low-oxidation catalysts. Some of the plants also use improved air heater elements and intensive soot blowing to remove the deposits. A small amount of ammonium bisulfate may still deposit despite these practices, but it does not affect SCR operation. If necessary, the deposits can be removed when the boiler is shut down for its annual maintenance; in Japan larger boilers are required by law to perform this yearly maintenance.

Water washing also has been used to remove the bisulfate deposits. About 24 hours must be allowed for washing, which includes time for cooling, washing, and drying. When water washing is necessary two or more times a year, one of the two parallel air preheaters is shut down for each washing while the boiler operates at a half load using the other air preheater. Recently a new technology - thermal cleaning - was developed for air preheater cleaning (Section 4.3.4).

4.2 SCR PLANTS OF CHUBU ELECTRIC POWER COMPANY

4.2.1 Introduction

Chubu Electric Power Company is the third largest utility company in Japan with power stations located in the Chubu area which is between the Kanto Area (including Tokyo) and the Kansai Area (including Osaka). Since most of its steam power generating stations are close to cities and industrial regions, extensive air pollution countermeasures have been taken. These include FGD and the use of low-sulfur fuels for SO_x abatement, and combustion modification, SCR, and selective noncatalytic reduction (SNR) for NO_x abatement.

Chubu Electric's SCR plants are shown in Table 4-2. Since the three plants constructed at the Chita Station in 1978 and 1980 worked so successfully, Chubu Electric installed nine more units in 1980 and 1981 and will construct four more in 1982 and 1983.

4.2.2 Chita Power Station

The Chita Power Station, near Nagoya City (population, 2 million), has six boilers (Table 4-3) which use the most advanced NO_x control systems for utility boilers in Japan.

Extensive combustion modification has been applied to the boilers at the Chita Station, including staged combustion, flue gas recirculation, low excess air combustion, and low NO_x burners. The 350 ppm NO_x concentration in flue gas from oil-fired boilers is reduced to about 100 ppm (a 70 percent removal rate) by combustion modification.

The No. 5 and No. 6 LNG-fired boilers began operation in 1978. In order to obtain permits from the local authorities (Aichi Prefecture and Chita City) for the construction of two new boilers, Chubu Electric promised to use LNG fuel and to install SCR units to minimize NO_x emissions. In addition, Chubu Electric installed an SNR system for the No. 2 boiler and an SCR unit for the

TABLE 4-2. CHUBU ELECTRIC'S SCR PLANTS

Station	Boiler No.	Capacity (MW)	N/R*	Fuel	NO (ppm)		Removal (Percent)	Completion Date
					Inlet ^x	Outlet		
Chita	5	700	N	Gas	50	10	80	Mar. 1978
	6	700	N	Gas	50	10	80	Apr. 1978
	4	700	P	Gas, oil	100	20	80	Mar. 1980
	1	375	R	Oil	135	70	50	Dec. 1982
Nishinagoya	6	500	R	Oil	100	20	80	Jul. 1980
	4	375	R	Oil	100	20	80	Mar. 1981
	3	375	R	Oil	100	20	80	Jan. 1982
Atsumi	3	700	N	Oil	80	16	80	May 1981
	4	700	N	Oil	80	16	80	June 1981
Shinnagoya	3	220	R	Oil	75	50	33	Sept. 1980
	2	220	R	Oil	90	60	33	Apr. 1981
	5	220	R	Oil	75	50	33	Sept. 1981
	6	220	R	Oil	85	60	29	May 1981
Chita	1	700	N	Gas	50	10	80	May 1983
No. 2	2	700	N	Gas	50	10	80	Jul. 1983

*New or retrofit.

TABLE 4-3. CHITA STATION BOILER AND NO_x ABATEMENT DATA

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Boiler						
Capacity, MW	375	375	500	700	700	700
Boiler Maker	MHI ^a	MHI	MHI	MHI	BHK ^b	BHK ^b
Operation Start-up	1965	1966	1967	1974	1978	1978
Fuel	Oil	Oil	Oil	Oil, LNG	LNG	LNG
NO _x , ppm	120-140	120-140	90-100	95-100	35-50	35-50
NO _x limitation, ppm	150	100	105	20	11	11
Denitrification Plant						
Process	-	SNR ^c	-	SCR ^d	SCR ^d	SCR ^d
Constructor	-	MHI	-	MHI	Hitachi	Hitachi
Completion	-	1977	-	1980	1978	1978
NO _x Concentration	-	80-100	-	15-20	7-10	7-10
after treatment, ppm						
NH ₃ Emitted, ppm	-	10-15	-	Below 5	Below 5	Below 5

^aMitsubishi Heavy Industries^bBabcock-Hitachi^cSelective noncatalytic reduction^dSelective catalytic reduction

TABLE 4-4. EMISSION LIMITS AT THE CHITA POWER STATION

Item	Regulation	Compliance Technique
Water		
COD, mg/L	≤ 10	• Chemical treatment
TSS, mg/L	≤ 15	
Oil, mg/L	≤ 1	• Rainwater to oil separator
pH	5.8 - 8.6	
Air		
NO _x	As shown in Table 4-1	• Combustion modifications (controlled mixing and OFA) • SCR with NH ₃ • SNR with NH ₃
SO ₂	-	• Low sulfur fuel
Ash, mg/Nm ³	≤ 20	• ESP's on boilers 1, 2, 3, and 4
Noise, phones	≤ 50	• Walls around transformer • FD fan insulated • Valves covered

No. 4 boiler so that the total NO_x emissions would not increase with the addition of boilers No. 5 and No. 6. The SNR system is described in Section 6.2.4.

Table 4-4 shows the water, NO_x , SO_2 , particulate, and noise emission limits which apply to the Chita Power Station.

4.2.3 SCR Units at the Chita Station

Two full scale SCR units for the new No. 5 and No. 6 700-MW LNG-fired boilers were constructed by Babcock-Hitachi using a pellet catalyst supplied by Hitachi Ltd. (Table 4-5). Flue gas (1,900,000 Nm^3/hr per boiler) from the boiler economizer at 350°C (full load) and 290°C (250 MW load) is injected with air-diluted NH_3 and sent into two parallel reactors. Each reactor measures $10.5 \times 11.5 \times 12.0$ m and has four 11 cm-deep layers of a pellet catalyst (Figure 4-7). The flue gas passes through one of the layers in which the SV is $20,000 \text{ hr}^{-1}$. Because of good combustion control the inlet NO_x concentration is only 35-45 ppm. By adding about 0.9 mol NH_3 to 1 mol NO_x , over 80 percent NO_x removal is attained while unreacted NH_3 is maintained below 5 ppm. The plant has operated without problems since its startup in April 1978. Since that time the catalyst has not been changed; a catalyst life of over 5 years is expected. The installation cost for the plant was 2400 yen/kW including the initial charge for the catalyst.

TABLE 4-5. DATA SUMMARY ON BABCOCK-HITACHI SCR SYSTEM -
No. 5 and No. 6 BOILER, CHITA POWER STATION

Reactors per unit	2
Catalyst Type	Pellet
Catalyst Size, mm	5 x 5
$\text{NH}_3:\text{NO}_x$ Mole Ratio	0.9
NO_x Removal, design, %	80
NO_x Inlet, ppm	35-45
NO_x Outlet, ppm	7-9
Catalyst Manufacturer	Hitachi Ltd.

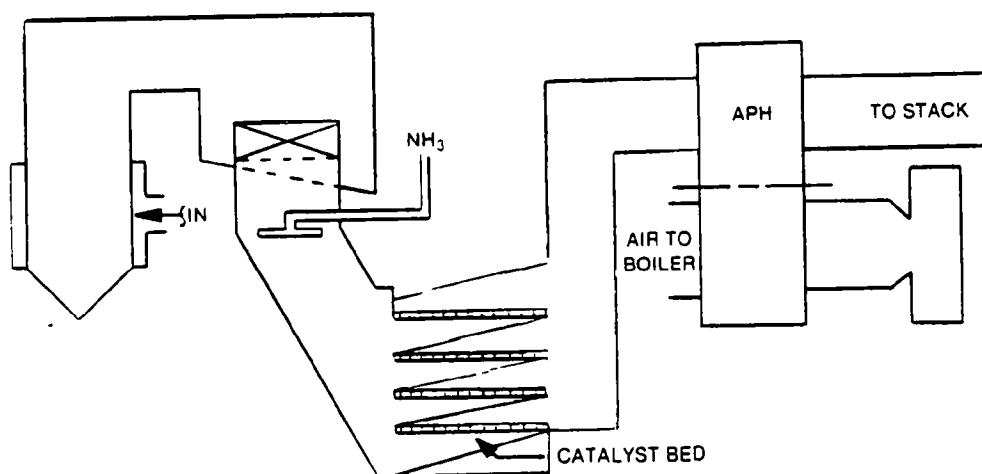


Figure 4-7 SCR Reactor and Catalyst Bed. (No 5 and No 6 Boilers, Chita Station) (3)

The SCR unit for the existing No. 4 boiler at the Chita Station was supplied by MHI and began continuous operation in March 1980. The design data for the unit are shown in Table 4-6. The unit's reactor and catalyst arrangements are shown in Figure 4-8. Within the reactor, a coated hexagonal honeycomb catalyst with a 6.8 mm channel diameter and a 1.2 mm wall thickness, is stacked in four stages. Each stage consists of two layers of catalyst packages; each package contains 50 elements.

Since startup, the SCR unit has operated without problems and has succeeded in reducing NO_x from about 100 ppm to about 18 ppm by using about 0.85 mol NH_3 to each mol of NO_x . Unreacted NH_3 has been maintained at 1-2 ppm. For fuel, the No. 4 boiler uses both low-sulfur oil and LNG, mostly the latter. There has been no ammonium bisulfate problem with the air preheater because of the low SO_x content of the flue gas and the very low level of leakage NH_3 .

The cost of this SCR installation is 2.5 billion yen (3,430 yen/kW) and therefore is relatively expensive. This is a result of the required retrofitting of extensive ductwork. The unit also uses a relatively large amount of catalyst ($\text{SV } 5,430 \text{ hr}^{-1}$) to treat flue gas from oil containing SO_x and particulates, with a low level of leakage NH_3 .

4.2.4 SCR Plants at Other Stations

In 1980 and 1981, eight SCR plants were completed at three of Chubu Electric's stations - Nishinagoya, Atsumi, and Shinnagoya - as shown in Table 4-2.

Two of the SCR plants at Atsumi are used with new 700-MW oil-fired boilers. These plants have square (grid) honeycomb catalysts with a 7 mm pitch (channel diameter plus wall thickness) and an SV of $5,200 \text{ hr}^{-1}$. A low-sulfur oil containing about 0.2 percent sulfur is burned with combustion modification using a low- NO_x burner to yield a flue gas containing about 100 ppm SO_x and 80 ppm NO_x . The gas is treated by SCR to reduce NO_x below 16 ppm. These plants have not experienced any problems to date.

TABLE 4-6. DESIGN DATA FOR THE MHI SCR SYSTEM USED WITH THE NO. 4
BOILER AT THE CHITA POWER STATION (3)

<u>General</u>	
Gas Volume, Nm ³ /hr	1,960,000
NO _x Removal, percent	80
NO _x Inlet, ppm	100
NO _x Outlet, ppm	< 20
<u>Reactor</u>	
Temperature, °C	388
<u>NH₃</u>	
NH ₃ : NO _x Mole Ratio	0.9
NH ₃ Outlet, ppm	< 10
<u>Catalyst</u>	
Space Velocity, hr ⁻¹	5430
Material	Transition Metal Oxide
Shape	Hexagonal Honeycomb
Pitch, mm	8
Manufacturer	NGK

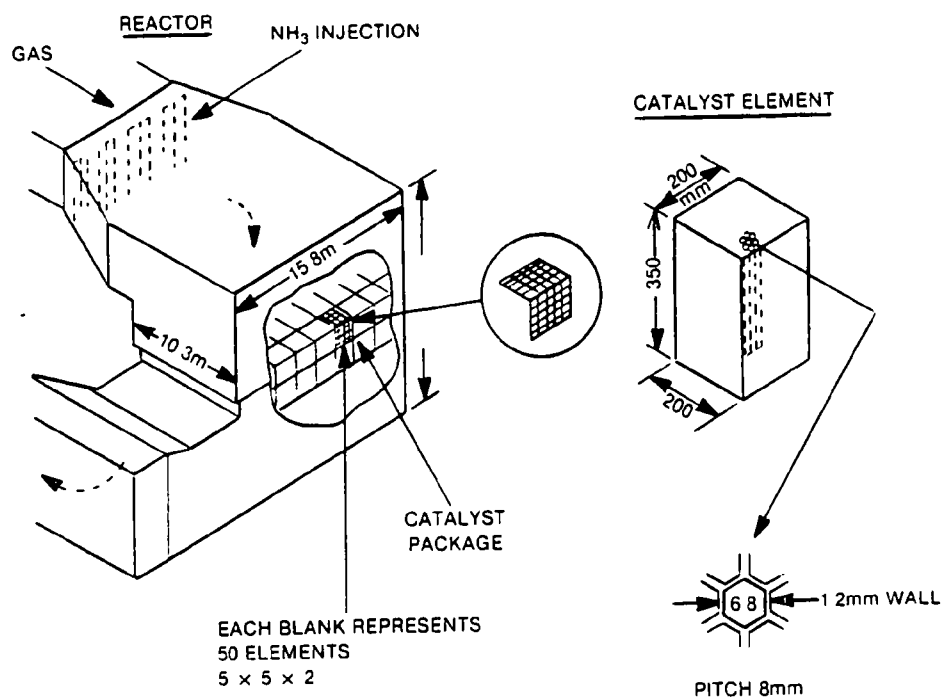
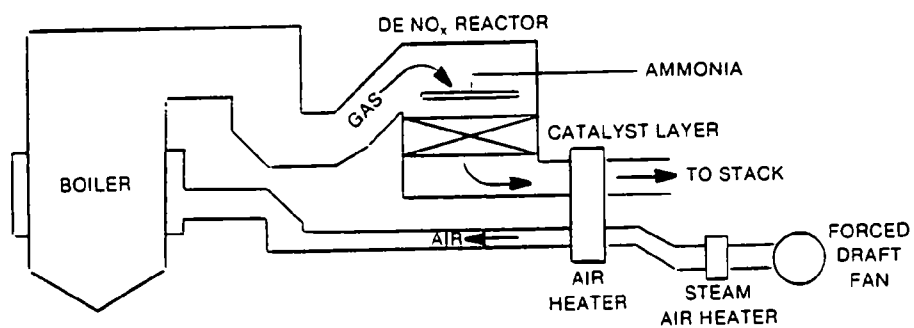


Figure 4-8 SCR Catalyst and Reactor Arrangement (No. 4 Boiler, Chita Station) (3)

The five other SCR plants are applied to existing boilers; all use honeycomb catalysts. Those at the Nishinagoya Station achieve an 80 percent NO_x removal rate, while those at the Shinnagoya Station are designed for about 30 percent NO_x removal and use a smaller amount of catalyst placed in the existing duct between the boiler economizer and the air preheater. All of these SCR plants have operated without problems.

4.3 SCR UNITS AT KUDAMATSU STATION, CHUGOKU ELECTRIC

4.3.1 Introduction

Chugoku Electric's Kudamatsu Station is located near the Tokuyama Industrial Complex and has three oil-fired boilers as shown in Table 4-7.

TABLE 4-7. BOILERS AT THE KUDAMATSU STATION

Boiler No.	Capacity (MW)	Year of Completion	NO _x (ppm)	NO _x allowed	
				(ppm)	(Nm ³ /hr)
1	156	1964	140-160	160	70
2	375	1973	130-160	32	34
3	<u>700</u>	1979	110-130	26	<u>50</u>
TOTAL	1,231				154

The No. 1 boiler was completed in 1964 and the No. 2 boiler in 1973. In order to obtain a construction permit for the No. 3 boiler, Chugoku Electric agreed to maintain total NO_x emissions below 154 Nm³/hr for the entire station. To do this, SCR plants were installed not only for the No. 3 boiler but also to remove 80 percent of NO_x from the No. 2 boiler (Table 4-7).

IHI constructed both the boilers and the SCR units at Kudamatsu. A honeycomb catalyst (square) is used in the SCR units. The SCR unit for the No. 2 boiler has a single reactor and began operation in April 1979. The No.

3 boiler's SCR unit has two reactors in parallel and began operation in September 1979 when the boiler also began operation.

Chugoku Electric also made agreements with the local government regarding SO_x and particulate emissions from the Kudamatsu Station. Emissions of SO_x must be maintained below $373 \text{ Nm}^3/\text{hr}$ by using low-sulfur oils --- 0.8 percent S for the No. 1 boiler and 0.2-0.25 percent S for Nos. 2 and 3. Particulate emissions from the station must be maintained below 20 mg/Nm^3 and below 68.6 kg/hr by using combustion control and ESP.

4.3.2 SCR Units

Flowsheets for the No. 2 SCR unit are presented in Figures 4-9 and 4-10; SCR system specifications are presented in Table 4-8. Figure 4-9 also gives the timetable for the retrofit construction; about one year was required for the SCR installation. New ducts were connected to the existing economizer and air preheaters during the annual boiler shutdown period in February and March 1979. The flowsheet of the SCR units for the No. 3 boiler is similar to the flowsheets in Figures 4-1 and 4-2.

The reactors in the SCR units each have two layers of a square ceramic honeycomb catalyst with horizontal gas flow as shown in Figure 4-11. The catalyst was produced by Sakai Chemical and Catalyst and Chemicals, Inc. Pilot plant tests by IHI indicate that the catalysts produced by the two companies meet the specifications equally well.

The $275\text{--}380^\circ\text{C}$ flue gas from the boiler economizer is injected with ammonia and introduced into the reactor. The gas is then sent through an air preheater and ESP. In the SCR plant for the existing No. 2 boiler, induced fans were installed to compensate for the pressure drop caused by the SCR reactor. The plant for the new No. 3 boiler does not have a fan.

TABLE 4-8. SCR PLANT SPECIFICATIONS (KUDAMATSU STATION, CHUGOKU ELECTRIC)

	No. 2 Boiler	No. 3 Boiler
New or retrofit	Retrofit	New
Power generation capacity, MW	375	700
Flue gas volume, Nm ³ /hr	1,050,000	1,900,000
Number of SCR reactors	1	2
Type of catalyst	Honeycomb	Honeycomb
Number of catalyst layers	2	2
Space velocity, SV ⁻¹	5,500	5,500
Catalyst volume, m ³	190	347
Flue gas temperature, °C	275-385	275-380
Type of fuel	Heavy oil	Heavy oil
Sulfur content of oil, %	0.25	0.25
Inlet NO _x , ppm (O ₂ 4%)	150-160	110-130
NH ₃ /NO _x mole ratio	0.90 (0.85) ^a	0.90 (0.85) ^a
NO _x removal, %	80 (81-83) ^a	80 (81-83) ^a
Leak NH ₃ , ppm	10 (4-6) ^a	10 (6-8) ^a
Catalyst life, year	1 (3) ^a	1 (3) ^a
Pressure drop through reactor, mm H ₂ O	102 (70) ^a	102 (70) ^a
Start-up	April 1979	Sept. 1979

^aFigures in parentheses are actual ones.

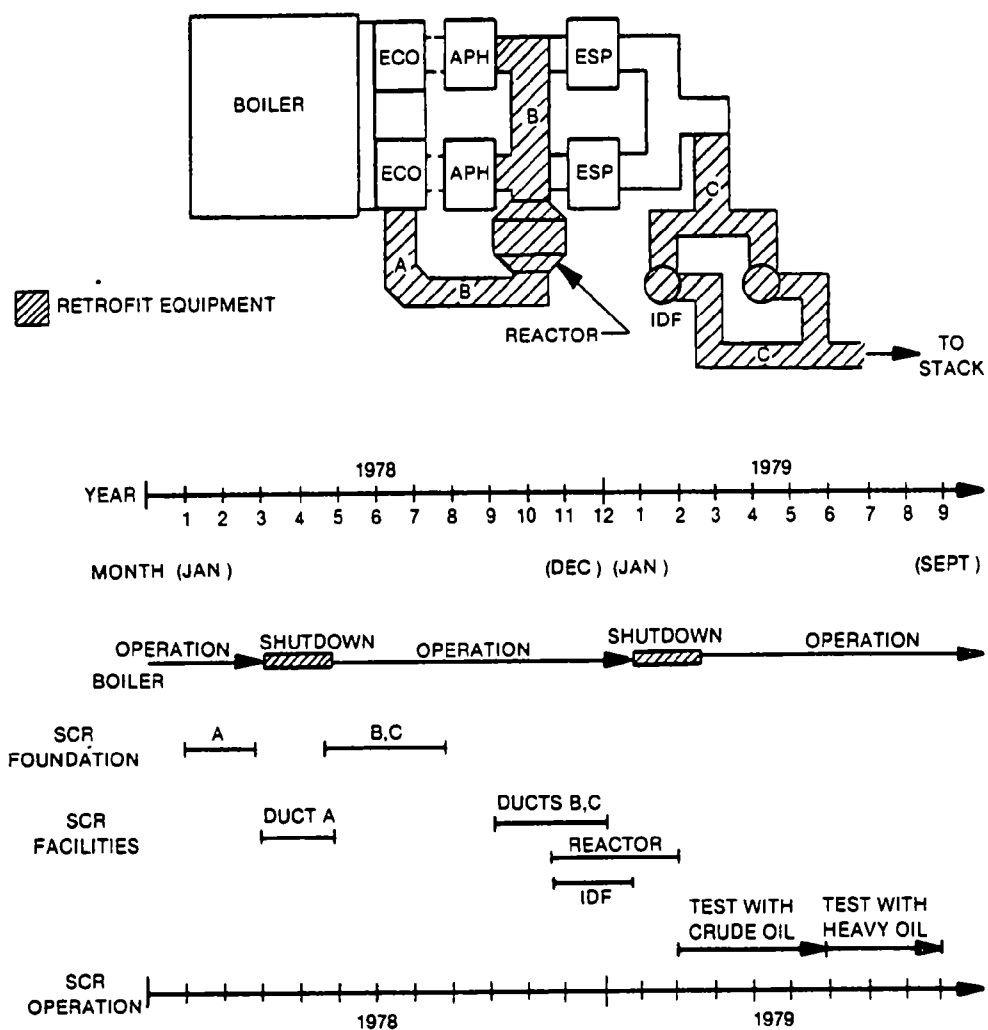


Figure 4-9 Retrofit Construction of the SCR System for the No. 2 Boiler at Kudamatsu Station

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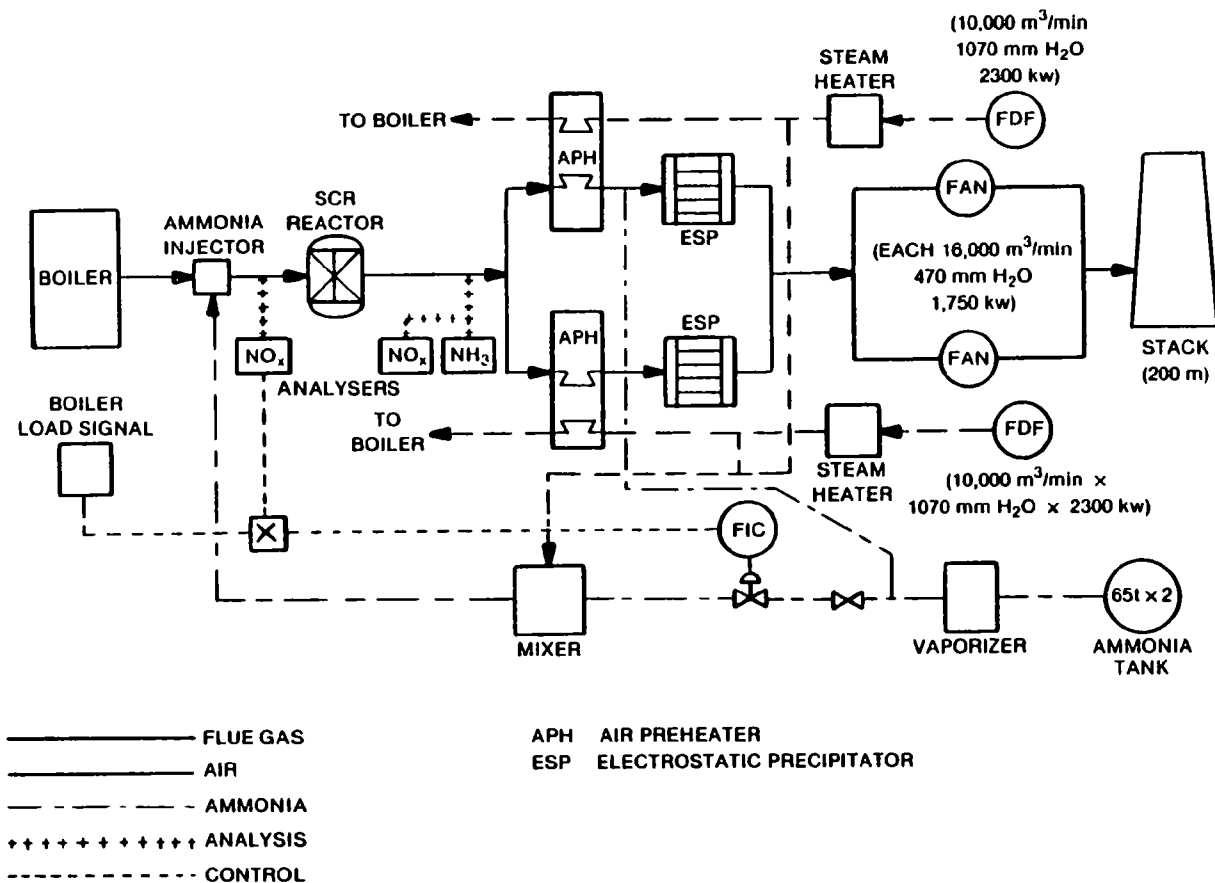


Figure 4-10 Flowsheet of the SCR System for the No. 2 Boiler at Kudamatsu Station.

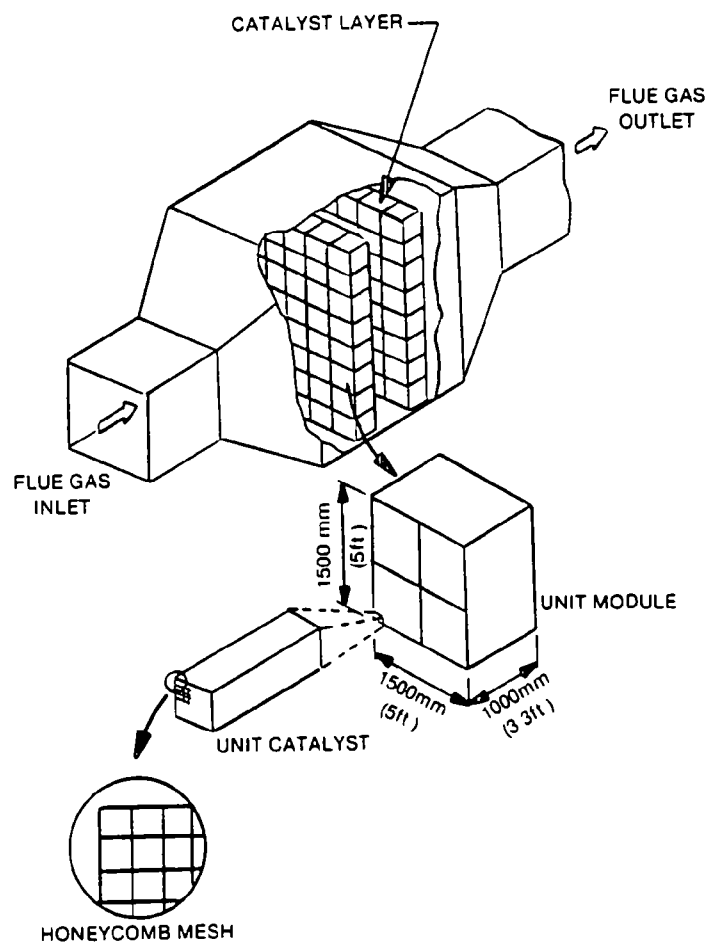


Figure 4-11 Fixed Bed Reactor for Oil Fired Applications. (horizontal gas flow)

The correct amount of ammonia that should be injection is determined by measuring the boiler load and the inlet NO_x concentration. Outlet NO_x and ammonia concentrations are also measured to trim the system. NO_x concentrations are measured by chemiluminescence and the outlet NH_3 concentration after NO conversion is continuously analyzed by catalytic oxidation (Section 3.7.6). Since this method of NH_3 analysis is not highly reliable, manual analysis is periodically used for calibration.

4.3.3 SCR System Performance

IHI guarantees that the NO_x removal efficiency of its SCR systems will be over 80% if an NH_3/NO_x mole ratio of 0.9 is used for more than a year. By using a mole ratio of 0.9, an 85-87% NO_x removal efficiency was attained initially at Kudamatsu. For normal operation, a mole ratio of 0.85 has been used for both systems. Currently the NO_x removal efficiency of the system is 81-82%, while in 1980 it was 82-83%. Unreacted NH_3 has been maintained at about 5 ppm. Based on these results the catalyst life is expected to be more than 4 years.

At a boiler load of one-third, the economizer outlet gas temperature drops to 275°C. When the boiler load goes below one-third, ammonia injection is discontinued. At this low boiler load level the NO_x concentration is already low enough to meet the established emission limit.

The pressure drop of the flue gas is 50-60 mm H_2O through the catalyst beds and nearly 100 mm H_2O through the entire SCR system, including the reactor and the connecting ducts. No increase in the pressure drop has been noticed during the more than 3-year operation period. Soot blowing systems have been installed for the reactors but have not been used because the catalyst beds have remained clean.

The No. 1 and No. 2 boilers at the Kudamatsu Station are operated by 10 persons per shift while the No. 3 boiler is operated by 4 persons per shift. No additional personnel are needed to operate the SCR system. If necessary,

the catalyst will be replaced during the annual maintenance shutdown of the boiler.

Ammonia consumption is 80-150 t/month for the two SCR plants. Two 65-ton ammonia tanks have been installed at the station. Prior to the application of SCR, ammonia was injected into the flue gas as it left the air preheater. This was done in order to neutralize the sulfuric acid mist and to prevent the corrosion of the ESP. It produced a flue gas containing nearly 10 ppm NH_3 .

The operation of the SCR units at Kudamatsu has been trouble-free except for the ammonium bisulfate problem in the air preheater which is described in the following section.

4.3.4 Ammonium Bisulfate Deposition in the Air Preheater

The flue gases from the No. 2 and No. 3 boilers contain about 1 ppm SO_3 with about 100 ppm SO_2 . After the gas passes through the SCR reactor, its SO_3 concentration increases to 5-7 ppm. The oxidation ratio of SO_2 to SO_3 is high (4-6%), because the catalyst was designed before low-oxidation catalysts were developed. In the air preheater, the flue gas containing about 5 ppm of NH_3 is cooled to 145°C and 137°C in the No. 2 and No. 3 systems, respectively.

A substantial amount of ammonium bisulfate deposits in the air preheaters of the SCR unit. In the No. 2 system, soot blowing is applied from the cold end of the preheater using 14 kg/cm² air for 2-hour periods, 3 times a day. The pressure drop of the gas through the preheater is normally about 150 mm H_2O . After the system has been operating for three or four months, the pressure drop begins to increase rapidly. When it reaches 300 mm H_2O after about four months operation, the boiler is shut down for cleaning of the preheater. One washing requires 2,500 tons of water. The wash water containing ammonium bisulfate is stored, neutralized at a rate of 50 t/hr and stored again in preparation for reuse. One washing takes about 20 hours including the drying of the preheater. Washing is usually done on weekends when the power demand is low.

The preheaters for the No. 3 boiler have soot blowing systems at both cold and hot ends. Three times a day air blowing is applied from the cold end of the preheater; steam soot blowing from the hot end is used once a day. Even with the increased blowing, water washing is necessary only once every two or three months. Five thousand tons of water are normally used to wash both of the preheaters. Each preheater is washed while the other preheater is in use and the boiler is operating at half load.

To solve the bisulfate deposition problem in the No. 3 system, a number of measures were taken during the annual maintenance shutdown of the boiler in late 1980. First, the soot blowing system at the cold end of the preheater was modified to provide a stronger blowing action. Second, a small amount of catalyst was added to the reactor in order to reduce the unreacted NH_3 from 6-8 ppm to 4-5 ppm. There was room in the catalyst container to hold the additional catalyst. Third, since dust tends to increase bisulfate deposition, the dust content of the flue gas was reduced by about one-half. The amount of dust was reduced by reducing the ratio of the flue gas recirculation and the staged combustion. This also had the effect of increasing the NO_x concentration of the flue gas from 105-110 ppm to 115-120 ppm.

So far, these modifications have proven successful with no increase in the pressure drop. The reinforced soot blowing at the cold end of the preheater is considered to be very effective; soot blowing from the hot end has been abandoned. There is no plan to add catalyst in the No. 2 system, although its soot blowing system may be reinforced in the future.

Recently Chugoku Electric, jointly with IHI, studied a new technology to remove the deposits--thermal cleaning. With this type of cleaning, the hot gas is passed through the preheater as usual while air is stopped to allow heating of the preheater elements to about 300°C. This causes the partial decomposition of the deposits. Intense soot blowing is applied during the heating process to dislodge the deposits. Test results have thus far not been disclosed.

4.3.5 Economics

The total investment cost of the Kudamatsu SCR plant was 2.2 billion yen for the No. 2 unit and 2.5 billion yen for the No. 3 unit. These costs include civil engineering, labor, and performance testing. The No. 2 unit was relatively expensive because of the complex ductwork needed for the retrofitting process as well as the installation of the induced fans.

A breakdown of capital costs for the No. 3 SCR system is given in Table 4-9. The entire No. 3 boiler and generator system cost 55 billion yen, including 2.5 billion yen for the SCR plant and 1.2 billion yen for the ESP system. In this case the SCR system accounts for 4.5% of the total cost of the boiler-generator system.

The annual cost for the No. 3 SCR plant is given in Table 4-10. The cost assumes 70% boiler utilization or actual power generation of 4,292,400 MWhr/yr. The annualized cost for SCR adds up to 0.28 yen/kWhr (assuming a 3-year catalyst life) which is equivalent to about 1.3% of the power generation cost. This cost would increase to 0.32 yen/kWhr if the catalyst life is 2 years, and would decrease to 0.26 yen/kWhr with a 4-year catalyst life. Although a small amount of catalyst was added to the No. 3 reactor, as mentioned above, it is not certain whether the addition was really needed to reduce bisulfate deposition. A 4-year catalyst life may be attained without the addition of the catalyst.

The power consumption of the SCR system represents 0.15% of the total power generated by the boiler. This is less than one-tenth of the power consumption of conventional FGD systems. The investment cost for the No. 3 plant is 3,570 yen/kW, approximately one-fifth that of a conventional FGD system.

4.3.6 Evaluation

The smooth operation of the reactor and the long life of the catalyst at Kudamatsu have demonstrated the reliability and utility of SCR for flue gas from low-sulfur oil. The ammonium bisulfate deposition problem is largely due

TABLE 4-9. CAPITAL COST BREAKDOWN OF SCR SYSTEM ON NO. 3 BOILER (700 MW)
CHUGOKU ELECTRIC, KUDAMATSU POWER STATION (\$1 = ¥250) (3)

Component	Capital Cost		Percent
	¥10 ⁹	\$10 ⁶	
Catalyst	1.1	4.4	44
Reactor	0.7	2.8	28
NH ₃ System	0.24	0.96	10
Testing and Start-Up	0.16	0.64	6
Other	<u>0.30</u>	<u>1.2</u>	<u>12</u>
TOTAL	2.5	10.0	100

TABLE 4-10. OPERATING COST BREAKDOWN OF SCR SYSTEM ON NO. 3 BOILER (700 MW)
CHUGOKU ELECTRIC, KUDAMATSU POWER STATION (\$1 = ¥250)

Component	Cost/Year		Percent
	¥10 ⁶	\$10 ⁶	
Interest	250	1.00	21
Depreciation	321	1.28	27
Tax	35	0.14	3
Catalyst	367	1.47	31
Power	83	0.33	7
NH ₃	76	0.30	6
Others	<u>62</u>	<u>0.25</u>	<u>5</u>
TOTAL	1194	4.77	100

Basis: 7 years depreciation
10% interest
3 years catalyst life

Note: Japanese utility power company economics include the catalyst cost both in the investment cost (which is depreciated) and in the operating cost.

to the high oxidation ratio of SO_2 to SO_3 which occurs with certain catalysts. The new low-oxidation catalysts greatly reduce this problem.

The applicability of thermal cleaning may be related to the intensity of the soot blowing and the specific composition of the deposits. Usually, bi-sulfate reacts with preheater construction material to form various compounds. Combinations of some of the compounds may be difficult to remove with thermal cleaning.

4.4 SCR UNIT AT THE SHIMONOSEKI PLANT, CHUGOKU ELECTRIC

4.4.1 Introduction

The Shimonoseki Station of the Chugoku Electric Power Company has two boilers--a 175 MW coal-fired boiler (No. 1) and a 400 MW oil-fired boiler (No. 2). The air and water pollution regulations which apply to the station are listed in Table 4-11.

TABLE 4-11. REGULATIONS FOR SHIMONOSEKI STATION

Pollutant	Regulated Level
<u>Air Pollution Control</u>	
k Value	2.7 (Ground level concentration 0.0047 ppm)
SO_x , Nm^3/hr	Below 412
Particulates, kg/hr	Below 130
No. 1 boiler, mg/Nm^3	Below 200
No. 2 boiler, mg/Nm^3	Below 40
NO_x , Nm^3/hr	Below 330
No. 1 boiler, ppm	Below 350
No. 2 boiler, ppm	Below 170
Suspended particulates, mg/m^3	Below 0.2
<u>Water Pollution Control</u>	
pH	5.8 - 8.6
Suspended solids, kg/day	Below 12
mg/liter	Below 15
Normal hexane soluble material	
kg/day	Below 0.8
mg/liter	Below 1
Chemical oxygen demand, kg/day	Below 12
mg/liter	Below 15

The No. 1 boiler was completed in 1967 and burned coal and oil at a 25/75 ratio before a full scale MHI limestone-gypsum FGD plant was completed in July 1979. After the FGD plant began operation, a 50/50 coal and oil ratio was used. Although the NO_x regulation may be met by combustion modification, even with coal as the only fuel, it is likely that more stringent NO_x reduction may be required in future. For this reason, Chugoku Electric decided to install a full-scale SCR unit to allow for the burning of coal as the sole fuel. This unit, completed in March 1980, is the first full-scale SCR plant for a coal-fired boiler in the world and is considered to be a demonstration plant.

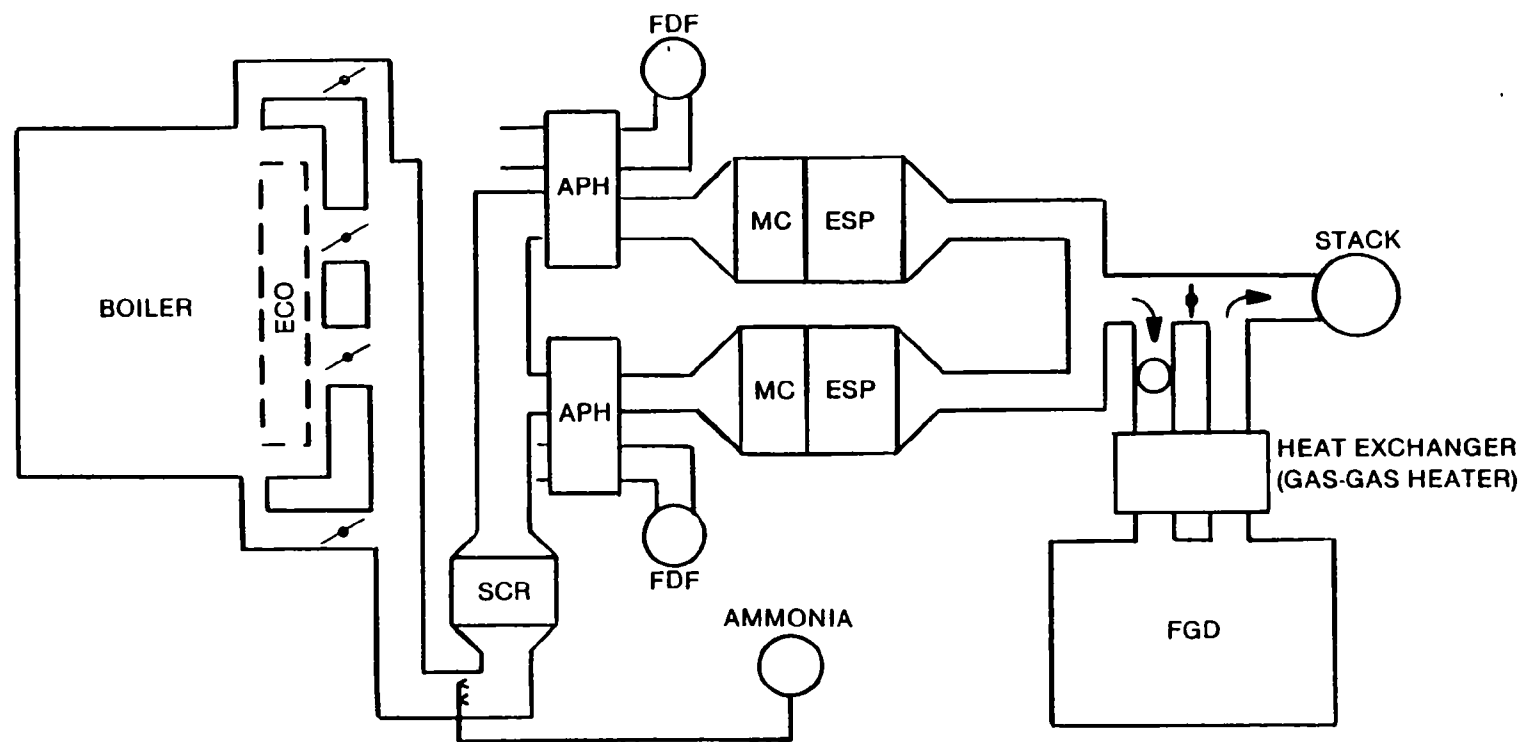
Figure 4-12 shows the combined SCR/FGD system for the No. 1 boiler. In the system, the flue gas is first subjected to SCR at 350-400°C, then passed through two trains of air preheaters and dust collectors (multi-cyclone and ESP), and finally subjected to FGD after passing through a heat exchanger.

The No. 2 boiler is a relatively new one and uses a high sulfur oil. The boiler uses combustion modification for NO_x abatement and an MHI limestone-gypsum FGD unit to reduce SO_2 .

4.4.2 SCR System

The design data for the Shimonoseki SCR system are given in Table 4-12.

The No. 1 boiler is used for the station's base load and the 370°C gas temperature at its economizer outlet is suitable for SCR. The load is sometimes lowered to 25% which causes a drop in the gas temperature. Since ammonium bisulfate may deposit on the catalyst at the low temperature and thereby lower catalytic activity, an economizer by-pass system was installed (Figure 4-12). The system mixes a portion of hot gas with the economizer outlet gas at the low load in order to maintain a gas temperature of about 350°C.



SCR SELECTIVE CATALYTIC REDUCTION OF NO_x
 MC: MULTICYCLONE
 APH: AIR PREHEATER
 FDF: FORCED DRAFT FAN
 ECO ECONOMIZER

**Figure 4-12 Flue Gas Treatment System for No. 1 175 MW Coal-Fired Boiler.
 (Shimonoseki Power Station, Chugoku Electric)**

TABLE 4-12. DESIGN DATA FOR THE MHI SCR SYSTEM INSTALLED AT THE SHIMONOSEKI POWER STATION

Item	Design Value
Flue gas flow rate	550,000 Nm ³ /hr
Inlet temperature	370°C
Inlet NO _x	500 ppm
NO _x removal	50% (Reactor sized for 80%)
NH ₃ /NO _x mole ratio	<0.51
NH ₃ emissions from reactor	<10 ppm
Inlet SO ₂	1600 ppm
Inlet SO ₃	32 ppm
Reactor dimensions	11.8m W x 8.5m D x 13.3m H
Space velocity	3000 hr ⁻¹
Catalyst	Honeycomb, solid square type. 10 mm pitch (channel diameter plus wall thickness).

An SCR reactor was installed adjacent to the boiler so that the treated gas could be sent to the existing air preheater (Figure 4-13). The reactor contains five horizontal layers of honeycomb catalyst (Figure 4-14) through which the gas passes downward. On top of the first honeycomb layer is a dummy layer made of inactive hard ceramic material with the same cross section as the honeycomb catalyst. This layer maintains a uniform parallel gas flow and prevents the erosion of the catalyst by fly ash. There is an open space at the bottom of the reactor where an additional catalyst layer could be placed to attain a higher NO_x removal efficiency.

The planning and design of the SCR system at Shimonoseki began in July 1979; construction followed in October 1979. The boiler was modified and the reactor connected during the boiler's annual maintenance shutdown period between February and March 31, 1980. Since startup in April 1980, the boiler, SCR system, and FGD system all have been operated without problems. Normally, a 0.51-0.56 mol NH₃ to 1 mol NO_x ratio has been used to remove 50-55% of NO_x. This meets the NO_x regulation and keeps unreacted NH₃ below 2 ppm. The system can be operated without an attendant.

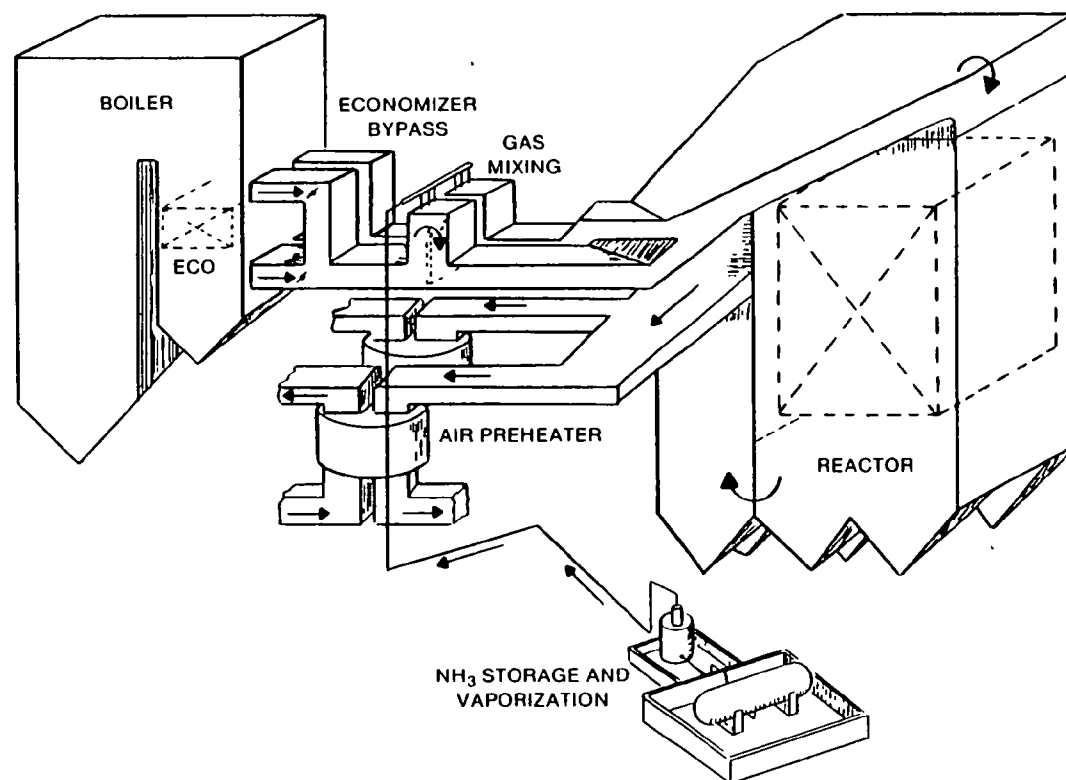


Figure 4 13 Isometric Flow Diagram of Boiler and SCR Reactor (Shimonoseki Power Station) (3)

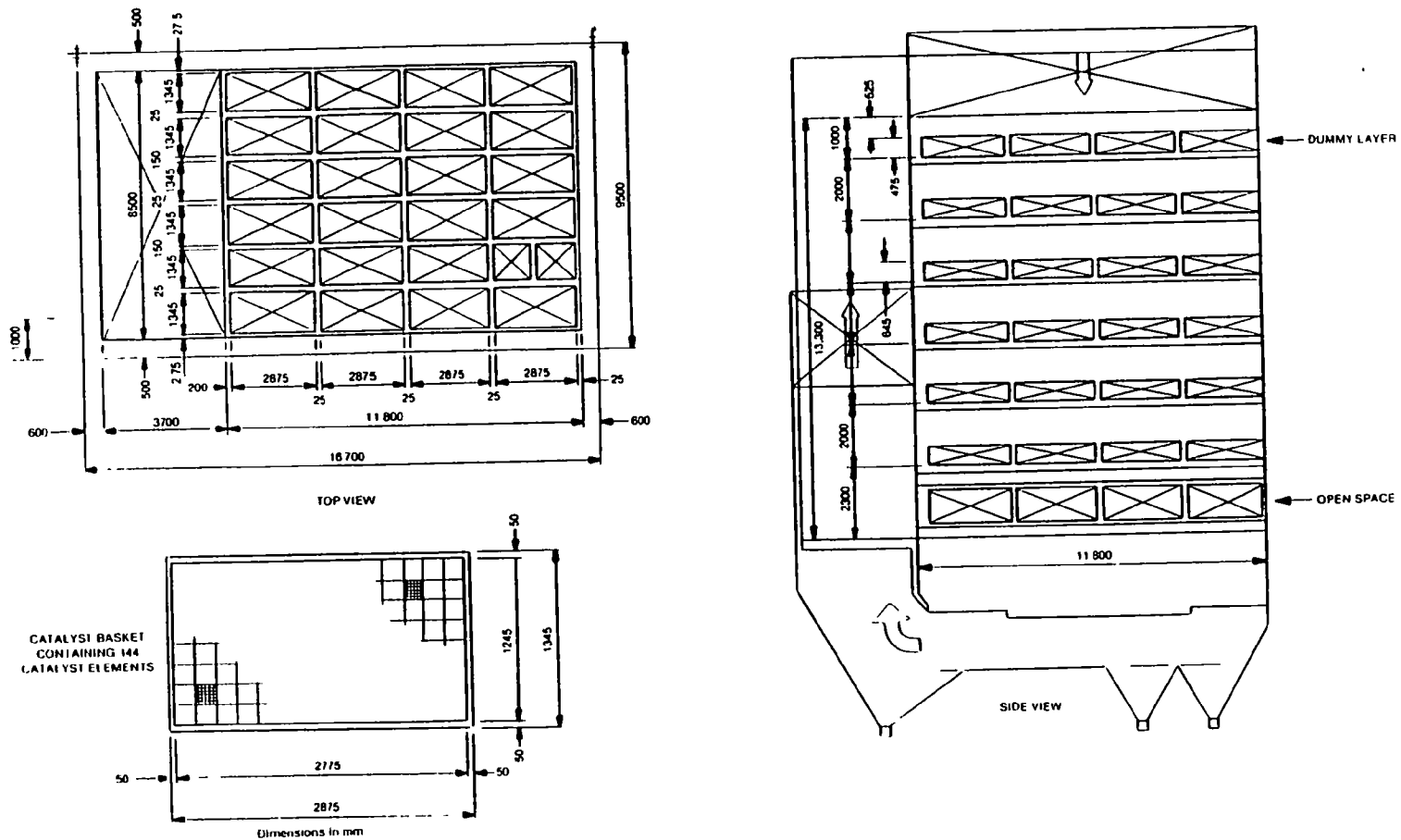


Figure 4 14 SCR Reactor and Catalyst Basket at Shimonoseki Power Station

MHI guarantees a catalyst life of one year for its SCR system. At Shimonoseki, the catalyst was used for more than two years without any degradation, except for some very minor erosion observed at the inlet edge of the first reactor layer. Three years of catalyst life is expected and the catalyst may be replaced during the annual boiler maintenance period. The reactor has a soot blowing system but it has not been used thus far because the catalyst has remained clean.

In this system the air preheater also has been kept clean. Originally, the air preheater contained dual-undulated elements for high- and medium-temperature zones and notched flat elements for the low-temperature zone. It also was equipped with a soot blowing system at the cold end which was operated for 2-hour periods, 4 times daily. When the SCR unit was installed, a notched flat element was substituted for the dual-undulated element in the medium temperature zone: the former can be more easily cleaned by soot blowing. An additional soot blowing system was installed at the hot end of the preheater. Since the startup of the SCR system, soot blowing from both ends has been used for 2-hour periods, 4 times daily. Thus the air preheater has been kept clean and has not caused an increase in the pressure drop.

The total investment cost of the Shimonoseki SCR system was about 2 billion yen in 1980 including 1.7 billion yen paid to the builder (3).

In the future, when 80% NO_x removal is required, a small amount of catalyst will be added so that 80% removal is attained.

4.4.3 Problems Related to Unreacted NH₃

The amount of ammonia injected in the SCR reactor at Shimonoseki is determined by the flue gas volume and inlet NO_x concentrations in a manner similar to that used at other SCR plants. The concentration of the unreacted NH₃ can be measured but has not been used to determine ammonia injection because the method of measurement is less reliable than those used for other parameters. Recently the Shimonoseki station began using a new method of analyzing unreacted NH₃ developed by Shimazu (Figure 4-15). A sample portion

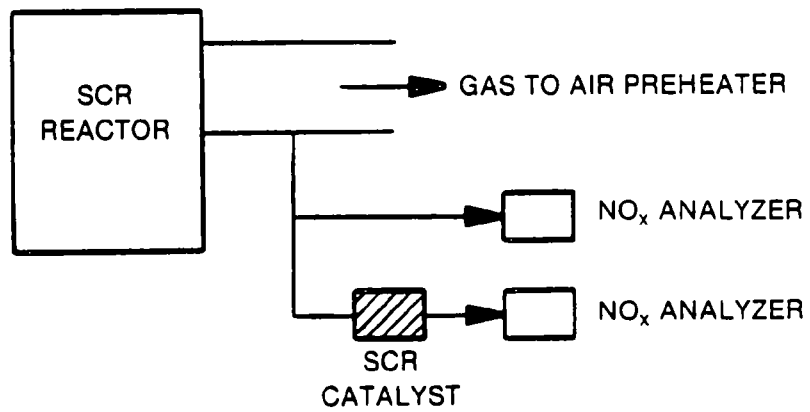


Figure 4-15 Principle of Unreacted NH_3 Analysis.

of the reactor outlet gas is sent through the reactor (with the SCR catalyst) where all of the unreacted NH_3 is converted to N_2 and H_2O after reacting with the NO in the gas. The amount of NH_3 in the gas is calculated by determining the difference between the NO_x concentrations in the gas which has been sent through the reactor and that which has not been exposed to the catalyst. This method seems suitable for analyzing a low level of unreacted NH_3 .

The product fly ash at Shimoseki contains very little ammonia and can readily be used for cement, concrete, or landfill material. It is assumed that the ammonia contamination of the fly ash will not be extensive as long as unreacted NH_3 is kept below 5 ppm.

The unreacted NH_3 is eventually caught by the FGD system downstream of the air preheater. The NH_3 has not caused any problems in the FGD system or with wastewater treatment because of its low concentration level.

The Shimonoseki Station's No. 2 boiler uses a high sulfur oil. For this reason, ammonia is injected into the flue gas as it leaves the air preheater in order to prevent ESP corrosion and also to increase particulate removal efficiency. Thus, the flue gas which is sent into the FGD system contains about 5 ppm NH_3 , which is more than that found in the No. 1 boiler flue gas after SCR. The FGD system for the No. 2 boiler, as well as the wastewater treatment system, has had no problem with the ammonia.

4.4.4 Evaluation

The smooth operation of the SCR system at Shimonoseki has demonstrated the commercial applicability of the high dust system for coal-fired boiler flue gas. The use of a dummy layer in the reactor successfully prevents catalyst erosion and is responsible for a catalyst life expectancy of more than 3 years.

The gas temperature at the SCR reactor has been kept above about 330°C . The critical temperature at which ammonium bisulfate deposits on the catalyst differs with the inlet SO_x concentration, the catalyst-induced oxidation

ratio of SO_2 to SO_3 and other factors. It has been found that with flue gas from heavy oil or crude oil, the oxidation ratio increases with time due to the deposition on the catalyst of vanadium derived from oil. This increase in oxidation may not occur with coal, particularly with the high dust system. Those problems warrant additional future study at Shimonoseki.

Since the catalyst has proved to be free from dust plugging and erosion problems, even for flue gas with a full dust load, MHI has decided to use a more efficient catalyst with a 7-mm pitch for future high-dust system SCR plants. This efficient catalyst has already been used at SCR plants for three coal-fired boilers (75 MW, 75 MW, and 125 MW) at Chugoku Electric's Shin-Ube Station, which began operation in early 1982. By using an SV of 4,000 hr^{-1} and a NH_3/NO_x mole ratio of 0.66, 65% of NO_x has been removed with 2 ppm unreacted NH_3 . The plants have operated successfully and the unreacted NH_3 has not caused any effect on the air preheater, FGD system, or fly ash composition.

4.5 SCR SYSTEM AT TOMATO-ATSUMA STATION, HOKKAIDO ELECTRIC

4.5.1 Introduction

In October 1980, Hokkaido Electric completed a new 350 MW coal-fired boiler at Tomato-Atsuma. The station is located in a new industrial district developed by the Hokkaido government. The flue gas treatment system for the Tomato-Atsuma boiler is shown in Figure 4-16. In accordance with local regulations, NO_x emitted from the boiler is less than 184 Nm^3/hr (158 ppm); SO_x is kept below 152 Nm^3/hr (130 ppm). The boiler burns domestic low-sulfur coal containing 0.3% sulfur and 1.2% nitrogen. A hot-side ESP has been installed to maintain a high dust removal efficiency. This unit is the first hot-side ESP installed in Japan for a utility boiler. At the plant, combustion modification including staged combustion, flue gas recirculation, and a low- NO_x burner, is used to reduce NO_x to 200 ppm. To meet the NO_x regulatory requirement, one-fourth of the flue gas is treated by SCR to achieve over 80% NO_x removal. A limestone-gypsum FGD system has been installed which removes over 90% of the SO_x from half of the flue gas.

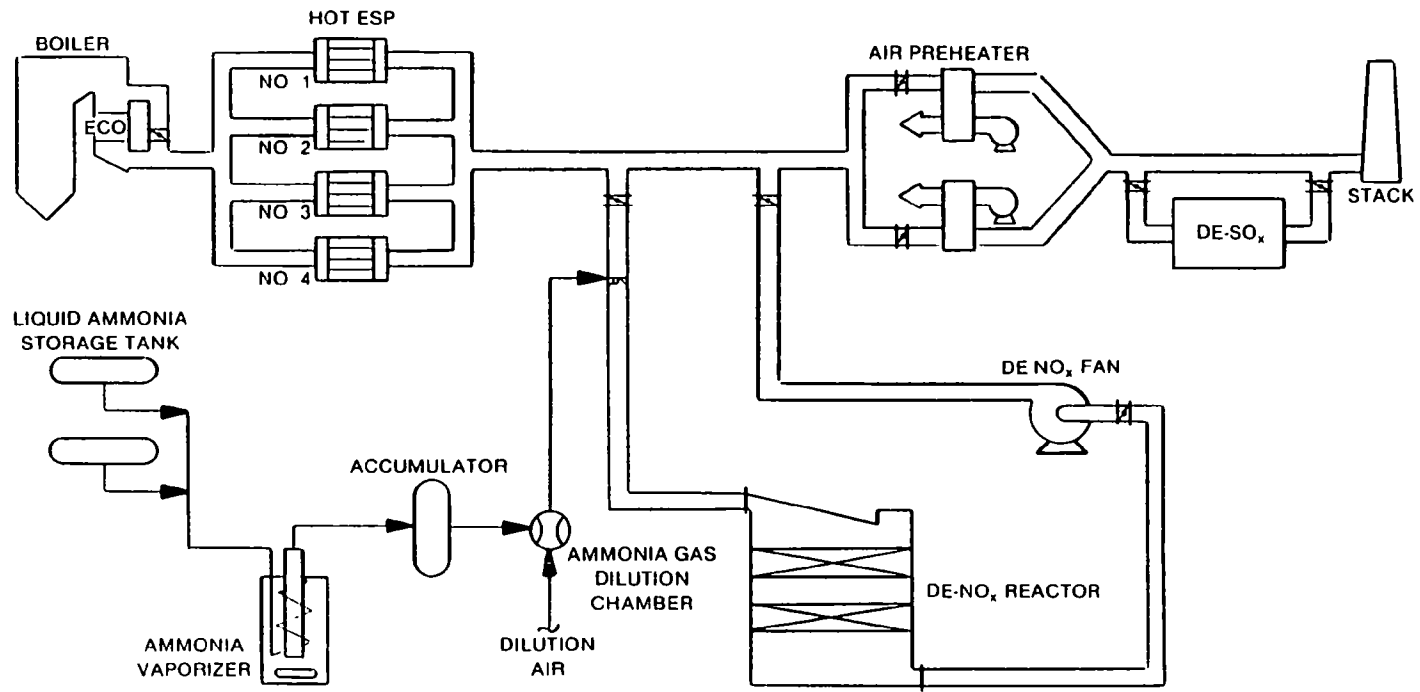


Figure 4-16 Flowsheet for the De NO_x System at the Tomato Atsuma Station
(Hokkaido Electric Power Co.)

The total investment cost for the power station at Tomato-Atsuma was 70 billion yen including 11-13 billion yen for pollution control facilities. The boiler, SCR unit, and FGD unit all were constructed by Babcock Hitachi Ltd. Since its startup in October 1980, the entire system has operated smoothly, except for a few minor problems with the FGD wastewater treatment system.

4.5.2 SCR System

The design conditions and equipment specifications for the Tomato Atsuma SCR unit are listed in Tables 4-13 and 4-14, respectively. A plate catalyst (1 mm thick with 10 mm pitch) produced by Hitachi Ltd. is used in the unit (Figure 4-17).

TABLE 4-13. DESIGN CONDITIONS FOR SCR UNIT, TOMATO-ATSUMA STATION, HOKKAIDO ELECTRIC POWER COMPANY

Items	Design Base	Remarks
Gas flow	280,000 Nm ³ /hr	350 MW x 1/4
Inlet gas temperature	356°C	
Inlet NO _x concentration	Max. 200 ppm	
Outlet NO _x concentration	<40 ppm	
NO _x removal efficiency	>80%	(Guaranteed)
Inlet dust load	45 mg/Nm ³	
Slip ammonia concentration	<10 ppm	
Inlet gas humidity	8.16 Vol. %	

The 360°C flue gas leaving the boiler economizer is sent through the hot-side ESP where its dust content is lowered from about 23 g/m³ to 45 mg/Nm³, a removal efficiency of 99.8%. Then the gas is sent downward through an SCR reactor. Gas velocity in the reactor is about 4 m/sec. This rate is sufficient to prevent both erosion and dust plugging of the catalyst. Eighty to 85% of the NO_x is removed in the reactor by using a ratio of 0.85 to 0.9 mol NH₃ to 1 mol NO (Table 4-15).

TABLE 4-14. PRIMARY PLANT EQUIPMENT SPECIFICATIONS

Equipment	Item	Description
DeNO _x Reactor	Type	Vertical Type Parallel Flow
	Number	1
	Size	6.6m W x 17m H x 8.8m L
	Material	Carbon Steel
Catalyst	Type	Plate Type (1 mm x 10 mm Pitch)
	Number	Two layers
	Material	Titanium base
DeNO _x Fan	Type	Double Suction Turbo Fan
	Number	1
	Flow	11,900 m ³ /min at 356°C
	Pressure	-340 mmH ₂ O (Inlet)
		-170 mmH ₂ O (Outlet)
	Motor	480 kW, 50 Hz, 10 P
Liquid Ammonia Storage Tank	Type	Horizontal Cylinder with Pillow Support
	Number	2
	Capacity	10 t
	Material	SB46N2SR (carbon steel)
Ammonia Vaporizer	Type	Vertical Spiral Tube
	Number	1
	Capacity	Max. 113 Kg/h
	Material	SS41, STPG38
Ammonia Accumulator	Type	Vertical Cylinder
	Number	1
	Capacity	0.5 m ³
	Material	SM41B
Ammonia Gas Dilution Chamber	Type	Horizontal Cylinder
	Number	1
	Material	STPG38

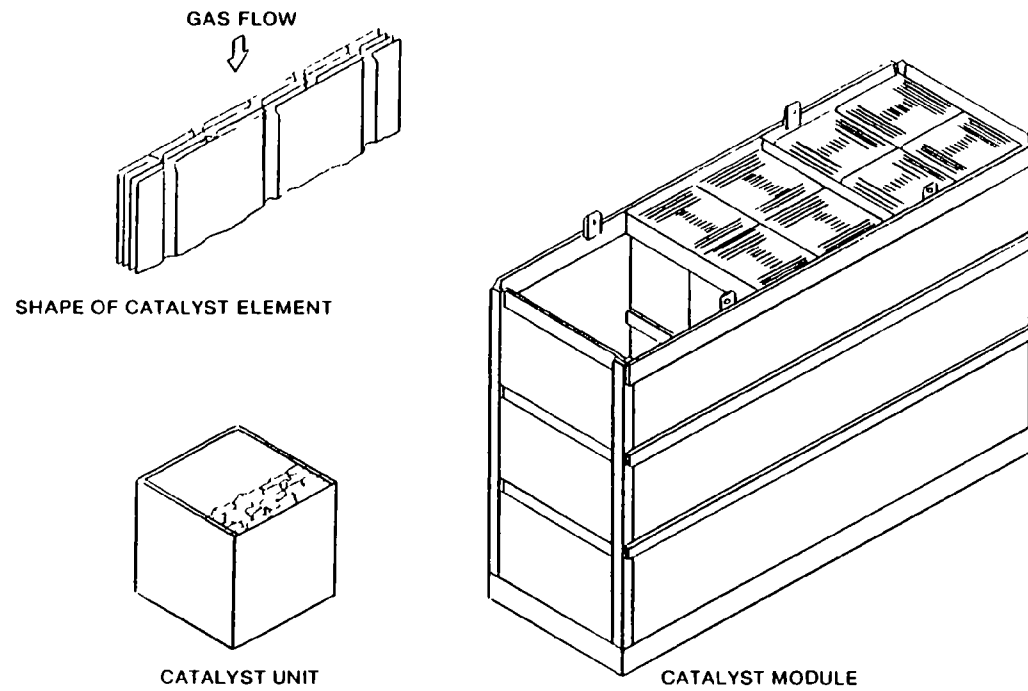


Figure 4 17 Catalyst Used in the Tomato-Atsuma SCR Unit

TABLE 4-15. DATA, TOMATO-ATSUMA SCR UNIT, HOKKAIDO ELECTRIC POWER COMPANY

Items	Design	Actual
Gas flow, Nm ³ /hr	280,000	287,000
Inlet gas temperature, °C	356	332
Inlet NO _x concentration, ppm (O ₂ 6%)	200	181
Outlet NO _x concentration, ppm (O ₂ 6%)	40	34
NO _x removal efficiency, %	80	81.2
(NH ₃)/(NO _x) Mole Ratio	0.85	0.85
Slip ammonia concentration, ppm	10	1.9
Inlet gas humidity, vol %	8.16	10.0

The amount of inlet ammonia injected is determined by the inlet flue gas volume and NO_x concentration. Outlet NH₃ concentration is sometimes measured manually; usually, the outlet NH₃ is kept below 5 ppm.

In May 1981, the entire system, including the boiler, was shut down for a 4-day scheduled inspection period. The SCR catalyst was found to be clean although a soot blowing system had not been installed. In addition, the air preheater had almost no deposits in it and required no cleaning. During the nearly 2-year operation period, the system did not experience any increase in the pressure drop of the preheater nor any decrease in NO_x removal efficiency. Although catalyst life is guaranteed for 1 year, it is expected that the catalyst will be used for more than 2 years to maintain over 80% NO_x removal efficiency with less than 10 ppm leakage NH₃.

The cleanliness of the air preheater is due to the following factors:

1. Low leakage NH₃ in the gas (below 5 ppm) which is further diluted when the gas is mixed with untreated flue gas before entering the preheater.
2. Low SO_x concentration in the gas, the low oxidation ratio of SO₂ to SO₃ (about 0.2%) caused by the catalyst, and the dilution by untreated flue gas.

3. Low dust content of the gas.

4. The use of soot blowing.

4.5.3 Future Construction

In 1985, Hokkaido Electric will complete the construction of a 600-MW coal-fired boiler at the Tomato-Atsuma station. This No. 2 boiler will be constructed by IHI; Hitachi Ltd will supply the turbines. Imported coal, containing 1.2% S and 1.8% N, will be used with extensive combustion modification to maintain NO_x below 170 ppm. This combination will enable the boiler to comply with the regulations without requiring SCR. The flue gas leaving the air preheater will be treated by a cold ESP and an MHI limestone-gypsum FGD system. Although the No. 2 boiler will not have an SCR reactor, a space between the boiler economizer and air preheater will be reserved for future installation of a high-dust SCR system.

4.5.4 Evaluation

The SCR unit at Tomato-Atsuma is the first commercial low-dust SCR unit to use a hot ESP for flue gas from coal. The smooth operation of the plant demonstrates that the low-dust system, as well as the high-dust system, is feasible. The Hitachi plate catalyst is very efficient and removes over 80% of NO_x with only a small amount of unreacted NH₃.

Several years ago when Hokkaido Electric decided to use the low-dust system, the high-dust system had not yet proved to be viable; now Hokkaido Electric is interested in using the high-dust system. Although the company currently has no plans to install an SCR system for the No. 2 boiler, a high-dust system will be installed if SCR proves to be necessary.

4.6 KANSAI ELECTRIC'S SCR PLANTS

4.6.1 Large Scale Testing of SCR

Kansai Electric, the second largest utility company in Japan, first installed an SCR test plant in 1977. The plant is capable of treating one-fourth of the flue gas from an existing 450 MW oil-fired boiler at the Kainan Station. Initially, a ring tube catalyst was used in a fixed bed. The flue gas contains about 100 ppm each of SO_x and NO_x with about 20 mg/ Nm^3 of particulates. The 330-380°C flue gas leaving the boiler economizer enters the SCR reactor where over 80% of NO_x is removed and unreacted NH_3 is maintained at around 10 ppm. At first, the reactor had dust plugging problems and as a result, the ring tube catalyst was replaced by a Hitachi plate catalyst. With the new catalyst, the SCR system has experienced trouble-free operation.

In 1977, Kansai Electric also installed a Thermal De NO_x SNR system for an existing 156 MW boiler at its Himeji Station. In 1978, a small amount of a honeycomb SCR catalyst was installed in the duct between the boiler economizer and the air preheater in order to increase NO_x removal efficiency and reduce unreacted NH_3 . The SNR unit was removed in 1979. Since then, about 30% of the NO_x has been removed by the catalyst and a small amount of ammonia has been injected between the boiler economizer and the catalyst bed.

Both of the plate catalysts at Kainan and the honeycomb catalyst at Himeji have been used with little degradation for about 4 years. Based on these results, Kansai Electric has installed many commercial SCR plants which use honeycomb and plate catalysts (Table 4-1).

4.6.2 Commercial SCR Plants

As shown in Table 4-1, Kansai Electric has 25 commercial SCR plants for existing oil- and gas-fired boilers and plans to install 6 plants for new oil-fired boilers. Twenty-one plants which use honeycomb catalysts have been or will be constructed by MHI and IHI; Babcock Hitachi has or will construct

another 10 plants which use plate catalysts. All of the SCR reactors are placed between the boiler economizer and air preheater.

As shown in Figure 4-18, the SCR reactors for the Sakaiko Station's No. 2, 4, 6 and 7 boilers (250 MW each) are each placed in a small space at the economizer outlet. The reactors use MHI honeycomb catalysts with a space velocity of $5,070 \text{ hr}^{-1}$ so that flue gases from both oil and gas burning can be treated.

The SCR system performance for the No. 6 boiler which fires LNG is shown in Figure 4-19. The flue gas contains about 110 ppm NO_x . By using 0.8 mol NH_3 per mol of NO_x , over 75 percent of the NO_x is removed with less than 5 ppm of unreacted NH_3 . During 13,000 hours of operation, the SCR system showed only a slight decrease in NO_x removal efficiency--from 77-78% at the beginning to 76-77% at the end.

Figure 4-20 shows the retrofitting of the SCR reactor for the existing No. 2 boiler (156 MW) at Kansai Electric's Osaka Station. The SCR reactor is positioned just above the vertical flow preheater so that the gas is sent downward through the reactor. SCR reactors also have been installed for the Nos. 3 and 4 boilers. These boilers burn 1% sulfur oil and produce flue gas containing about 500 ppm SO_2 with a small amount of SO_3 . To meet regulatory requirements, a low oxidation honeycomb catalyst is used to remove 75% of NO_x and to maintain unreacted NH_3 below 5 ppm.

As of July 1982, the SCR systems for boiler Nos. 2 and 4 have operated without problems for about 9,000 hours. There has been no ammonium bisulfate deposition in the air preheaters, which may be due to the low levels of unreacted NH_3 and SO_3 .

Osaka Station's No. 1 oil-fired boiler (156 MW) has a simple SCR system which uses a small amount of catalyst in the duct between the boiler economizer and air preheater. This system removes about 30% of NO_x .

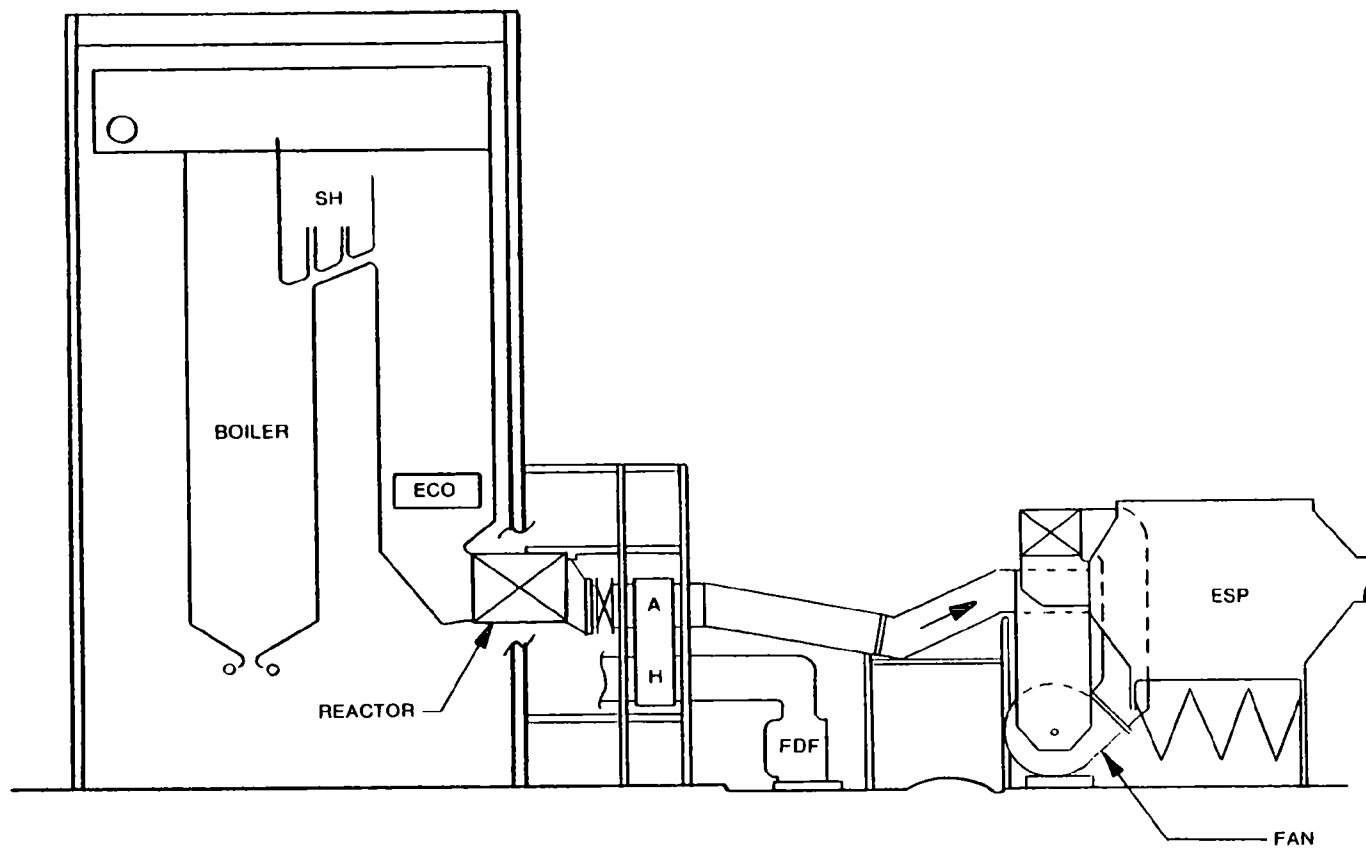
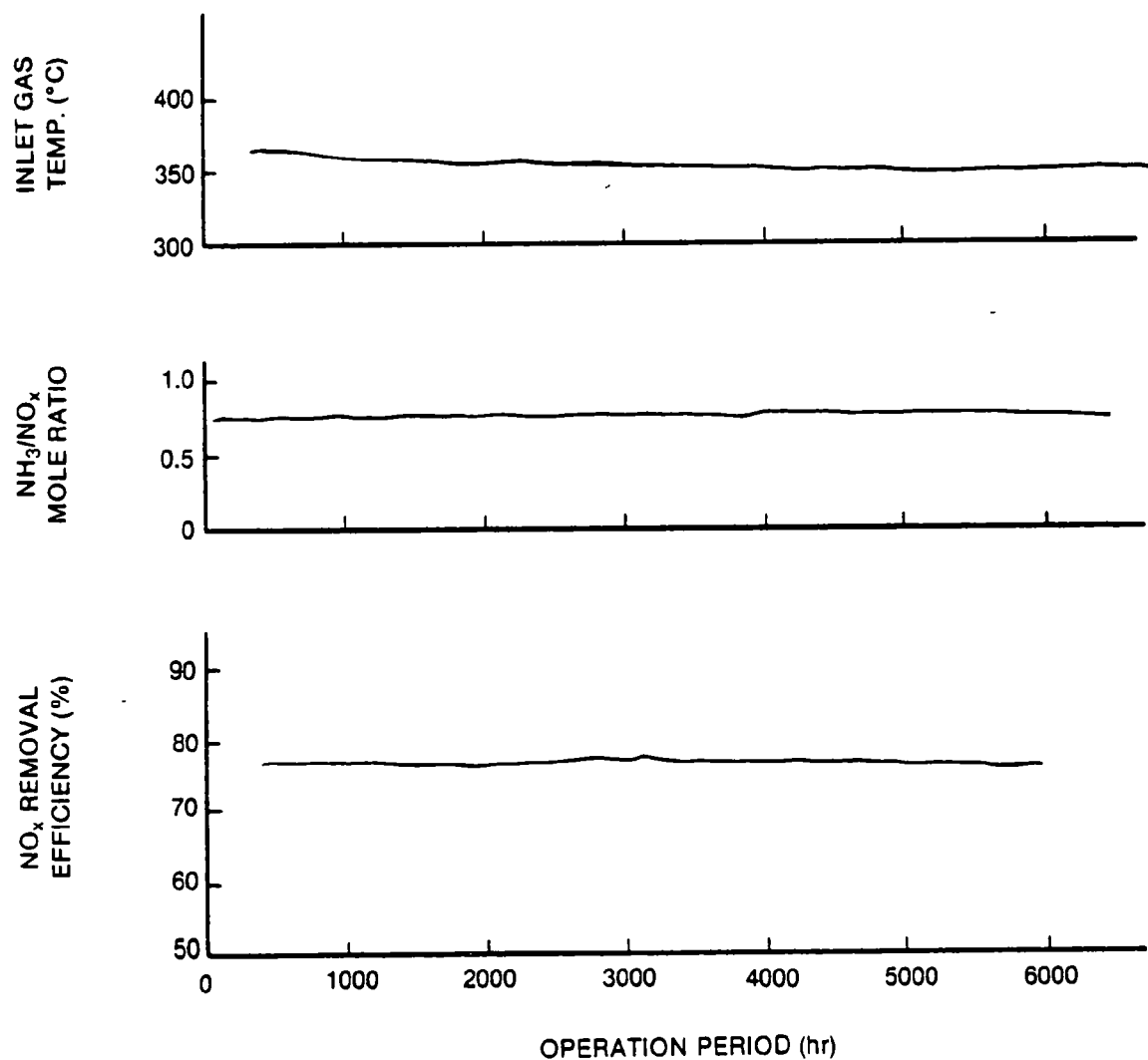


Figure 4 18 SCR Reactor Retrofitted to Boiler Nos 2, 4, 6, and 7
(Sakai Station, Kansai Electric Power Company)



(Figures plot data once a day at full load)

Figure 4-19 Performance of the SCR Unit for the 250 MW, LNG-Fired No. 6 Boiler.
(Sakaiko Station)

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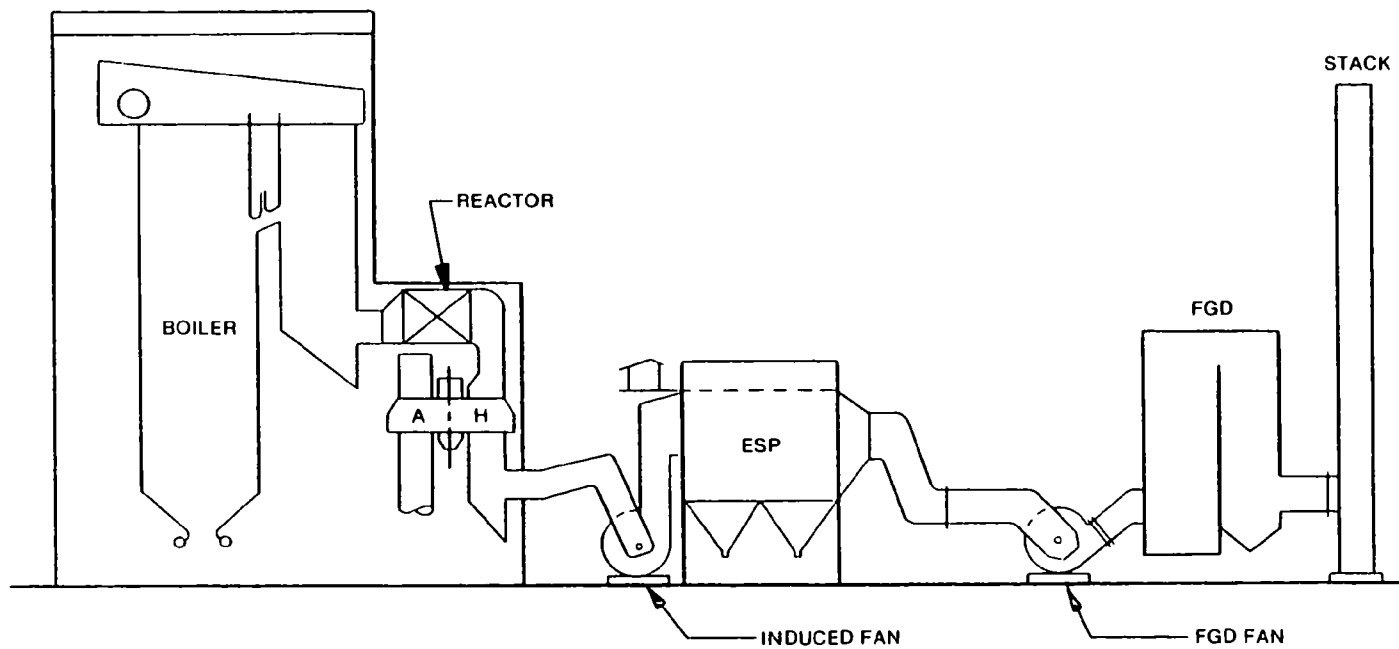


Figure 4 20 SCR Reactor Retrofitted to Boiler Nos. 2, 3, and 4
(Osaka Station, Kansai Electric Power Company)

Figure 4-21 shows the SCR reactor which was retrofitted to the existing No. 6 boiler (600 MW) at Kansai's Himeji No. 2 Station. The boiler burns either oil or gas. IHI constructed the SCR plant which uses a honeycomb catalyst; a large additional amount of ductwork was required to connect a large reactor between the boiler economizer and air preheater. The boiler has two trains of air preheater-ESP systems and therefore required an SCR reactor for each of the trains. The boiler burns LNG currently and the SCR systems have been operated without problems.

4.6.3 Evaluation

Kansai Electric's SCR units have been operated without problems. The lack of a bisulfate deposition problem in the unit's air preheaters may be due to the use of a catalyst with a low SO_2 oxidation capability and to a low level of unreacted NH_3 .

4.7 SCR TESTS AT THE NAKOSO STATION (5)

4.7.1 Test Plant

Tokyo Electric Power Company, Tohoku Electric Power Company, Joban Joint Power Company, and MHI conducted extensive testing of SCR with flue gas (4,000 Nm^3/hr) from the No. 7 boiler at Joban's Nakoso Station. The tests were run from April 1979 to November 1980. The No. 7 boiler burned 40% coal and 60% oil in the daytime and 60-70% coal/30-40% oil during the reduced load period at night.

The flowsheet of the test plant is shown in Figure 4-22. The plant consisted of both high-dust and low-dust SCR systems in combination with wet limestone-gypsum FGD system. The high-dust system treated flue gas with a full dust load of 6-10 g/Nm^3 . It used 2 downflow SCR reactors with honeycomb or plate catalysts. In the high-dust system, a ceramic dummy spacer was placed above the catalyst layer to protect the catalyst from fly ash erosion. In the low-dust system, the flue gas first was sent through a hot ESP where the dust content was reduced to 0.1-0.3 gram/Nm^3 . From there, the gas went

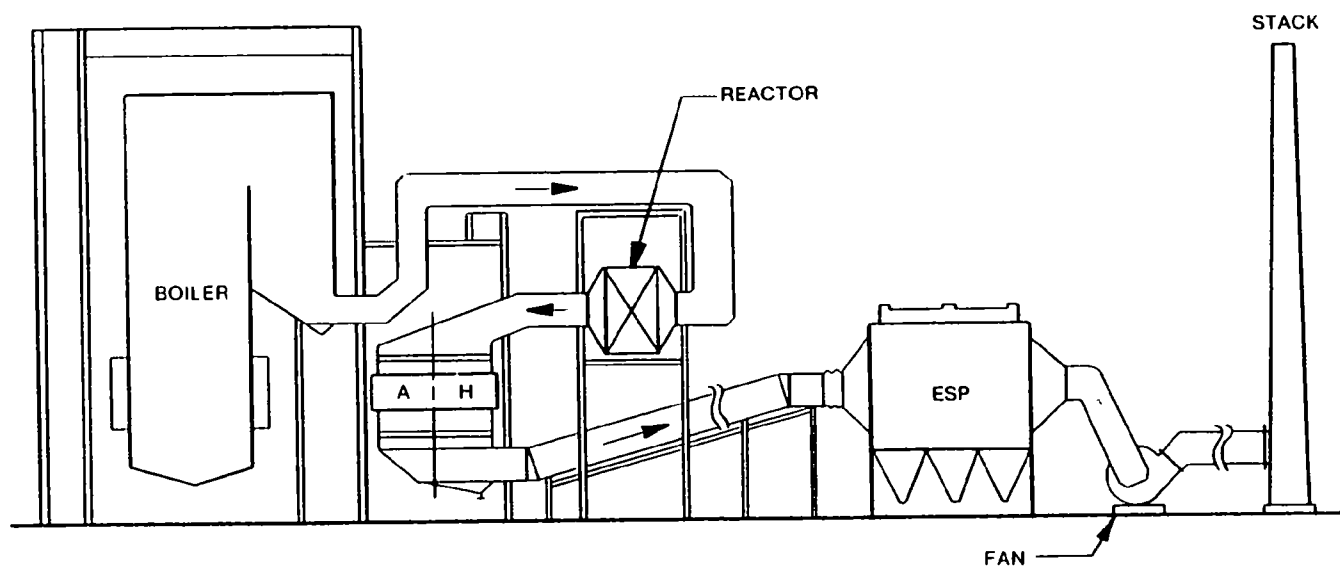


Figure 4-21 SCR Reactor Retrofitted to Boiler No. 6 (Himeji Station, Kansai Electric Power Company)

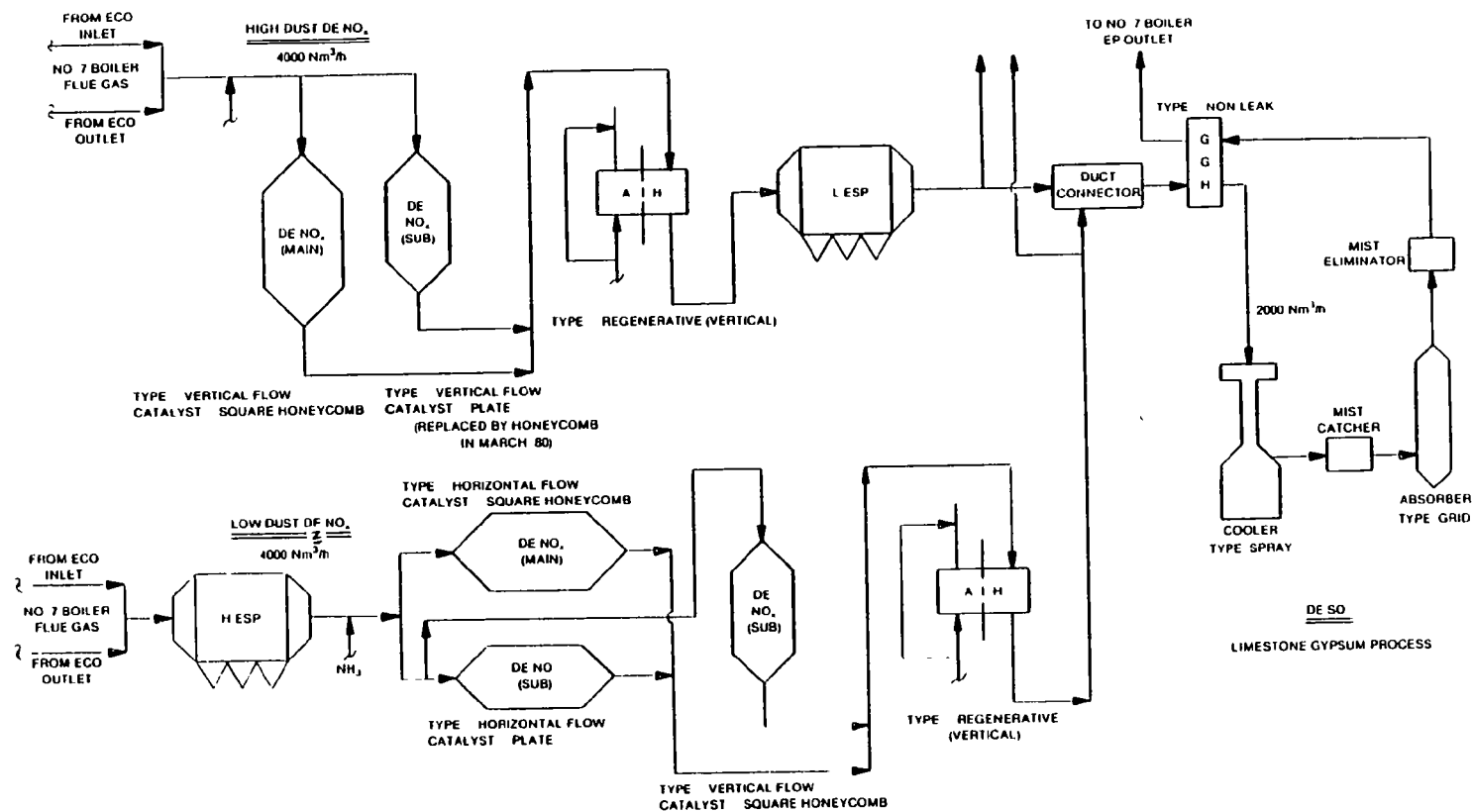


Figure 4 22 Flowsheet of the Nakoso SCR Test Plant

into 3 SCR reactors in parallel. Two of the reactors used either a honeycomb or plate catalyst with horizontal gas flow while the third used a honeycomb catalyst with gas downflow. A vertical flow air preheater was installed downstream of each of the reactors.

4.7.2 Test Results

Tests were conducted for a total of 10,600 hours, excluding monthly shutdown periods for inspection. These shutdown periods typically lasted several days.

Figure 4-23 summarizes 1979 test results for the high-dust system. An NO_x removal efficiency of 80% was attained throughout the test period. The catalysts were kept clean and showed no degradation; the dummy layer successfully prevented catalyst erosion.

During the test period the pressure drop of the gas through the catalyst bed remained at about 25 and 15 mm H_2O for the main and sub reactors, respectively, without soot blowing.

The air preheater contained dual-undulated elements for high- and intermediate-temperature zones and a notched flat element for the low-temperature zone. Soot blowing was applied once a day to keep the preheater clean. There was no increase in the pressure drop through the preheater during the entire 10,600 hour test period. Unreacted NH_3 was maintained at 1-3 ppm. Results of the first 5,000 hours of testing are given in Figure 4-24.

Figures 4-25 and 4-26 present results of tests on the low-dust system. Without soot blowing, fine particles of fly ash deposited horizontally on the inlet edge of the honeycomb catalyst. This caused an increase in the pressure drop and a decrease in the NO_x removal efficiency. The ash deposits were removed by soot blowing. Deposition can be reduced by using a honeycomb with a larger channel diameter or with a higher gas velocity, but these measures will not prevent the large increase in the pressure drop which occurs when

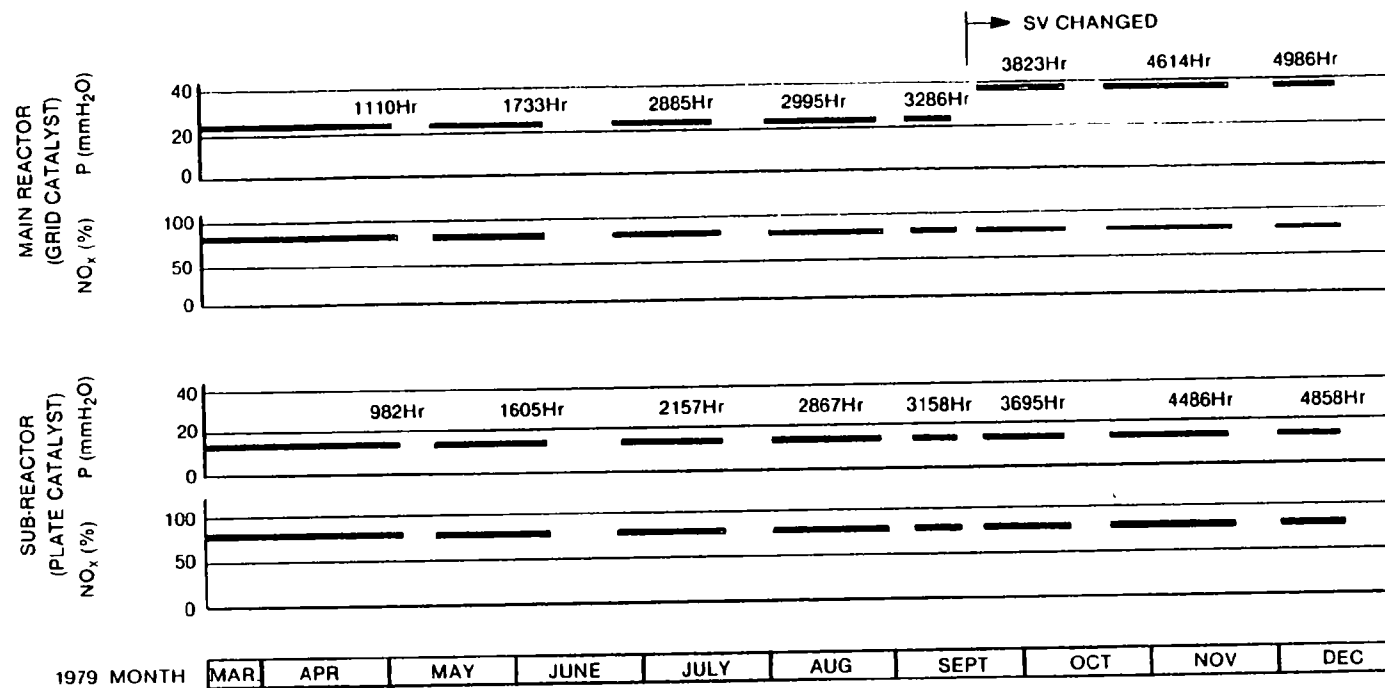


Figure 4 23 Operating Experience of High Dust De NO_x System

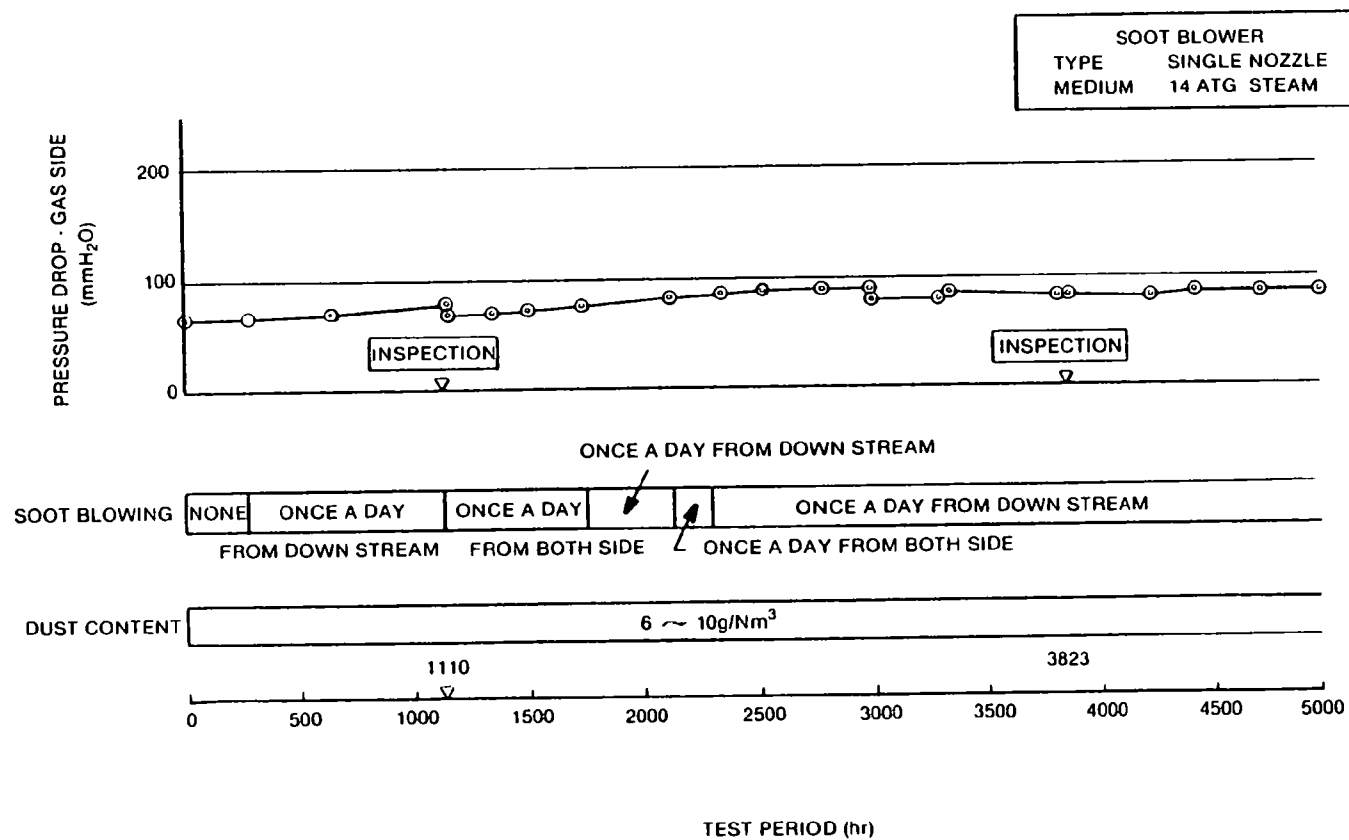


Figure 4-24 Operating Experience of Air Preheater vs Soot Blowing (high dust content)

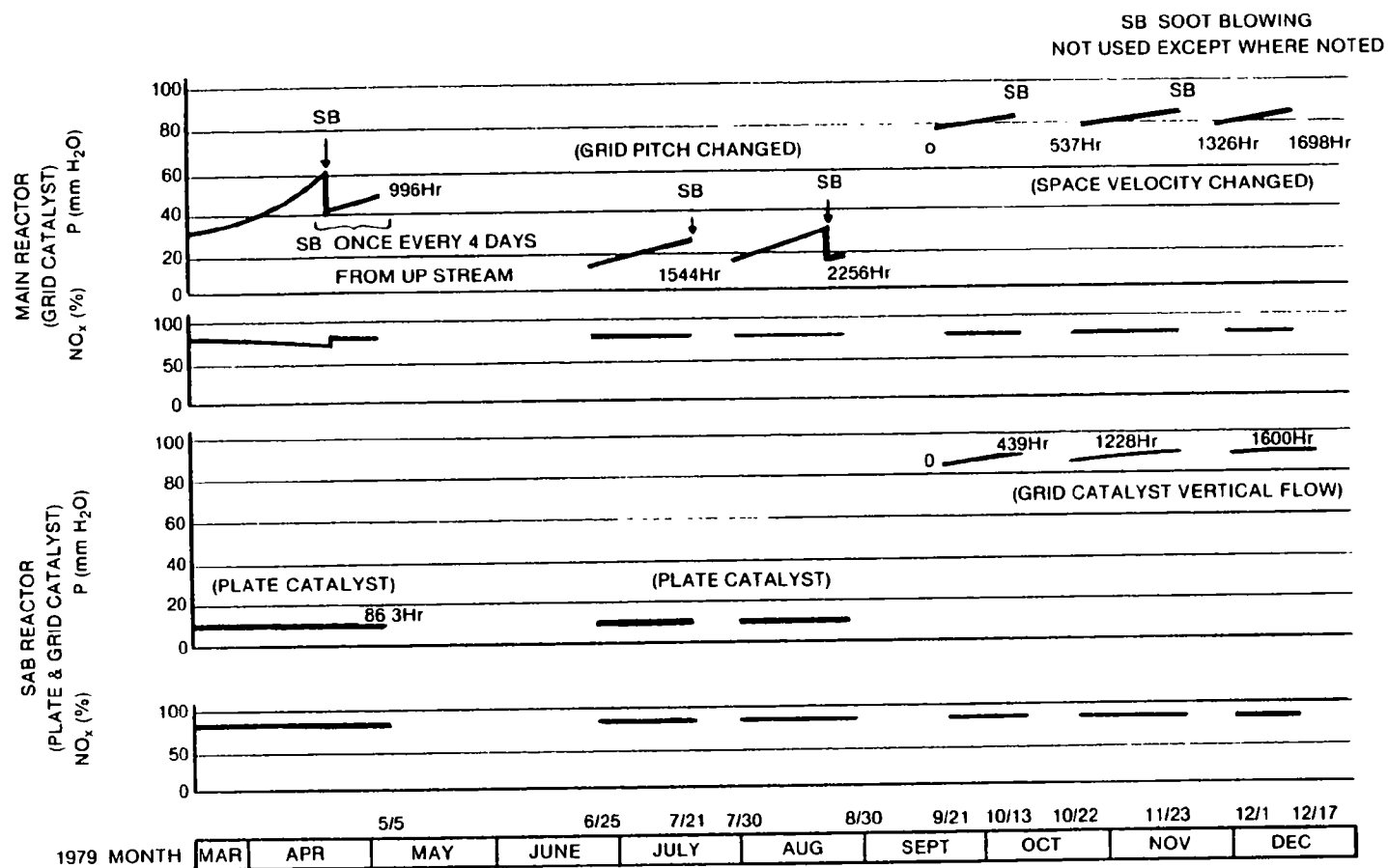


Figure 4 25 Operating Experience of Low-Dust De NO_x System

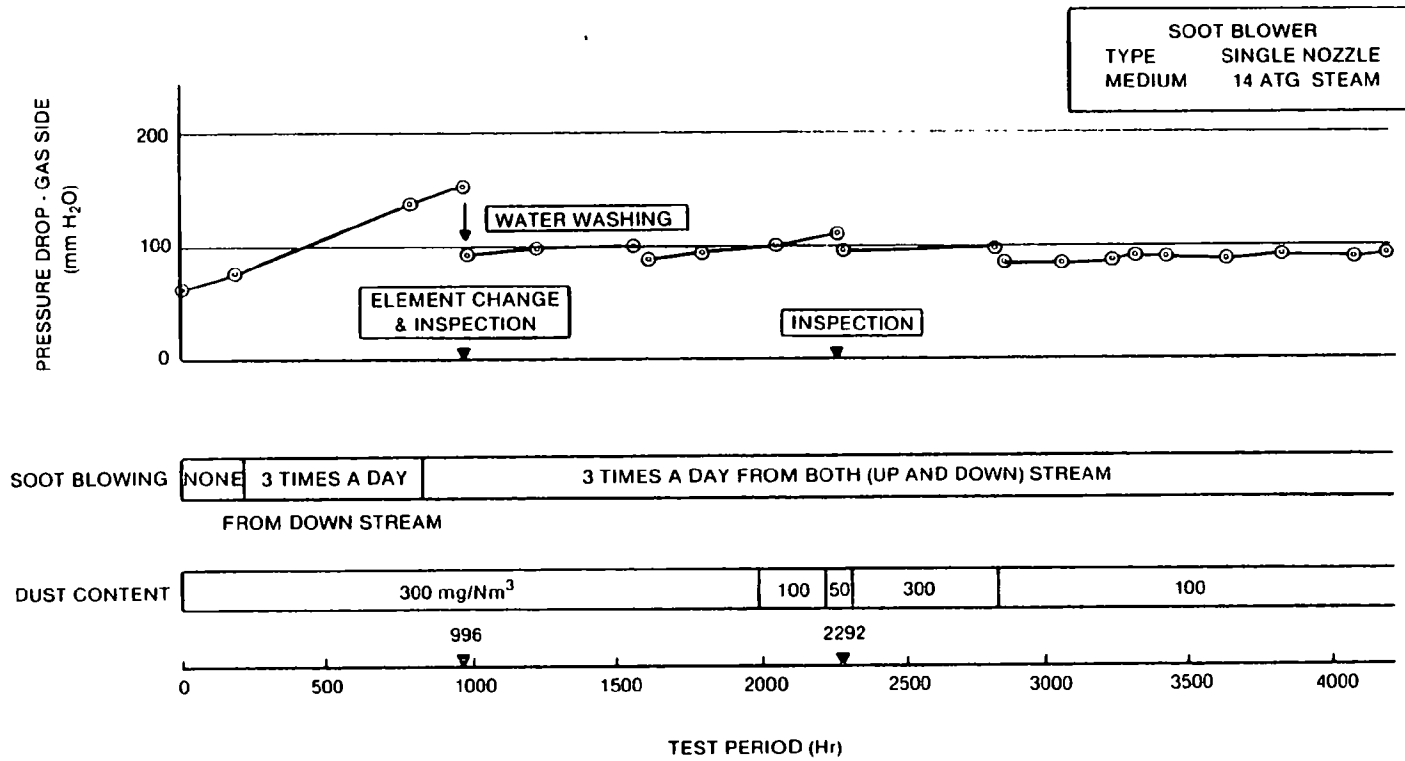


Figure 4 26 Operating Experience of Air Preheater vs Soot Blowing (low dust content)

soot blowing is not used. About 80% NO_x removal efficiency and unreacted NH₃ in the range of 1-3 ppm was achieved throughout the test period.

The air preheater experienced ammonium bisulfate problems when it contained the standard types of elements. As shown in Figure 4-26, the pressure drop increased markedly even with soot blowing three times a day. After 996 hours of operation, the preheater was washed with water and the elements in the intermediate- and low-temperature zones were replaced with new notched-flat elements which permit soot blowing to work more efficiently. After the change of elements, any increase in pressure drop was prevented by applying soot blowing three times a day from both cold and hot sides of the preheater.

4.7.3 Evaluation

Based on these tests, Tokyo Electric considers both the high-dust and low-dust SCR systems to be commercially applicable to coal-fired boilers, the high dust being superior to the low-dust. Two commercial SCR plants under construction for the Nos. 8 and 9 coal/oil-fired boilers at the Nakoso Station (600 MW each) will use the high-dust system.

However, the high-dust system does have two problems associated with it (1) contamination of fly ash by ammonia, and (2) a relatively low cold ESP efficiency for fly ash from low-sulfur coal. As the tests have demonstrated, contamination of the fly ash can be eliminated by maintaining unreacted NH₃ at a very low level. The problem of the low ESP efficiency can be solved by applying wet process FGD which is very effective at removing particulates. The tests at Nakoso showed that a particulate concentration of 300 mg/Nm³ can be reduced to about 30 mg/Nm³ by FGD (5).

4.8 EPDC'S SCR ACTIVITIES (6)

4.8.1 Introduction

In cooperation with five major SCR process developers, EPDC conducted extensive pilot plant tests of both high- and low-dust SCR systems with coal-fired flue gas. For the full-scale demonstration plant (250 MW) and for a commercial plant for a new 700-MW coal-fired boiler, EPDC tested the low-dust system. This section was made in order to maintain a low dust emission level with various types of imported coals and to eliminate ammonia contamination of the fly ash.

4.8.2 Pilot Plant Tests with KHI (7)

Figure 4-27 is the flowsheet of the Takehara SCR pilot plant. In the plant, the 150°C flue gas leaving the existing ESP is heated by a heat exchanger and electric heater to 300°-400°C. The composition of the flue gas and the properties of the fly ash are shown in Table 4-16. The composition of the fly ash is shown in Table 4-17.

TABLE 4-16. FLUE GAS COMPOSITION AND FLY ASH PROPERTIES, SCR PILOT PLANT, TAKEHARA STATION

Flue gas contents:	
NO _x , ppm	200 ~ 410
SO ₂ ^x , ppm	1100 ~ 1720
SO ₃ , ppm	1 ~ 2
O ₂ , %	5 ~ 10 %
H ₂ O, %	8 ~ 9 %
Dust, mg/Nm ³	46 ~ 255 mg/Nm ³
Dust properties:	
Particle size, μ	10 ~ 30μ
Specific gravity	ca. 2.1 (absolute)

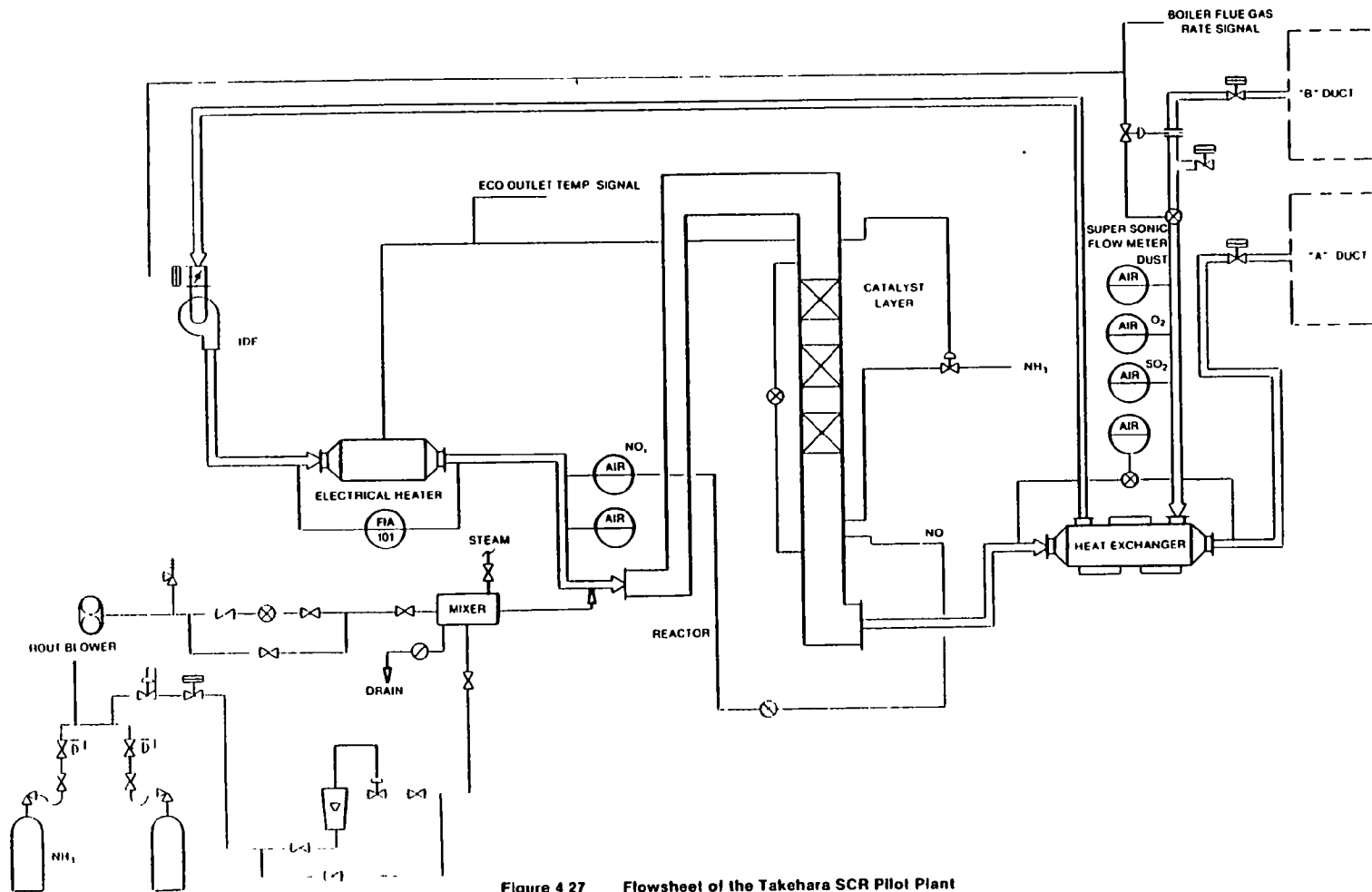


Figure 4 27 Flowsheet of the Takehara SCR Pilot Plant

TABLE 4-17. FLY ASH COMPOSITION.

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	V ₂ O ₅
56.91	4.92	21.5	1.57	1.28	0.04
Na ₂ O	K ₂ O	PbO	MnO	TiO ₂	CuO
0.57	0.22	0.03	0.04	1.67	0.01
ZnO	NH ₄ ⁺	Cl ⁻	SO ₄ ⁻⁻⁻	CO ₃ ⁻⁻⁻	C
0.02	<0.01	Nil	0.77	0.44	3.5

The pilot plant uses a vertical SCR reactor with a gas down flow and a tubular catalyst. The objective of the pilot plant test was to attain 80% NO_x removal efficiency with unreacted NH₃ less than 5 ppm. The SO₂ oxidation ratio caused by the catalyst was about 1%.

Figure 4-28 shows the relationship between the gas velocity in the reactor (linear velocity), space velocity, gas temperature, and NO_x removal efficiency. Over 90% of NO_x was removed at temperatures above 350°C with an SV of 4,160 hr⁻¹ or less and an NH₃/NO_x mole ratio of 1.0, although a considerable amount of unreacted NH₃ was released.

Figure 4-29 shows that by using a mole ratio of 1.0 at the SV of 3,120 hr⁻¹, unreacted NH₃ exceeded 5 ppm, although the NO_x removal efficiency exceeds 90%. In order to keep the level of unreacted NH₃ below 5 ppm, the mole ratio should be smaller than 0.9, which will result in an NO_x removal efficiency below 90%. An SV smaller than 3,000 hr⁻¹ may be used in large-scale SCR units to achieve the same results. Figure 4-30 shows that catalytic activity did not decrease during the 4,000 hour test period. Nor did the pressure drop, which indicates that no dust plugging occurred.

Figures 4-31 and 4-32 illustrate the results of special tests using one-third the normal amount of catalyst. In one of the tests, the gas temperature was varied between 360° and 290°C with a temperature change rate of 3.3°C/min. for the descending rate and 3.1°C/min. for the ascending rate (Figure 4-32).

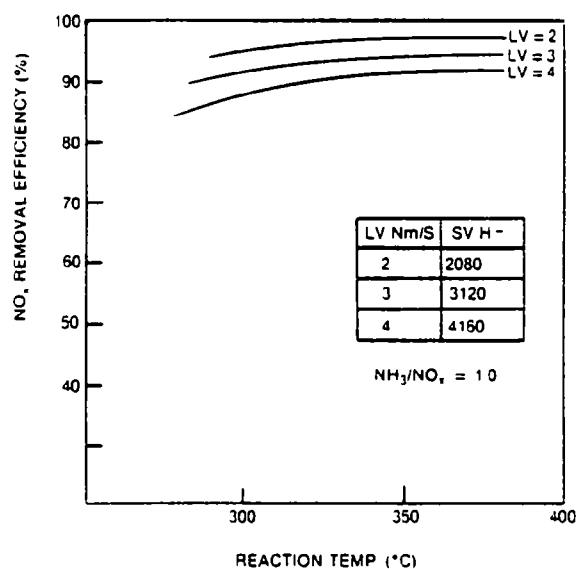


Figure 4-28 Effect of Reaction Temperature on NO_x Removal Efficiency, SCR Pilot Plant, Takehara Station

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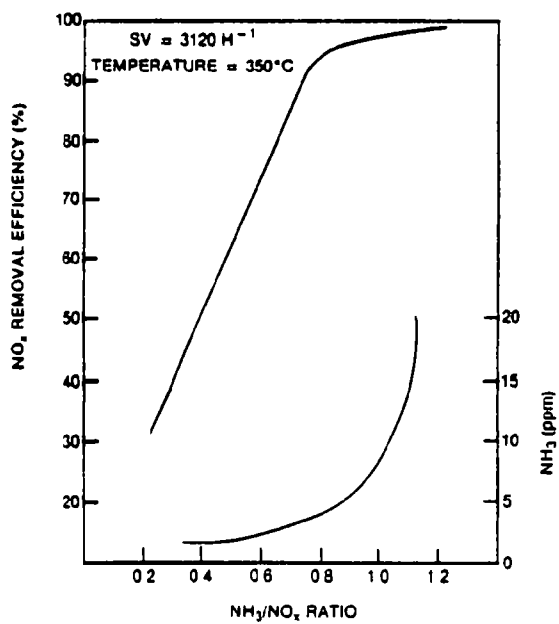


Figure 4-29 Effect of NH_3/NO_x Ratio on NO_x Removal Efficiency and Unreacted NH_3 , SCR Pilot Plant, Takehara Station

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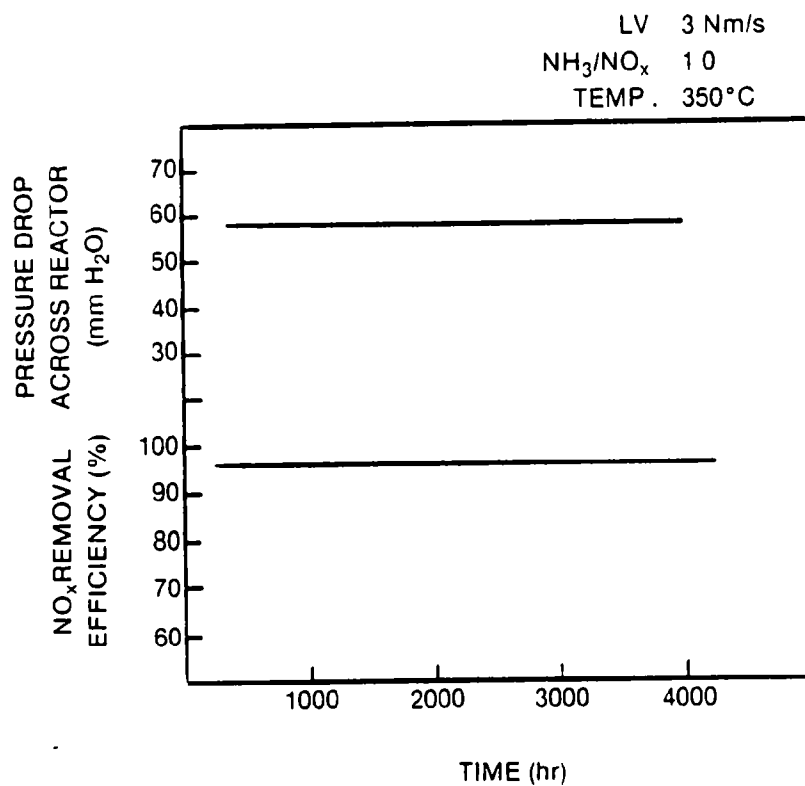


Figure 4-30 NO_x Removal Efficiency and Pressure Drop During 4000 hr Test Period, SCR Pilot Plant, Takehara Station.

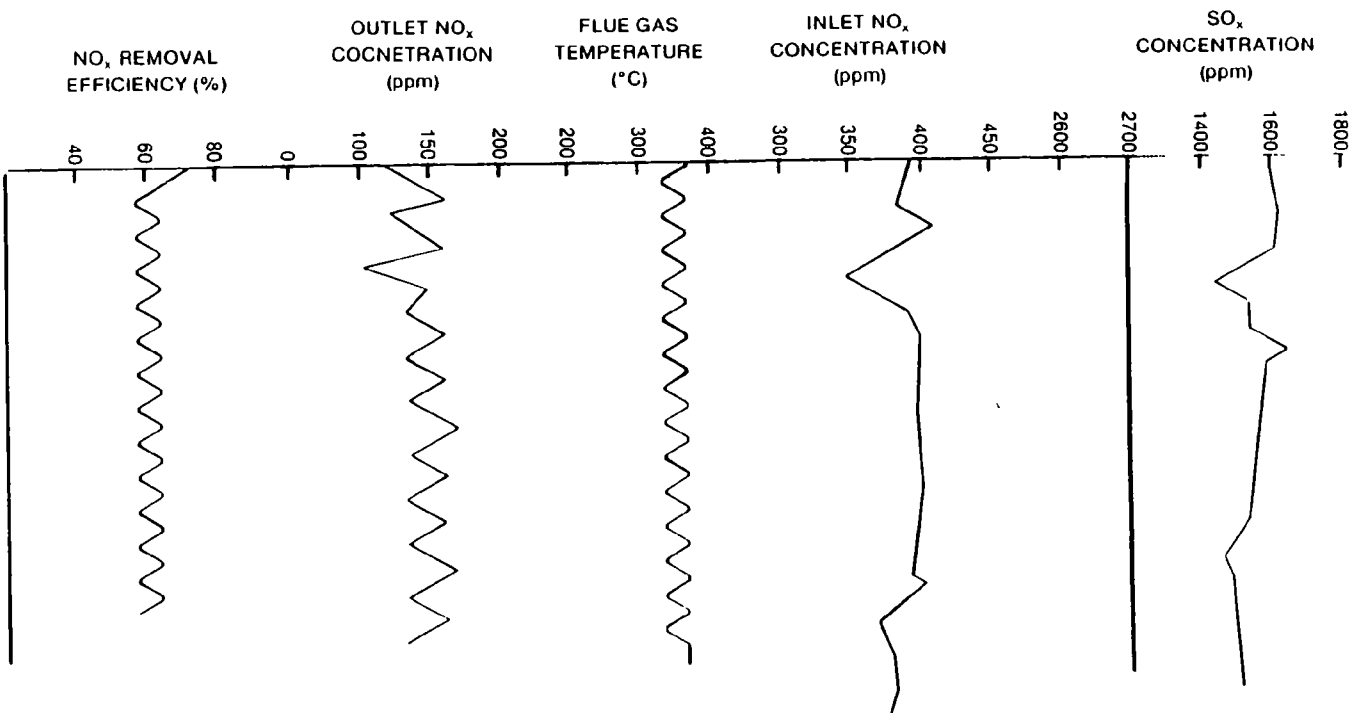


Figure 4.31 Temperature Swing Test Results, SCR Pilot Plant, Takehara Station

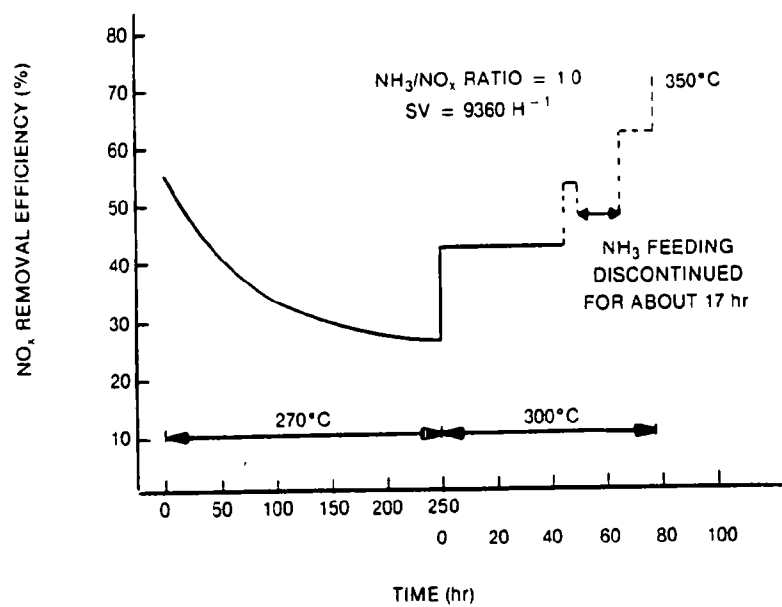


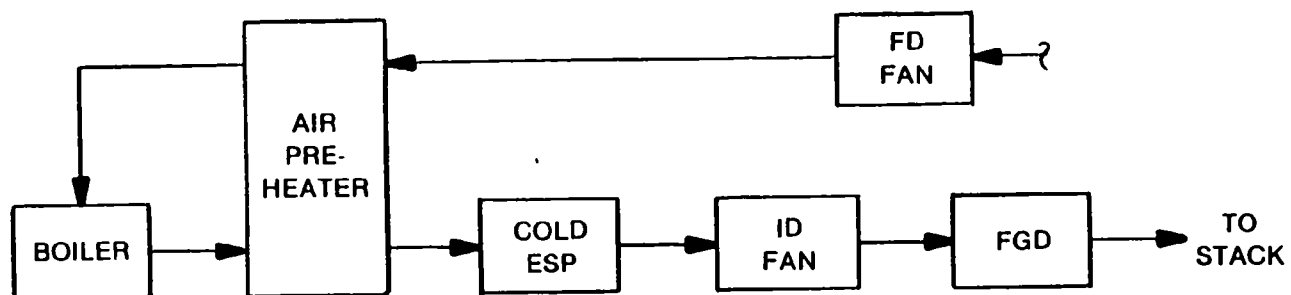
Figure 4-32 NH_3 Injection at Low Temperature and Recovery Test,
 SCR Pilot Plant, Takehara Station

No change in the NO_x removal efficiency was observed before or after the test. Figure 4-33 shows that the NO_x removal efficiency decreased from 60% to about 30% when the gas temperature was maintained at 270°C for 250 hours due to ammonium bisulfate deposition on the catalyst. When the gas temperature was raised to 300°C , the NO_x removal efficiency increased to over 40%. When the gas was heated even more (350°C), catalytic activity returned to its initial level. These results indicate that the catalyst was resistant to attack by the ammonium bisulfate.

4.8.3 Demonstration Plant

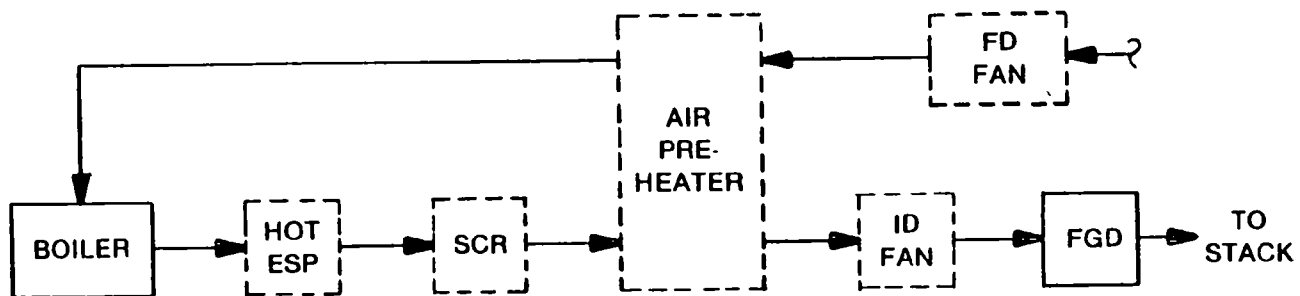
Basic information on the SCR demonstration plant at the Takehara Station is presented in Table 4-18 and Figures 4-33 and 4-34. The No. 1 coal-fired boiler (250 MW) has two trains of air preheater/cold ESP/ ID fans. After passing through this system, all of the boiler flue gas is treated by wet limestone/gypsum FGD. For the demonstration test, a system with two trains of hot ESP/SCR/fans and modified air preheaters was installed. One of the SCR reactors is manufactured by BHK and uses a plate catalyst similar to the one used at Hokkaido Electric's Tomato-Atsuma Station (Section 4.5) with an SV of $2,300 \text{ hr}^{-1}$; the other is manufactured by KHI and uses a tubular catalyst with an SV of about $2,000 \text{ hr}^{-1}$.

The air preheater used in the demonstration has a modified arrangement of elements and soot blowers as shown in Figure 4-35. Ammonium bisulfate tends to deposit between the intermediate- and low-temperature zones in a conventional air preheater and is difficult to remove by conventional soot blowing. To solve that problem a combined intermediate- and low-temperature element was installed which permits soot blowing to work efficiently. The new fans installed in the SCR demonstration plant are compared with the existing ones in Table 4-19. The increase in the capacity of the induced fans is designed to compensate for the increase in the pressure drop caused by SCR reactor and hot ESP. An increased capacity in the forced draft fans is required by the large distance between the fan and the boiler caused by the retrofitting of the SCR system.



EXISTING ARRANGEMENT

————— EXISTING
 - - - - - NEW



MODIFIED ARRANGEMENT

Figure 4-33 Equipment Modifications Made for SCR System Installation at EPDC's Takehara Station. (8)

TABLE 4-18. DESCRIPTION OF SCR DEMONSTRATION PLANT, TAKEHARA STATION NO. 1 UNIT

Item	Manufacturer	Type	Capacity	Efficiency (Guaranteed)	Remarks
(1) Existing Plant					
(a) Boiler	BHK	Reheat Type Radiant Boiler	810 T/h	-	Fuel: coal
(b) Plant output	-	-	250 MW	-	
(2) Demonstration Plant					
(a) SCR	BHK	Plate Catalyst	400,000 Nm ³ /h	>80%	
	KHI	Tube Catalyst	400,000 Nm ³ /h	>80%	
(b) Air Preheater	Gadilius	Long element Ljungstrom	400,000 Nm ³ /h x 2	-	New Air Preheater
(c) NH ₃ Removal from FGD Blowdown	KZ	Activated Sludge	1,000 m ³ /Day	<10 ppm as total N	

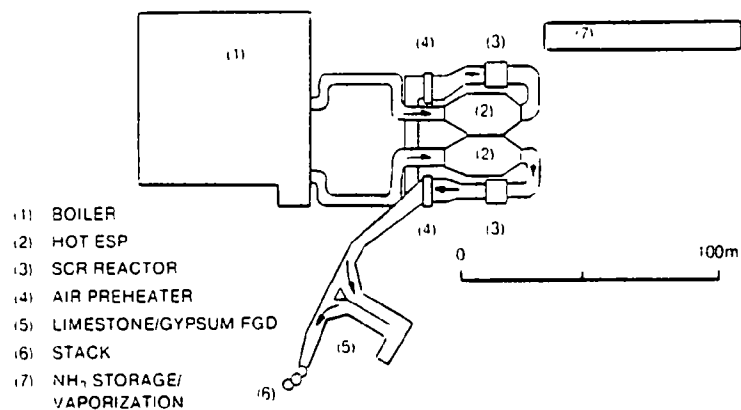
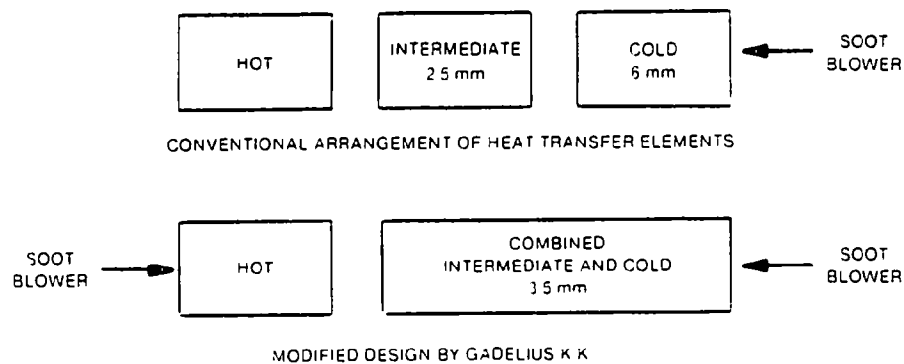


Figure 3 34 Arrangement of the SCR Demonstration Plant Takehara Station EPDC (3)

GA 500 1



(Figures show clearance between the elements)

Figure 4 35 Conventional and Modified Air Preheater Designs (9)

TABLE 4-19. COMPARISON OF EXISTING AND NEW FANS AT TAKEHARA POWER STATION (KW)

Fan	Existing	New
Forced Draft (air)	630 x 2	1350 x 2
Induced Draft (flue gas)	1350 x 2	2350 x 2

The Takehara SCR units began operation in 1981 and have since been operated with an NO_x removal efficiency over 80% and 5 ppm of unreacted NH₃. An ammonium bisulfate problem occurred in the air preheater during the initial stage of operation when unreacted NH₃ was about 10 ppm.

The small amount of ammonia contained in the flue gas after SCR is caught by the wet FGD system. The FGD scrubbing liquor also contains nitrates derived from NO_x. In order to reduce the nitrogen concentration to below 10 ppm in the FGD system wastewater, a conventional activated sludge treatment system has been constructed by Hitachi Zosen.

The total investment cost for the demonstration plant was 8 million yen including the cost of the hot ESPs, air preheaters, fans and wastewater treatment system. This cost is relatively high, due to the expense of retrofitting, as well as the cost of equipment required for the demonstration tests. According to EPDC personnel, the investment cost for an SCR system designed to remove 80% of the NO_x from coal-fired boiler flue gas was 7,000 yen/kW in 1981. Assuming a 2-year catalyst life, the annualized cost for this same system was about 0.6 yen/kWhr (including a 7-year depreciation schedule).

4.9 SCR COSTS

4.9.1 Investment Costs

Table 4-20 shows the investment costs of 9 SCR plants for utility boilers. Chubu Electric's 2 SCR plants for LNG-fired boilers at its Chita Station

TABLE 4-20. INVESTMENT COSTS OF SCR PLANTS FOR UTILITY BOILERS

Company	Station	Fuel	Size (MW)	N/R	NO ₃ removal (%)	Outlet NO _x (ppm)	Vendor	Start- Up	Cost (yen/kW)
Chubu Electric	Chita	LNG	700	N ^a	80	8	BH ^c	1978	2400
		LNG	700	N _b	80	8	BH	1978	2400
		Oil	700	R ^b	80	18	MHI ^d	1980	3600
Chugoku Electric	Kudamatsu	Oil	375	R	80	32	IHI ^e	1979	5900
		Oil	700	N	80	26	IHI	1979	3200
	Shimonoseki	Coal	175	R	50	200	MHI	1980	9700 ^g
Hokkaido Electric	Tomato-Atsuma	Coal	350x1/4	N	>80	>40	BH	1980	10000 ^h
EPDC	Takehara	Coal	250x1/2	R	80	80	BH	1981	7000 ^h
		Coal	250x1/2	R	80	80	KHI ^f	1981	7000 ^h

^aNew^bRetrofit^cBabcock Hitachi^dMitsubishi Heavy Industries^eIshikawajima-Harima Heavy Industries^fKawasaki Heavy Industries Reactor has a capacity for 80% NO_x removal.^gIncluding boiler modification for economizer by-pass.^hRough approximation

are less costly (2400 yen/kW) than the other plants because they use clean gas treatment which permits the use of small amounts of a pellet catalyst with an SV of 20,000 hr⁻¹. The SCR plant for the existing oil-fired boiler at the Chita Station cost 3,600 yen/kW using a honeycomb catalyst with an SV of 5,100 hr⁻¹.

Chugoku Electric's SCR plants for oil-fired boilers at the Kudamatsu Station cost 5,900 yen/kW for the existing boiler and 3,200 yen/kW for the new boilers. Both systems use a honeycomb catalyst with an SV of about 5,100 hr⁻¹. The relatively high cost of the plant for the existing boiler was a result of the cost of the extensive ductwork required for retrofitting, and the installation of new fans needed to compensate for the pressure drop caused by the SCR system (Section 4.3). The SCR plant for the existing oil-fired boiler at the Chita Station did not require an additional fan because the existing boiler fan was able to compensate for the increased pressure drop on its own.

The SCR plant for the existing coal-fired boiler at the Shimonoseki Station cost nearly 10,000 yen/kW including the cost for the boiler modification needed for installation of the economizer by-pass system (Section 4.4). Hokkaido Electric's SCR plant at the Tomato-Atsuma Station cost about 10,000 yen/kW and has a capacity of treating one-fourth of the flue gas from a new 350 MW boiler. The relatively high cost of this SCR system for a new boiler may be due to the small size of the plant (88 MW equivalent) and the fact that it removes 90% of NO_x. EPDC's two SCR plants for existing coal-fired boilers at the Takehara Station cost about 7,000 yen/kW each. Generally speaking, an SCR plant which achieves 80% NO_x removal for a new coal-fired utility boiler may cost 6,000 - 8,500 yen, depending on inlet SO_x and NO_x concentrations and the amount of unreacted NH₃ allowed.

4.9.2 Estimated Investment and Annualized Costs

Tables 4-21 and 4-22 show the estimated investment and annualized costs of SCR for new 700-MW utility boilers burning coal, oil, and gas. In preparing these cost estimates the following assumptions were made, based on a study of the costs of commercial and demonstration SCR plants.

TABLE 4-21 CALCULATED COSTS FOR AN SCR PLANT FOR A NEW 700 MW COAL-FIRED BOILER (70% Boiler Utilization 4,292,000 MWhr/year, 1981 yen)
(flue gas flow rate 2,300,000 Nm³/hr, honeycomb catalyst ceramic square type, 3.5 million yen/m³, 2 year life)

Boiler basis	Parameter	High S Coal		High S Coal		Low S Coal		Low S Coal	
	NO _x , ppm	600		300		300		300	
	SO ₂ , ppm	2500		2500		600		600	
	Particulates, Nm ³	15-25 ⁱ		15-25 ⁱ		15-25 ⁱ		0.05-0.20 ^j	
Design data	Catalyst size, mm	7.4 + 1.6 ^h		7.4 + 1.6 ^h		7.4 + 1.6 ^h		6.6 + 1.4 ^h	
	NH ₃ emissions, ppm	4-5		4-5		4-5		2-3	
	NO _x removal, %	80 90		80 90		80 90		80 90	
	NH ₃ /NO _x mole ratio _{in}	0.82 0.92		0.83 0.93		0.83 0.93		0.82 0.92	
	Space velocity, hr	2200 1600		2700 2000		3000 2200		3000 2200	
	Catalyst volume, m ³	1045 1438		852 1150		767 1045		767 1045	
	Reactor pressure drop, mm/H ₂ O	130 150		115 135		110 130		110 130	
	Power consumption, %	0.20 0.24		0.18 0.22		0.17 0.20		0.19 0.20	
Investment costs	Catalyst, 10 ⁶ yen	3.66 5.03		2.98 4.02		2.68 3.66		2.68 3.66	
	Other, 10 ⁶ yen ^b	2.25 2.50		2.10 2.35		2.00 2.30		2.00 2.30	
	Total, 10 ⁶ yen ^b	5.91 7.53		5.08 6.37		4.68 5.96		4.68 5.96	
	Total, yen/kW ^d	8440 10760		7260 9100		6690 8510		6690 8510	
Annual costs	Fixed cost, 10 ⁶ yen ^c	0.92 1.13		0.83 0.99		0.77 0.95		0.77 0.95	
	Catalyst, 10 ⁶ yen ^d	1.83 2.52		1.49 2.01		1.34 1.83		1.34 1.83	
	Ammonia, 10 ⁶ yen ^e	0.53 0.59		0.27 0.30		0.27 0.30		0.26 0.29	
	Other, 10 ⁶ yen ^f	0.20 0.24		0.18 0.22		0.16 0.20		0.16 0.20	
	Total, 10 ⁶ yen	3.48 4.48		2.77 3.52		2.54 3.28		2.53 3.27	
Annualized cost, yen/kWhr		0.81 1.04		0.65 0.82		0.59 0.76		0.59 0.76	
Cost effectiveness, yen/Nm ³ of NO _x removed		514 588		826 924		749 861		749 861	
dollars/lb of NO _x removed ^g		0.45 0.51		0.73 0.81		0.66 0.76		0.66 0.76	

^aPercent of power generated by the boiler

^bIncluding civil engineering and test operation

^c10% of catalyst and 25% of investment excluding catalyst

^dCatalyst cost divided by life (years)

^eAt 100 000 yen/ton

^fMainly for power (18 yen/kWhr)

^gΔI = V250, NO_x as NO₂

^hChannel diameter plus wall thickness

ⁱWith full dust load

^jLeaving a hot ESP

TABLE 4-22 (A) ESTIMATED COSTS FOR SCR FOR NEW 700 MW OIL- AND GAS-FIRED BOILERS (70% boiler utilization 4,292,000 MWhr/year) (1981 costs, flue gas flow rate 2,000,000 Nm³/hr, ceramic square honeycomb and pellet catalysts)

Boiler basis	Parameter	High S Oil		Low S Oil		Low S Oil		Gas	
Design data	Fuel	200		200		100		60	
	NO _x , ppm	1,500		100		100		1	
	SO ₂ , ppm	0.05-0.20		0.02-0.05		0.02-0.05 ^j		0.005-0.02 ^j	
	Particulates, g/Nm ³	Honeycomb		Honeycomb		Honeycomb		Pellet	
	Catalyst size, mm	6.6 × 1.4 ^b		5.8 × 1.2 ^b		5.8 × 1.2 ^b		5	
	Catalyst life, year	3		3		3		4	
	Catalyst cost, 10 ³ yen/m ³	3.3		3.3		3.3		3.0	
	NO _x emissions, ppm	2-3		4-5		4-5		6-8	
	NO _x removal, %	80	90	80	90	80	90	80	90
	NH ₃ /NO _x mole ratio	0.83	0.93	0.84	0.94	0.88	0.98	1.00	1.10
	Space velocity, hr ⁻¹	2800	2000	4300	3100	5100	3700	18000	13000
	Catalyst volume, m ³	714	1000	465	645	392	541	111	154
	Reactor pressure drop, mm/H ₂ O	120	140	105	115	100	110	120	140
	Power consumption, %	0.17	0.20	0.16	0.17	0.15	0.16	0.17	0.20
Investment cost	Catalyst, 10 ³ yen	2.36	3.30	1.53	2.13	1.29	1.78	0.33	0.46
	Other, 10 ³ yen ^d	2.00	2.25	1.70	1.90	1.60	1.80	1.40	1.50
	Total, 10 ³ yen ^d	4.36	5.55	3.23	4.03	2.89	3.58	1.73	1.96
	Total, yen/kW ^e	6230	7930	4610	5760	4130	5110	2470	2800
Annual costs	Fixed cost, 10 ³ yen ^c	0.73	0.89	0.58	0.69	0.53	0.63	0.38	0.42
	Catalyst, 10 ³ yen ^d	0.79	1.10	0.51	0.71	0.43	0.59	0.08	0.12
	Ammonia, 10 ³ yen ^f	0.16	0.17	0.16	0.18	0.08	0.09	0.05	0.06
	Other, 10 ³ yen ^g	0.20	0.24	0.18	0.19	0.17	0.19	0.20	0.24
	Total, 10 ³ yen	1.88	2.40	1.43	1.77	1.21	1.50	0.71	0.84
Annualized cost	(yen/kW/hr)	0.44	0.56	0.33	0.41	0.28	0.35	0.17	0.20
Cost effectiveness	(yen/Nm ³ of NO _x removed)	958	1087	719	794	1215	1343	1205	1270
	(dollars/lb of NO _x removed) ^h	0.84	0.96	0.63	0.70	1.07	1.18	1.05	1.12

- ^a Percent of power generated by the boiler
^b Including civil engineering and test operation
^c 10% of catalyst and 25% of investment excluding catalyst
^d Catalyst cost divided by life (years)
^e At 100,000 yen/ton
^f Mainly for power (21 yen/kWhr)
^g $\frac{1}{2}$ = V250 NO_x as NO₂
^h (channel diameter plus wall thickness)
ⁱ With full dust load
^j Leaving a hot 15P

- (1) As shown in Figure 4-36, flue gas from the boiler economizer is treated in the two trains of the SCR system. In most systems, the gas is first injected with ammonia and sent into the SCR reactor. The exception is the low-dust system for coal (C in Figure 4-36) in which the flue gas is sent through a hot ESP and then into a reactor.
- (2) A square honeycomb catalyst is used except in the case of the the system for the gas-fired boiler which uses a pellet catalyst. The channel diameter of the honeycomb is 7.4 mm for coal with a full dust load, 6.6 mm for coal with the low-dust system and high-sulfur oil, and 5.8 mm for low-sulfur oil. The catalyst cost is 3.5 million yen/m³ for coal, 3.3 million yen for oil, and 3 million yen for gas. (Plate catalysts may be used instead of honeycombs for the same or a slightly lower cost.)
- (3) Unreacted NH₃ is maintained at 4-5 ppm for coal with a full dust load and low-sulfur oil. It is maintained at 2-3 ppm for coal with a low-dust system and high-sulfur oil because, in these cases, ammonium bisulfate deposition in the air preheater may become a serious problem if the unreacted NH₃ concentration is any higher.
- (4) NO_x removals of 80% and 90% were assumed, which actually require 81-82% and 91-92% removal, respectively. For 90% NO_x removal, 35-40% more catalyst is used than for 80% removal. A higher inlet NO_x concentration also requires a larger amount of catalyst.
- (5) The catalyst-induced SO₂ oxidation ratio is maintained below 0.5% for high-sulfur fuels and below 1% for low-sulfur fuels.
- (6) The annual power generation is 4,292,499 MW (70% of full capacity).

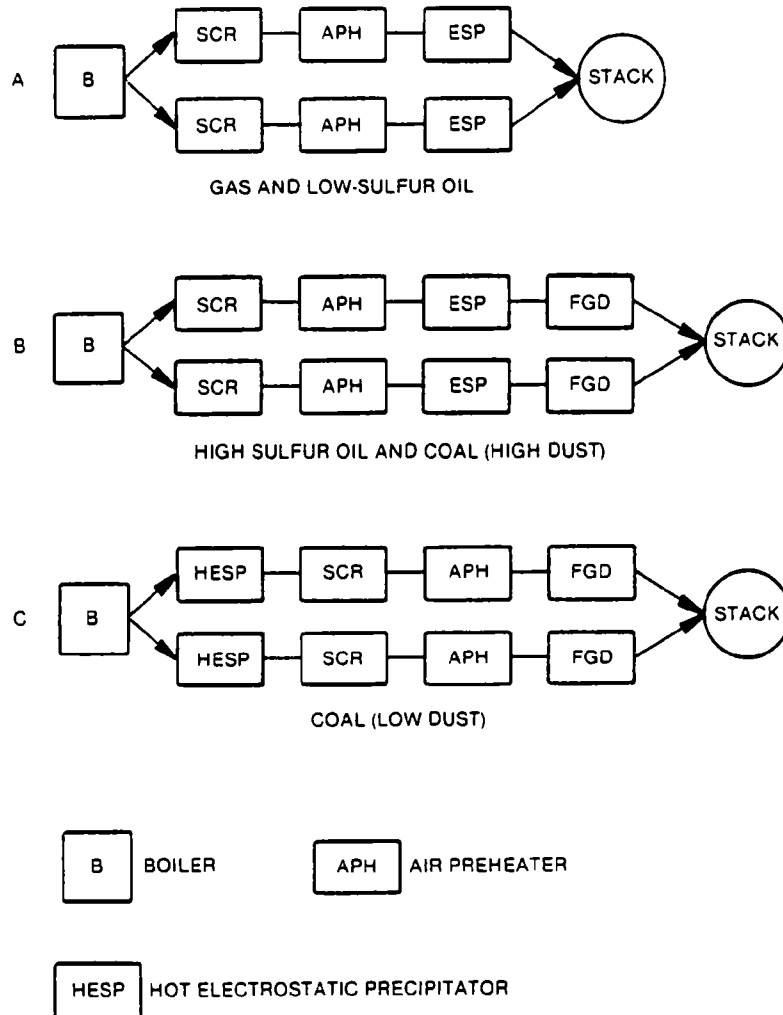


Figure 4-36 Flue Gas Treatment Systems.

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- (7) The investment cost includes costs for reactor, catalyst, ducts, ammonia tank and injection system, soot blowing system, control system, civil engineering services, and test operation.
- (8) The fixed capital cost includes a 25% investment cost excluding catalyst expense and 10% interest for the initial charge of the catalyst.
- (9) The catalyst life is 2 years for coal, 3 years for oil, and 4 years for gas. The annualized cost includes the catalyst cost divided by the catalyst life (years).
- (10) The cost of ammonia is 100,000 yen (\$400)/ton. The power cost is 18 yen/kWhr for coal and 21 yen/kWhr for oil and gas.

Table 4-21 shows that the investment cost for 80% NO_x removal is 8,440 and 7,260 yen/kW for high-sulfur coal with 600 and 300 ppm inlet NO_x concentrations, respectively. The cost for low-sulfur coal is 6,690 yen/kW for both the high-dust and low-dust systems. Compared with the high-dust system, the low-dust system uses the same amount of more efficient catalyst to maintain a lower level of unreacted NH₃. The investment cost for 90% NO_x removal is about 30% higher than that for 80% removal. The catalyst cost makes up over 55% of the investment cost for 80% removal and over 65% for 90% removal.

The annualized cost for 80% NO_x removal is 0.81 and 0.65 yen/kWhr for high sulfur coal with 600 and 300 ppm inlet NO_x concentrations, respectively, and is 0.59 yen/kWhr for low-sulfur coal. Ninety percent NO_x removal costs about 30% more than 80% removal.

Although the annualized cost for NO_x removal with 600 ppm inlet NO_x is about 25% more than that for 300 ppm NO_x, the cost effectiveness is much lower --- 45 cents vs. 73 cents per lb of NO_x removed for 80% removal. With 90% NO_x removal it is nearly 20% more cost effective to remove NO_x from gas containing 300 ppm than from gas with 600 ppm NO_x.

In actual practice it is difficult to consistently maintain 90% NO_x removal with less than 5 ppm of unreacted NH₃ when treating a large amount of NO_x-rich flue gas such as that from a large coal-fired boiler. This is true for two reasons. First, the NO_x concentration as well as the gas velocity may be considerably different in different areas of the large duct and reactor inlet. Second, the boiler load is not constant, resulting in a fluctuation in both gas volume and NO_x concentration, and the NO_x analyzer has a delay time of several minutes. In order to reduce NO_x from a large boiler by 90%, the combination of combustion modification for 35-50% removal and SCR for 80-85% removal may be more practical and economical than the use of SCR by itself.

Table 4-22 lists the costs of SCR systems for oil- and gas-fired boilers. The most common type of SCR plant in Japan is used for 80% NO_x reduction in flue gas from an oil-fired boiler containing about 100 ppm NO_x. The investment cost is 3,860 yen/kW, the annualized cost 0.27 yen/kW. NO_x removal of 200 ppm inlet NO_x in low-sulfur oil flue gas costs about 20% more than this; removal of NO_x from gas-fired boiler flue gas containing 60 ppm NO_x costs about half as much.

SCR for boilers which burn high-sulfur oil may require about 60% more catalyst than those which burn low-sulfur oil, given the same inlet NO_x concentration and NO_x removal ratios. This occurs for two reasons: (1) In the high-sulfur oil system the catalyst is less reactive. This is because of the low SO₂ oxidation ratio and the larger channel diameter needed for the larger amount of dust. (2) It is necessary to maintain unreacted NH₃ at a lower level in the high-sulfur oil system in order to reduce ammonium bisulfate deposition in the air preheater. Thus, the SCR system costs for high-sulfur oil-fired boilers are about 40% more than those for low-sulfur oil-fired boilers and are similar to SCR system costs for low-sulfur coal-fired boilers.

The investment cost for an SCR system applied to an existing boiler may be 10-40% more than that for a new boiler because of the retrofitting requirements and the possible need for new fans. When an SCR system is applied to 150°C flue gas leaving an air preheater, the system investment cost may be 40-

60% more and the annualized cost 50-80% more than that for SCR applied at the economizer outlet because of the requirement for gas heating. Although low-temperature catalysts which work at 150-200°C have been developed, these catalysts experience ammonium bisulfate problems. Applying SCR to the economizer outlet is more economical than using low-temperature catalysts at the air preheater outlet, even for existing boilers.

4.9.3 Power Generation and Flue Gas Treatment Costs

Table 4-23 gives estimated costs for a new coal-fired power station with flue gas treatment systems in Japan. The total investment cost is 220,00 yen/kW, 10% of which is for FGD, 32% for SCR, and 1.8 for ESP. The total annualized cost, including the cost of flue gas treatment is 18 yen/kW. Of the total amount, 10% is for FGD, 4% for SCR, and 0.5% for ESP. The annualized cost for this coal-fired station is less than the cost of an oil-fired power station that uses ESP without FGD and SCR.

TABLE 4-23. POWER GENERATION COST FOR A COAL-FIRED BOILER IN JAPAN (1981)

Investment cost (yen/kW)	
ESP (99% removal)	4,000
SCR (80% NO _x removal)	7,000
FGD (90% SO ₂ removal)	30,000
Total Power Plant (including boiler, turbine, generator, coal treatment, flue gas treatment, plant site, and auxiliary facilities)	260,000
Annualized cost including capital cost (yen/kWhr)	
ESP	0.1
SCR	0.7
FGD	1.9
Total power cost (including flue gas treatment)	18.0

4.10 USE OF JAPANESE SCR TECHNOLOGY IN THE UNITED STATES

4.10.1 Introduction

As Japanese SCR technology has become more reliable and less costly some U.S. utility companies have become interested in using it. Various Japanese SCR processes have been licensed to U.S. firms (Table 4-24) and a number of pilot and demonstration plants have been constructed.

The U.S. Environmental Protection Agency (EPA) sponsored an 0.5 MW pilot plant test of the Hitachi Zosen SCR process at Georgia Power Company's Mitchell Station. The Electric Power Research Institute (EPRI) constructed a 2.5 MW pilot plant which uses KHI's SCR system at Public Service Co. of Colorado's Arapahoe Station. Southern California Edison has constructed a 107.5 MW KHI SCR demonstration facility with a capacity of treating one-half of the gas from a 215 MW oil-fired boiler at its Huntington Beach Station. In addition, IHI's SCR catalyst will be used at an SCR pilot plant for an industrial boiler.

This section describes the pilot plant tests of the Hitachi Zosen process at Georgia Power Company's Mitchell Station.

4.10.2 Hitachi Zosen Technology Pilot Plant Tests at the Mitchell Station (1)

Hitachi Zosen received an order from EPA for a 1,700 NM³/hr (0.5 MW equivalent) capacity demonstration SCR plant which would remove 90% of NO_x from coal-fired boiler flue gas.

Chemico Air Pollution Control Corporation, Hitachi Zosen's North American licensee, constructed the demonstration plant at Georgia Power Company's Mitchell Station. The boiler burns Kentucky coal containing about 1% sulfur. For the test, flue gas (1,700 Nm³/hr) from the boiler economizer with a full dust load was used. Since the gas cools while passing through a long duct

TABLE 4-24. PRINCIPAL VENDOR CONTACTS FOR JAPANESE NO_x SCR TECHNOLOGY (3)

Process	Japan Representative	U.S. Licensee or Partner
Babcock-Hitachi (Hitachi, Ltd.)	Eiuroshi Kuroda Kure Works. Babcock- Hitachi K.K. No. 6-9 Takara-Machi Kure-shi, Hiroshima-Ken, 737, Japan (0823) (21) 1161 Telex 6624-21 BHK KRE-J	Greg T. Bielawski Babcock and Wilcox FPG-ECS P.O. Box 351 Barbarton, Ohio 44203 216/753-451
Hitachi-Zosen (Hitachi Ship- building and Engineering)	Shingo Tanaka Hitachi Shipbuilding & Engineering Co., Ltd. Palaceside Building 1-1, Hitotsubashi, 1-Chome Chiyoda-Ku, Tokyo, Japan Tokyo (213) 6611 Telex J22363 • J24490	
Ishikawajima- Harima Heavy Industries (IHI)	Nobuo Aoki Ishikawajima-Harima Heavy Industries Co., Ltd. Tokyo Genboku Kaikan 30-13 • 5-chrome, Tokyo Koto-Ku, Tokyo, 135, Japan (03) 649-1111 Telex (IHI CO) J22232	John Cvicker Foster Wheeler Energy Corp 9 Peach Tree Hill Road Livingston, NJ 07039 201/533-2687
Kawasaki Heavy Industries (KHI)	Senji Niwa Kawasaki Heavy Industries, Ltd. 14, 2-Chome Higashikawasaki-Cho Ikuta-Ku, Kobe, 650-91 Japan Tel. Kobe (078) 671-5001 Telex 5624-032 KHI CPL J	Joy Manufacturing Western Precipitation Div. P.O. Box 2744 Los Angeles, CA 90051 213/240-2300
Mitsubishi Heavy Industries (MHI)	Tadamasa Sengoku Mitsubishi Heavy Industries, Ltd. Shin-Tamachi Bldg. 34-6, Shiba 5-chome Minato-Ku, Tokyo 108 Japan (03) 455-5711 Telex J22282 HISHIJU J28578 MHITAM	Donald J. Frey Manager, Fuel Systems Engineering CE Power Systems Combustion Engineering, Inc., 1000 Prospect Hill Road Windsor, Conn. 16093 203/688-1911 Ext. 2241

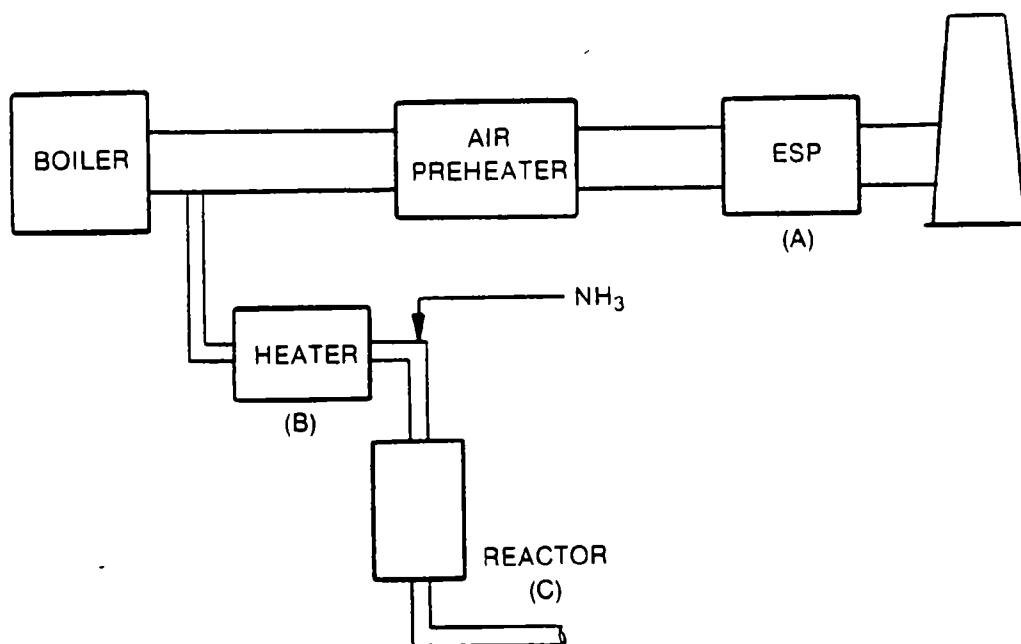


Figure 4-37 SCR Pilot Plant and Fly Ash Sampling Points,
Mitchell Station, Georgia Power Co.

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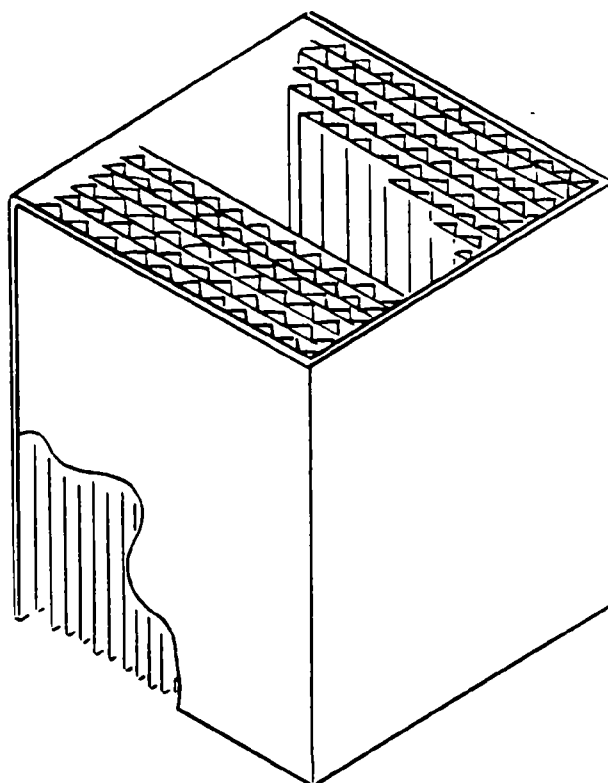


Figure 4-38 NOXNON 600 Catalyst.

(14" diameter), it is electrically heated to about 400°C and then injected with ammonia before it passes down through the SCR reactor (Figure 4-37).

A NOXNON 500 catalyst was used for the first and second pilot plant tests. The catalyst was prepared by treating the surface of a special alloy plate; it is similar in shape to the NOXNON 600 catalyst used for the third test (Figure 4-38).

The first test using the NOXNON 500 catalyst and an NH_3/NO_x mole ratio of 1.0 initially produced a 90% NO_x removal rate. However, this efficiency decreased during the course of the 2,000-hour test run as the pressure drop increased. Tests on the used catalyst showed that the decrease in efficiency was not caused by poisoning of the catalyst but instead, by fly ash deposition on the catalyst surface.

For the second test, a new NOXNON 500 catalyst was used and soot blowing was added. Despite these measures, the NO_x removal efficiency still decreased during the 2,000 hour test period.

A NOXNON 600 catalyst was used for the third test. The NOXNON 600 has a stainless steel mesh base which is coated with catalyst material and shaped as shown in Figure 4-38. The pitch of the NOXNON 600 catalyst is 14 mm whereas the NOXNON 500 has a pitch of 8 mm. Because of the wider pitch of the former catalyst, the reactor was lengthened for the third test to enable it to attain 90% removal. Use of this catalyst greatly reduced the reactor's dust clogging tendency.

Results of demonstration tests conducted from May through October 1980 using the NOXNON 600 catalyst are shown in Figure 4-39 (9). The results represent over 3500 hours of operation. During the first 90 days of operation the NO_x removal efficiency averaged over 90 percent. For the entire test period of 160 days of continuous operation, the average NO_x reduction was only slightly lower--89.8 percent. Figure 4-39 also illustrates that when it remains in the range of 2100 to 2400 Nm^3/hr , the flow rate has essentially no effect on the SCR system's NO_x removal efficiency.

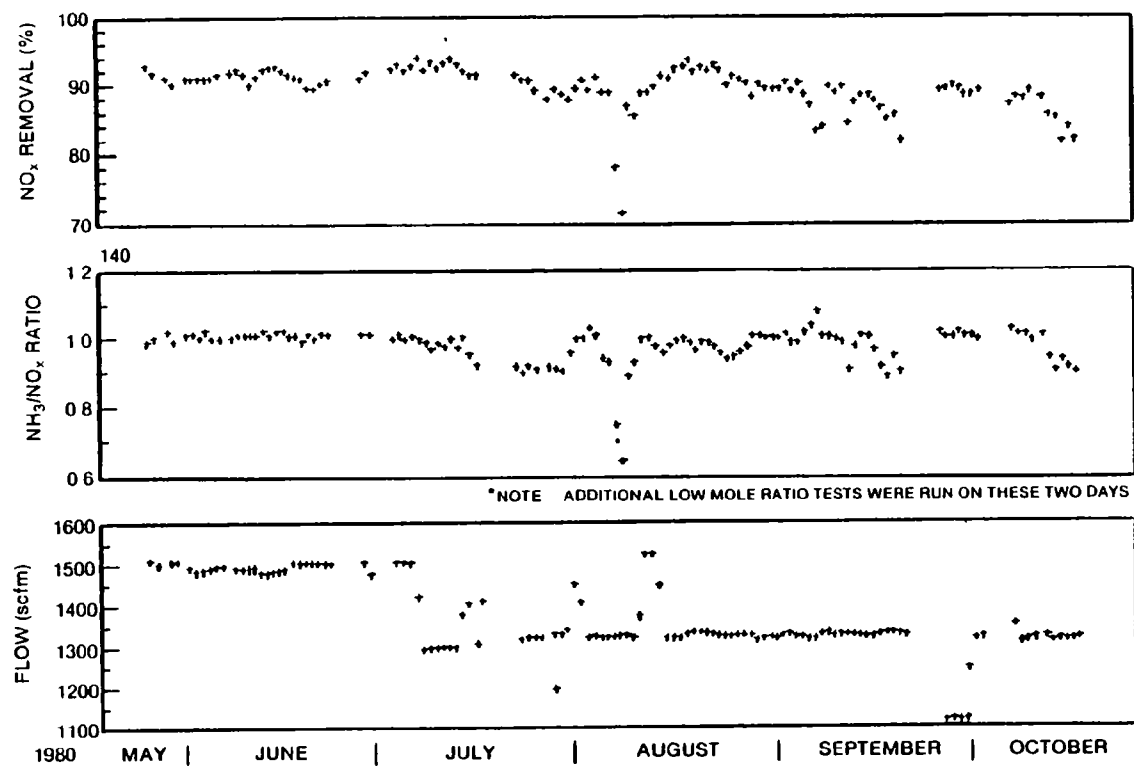


Figure 4-39 Demonstration Test Results from the SCR Pilot Plant, Mitchell Station, Georgia Power Co. (9)

Since catalytic activity decreased slightly during the 3,500-hour test period, a regeneration technique was developed to restore the activity to its initial level.

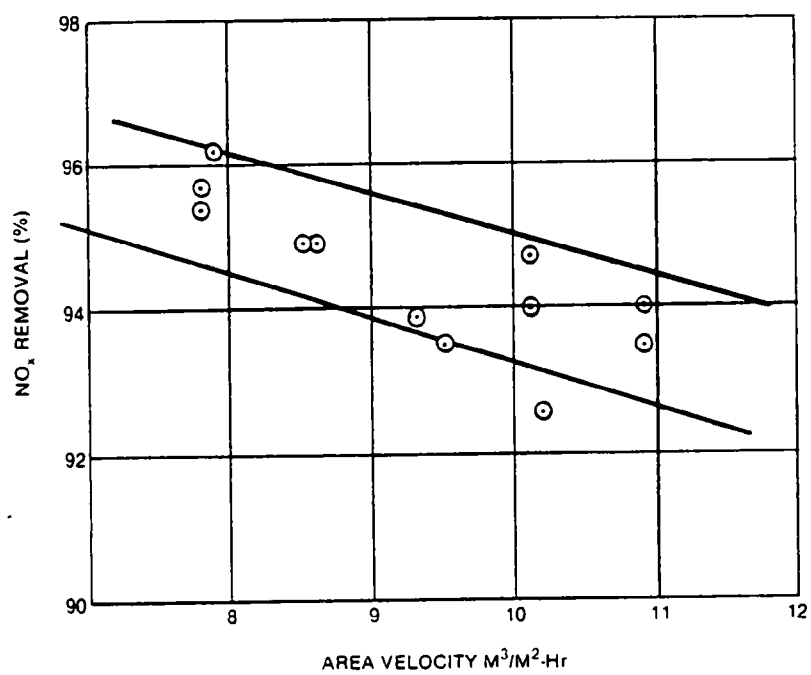
Figures 4-40 and 4-41 show the results of tests using NOXNON 600 with different area velocities and NH_3/NO_x mole ratios. Over 90% NO_x removal was attained with a mole ratio of 1.0 and an area velocity smaller than $12 \text{ m}^3/\text{m}^2 \text{ hr}$. However, with the mole ratio of 1.0, unreacted NH_3 exceeds 30 ppm. One gas analysis at the pilot plant indicated that at 90% NO_x removal, unreacted NH_3 reached about 50 ppm and that the SO_3 content of the gas was 8.4 ppm at the reactor inlet and increased to 20.7 ppm at the outlet. (10)

4.10.3 Evaluation

The SCR pilot plant tests at the Mitchell Station indicated that with a 90% NO_x removal, both unreacted NH_3 and SO_3 levels are high and can contaminate the fly ash. To lower unreacted NH_3 to below 5 ppm, a mole ratio of 0.82-0.83 should be used to remove 82-83% of NO_x . In order to reduce SO_3 , a low-oxidation, and therefore less active, catalyst should be used. An 80% NO_x removal efficiency appears to be a practical target for treating a large amount of flue gas with a high NO_x concentration.

The NOXNON 500 catalyst proved to have a considerable dust clogging problem. With its wider pitch, the NOXNON 600 performed well, but still was not free of the dust clogging problem. On the other hand, during Hitachi Zosen's SCR test at EPDC's Isogo Station, the NOXNON 500 catalyst experienced no dust clogging problem. This indicates a difference in the nature of the fly ash at the two test sites.

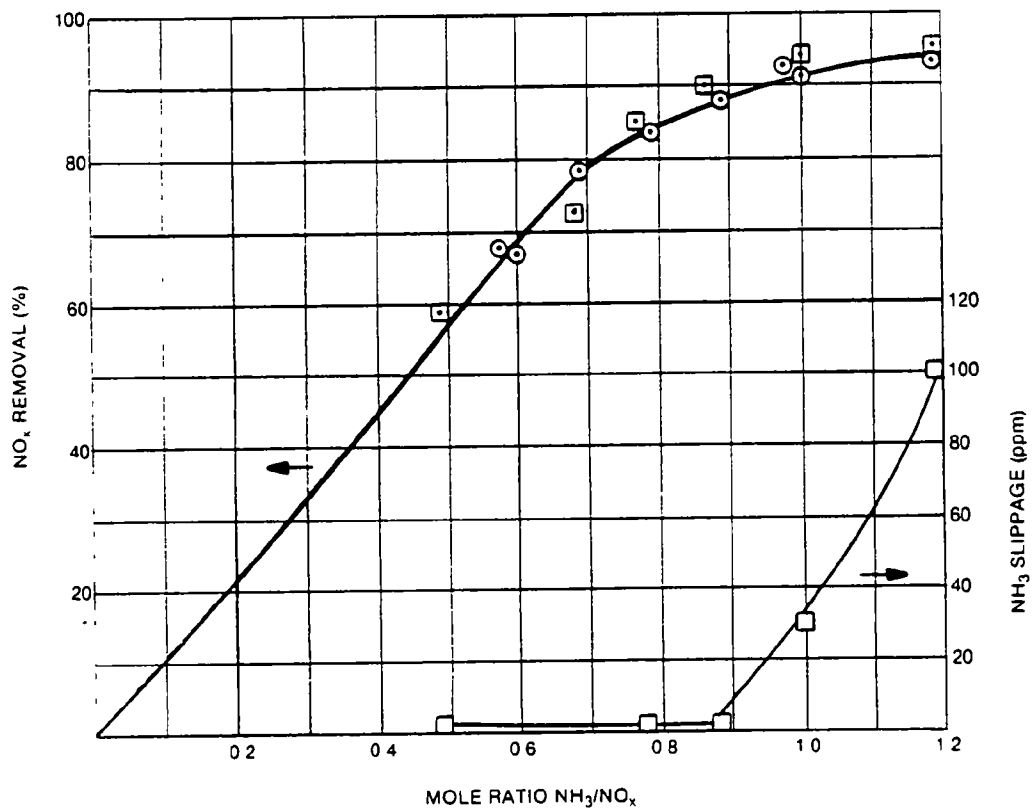
In order to determine the reason for this difference, the author tested samples of fly ash obtained from three locations at the Mitchell Station pilot plant (Figure 4-37, A, B, and C): the commercial ESP, the heater, and the reactor.



MOLE RATIO 1.0
REACTOR TEMP 720°F
INLET NO_x CONCENTRATION 400-450 ppm

Figure 4-40 NO_x Removal vs. Area Velocity (1)

70A2679



CATALYST NOXNON 600
 TEMP 700-710°F
 FLOW RATE 1500 scfm
 1300 scfm
 INLET NO_x 400-500 ppm

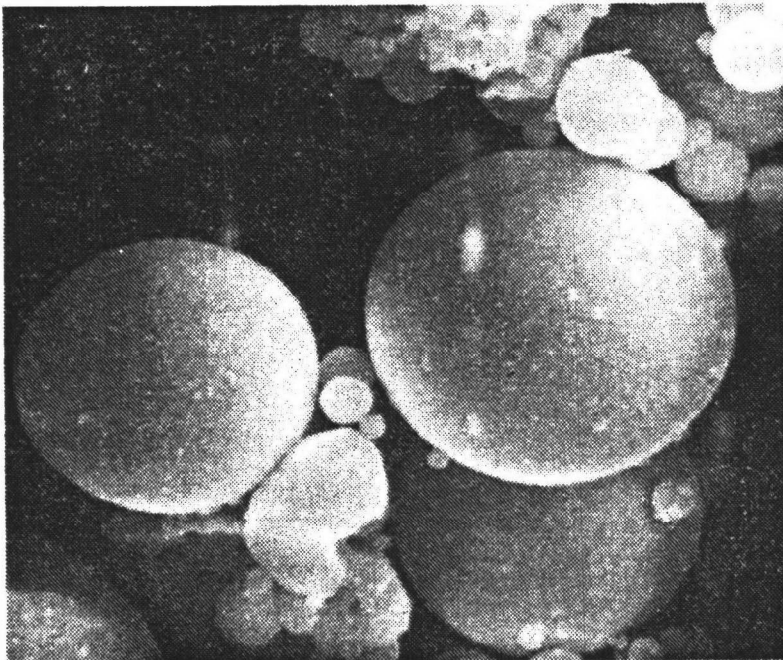
Figure 4-41 NO_x Removal vs Mole Ratio (1)

70A2680

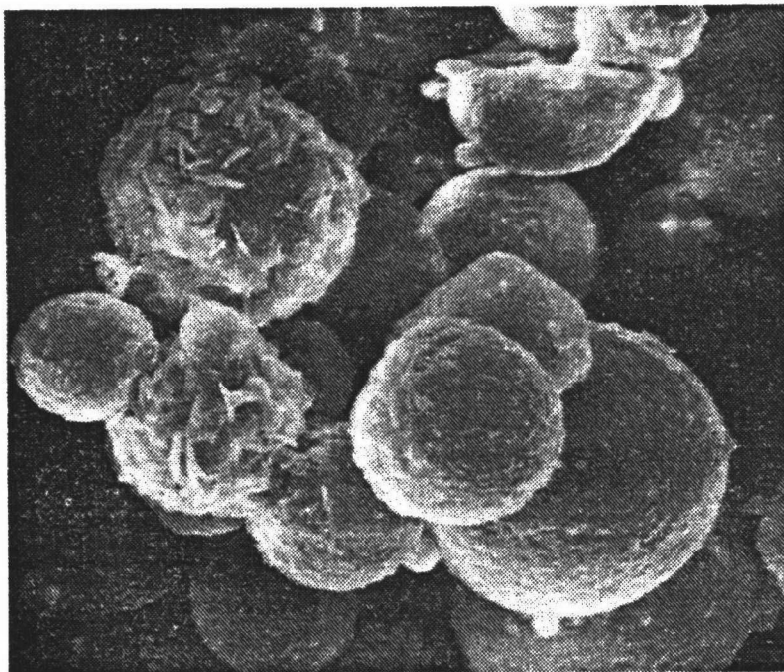
Figures 4-42 and 4-43 are scanning electron microscope photographs of the samples. The author compared these samples with fly ash samples obtained at SCR plants in Japan. The chemical composition of the samples is shown in Table 4-26. Ash A has a clean smooth surface similar to the Japanese ashes as shown in Figure 4-42. By contrast, ashes B and C have many deposits on their surface. Such deposits appear to give the ash an adhesive quality. Some of the ash B particles contain crystals which have grown perpendicularly on their surfaces as shown in Figure 4-42. This indicates crystal growth caused by gas phase reaction.

The author presumes that these deposits on the ash, including the well-grown crystals, were formed by the reaction of SO_2 and metallic vapor in the combustion gas. It seems likely that a considerable amount of SO_2 is formed in the heater at the Mitchell Station. This heater contains fine stainless steel tubes which are at a temperature above 400°C . Stainless steel has been known to act as a good oxidation catalyst of SO_2 to SO_3 . Although a similar heater has been used by Hitachi Zosen at Isogo, the SO_2 content of the flue gases at the two stations are different---about 1,000 ppm at the Mitchell Station and about 300 ppm at Isogo. At the Mitchell Station a much larger amount of SO_3 may form on the surface of the hot tubes. It is on these same tubes that the fly ash deposits and undergoes the reaction described above. It has been found that various metallic components in coal vaporize upon combustion and condense on the ash surface during cooling. As shown in Table 4-25, ashes B and C contain more than 10 times the amount of potassium that the Japanese ashes contain; potassium is volatile at high temperatures. Other metallic components also may be involved in the formation of the deposits.

The author presumes that the combination of those two factors caused deposit formation and made the ash adhesive; the deposits have a much lower melting point than that of the ash particles themselves and may be quite adhesive at 400°C . The well-grown crystals may have been formed while the ash remained on the surface of the stainless steel tube. Some of the ash particles may occasionally dislodge and deposit on the catalyst.

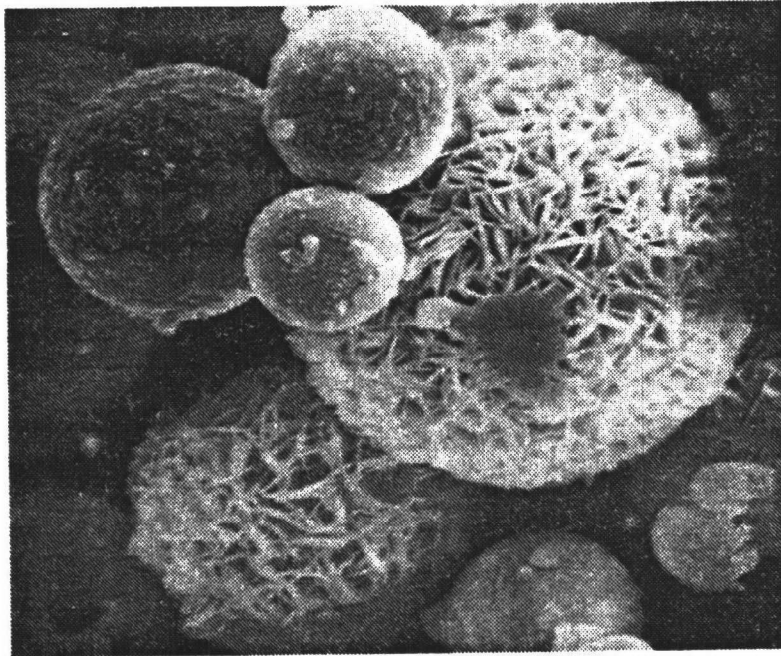


(A) (FROM ESP)

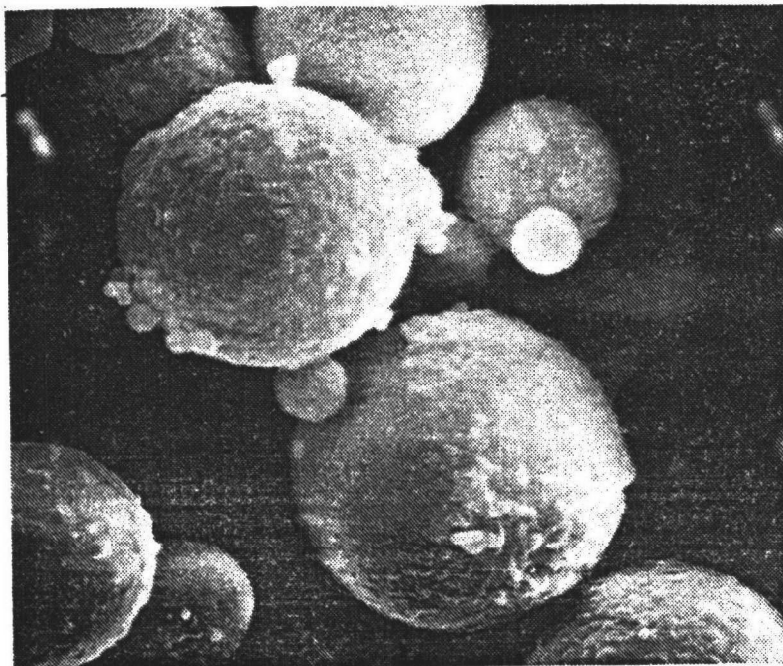


(B) (FROM HEATER)

Figure 4-42 Scanning Electron Microscope Photographs of Fly Ash at Plant Mitchell (I) (x3000)



(B) (FROM HEATER)



(C) FROM REACTOR)

Figure 4-43 Scanning Electron Microscope Photographs of Fly Ash at Plant Mitchell (II) (x3000)

TABLE 4-25. COMPOSITION OF FLY ASH (%)

	Mitchell Station		Isogo	
	B	C	(1)	(2)
SiO ₂	48.0	47.8	45.1	44.5
Al ₂ O ₃	32.1	31.3	21.5	22.2
Fe ₂ O ₃	12.1	10.7	5.2	5.7
TiO ₂	1.3	1.2	1.4	1.3
CaO	1.8	1.8	1.1	4.7
MgO	1.3	1.4	1.8	1.9
Na ₂ O	0.3	0.3	0.9	0.6
K ₂ O	2.8	3.0	0.08	0.24
SO ₄	— ^a	— ^a	9.1	5.3
NH ₃	— ^a	0.2	— ^a	— ^a

An example of dust clogging on an SCR catalyst in Japan took place during treatment of flue gas from an iron-ore sintering machine. The gas contained large amounts of SO₂, Fe₂O₃ dust, and potassium vapor which resulted in deposits of a double salt and potassium ferric sulfate on the catalyst.

Since ash A has a clean smooth surface and is not adhesive, it is possible that the fly ash at the Mitchell Station would not be adhesive if the stainless steel heater were not used. On the other hand, surfaces of ash particles obtained at Isogo, Takasago, and the Mitchell Station (A) are not entirely clean, but have many fine deposits, although the amount of deposition is far less than that of ashes B and C. Further study on the surface properties of these ashes may be needed.

A gas analysis of the SO₂ concentrations at the inlet and outlet of the SCR reactor at Mitchell indicates that the SO₂ oxidation ratio was about 1.2%. Although the oxidation ratio is not very high, a low-oxidation catalyst may be desirable for treating SO₂-rich gas. In addition, oxidation at the catalyst surface may have promoted dust clogging.

Catalyst shape also has an effect on dust clogging. As shown in Figure 4-44, the wave catalyst has many corners with small angles in which the actual gas velocity is slow. This results in dust deposition in the corners and soot blowing does not efficiently remove these deposits. Triangle catalysts, such as NOXNON 500 and 600 also have a tendency for dust plugging at the corners. Hexagonal or simple plate catalysts are the best type of catalysts for avoiding dust plugging.

Dust plugging also may be prevented by using a suitably-shaped low oxidation catalyst along with an adequate gas velocity.

4.10.4 Costs of SCR for Coal-Fired Boiler Applications in the U.S.

Tables 4-26 and 4-27 show the estimated investment and annual costs of SCR applied to a 500-MW coal-fired boiler in the U.S. for 90% removal using Hitachi Zosen's catalyst. The total investment cost equals \$51/kW and is close to the 10,760 yen for \$43/kW shown in Table 4-21 for 90% NO_x removal with 600 ppm inlet NO_x, although the basis of the cost calculation may be a little different. The total annual cost for a 7000-hour SCR operation period at the 500 MW plant is estimated at \$11,160,000. Assuming an average 90% load during operation hours, the annualized cost accounts for 3.54 mil/kWhr, which is slightly less than the cost shown in Table 4-21.

Tables 4-26, 4-27 and 4-21 show a variation in the estimated cost of the catalyst. Tables 4-26 and 4-27 assume the initial charge of the catalyst to be \$10.50/kW combined with a catalyst life of 1 year. Table 4-21 assumes the initial charge of the catalyst to be 5230 yen (\$20.90)/kW with a catalyst life of 2 years, yielding an annualized catalyst cost of \$10.50/kW.

In Japan, the life of an SCR catalyst used with a coal-fired boiler is usually guaranteed for one year although in practice it may last for 2 years. Only one catalyst has been used for 2 years (at Shimonoseki) and it operated at 50% removal. With regeneration, Hitachi Zosen's catalyst may be used for 2 years which would mean a lower annualized cost. On the other hand, a larger

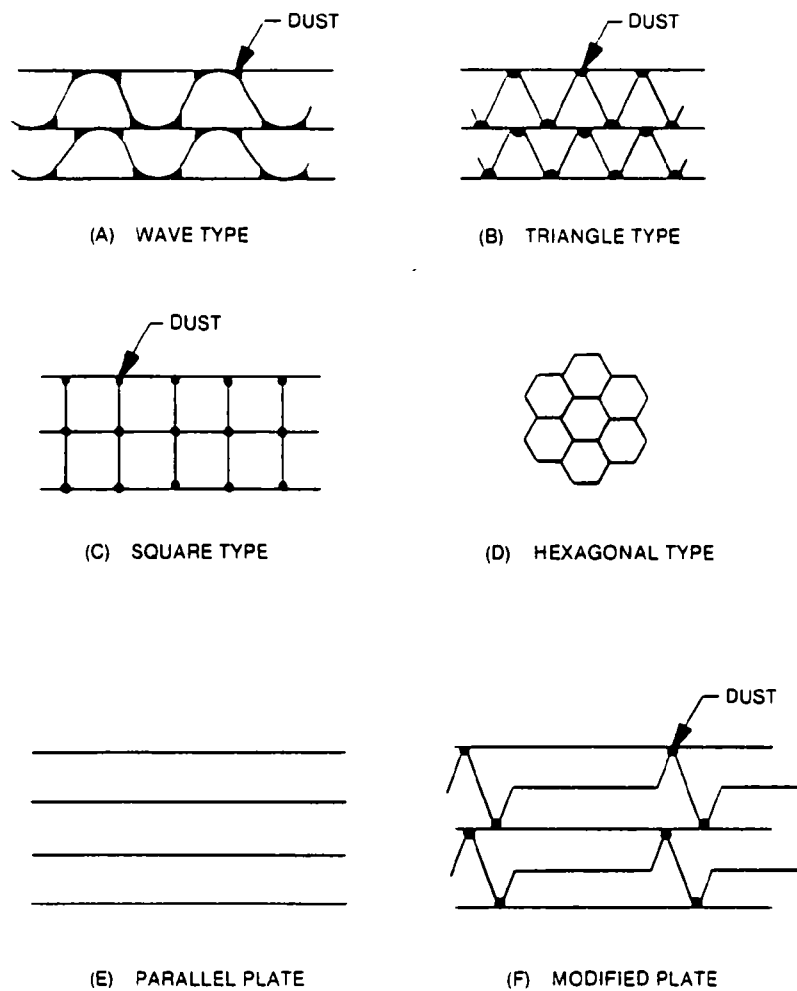


Figure 4-44 Parallel Flow Catalysts and their Dust Clogging Tendencies

TABLE 4-26. ESTIMATED CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS IN THE U.S.^a (9)

	Investment, \$	% of total direct investment
<u>Direct Investment</u> ^b		
NH ₃ storage and injection	692,000	5.0
Reactor section	10,247,000	74.7
Gas handling	472,000	3.4
Air preheater modifications	<u>1,534,000</u>	<u>11.2</u>
Sub-total direct investment (DI)	12,945,000	94.3
Services, utilities (0.06 x DI)	<u>777,000</u>	<u>5.7</u>
Total direct investment (TDI)	13,722,000	100.0
<u>Indirect Investment</u>		
Engineering design and supervision	298,000	2.2
Architect and engineering contractor	75,000	0.5
Construction expense		
= 0.25 (TDI x 10 ⁻⁶) ^{0.83}	2,198,000	16.0
Contractor fees = 0.096 (TDI x 10 ⁻⁶) ^{0.76}	<u>703,000</u>	<u>5.1</u>
Total indirect investment (IDI)	3,274,000	23.8
Contingency = 0.2 (TDI + IDI)	<u>3,399,000</u>	<u>24.8</u>
Total fixed investment (TFI)	20,395,000	148.6
<u>Other Capital Charges</u>		
Allowance for startup and modifications		
= (0.1) (TFI)	2,040,000	14.9
Interest during construction		
= (0.12) (TFI)	<u>2,447,000</u>	<u>17.8</u>
Total depreciable investment	24,882,000	181.3
Land	5,000	-
Working capital	270,000	3.4
Royalty fee	<u>300,000</u>	<u>2.2</u>
TOTAL CAPITAL INVESTMENT	25,657,000	186.9

^aBasis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% NO_x removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

^bEach item of direct investment includes total equipment costs plus installation labor, and material costs for electrical, piping, ductwork, foundations, structural, instrumentation, insulation, and site preparation.

TABLE 4-27. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSIN PROCESS IN THE U.S.^a (9)

Item	Annual Quantity	Unit Cost (\$)	Annual Cost (\$)	% of annual revenue required
<u>Direct Costs</u>				
Raw materials				
NH ₃	5.28x10 kg	0.165/kg	871,000	7.8
Catalyst			5,250,000	47.0
Total raw materials			6,121,000	54.8
Conversion costs				
Operating labor and supervision	8,760 labor hrs.	12.50/ labor hrs.	110,000	1.0
Utilities				
Steam	85,800 GJ	1.90/GJ	163,000	1.5
Electricity	18,226,000 kWh	0.029/kWh	529,000	4.8
Heat credit	125,200 GJ	-1.90/GJ	(214,000)	(1.9)
Maintenance = 0.04 x TDI			549,000	4.9
Analyses	2,920 labor hrs.	17.00/ labor hrs.	50,000	0.4
Total conversion costs			1,187,000	10.7
Total direct costs			7,308,000	65.5
<u>Indirect Costs</u>				
Capital charges				
Depreciation = (0.06) (total depreciable investment)			1,493,000	13.3
Average cost of capital = (0.086) x (total capital investment)			2,207,000	19.8
Overheads				
Plant = (0.5) (conversion costs minus utilities)			355,000	3.2
Administrative = (0.1) (operating labor costs)			11,000	0.1
Total indirect costs			4,066,000	36.4
Spent catalyst disposal			(214,000)	(1.9)
Gross average revenue requirement			11,160,000	100.0
TOTAL ANNUAL REVENUE REQUIREMENTS			11,160,000	100.0

^a Basis: 500 MW new coal-fired power plant, 3.5% S coal, 90% NO_x reduction, 90% SO₂ removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 MG/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment \$13,722,000; total depreciable investment \$24,882,000; and total capital investment \$24,657,000.

amount of catalyst than that upon which these figures are based may be needed to reduce unreacted NH_3 to a level of 5 ppm or below.

In the U.S., the reduction of unreacted NH_3 may be important for coal-fired boilers. This is because it is necessary to maintain an appropriate ammonia content in the large amounts of fly ash and sludge produced by the lime/limestone FGD process. Based on this assumption, catalyst costs in the U.S. may be similar to those listed in Table 4-21.

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SECTION 5

SCR FOR INDUSTRIAL GAS SOURCES

5.1 GENERAL DESCRIPTION

5.1.1 SCR Units for Industrial Gas Sources

SCR units for industrial gas sources with a capacity greater than 10,000 Nm³/hr are listed in Tables 5-1 through 5-3. Of a total of 62 units, 58 are commercial and four are test units (Nos. 33, 35, 65, and 72).

Most of the SCR units were constructed between 1975 and 1978, when the ambient NO₂ standard was extremely stringent—0.02 ppm as a daily average. This standard is equivalent to 0.01 ppm as a yearly average and is less than half of the 0.05 ppm equivalent U.S. daily average standard. In order to achieve this stringent standard, local governments reduced NO_x as much as possible.

Few SCR units for industrial gas sources have been constructed since 1979 partly because the ambient standard was relaxed in 1978 to 0.04-0.06 ppm as a daily average, and partly because of the economic recession which slowed the construction of new factories requiring NO_x flue gas treatment.

Most of the SCR units use granular (or pellet) catalysts for the following reasons: (1) many units treat clean flue gas; (2) parallel flow catalysts were not well developed before 1978; and (3) some of the units use granular catalysts in a moving bed. Moving bed systems can remove 70-80% of the dust

TABLE 5-1. SCR PLANTS FOR OIL, PETROCHEMICAL, AND GAS COMPANIES (Gas Flow Greater than 10,000 Nm³/hr)

No.	User	Plant Site	Gas Source	Fuel	Capacity (1,000 Nm ³ /hr)	New or Retrofit	Vendor	Catalyst	Start Up
<u>Oil Companies</u>									
1	Fuji Oil	Sodegaura	CO Boiler	CO, H ₂ ^a	70	R	JGC	PP ^b	1976
2	Fuji Oil	Sodegaura	Boiler	H ₂	200	N	Mitsubishi H.I.	H ^c	1978
3	Idemitsu Kosan	Anegasaki	Furnace	LCC gas	350	R	Hitachi Zosen	G ^d	1975
4	Kansai Oil	Sakai	Boiler	H ₂	150	R	Hitachi Zosen	G	1979
5	Kashima Oil	Kashima	Furnace	Offgas	58	R	JGC	PP	1975
<u>Petrochemical Companies</u>									
6	Chiba Pet. Chem.	Chiba	Boiler	H ₂	10	R	Ube Kosau	G	1975
7	Idemitsu Pet. Chem.	Anegasaki	Furnace	LHG	300	R	Mitsui Toatsu	G	1977
8	Mitsui Pet. Chem.	Chiba	Boiler	FCC Gas	240	R	Mitsui Engineering	G	1975
9	Mitsubishi Pet. Chem.	Yokkaichi	Boiler	H ₂	150	R	Hitachi Ltd.	G	1976
10	Nihon Pet. Chem.	Chiba	Boiler	H ₂	100	R	Mitsubishi Kakoki	T ^e	1976
11	Osaka Pet. Chem.	Sakai	Furnace	Offgas	91	R	Mitsui Toatsu	G	1976
12	Shindaiyowa Pet. Chem.	Yokkaichi	Boiler	H ₂	440	R	Hitachi Zosen	G	1975
13	Ukishima Pet. Chem.	Chiba	Boiler	H ₂	260	N	Mitsui Engineering	T	1978
<u>Gas Companies</u>									
14	Osaka Gas	Senpoku	Generator	Naphtha	64	R	Mitsubishi H.I.	G	1975
15,16	Osaka Gas	Senpoku	Boiler	Gas	30 x 2	R	Mitsubishi H.I.	G	1976
17,18	Toho Gas	Chiba	Generator	Naphtha	42 x 2	R	Mitsubishi Kakoki	G	1977
19	Toho Gas	Chiba	Boiler	Kerosene	30	R	Mitsubishi Kakoki	G	1977
20	Toho Gas	Sorami	Reformer	Naphtha	19	R	Mitsubishi Kakoki	G	1976
21,22	Toho Gas	Sorami	Reformer	Naphtha	31 x 2	R	Sumitomo Chem. Eng.	G	1977
23	Toho Gas	Sorami	Boiler	Naphtha	23	R	Sumitomo Chem. Eng.	G	1977

^aHeavy Oil^bParallel Passage Reactor^cHoneycomb^dGranular^eTubular

TABLE 5-2. SCR PLANTS FOR STEEL AND METAL INDUSTRIES (Larger than 10,000 Nm³/hr)

No.	User	Plant Site	Gas Source	Fuel	Capacity (1,000 Nm ³ /hr)	New or Retrofit	Vendor	Catalyst	Start Up
<u>Steel Producer</u>									
31	Kawasaki Steel	Chiba	Coke Oven		500	N	Hitachi Ltd.	GM ^a	1976
32	Kawasaki Steel	Chiba	Sintering Machine		762	N	Hitachi Zosen	G ^b	1977
33	Kobe Steel	Amagasaki	Coke Oven		104	R	Kobe Steel	GM ^c	1977
34	Nippon Yohan	Ogishima	Sintering Machine		1,320	R	Nippon Kokan	GM ^c	1979
35	Nippon Steel	Kimizu	Coke Oven		133	N	JGC	PP	1978
36	Nisshin Steel	Amagasaki	Boiler	(HO) ^d	19	R	Hitachi Ltd.	GM	1977
37	Toshin Steel	Himeji	Furnace	(HO)	71	R	Hitachi Zosen	G	1976
<u>Metal Producer</u>									
38	Nihon Seitetsu	Katsuma	Furnace	(HO)	10	R	Hitachi Zosen	G ^c	1976
39	Nippon Yakin	Kawasaki	Boiler	(HO)	15	R	Mitsubishi Kakoki	R ^c	1976
40	Seitetsu Kagaku	Boiler	Boiler	(HO)	15	R	Seitetsu Kagaku	R	1975

^aGranular catalyst, moving bed.^bGranular catalyst (fixed bed).^cGranular iron ore is used as catalyst in moving bed.^dHeavy oil.^eReplaced in 1977 with ring-tube catalyst stacked regularly to achieve parallel flow.

TABLE 5-3. SCR PLANTS FOR OTHER INDUSTRIES (Larger than 10,000 Nm³/hr)

No.	User	Plant Site	Gas Source	Fuel	Capacity (1,000 Nm ³ /hr)	New or Retrofit	Vendor	Catalyst	Start Up
51,52	Aito	Chiba	Boiler	LNG	30 x 2	N	Mitsubishi H.I.	G ^c	1978
53	Ajinomoto	Kawasaki	Boiler	HO ^a	180	R	Ishibawajima H.I.	G	1978
54	Asahi Glass	Keihio	Furnace	HO	75	R	Asahi Glass	GM ^d	1976
55	Atomic Power Res.		Boiler		50	N	Kawasaki H.I.	G	1977
56	Catalyst Chem.	Wakamatsu	Furnace	HO	10	R	JGC	GM	1976
57	Chiyoda Kenzai	Kaisuka	Boiler	HO	15	R	Babcock Hitachi	G	1976
58	Chiyoda Kenzai	Atsugi	Boiler	HO	19	R	Lbara	G	1977
59	Dainippon Ink	Sakai	Boiler	LNG	30	N	Mitsubishi H.I.	G	1978
60	Green Chemical	Kashima	Furnace	LPG	10	N	Hitachi Zosen	G	1974
61	H. N. Methanol	Sodegaura	Reformer	LPG	200	N	Sumitomo Chem. Eng.	G	1974
62	J. National Railway	Kawasaki	Gas Turbine	Kerosene	1,024	N	Babcock Hitachi	GM	1981
63	Kansai Plant	Amagasaki	Boiler	Kerosene	16	R	Babcock Hitachi	G	1978
64	Kawasaki H.I.	Akashi	Boiler	HO	25	R	Kawasaki H.I.	G	1978
65	Kurabo	Hirakata	Boiler	H.O.	30	R	Kurabo	GM	1975
66,67	Mitsui Toatsu	Osaka	Reformer	Buthane	84 x 170	R	Mitsui Toatsu	G	1976
68	Nihon Ammonia	Sodegaura	Reformer	LPG	290	N	Sumitomo Chem. Eng.	G	1975
69	Nihon Oil & Fat	Amagasaki	Boiler	LPG	20	N	Babcock Hitachi	G	1978
70	N. N. Methanol	Sodegaura	Reformer	Buthane	323	N	Mitsui Toatsu	G	1976
71	Sekisui Chem.	Sakai	Boiler	LPG	20	N	Mitsui Toatsu	G	1980
72	Sumitomo Chem.	Sodegaura	Boiler	HO	30	R	Sumitomo Chem. Eng.	G	1973
73	Sumitomo Chem.	Niihama	Reformer	LPG	200	R	Sumitomo Chem. Eng.	G	1975
74,75	Sumitomo Chem.	Ahegasaki	Boiler	LPG	100 x 200	R	Sumitomo Chem. Eng.	G	1975
76,77	Sumitomo Chem.	Sodegaura	Boiler	HO	250 x 350	R	Sumitomo Chem. Eng.	G	1976
78	Tokyo Metropolis	Sunamachi	Incinerator	Sludge	100	N	Mitsui Eng.	H ^e	1979
79	Unitika	Uji	Diesel Engine	LO ^b	70	N	Unitika	G	1978

^aHeavy oil.^bLight oil.^cGranule.^dGranule in moving bed^eHoneycomb.

in the flue gas along with 80-90% of NO_x and are suitable for certain gas sources which do not have ESPs.

There are 8 industrial SCR units which use parallel flow reactors. Nos. 1, 5, and 35 use a parallel passage reactor, Nos. 2 and 78 use a honeycomb catalyst, and Nos. 10, 13, and 39 use tube or ring-tube catalysts. Since parallel flow catalysts provide simple reliable operation, they are generally preferred to the moving bed reactor with a granular catalyst except for cases in which dust removal by the bed is important. A moving bed reactor may be useful for very dirty gases such as flue gas from a glass melting furnace which contains alkaline vapor or for low-temperature gas containing SO_x , which tends to deposit sodium sulfate or ammonium bisulfate on the parallel flow catalysts (Nos. 54 and 33).

Most of the SCR units have been operated without problems. However, several units have been shut down or operated intermittently due to the 1978 relaxation of the NO_x regulation and the downturn in the economy which reduced NO_x emissions made continuous operation of the SCR system unnecessary.

Unit Nos. 1, 3, 5, 76, and 77 are the only major units which have not been in use for over one year. These five units were constructed in 1975 and 1976, at an early stage in the development of SCR. Unit No. 12 has been operated intermittently. Unit Nos. 1, 3, and 12 require fuel for gas heating, and therefore have high operating costs.

Some of the catalysts produced before 1976 either were not resistant to SO_x or experienced dust plugging problems; most of the catalysts produced in 1976 or later had few poisoning or plugging problems. For example, the Fe_2O_3 -based ring catalyst charged in 1976 for Unit No. 39 was not satisfactory and was replaced in 1977 with a TiO_2 -based ring-tube catalyst. The latter catalyst has treated flue gas from an industrial boiler burning heavy oil (2.5% sulfur) for over 4 years without replacement (Section 5.3). The honeycomb catalyst of Unit No. 2 has been used for over 4 years without renewal (Section 5.2).

Most of the units, particularly the smaller ones, remove 90% or more of NO_x using 1.0 - 1.2 mol NH_3 to 1 mol NO_x . Although unreacted NH_3 reaches 10 ppm in these units, an ammonium bisulfate problem is seldom encountered because the flue gas is usually discharged above 250°C. An ammonium bisulfate problem did occur in a few larger plants including Unit No. 12 (Shindaikyowa), which cools the gas below 250°C for better heat recovery. Units No. 2 and 12 recently used 0.6 - 0.7 mol NH_3 to 1 mol NO_x to remove 60-70% of NO_x . These units leaked NH_3 below 1 ppm and did not have a bisulfate problem.

5.1.2 Economics

The investment costs of seven SCR units are shown in Table 5-4. Costs are given for the SCR reactor, the initial charge of catalyst, connecting ducts, ammonia storage and injection facilities, NO_x and NH_3 analyzers, and control systems (unless otherwise noted). Some of the unit costs include costs for the heat exchanger, heater, and fans for gas heating purposes.

In general, SCR units were expensive during the early stages of development in 1975 and 1976. The costs were substantially lowered in 1977 and 1978 due to technology developments and have increased slightly since 1979 due to inflation. The individual cost of Unit Nos. 1, 12, 39, and 65, which were constructed in 1975 and 1976 exceeds 13,000 yen/kWhr although these units are for existing boilers and include heating or test facilities. By contrast, the two units constructed in 1978 for new boilers (Nos. 2 and 13) cost only 1,230 and 2,640 yen/kWh, respectively. Unit No. 78, constructed in 1979, is fairly costly—14,500 yen/kWh—because it was designed to remove both NO_x and odor from an existing incinerator and has a heat exchanger, heater, and fans.

As opposed to SCR units for utility boilers, units for industrial uses treat various kinds and amounts of gas under a variety of conditions. Therefore, although the operating costs of SCR units for large new industrial boilers may be close to those for new utility boilers, the investment costs vary widely.

TABLE 5-4. INVESTMENT COSTS OF SEVEN INDUSTRIAL SCR UNITS

No.	Owner	Gas Source	Capacity (MW) ^a	NO _x Removal (%)	New or Retrofit	Reactor (Catalyst)	SV ₁ (hr ⁻¹)	Cost		Year Completed
								(10 ⁴ yen)	(yen/kW)	
1	Fuji Oil	Boiler	23	95	R	PP ^b	4,200	480	20,870 ^c	1976
2	Fuji Oil	Boiler	53	80	N	II ^d	5,220	65	1,230 ^e	1978
12	Shindaiyowa	Boiler	150	90	R	Granule	10,000	2,000	13,300 ^f	1975
13	Hkushima	Boiler	87	85	N	Tube		200	2,640 ^f	1978
39	Nippon Yakin	Boiler	5	90	R	Ring Tube	3,900	66	13,200 ^f	1976
65	Kurebo	Boiler	10	90	R	MB ^g	10,000	130	13,000 ^h	1975
78	Tokyo Metro.	Incinerator	33	90 ⁱ	R	II	4,000	480	14,500 ^f	1979

^a Calculated from gas volume (300 Nm³/hr = 1 MW).^b Parallel Passage Reactor.^c Including Heater.^d Honeycomb.^e For catalyst and reactor.^f Including fan, heat exchanger and heater.^g Moving bed reactor.^h Including test facilities.ⁱ Removes both NO_x and offensive odor.

The operating costs for 8 units in 1979 are shown in Table 5-5. The costs range from 1,400 - 2,000 yen/kl oil or 0.33 - 0.46 yen/kWhr for the four units which do not require gas heating, and from 2,200 - 4,000 yen/kl or 0.49 - 0.93 yen/kWhr for the four units requiring gas heating. Unit No. 1 is the most expensive and has been shut down since 1977.

In 1981, the operation costs for SCR units may be slightly higher than those shown in Table 5-5 due to inflation. However, the application of SCR can be less expensive than the use of higher quality fuel for NO_x abatement, as will be discussed in Section 5.3.

5.2 SODEGAURA REFINERY, FUJI OIL

5.2.1 Introduction

Fuji Oil's Sodegaura Refinery is located in the Keiyo Industrial Region near Chiba City and Tokyo. This area is the largest industrial region where stringent NO_x and SO_x regulations have been applied by the local government. The Sodegaura Refinery now has five boilers as shown in Table 5-6. The total boiler capacity was almost doubled between 1974 and 1977. During the same time period the permissible total NO_x emissions from the refinery were cut almost in half, requiring extensive NO_x abatement by combustion modification and SCR (Tables 5-6 through 5-9).

5.2.2 SCR Unit for CO Boiler

The flow sheet of the CO boiler and the SCR unit at the Sodegaura Refinery is shown in Figure 5-1. The SCR unit was constructed for the existing CO boiler by JGC Corporation using JGC's catalyst and the Shell parallel passage reactor. Since it was difficult to install the SCR reactor between the boiler and the economizer, an inline heater first was installed to heat the 250-300°C economizer outlet gas to 360-400°C. The SCR reactor then was installed downstream of the heater. The SCR unit was completed in 1976 and was operated for about 6 months with an NO_x removal rate of 92-96% (Table 5-9). The pressure drop through the SCR reactor was 100-120 mm H₂O.

TABLE 5-5. OPERATING COSTS OF SCR UNITS IN 1979 (Heavy Oil-Fired Boiler Including 7 Years Depreciation)

No	Owner	Capacity (MW)	Reactor (Catalyst)	NO _x Removal (%)	Cost		Remarks
					(yen/kW)	(yen/kwhr)	
1	Fuji Oil	23	pp ^a	95	4,000	0.93	With gas heating
2	Fuji Oil	53	h ^b	70	1,400	0.32	
13	Ukushima	87	Tube	85	1,500	0.33	
36	Nisshin Steel	6.5	MB ^c	90	2,800	0.65	With gas heating
39	Nippon Yakin	5.0	Ring Tube	90	2,200	0.49	With gas heating
63	Kansai Paint	5.3	Ring	90	3,600	0.84	With gas heating
65	Kurabo	10	MB	90	2,000	0.46	
69	Nihon Oil & Fats	6.7	MB	90	1,800	0.41	

^aParallel passage reactor.

^bHoneycomb.

^cMoving bed.

TABLE 5-6. BOILERS AND NO_x ABATEMENT AT SODEGAURA REFINERY (1)

Boiler	Fuel	Steam Rate (ton/hr)	NO _x Abatement Methods
No. 4	Oil	75	LNB ^a
No. 5	Oil	160	LNB, TSC ^b , FGR ^c
No. 6	Oil	160	LNB, TSC, FGR
No. 7	Oil	160-200	LNB, TSC, SCR
CO Boiler	CO, Oil	45	SCR

^aLow-NO_x burner.^bTwo-stage combustion.^cFlue gas recirculation.TABLE 5-7. PERMISSIBLE EMISSIONS OF NO_x AND SO_x FROM THE SODEGAURA REFINERY

	1974	1975	1976	Since 1977
NO _x , Nm ³ /hr	157	124	107	92
SO _x , Nm ³ /hr	375	163	145	134

TABLE 5-8. VOLUME AND COMPOSITION OF FLUE GAS TO BE TREATED BY SCR AT THE SODEGAURA REFINERY

Boiler	Fuel	Gas Volume (Nm ³ /hr)	MW Equivalent	NO _x (ppm)	SO _x (ppm)	Dust (mg/Nm ³)
CO Boiler	CO + Oil	70,000	23	160-200	400-600	60-70
No. 7 Boiler	Oil	200,000	67	110-120	200	20

TABLE 5-9. SCR UNITS AT THE SODEGAURA REFINERY

Boiler	Vendor	Year Completed	SV ₋₁ (hr ⁻¹)	Inlet NO _x (ppm)	NH ₃ /NO _x Ratio ^x	Outlet NO _x (ppm)	Removal (%)	Leak NH ₃ (ppm)
CO Boiler	JGC ^a	1976	4,000	180	1.1-1.2	8-15	92-96	10-20
No. 7	MHI ^b	1977	6,400	115	0.5-0.8	57-23	50-80	<1

^aJGC Corporation (using parallel passage reactor).^bMitsubishi Heavy Industries (using honeycomb catalyst).

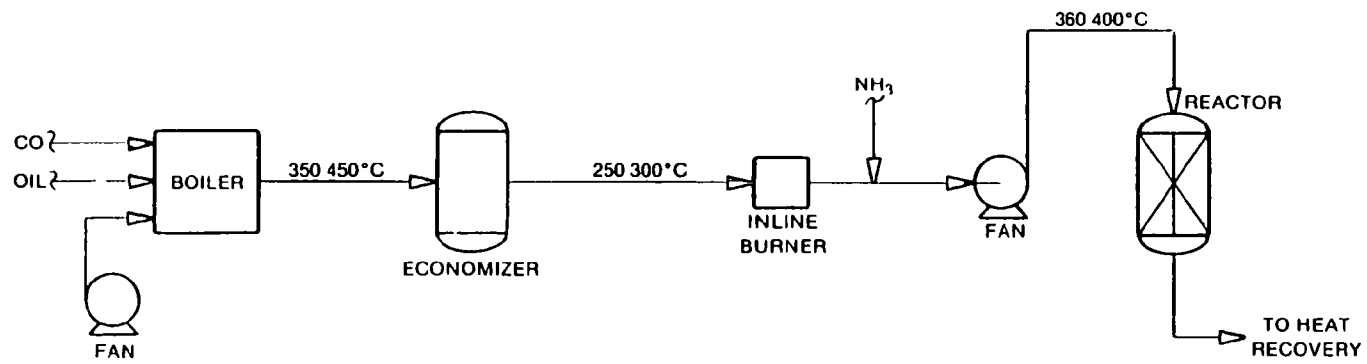


Figure 5-1 Flowsheet of CO Boiler and SCR Unit (Fuji Oil)

Operation of the SCR unit was expensive (Table 5-5) and not energy-efficient because of the fuel requirement for gas heating as well as the high pressure drop. The SCR unit was shut down after 6 months of operation, when the operational load of the refinery dropped to 70% of capacity. At that time, total NO_x emissions were lowered to meet the standard without operating the unit.

5.2.3 SCR Unit for Oil-Fired Boiler

A new oil-fired boiler SCR unit was constructed in 1978 by MHI. The unit uses a NGK honeycomb catalyst and has a capacity of treating 200,000 Nm^3/hr of flue gas containing about 120 ppm NO_x , 200 ppm SO_x , and 20 mg/Nm^3 of dust (Figure 5-2). The reactor exists in ductwork extended between the boiler and economizer and treats gas at temperatures of 330-370°C.

This SCR unit can remove about 90% of NO_x using 0.9 mol NH_3 to 1 mol NO_x . In order to eliminate the ammonium bisulfate problem with the economizer, the unit was operated from 1978 to 1980 with 0.7 mol NH_3 to 1 mol NO_x . This resulted in a NO_x reduction of nearly 70% and less than 1 ppm unreacted NH_3 . Since 1980 it has operated with 0.5 mol NH_3 to 1 mol NO_x and obtained 50% NO_x removal with less than 1 ppm unreacted NH_3 . A small amount of ammonium bisulfate still deposits on the tubes of the economizer, but the economizer can be operated without problems for more than a year at a time and is washed with water during the annual maintenance shutdown period.

After unit startup, a heavy oil additive was used for possible boiler operation improvement, and as a result a slight dust deposit was observed in the catalyst bed. The dust deposit has since been eliminated by not using the additive and applying soot blowing to the catalyst bed.

Catalytic activity tests indicated that the use of 1 mol NH_3 to 1 mol NO_x resulted in 93.5% NO_x removal with 5 ppm of unreacted NH_3 and less than 1% SO_2 oxidation during the first 2 years of operation. An 89.5% NO_x

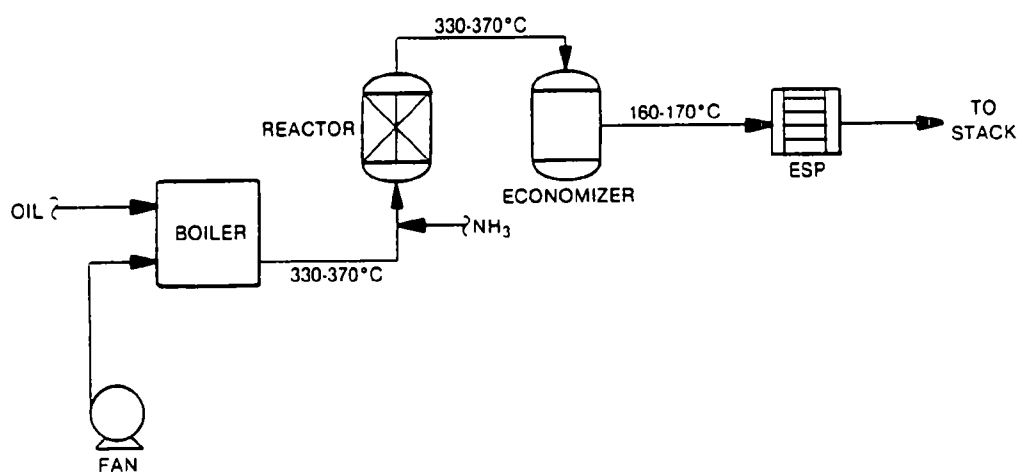


Figure 5-2 Flowsheet of Oil-Fired Boiler and SCR Unit. (Fuji Oil)

removal rate with 10 ppm unreacted NH_3 and about 5% SO_2 oxidation was reported after 2 years of operation. After 3-1/2 years of operation, the NO_x removal efficiency was 86.4% and the catalyst was still active.

5.2.4 Evaluation

The SCR unit for the CO boiler is one of the oldest in Japan and was designed at an early stage in the development of SCR technology when fuel was still inexpensive. Today, if an SCR unit were installed on a similar boiler, the reactor might be placed between the boiler and the economizer to treat the flue gas at 350-450°C, or a low-temperature catalyst might be used for the gas leaving the economizer at 250-300°C in order to save energy.

The SCR unit for the No. 7 oil-fired boiler is one of the oldest units using a honeycomb catalyst. Both investment and operation costs are reasonable (Tables 5-4 and 5-5). Although the catalyst shows a slight decrease in activity and an increase in the SO_2 oxidation ratio with time, it has been successfully used for over 4 years. The increase in the SO_2 oxidation ratio may be caused by the deposition of flue gas vanadium on the catalyst. Improvements in SCR catalysts since 1978 may result in better catalysts for this type of application.

5.3 KAWASAKI PLANT, NIPPON YAKIN

5.3.1 Introduction

Nippon Yakin is an alloy producer with a stainless steel factory in Kawasaki City adjacent to Tokyo. This area was very polluted about ten years ago and has since set stringent regulations for pollution control. The SO_x and NO_x concentrations in the factory's boiler flue gas are transmitted to the City Pollution Control Center.

The factory has 5 boilers, 2 of which use high-sulfur heavy oil ($\text{S}=2.5\%$), while the rest use gas. Each of the 2 oil-fired boilers has a capacity of producing 6 tons of steam per hour with a total gas flow rate of about

15,000 Nm³/hr (5 MW). According to the regulation, NO_x concentrations in the oil-fired flue gas must be kept below 60 ppm. Since the flue gas leaving the boiler contains about 250 ppm NO_x, 1,000 ppm SO_x, and about 100 mg/Nm³ of dust, both SCR and FGD have been applied. To be safe, NO_x is usually reduced to about 20 ppm by SCR, while SO_x is reduced to 20-25 ppm by sodium scrubbing.

The other three boilers use LPG gas and maintain NO_x concentrations below 50 ppm by combustion modification.

5.3.2 Process Description

A flowsheet of the combined SCR/FGD system used in the Kawasaki Plant is shown in Figure 5-3. Flue gas leaving the boiler at 280-300°C is heated to 330°C by a Rothemuehle heat exchanger and then to 370°C by oil-firing. After that, it is injected with ammonia, and then sent to an SCR reactor. The reactor and the heat exchanger were constructed by Mitsubishi Kakoki Kaisha (MKK) in 1976. The Sarc catalyst, a large ring-shaped catalyst based on Fe₂O₃ and V₂O₅, was used with a random packing during the first 6 months of operation. This resulted in a considerable increase in the pressure drop due to dust plugging, and a large decrease in catalytic activity. After 6 months the catalyst was replaced by an improved Sarc catalyst which was used for an additional 6 months without success.

In September 1977, the reactor was modified and a rashig ring type catalyst made by Catalyst and Chemicals, Inc., was charged. This catalyst has inner and outer diameters of 25 and 35 mm, a height of 40 mm, and is made of TiO₂ and V₂O₅. The catalyst was piled regularly to form tubes, inside and outside of which the gas passes in a parallel flow.

The new reactor went into operation in September 1977, and has operated for over four years without problems and without catalyst replacement. The volume of the catalyst is 4 m³, and the SV is 3,750 hr⁻¹. By using 1.2 mol NH₃ to 1 mol NO_x, 92% of the NO_x is removed and unreacted NH₃ is kept around

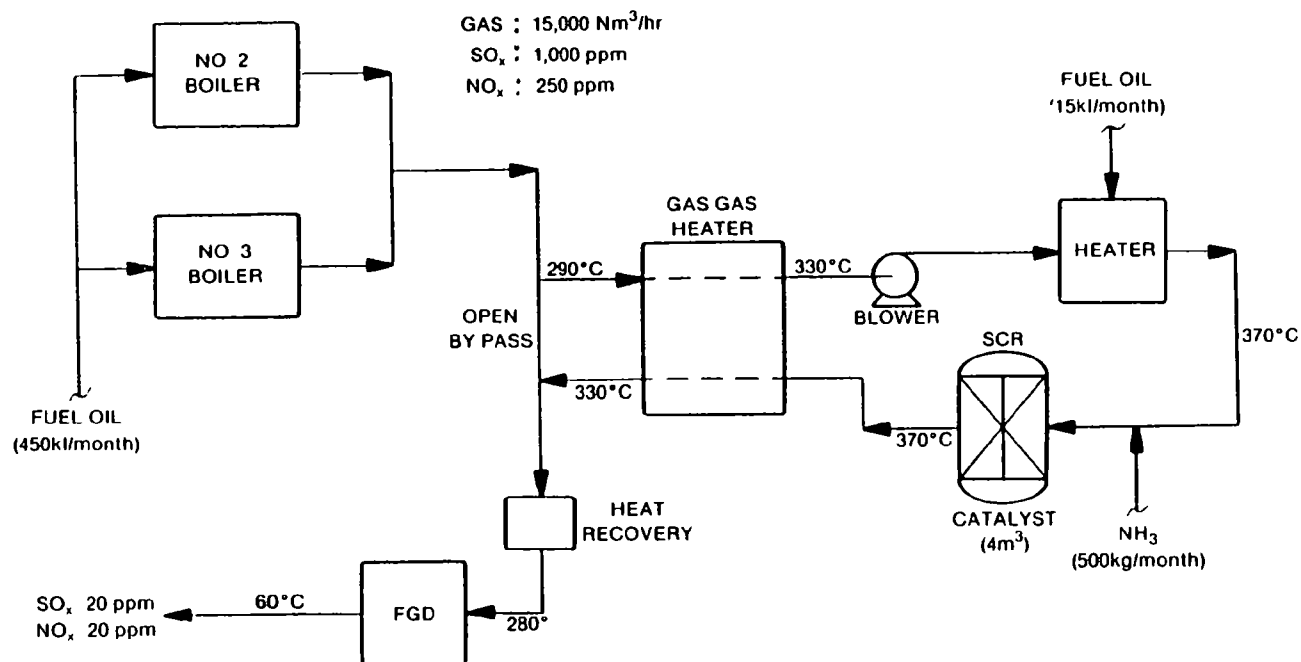


Figure 5 3 Flue Gas Treatment System at the Kawasaki Plant, Nippon Yakin

10 ppm. The pressure drop in the reactor was 210 mm H₂O at startup and increased to about 270 mm H₂O after 4 years of operation. The NO_x removal efficiency has remained over 90% during the 5 year period.

Flue gas leaving the SCR reactor is passed through the heat exchanger where it is cooled to 330°C. Although the gas contains considerable amounts of NH₃ and SO_x, ammonium bisulfate does not deposit in the heat exchanger because of the high flue gas temperature. The gas is then cooled to 280°C by a heat recovery system and subjected to FGD using a spray of sodium hydroxide solution to reduce SO_x to about 20 ppm. The liquor discharged from the scrubber contains sodium sulfite, sulfate, and a small amount of ammonia and is sent to a water treatment system and treated with other wastewaters from the factory.

The construction of the SCR and FGD plants required 4 months. Five days were needed to connect the plants to the boiler.

The boilers undergo a maintenance shutdown once a year. When one of the oil-fired boilers is down for maintenance, the other is in operation. Therefore, the SCR-FGD system has operated continuously for 5 years without total shutdown.

5.3.3 Economics

In 1976, the Kawasaki plant's SCR system (Section 3.6) cost 73 million yen including the cost of the heat exchanger and the heater, while the FGD system cost 63 million yen. The catalyst produced by Catalyst and Chemicals, Inc. cost 6 million yen (1.5 million yen/m³) in 1977. The operating cost of the SCR and FGD systems was 30 million yen in 1979, including about 16 million yen for sodium hydroxide and 5 million yen for gas heating fuel. The 1979 annual costs are summarized below.

Annual cost (million yen)	
Capital cost (25% of investment)	34.0
Catalyst (4 year life)	1.5
Others	30.0
Total	65.5
Annual Fuel Oil Consumption of the Boilers	5,400 kl
Annualized cost	12,130 yen/kl oil

In 1979, heavy oil cost 33,000 yen/kl while kerosene with the equivalent heating value cost 50,000 yen. Since the cost difference was 17,000 yen/kl, the use of heavy oil with the SCR-FGD system meant a 4,778 yen/kl saving. In 1981, heavy oil cost 50,000 yen/kl and kerosene with the equivalent heating value cost 70,000 yen while the annualized cost of the flue gas treatment system was estimated at 12,700 yen/kl. Therefore, the use of this system resulted in substantial savings.

5.3.4 Evaluation

More than 4 years of continuous catalyst use may be the longest record for an SCR catalyst used to treat high sulfur oil flue gas. The smooth operation of Nippon Yakin's Kawasaki plant is a good example of the reliability of an SCR system for industrial boilers.

The catalyst used at the Kawasaki Plant was designed by Catalyst and Chemicals Inc. more than 6 years ago. Further improvements in SCR catalysts made in the past 5 years may make SCR even more reliable.

The heat exchanger has had no ammonium bisulfate problems even though the gas leaving the SCR reactor contains a considerable amount of SO₂ with about 10 ppm unreacted NH₃, due to high gas temperatures (330°C). The gas is subsequently cooled to 280°C for heat recovery. Ammonium bisulfate will deposit when the gas is cooled to lower temperatures and reduction of unreacted NH₃ will be needed for additional heat recovery.

In the future, Nippon Yakin may replace the ring-tube catalyst with a tubular catalyst since the tubular type can be more easily packed.

5.4 SCR FOR COKE OVEN FLUE GAS (NIPPON STEEL)

5.4.1 Introduction

Nippon Steel, Japan's largest steel producer, Nippon Steel Chemical and JGC Corp. have conducted large-scale SCR tests with coke oven flue gas at Nippon Steel's Kimitsu Works Plant. The coke oven flue gas has a flow rate of 152,000 Nm³/hr and contains about 400 ppm NO_x, 15 ppm SO_x, and less than 35 mg/Nm³ of dust. The gas temperature ranges from 170-200°C. Since gas heating to 350°C for SCR is expensive, a low-temperature catalyst developed by JGC Corp. and a parallel passage reactor, originally developed by Shell, are used.

Because ammonium bisulfate gradually deposits on the catalyst and reduces its activity, the gas is periodically (once every several days) heated to above 350°C. The heating takes place in an inline heater for a few hours in order to volatilize the deposits. The SCR unit began operation in March 1978, and has operated since that time without trouble.

5.4.2 Process and Operation (3)

A flow sheet of the Nippon Steel SCR system is shown in Figure 5-4. The flue gas from the coke ovens is injected with ammonia, sent through two trains of inline heaters and SCR reactors, and finally into a stack.

Figure 5-5 shows examples of the change in NO_x removal efficiencies with the heating cycle during treatment of a gas containing 50 or 200 ppm SO_x. The efficiency was lowered more rapidly with gas richer in SO_x due to the deposition of larger amounts of bisulfate. After being heated at 400°C for two hours, the catalyst activity returned to its original level.

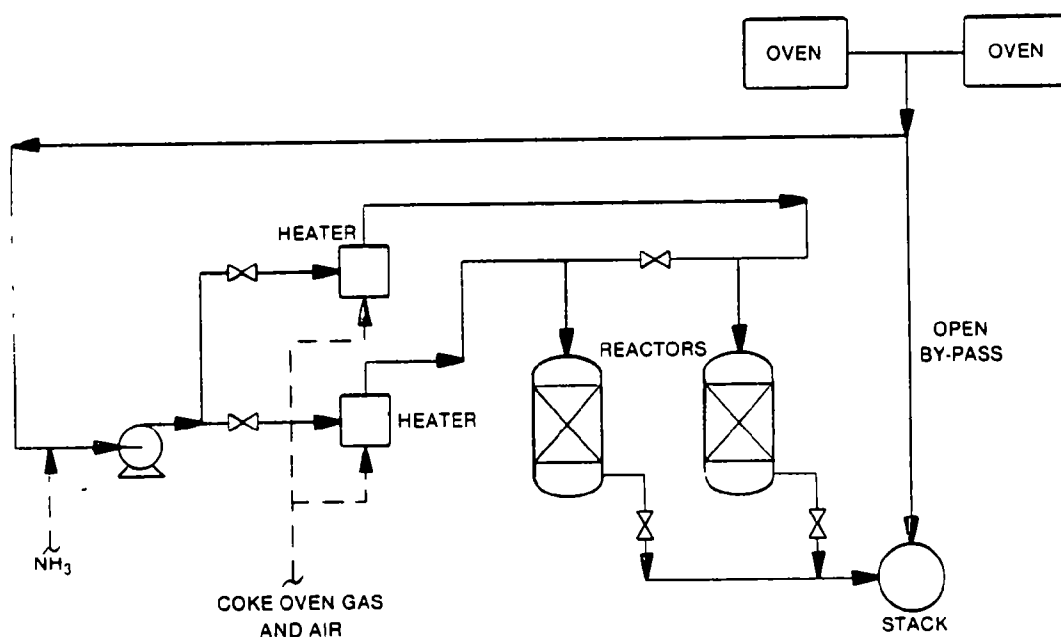
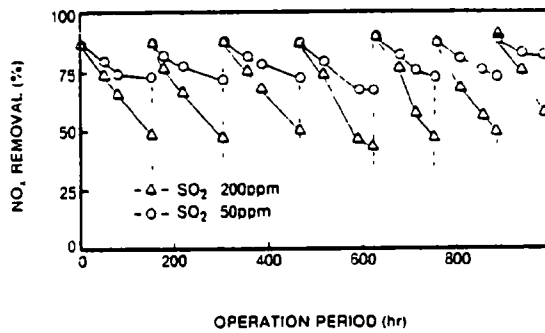


Figure 5-4 Flowsheet of an SCR System for a Coke Oven.



CATALYST JP 501 AT 250°C
 HEATING CONDITION 400°C 2 hours
 GAS COMPOSITION NO 200 ppm NH₃ 220 ppm
 O₂ 3% H₂O 10% N₂ balance

Figure 5-5 Change in NO_x Removal Efficiency During Heating Cycle. (4)

70A2820

CONCENTRATIONS (ppm)	TYPE OF TEST	SV (hr ⁻¹)	TEMP (°C)	NH ₃ NO _x	NO _x REMOVAL (%)		
					50	70	90
	STANDARD	2 700	200	1 3			
	AT 180°C	3 500	180	1 2			
	LOW NH ₃ (180°C)	3 500	180	0 9			
	LESS FREQUENT HEATING	3 500	180	0 9			
	WITHOUT HEATING	3 500	170	0 9			
	WITHOUT HEATING	3 500	170	0 7			

Figure 5-8 Operating Conditions and NO_x Removal Efficiency (3)

70A2821

Tests were conducted continuously for one year from April 1978 through March 1979 under varied conditions, as shown in Table 5-10.

TABLE 5-10. NIPPON STEEL SCR SYSTEM TEST CONDITIONS

Temperature (°C)	170,	180,	200	
SV (hr ⁻¹)	2,700,		3,500	
NH ₃ /NO _x mole ratio	1.3,	1.2,	0.9,	0.7

The NO_x removal efficiencies with different operating conditions are shown in Figure 5-6. With the standard condition of 200°C with an SV of 2,700 hr⁻¹ and a mole ratio of 1.3, the NO_x removal efficiency was 94-98%. The efficiency was 84-92% at 180°C with a mole ratio of 1.2 and an SV of 3,500 hr⁻¹, and 78-88% with a mole ratio of 0.9. When gas heating to 400°C took place over longer intervals, the NO_x removal efficiency was lowered. Tests were conducted using 170°C flue gas without gas heating. These tests indicated that the removal efficiency was 60-70% with a mole ratio of 0.9 and about 50% with a mole ratio of 0.7.

The NO_x removal efficiency under the standard condition was 98% at the beginning and 97% at the end of the tests, which indicated that there was little, if any, degradation of the catalyst during the one-year test period. Tests also have shown that, immediately after being heated to 400°C, the catalyst produced a relatively low NO_x removal efficiency for a short time period. For example, the NO_x removal efficiency was about 80% with 1 mol NH₃ to 1 mol NO_x at 180°C immediately after the heating, and increased to nearly 90% in a few hours. It appears that the catalyst absorbs more ammonia at lower temperatures than at higher temperatures. A considerable amount of ammonia is released from the catalyst when it is heated to 400°C. After being heated to 170-200°C, the catalyst absorbs ammonia in the flue gas until saturation is reached. Saturation results in a temporary shortage of ammonia which can react with NO_x in the flue gas.

The pressure drop in the reactor was 40-50 mm H₂O both at the beginning and the end of the test period indicating that there was no dust plugging problem.

5.4.3 Evaluation

Tests of Nippon Steel's SCR unit were conducted successfully with over 90% NO_x removal efficiency under the standard conditions. Neither catalyst degradation nor dust plugging was observed during the one-year test period. Although periodic gas heating to over 350°C is needed to remove ammonium bisulfate, the use of low-temperature catalysts may be less costly than the use of a standard catalyst with continuous gas heating to 350°C. Another advantage of the system is the simple thermal treatment in the fixed bed. Operation of this system is much easier than using a moving bed with a catalyst that is discharged from the reactor for NO_x treatment. However, low-temperature catalysts may not be suitable for SO_x-rich gas because of the requirement for frequent gas heating.

Parallel passage reactors are expensive because they use many steel gauze envelopes to hold the catalyst. On the other hand, smaller, very active catalysts can be used because less physical strength is needed in these reactors. Therefore, the reactor may be suitable for a low-temperature very active catalyst.

Although the SCR system at Kimitsu works well, it does require considerable investment costs, land space, and energy. At this time, Nippon Steel has no plans to construct a commercial plant using the system.

5.5 SCR USING AN IRON ORE CATALYST

5.5.1 Introduction

Nippon Kokan, one of the largest steel producers in Japan, constructed a full-scale SCR unit at its Keihin Works plant. The unit has a capacity of

treating 1,320,000 Nm³/hr of flue gas from an iron-ore sintering machine using iron ore as the catalyst in a moving bed reactor.

The flue gas is first subjected to dust removal by an ESP and then FGD by ammonia scrubbing, utilizing ammonia present in the coke oven gas (5). The FGD system began operation in 1976 and has operated successfully since that time. When further gas treatment for NO_x removal was requested by the local government, Nippon Kokan conducted pilot plant tests of SCR using iron ore as the catalyst (2). Based on these tests, the full-scale SCR unit was completed and began operation in 1979.

5.5.2 Process Description

The flow sheet of the gas treatment system at Keikin is presented in Figure 5-7. The 150°C flue gas from the sintering machine contains about 300 ppm SO_x, 200 ppm NO_x, and 500 mg/Nm³ of dust. It passes through an ESP, heat exchanger, and an FGD unit to remove over 90% of the SO_x. The flue gas leaving the FGD unit is further cleaned by a wet ESP and then heated to 110°C by a heat exchanger. An SCR unit was installed downstream of the FGD system. The gas is heated to 380-400°C by a heat exchanger and a heater, injected with ammonia, and sent into the moving bed reactor (SV=3,500 hr⁻¹) where 80% of the NO_x is removed. One specific kind of iron ore was found to be particularly active as a catalyst.

Since the flue gas after FGD still contains small amounts of SO_x, a portion of the iron ore reacts to form a powdery sulfate. The ore catalyst discharged from the reactor is screened and returned to the reactor; the iron ore fines containing sulfate are returned to the sintering machine.

The SCR unit cost 6.7 billion yen including the price of the heat exchanger and the heater.

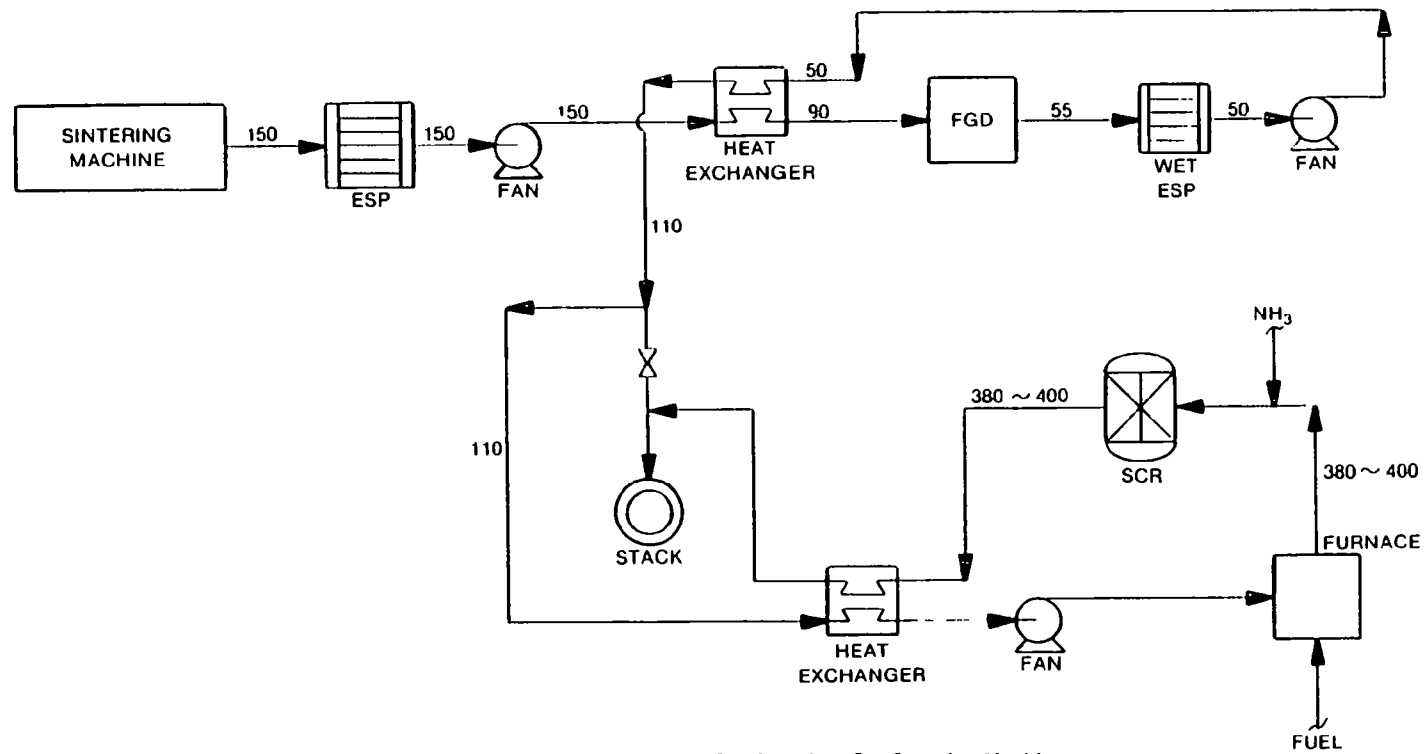


Figure 5-7 FGD/SCR System for Flue Gas from Iron Ore Sintering Machine (Keihin Works, Nippon Kokan)

5.5.3 Evaluation

The iron ore-catalyst SCR system may be best suited to flue gas treatment at steel works because iron ore is inexpensive and can be utilized for steel production after it is used as a catalyst. From this standpoint, the process is quite economical, compared with standard SCR processes for which the cost of the catalyst comprises more than half of the total investment and operation costs.

Treatment of flue gas from a sintering machine still may be fairly expensive because the gas temperature is low---about 150°C at the sintering machine outlet and even lower after wet FGD treatment---thus requiring a heat exchanger and fuel for the heater.

Use of a low-temperature catalyst might reduce the fuel requirement to some extent. JGC Corporation, with funding from the Steel Federation, conducted tests of SCR with a low-temperature catalyst for flue gas leaving a sintering machine (2). These tests were conducted at 290°C or above to avoid ammonium bisulfate deposition and thus required extensive gas heating.

The system at the Keihin Works may be one of the best solutions for treating flue gas from a sintering machine to meet stringent particulate, SO_x, and NO_x standards.

On the other hand, where the regulations are not very stringent, a moving bed reactor with iron ore may be the best way to treat flue gas from a sintering machine directly without an ESP. This system removes 70-80% of the dust and portions of the SO_x and NO_x, and requires only minimal gas heating.

5.6 LOW-TEMPERATURE CATALYST TESTS (KOBE STEEL)

5.6.1 Introduction

Kobe Steel, one of Japan's largest steel and heavy machinery producers, has developed low-temperature SCR catalysts for 180-250°C gases containing 50-

250 ppm NO_x , and 50-1,000 ppm SO_x . These catalysts have been tested at several pilot plants; the largest test plant has a capacity of treating 100,000 Nm^3/hr of flue gas.

Kobe Steel's low temperature catalysts are based on $\alpha\text{-Al}_2\text{O}_3$ or TiO_2 and are characterized by containing niobium in addition to vanadium. Both pellet and honeycomb catalysts have been produced and tested. Pellet catalysts in a movable bed have been used for low temperature gases containing SO_x . Bisulfates deposit on the honeycomb catalyst which means that the catalyst frequently must be discharged from the reactor for thermal treatment.

Unlike other process developers, Kobe Steel has found that the alumina-based catalyst containing Ti, V, and Nb performs well for low temperature gas. Kobe Steel has also developed a special technique for thermally treating a catalyst to recover its initial properties.

5.6.2 Catalysts and Plant Operation

The effect of niobium on the alumina-based $\text{TiO}_2\text{-V}_2\text{O}_5$ catalyst is shown in Figure 5-8. Niobium increases NO_x removal efficiencies especially well at low temperatures. Extensive pilot plant tests have indicated that the alumina-based catalyst is superior to the titanium-based catalyst for low temperature gases. When a titanium-based catalyst was used for a 180-250°C gas containing about 50 ppm SO_x (SV: 5,000 hr^{-1} ; NH_3/NO_x mole ratio:1), the initial NO_x removal efficiency of 98% dropped to about 80% within 8-10 days of continuous operation. Although catalytic activity can be recovered when the contaminated catalyst is heated to 400-450°C, frequent heating consumes considerable energy.

When the alumina-based catalyst is used under the same conditions, the initial 90% NO_x removal efficiency drops very slowly and requires 3,000-4,000 hours to reach 80%. The large specific surface area of the alumina-based catalyst---about 150 m^2/gram compared with about 50 m^2/gram for the titania-based catalyst---may be a factor which explains the long period of

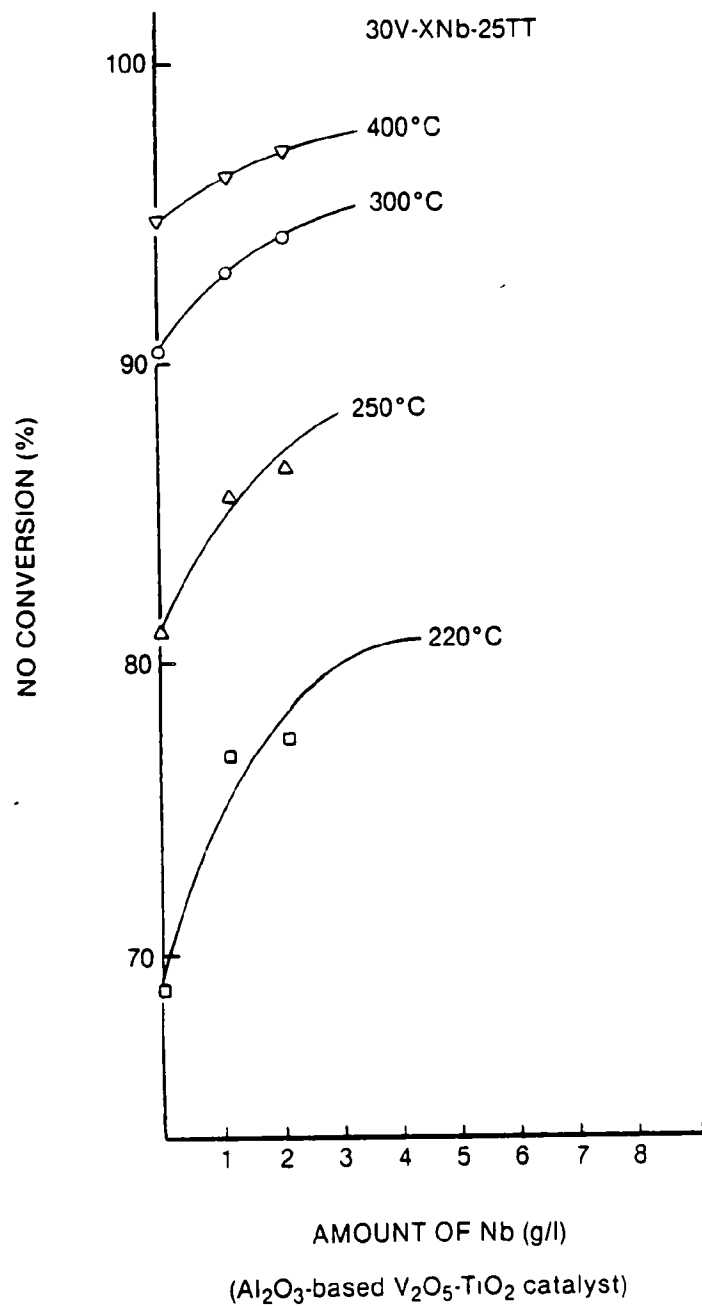


Figure 5-8 Effect of Niobium on NO_x Removal.

catalyst usefulness. Another reason may be the low oxidation rate of SO_2 to SO_3 caused by the niobium-containing alumina-based catalyst.

Figure 5-9 shows the thermal treatment system used to treat the contaminated aluminum-based catalyst. The catalyst is heated to $550\text{--}600^\circ\text{C}$ in several minutes to avoid degradation. With rapid heating for a short time, catalytic activity is restored to its original level without a loss in physical strength.

Kobe Steel's large test plant ($100,000 \text{ Nm}^3/\text{hr}$) has been operated for over 4 years, removing 90–80% of NO_x in the $200\text{--}220^\circ\text{C}$ flue gas which contains about 250 ppm NO_x , 50 ppm SO_x (including about 5 ppm of SO_3), and 10–50 mg/Nm^3 of dust. Thermal treatment is applied once every 3,000–4,000 hours. The catalyst retains a sufficiently high activity and physical strength during this time. Both the catalyst and thermal treatment system have been patented in several countries including the U.S.

5.6.3 Evaluation

Alumina-based catalysts for SCR were popular several years ago but they are no longer used for SO_x -containing gas by most process developers and users. Instead, SO_x -resistant TiO_2 -based catalysts have been developed. SCR operator experience indicates that alumina-based catalysts are often poisoned by SO_x to form aluminum sulfate when used at $300\text{--}400^\circ\text{C}$. The catalysts must be heated to 800°C in order to decompose the aluminum sulfate and recover their catalytic activity.

Kobe Steel's long-term SCR test has proved that the alumina-based catalyst is best suited to a low-temperature gas with a relatively low SO_x concentration. It appears that aluminum sulfate is not formed at lower temperatures, because ammonia in the flue gas readily combines with SO_3 before the SO_3 attacks the catalyst. Above 300°C , ammonia does not combine with SO_3 . Thus, heating the catalyst for several minutes at $550\text{--}600^\circ\text{C}$ can remove the sulfate formed on it.

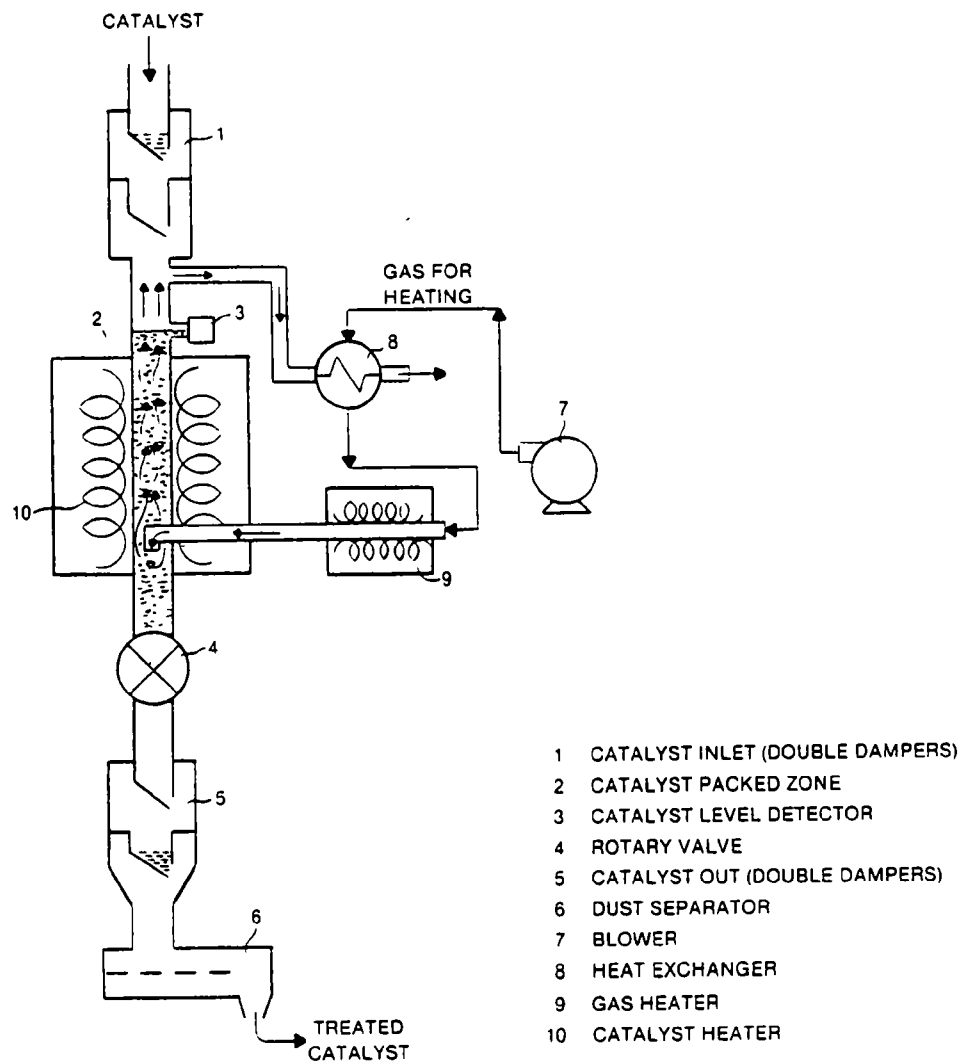


Figure 5 9 Thermal Treatment System

Another reason for the usefulness of the alumina-based catalyst is that not much SO_2/SO_3 oxidation occurs at low temperatures, although a large amount of oxidation occurs above 300°C . Some catalysts oxidize SO_2 considerably, even at 250°C , which results in reduced activity (Section 3.3.2). The alumina-based catalyst containing niobium does not appear to oxidize any SO_2 at $200\text{--}220^\circ\text{C}$ and yet is highly active.

The alumina-based catalyst can be used for 3,000–4,000 hours at a time and for over 4 years without degradation when used with a low-temperature gas. This amounts to a considerable energy and catalyst cost savings. The TiO_2 -based catalyst produced by Kobe Steel seems to perform similarly to TiO_2 -based catalysts manufactured by other producers.

When Kobe Steel's system using the alumina-based catalyst is compared with JGC's system using a TiO_2 -based catalyst (Section 5.4), it can be seen that the former requires higher heating temperatures— $550\text{--}600^\circ\text{C}$ versus 400°C . At the same time, the energy requirement may be much less for the Kobe Steel system because of a lower required heating frequency and the fact that the catalyst is heated in a separate vessel. However, overall the Kobe Steel system is more complex than the JGC system.

Further studies are needed to demonstrate the applicability of alumina-based catalysts to gases with various compositions at various temperatures.

5.7 SCR FOR INCINERATOR FLUE GAS

5.7.1 Introduction

In Tokyo, Mitsui Engineering constructed a commercial SCR unit to remove both NO_x and odor from its sewage sludge incinerator which produces 100,000 Nm^3/hr of flue gas. Prior to construction, Mitsui conducted extensive tests at the request of the Tokyo Metropolitan Government. The flue gas was found to contain over 100 ppm NO_x with considerable amounts of SO_x , HCl , various kinds of dust, and other odorous components (including aldehydes) which are difficult to remove by carbon adsorption or wet process oxidation.

The government-owned incinerators have sodium scrubbing systems and wet ESPs for gas cleaning. The treated gas contains about 100 ppm NO_x , 5 ppm each of SO_x and HCl , and has a considerable odor. Mitsui Engineering conducted tests on flue gases both before and after gas cleaning by the scrubber and ESP. They found that a certain kind of SCR catalyst is especially useful for odor removal and applicable to the cleaned flue gas, although there are problems involved in treating the uncleaned flue gas directly. A commercial SCR unit with a capacity of treating 108,000 Nm^3/hr of flue gas leaving the sodium scrubber and wet ESP subsequently was constructed; it began operation in October 1979.

5.7.2 Process Description (6)

The 108,000 Nm^3/hr flue gas from the incinerator contains about 100 ppm NO_x , about 5 ppm each of SO_x and HCl , less than 0.01 g/ Nm^3 of dust and about 10% O_2 , 8% CO_2 , 7% H_2O , and 75% N_2 at 40–50°C. The flowsheet of the unit is shown in Figure 5-10. The flue gas is heated to 280°C in a heat exchanger and then in a heater to 350°C, injected with ammonia, and sent into a reactor containing a honeycomb catalyst at an SV of 4,000 hr^{-1} and linear velocity of 7.7 m/sec. Over 90% of the NO_x and 80% of the odor are removed by using 1.1 mol NH_3 to 1 mol NO_x . No problems have been encountered since system start-up.

Figure 5-11 shows test results for the removal of various odorous gaseous compounds. A synthetic gas containing 10 ppm each of these compounds was sent through the SCR catalyst at different temperatures without ammonia addition. Over 90% of the compounds (except ammonia) were removed at 300°C or below, forming CO_2 , H_2O and SO_2 by oxidation. Tests with ammonia added to the gas indicated that ammonia did not substantially affect the removal ratio of these compounds.

5.7.3 Economics (6)

The Mitsui Engineering SCR unit cost 480 million yen including the price of the heat exchanger, heater, initial catalyst charge, and civil engineering

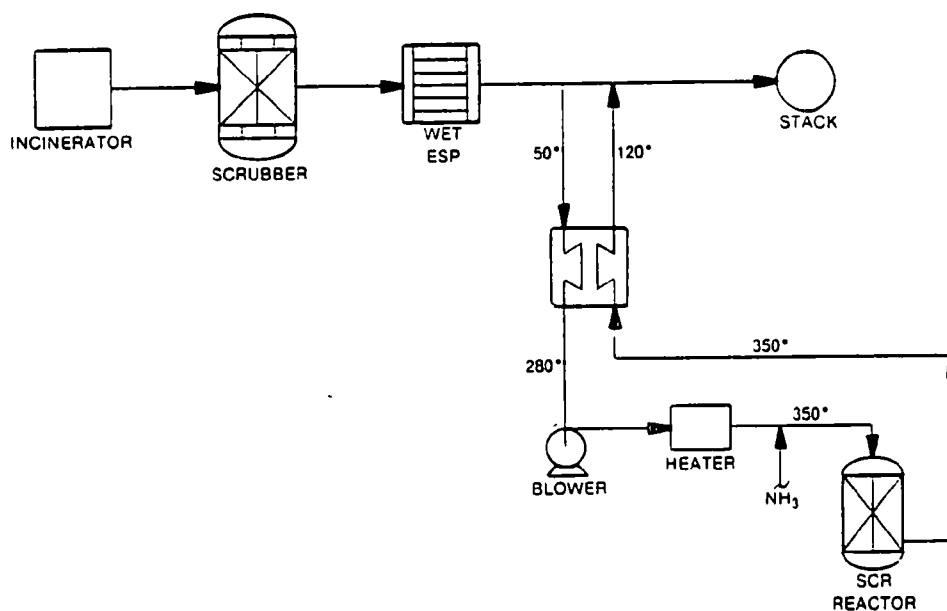


Figure 5-10 Flue Gas Treatment System for an Incinerator.

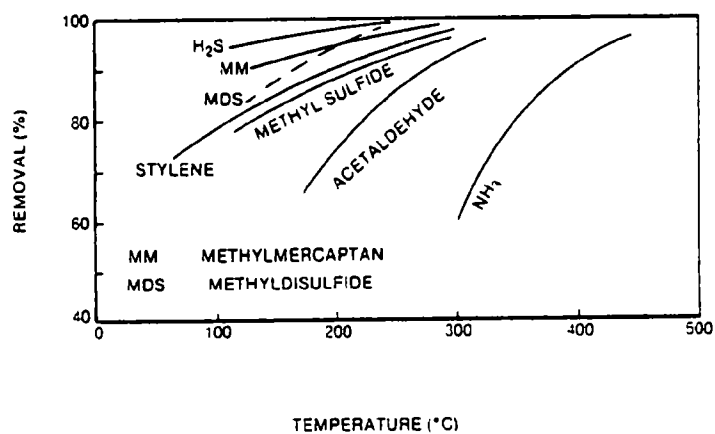


Figure 5-11 Odor Component Removal by Oxidation with the SCR Catalyst

services. The annual cost for flue gas treatment, based on 8,000 hours of operation in 1980, is shown in Table 5-11. The total treatment cost of 450 yen/1,000 Nm³ of flue gas includes the cost of kerosene for gas heating at 209 yen/1,000 Nm³. When SCR is not applied, the flue gas leaving the wet ESP must be heated. Therefore, the actual cost increase caused by the SCR unit is about 350 yen/1,000 Nm³.

5.7.4 Evaluation

This SCR unit may be the first one in the world to remove NO_x and odor simultaneously, and has various other NO_x and odor removal applications. It is known that the presence of NO_x increases the odors caused by other compounds. Therefore, NO_x removal is also helpful in reducing odor. The process may be considerably less expensive when applied directly to the flue gas leaving the incinerator. Direct treatment eliminates not only the heat exchanger and the heater, but also ammonia consumption, since the flue gas usually contains ammonia sufficient for SCR.

5.8 OTHER SCR UNITS

5.8.1 SCR Unit at Ukishima Chemical Petrochemical's Chiba Plant

For Ukishima Chemical Petrochemical, Mitsui Engineering constructed an SCR unit with a capacity of treating 260,000 Nm³ of flue gas from a new oil-fired boiler. The SCR unit has a tubular catalyst with an SV of 4,000 hr⁻¹. The unit began operation in 1978 with an investment cost of 260 million yen (2).

The 350-400°C flue gas from the boiler contains about 150 ppm NO_x, 50-300 ppm SO_x, and 100-150 mg/Nm³ of dust. By using 1 mol NH₃ to 1 mol NO_x, an 85% NO_x removal rate has been achieved. The removal efficiency decreased slightly during the first 2 years of operation. In 1980, one-third of the catalyst was replaced with a honeycomb catalyst to maintain the high removal efficiency. Mitsui Engineering currently prefers honeycomb to tubular catalysts.

TABLE 5-1 MITSUI COST CALCULATION (MITSUI ENGINEERING)

Conditions	Plant Design Capacity	(A) Capacity 100,000 Nm ³ /h	(B) Operation Hours 8,000 h/year		
	Investment Cost (1,000 Yen)	(C) Equipment	357,000		
		(D) Civil Work	48,000		
		(E) Catalyst	75,000	(F) Total Cost 480,000	
	Long Term Loan (1,000 Yen)	(G)	405,000	Interest 7%	
Short Term Loan (1,000 Yen)	(H)	82 925	Interest 9%		
		Annual Quantity	Unit Price	Annual Expense (1,000 Yen)	
Variable Cost	Utilities	Electricity	360 kW x (B) kWh	14 Yen/kWh	40,320
		Kerosene	380 l/h x (B) l	55 Yen/l	167,200
		Ammonia	7.6 kg/h x (B) kg	180 Yen/kg	10,944
		Tertiary Treatment Water	15 t/h x (B) t	5 Yen/t	600
		Catalyst	25m ³ /2 Years x 1.2 m ³	3,000 Yen/m ³	37,500
Direct Cost	Fixed Cost	Consumables	(C) x 0.005		1,785
		Total Variable Cost			258,349
		Depreciation Equip.	(C) x 0.9 ÷ 7		45,900
		Civil	(D) x 0.9 ÷ 20		2,160
		Fixed Property Tax	[(E) + (D)] x 0.016 x 1/2		3,240
	Insurance	(F) x 0.005		2,400	
	Labor	3 Men x 2,500,000 Yen Man/Year		7,500	
	Repair	[(C) + (D)] x 0.03		12,150	
	Total Fixed Cost			73,350	
	Total Direct Cost			331,699	
Indirect Cost	Interest	Overhead for Head Office	(F) x 0.01		4,800
		Long Term Loan	(G) x 0.007 x [(7 + 1)/(2 x 7)]		16,200
		Short Term Loan	(H) x 0.09		7,463
		Total Indirect Cost			28,463
Total Annual Expense 360,162					
Treatment Cost 450 Yen/1,000 Nm ³					

5.8.2 Shindaikyowa Petrochemical's Yokkaichi Plant

In 1975, Hitachi Zosen constructed an SCR unit with a capacity of treating 400,000 Nm³/hr of flue gas from an oil-fired boiler at Shindaikyowa Petrochemical's Yokkaichi plant. The flue gas is treated by sodium scrubbing using the Wellman-Lord process (2).

The 55-60°C flue gas leaving the scrubber contains about 150 ppm NO_x, 100 ppm SO_x, and 50 mg/Nm³ of particulates (including about 20 mg/Nm³ of sodium salts). The gas is heated to 330-340°C by a heat exchanger, then to 400-410°C by an oil burner, injected with ammonia and sent into a reactor with a pellet catalyst. About 80% of the NO_x is removed by using 1 mol NH₃ to 1 mol NO_x, producing about 10 ppm of unreacted NH₃. The treated gas is then passed through a heat exchanger where it is cooled to 160-170°C. A serious ammonium bisulfate deposit problem was encountered with the heat exchanger and frequent water washings were required.

Since the relaxation of the NO_x emission regulations in 1979, 0.6-0.7 mol NH₃ to 1 mol NO_x has been used to remove 60-70% of NO_x and maintain unreacted NH₃ below 1 ppm. This change eliminated the previous bisulfate deposition problem.

5.8.3 Kawasaki Steel's Chiba Plant

In 1976, Hitachi Zosen constructed an SCR unit with a capacity of treating 762,000 Nm³/hr of flue gas from an iron ore sintering machine (2) at Kawasaki Steel's Chiba Plant. The flue gas is treated by wet lime scrubbing and wet ESP, heated by a heat exchanger and heater to 400°C, and subjected to SCR. The SCR unit has been operated without problems for 4 years. In late 1980, the catalyst was replaced, although it was still active. The new catalyst (also supplied by Hitachi Zosen) works at lower temperatures and therefore saves energy.

5.8.4 SCR for Diesel Engine Flue Gas

In 1978, the Unitika Company constructed an SCR unit with a capacity of treating 70,000 Nm³/hr flue gas from a power-generation diesel engine fueled by 1.5% sulfur oil. The 350-400°C flue gas contains 900-1,100 ppm NO_x, 600 ppm SO_x and 100-150 mg/Nm³ dust with 13% O₂.

The SCR unit uses a 4 mm spherical TiO₂-based catalyst in an intermittent moving bed with an SV of 10,000 hr⁻¹. Nearly 85% of the NO_x is removed using 0.85 mol NH₃ to 1 mol NO_x and unreacted NH₃ is maintained at a barely detectable level. The SCR unit began operation in April 1978, and has been operated since that time without trouble. About 10% of the catalyst is replaced annually.

After SCR and heat recovery, the SO_x in the gas is adsorbed by activated carbon. The carbon is washed with water to recover sulfuric acid in the same manner as has been done with the flue gas from an industrial boiler (5). Unitika conducted tests of simultaneous NO_x and SO_x removal by activated carbon and ammonia with thermal regeneration of SO₂ (2). However, the tests were discontinued when carbon consumption was found to be unacceptably high.

5.8.5 SCR for Gas Turbine Flue Gas

Hitachi Ltd. and Babcock Hitachi constructed a combined-cycle power generation unit using kerosene, and an SCR unit for Japan National Railway's Kawasaki Plant. The gas and steam turbines have a capacity of 97.1 MW and 44.2 MW, respectively, with a total power generation capacity of 141.3 MW. They produce 1,024,000 Nm³/hr of flue gas. Since the flue gas temperature at the gas turbine outlet is too high for SCR, the gas is passed through one of the two boilers where it is cooled to 364°C, treated by SCR, and then sent into another boiler.

The kerosene fuel contains about 0.05 sulfur and the flue gas contains small amounts of SO_x and dust with about 75 ppm NO_x. A moving bed reactor with a pellet catalyst is used for SCR. The entire system was designed in

1977, when Hitachi's plate catalyst was not yet well developed. Since the system is operated about 14 hours a day with a shutdown at night, the catalyst undergoes startup heating and shutdown cooling every day. In 1977, Hitachi was not confident about the reliability of the plant catalyst under such conditions, but currently prefers the plate catalyst in a fixed bed rather than a moving bed for this type of gas.

The system began operation in April 1981, and has operated without problems since then. About 80% of the NO_x is removed by using 1 mol NH_3 to 1 mol NO_x , which produces unreacted NH_3 at a concentration of about 10 ppm. Because the SO_x content of the gas is low, the NH_3 has not caused any deposition problems in the downstream facilities.

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Section 6

OTHER PROCESSES FOR NO_x REMOVAL

6.1 CLASSIFICATION OF NO_x REMOVAL PROCESSES

NO_x removal processes other than selective catalytic reduction (SCR) may be grouped into two general categories: wet and dry. The processes in each category are listed in Table 6-1.

TABLE 6-1. NO_x REMOVAL PROCESSES OTHER THAN SCR

Dry Process

NO_x Removal Only

- Selective noncatalytic reduction (SNR)
- Combination of SNR and SCR
- MACT in-furnace NO_x removal
- Molecular sieve adsorption

Simultaneous NO_x/SO_x Removal

- Activated carbon adsorption
- Electron beam radiation
- Copper oxide absorption

Wet Process

NO_x Removal Only

- Sodium scrubbing (equimolecular absorption)
- Oxidation absorption

Simultaneous NO_x and SO_x Removal

- Oxidation reduction
- Absorption using complexing agent

Several years ago when SCR technology had serious problems and was very costly, many of these other processes were being actively tested. However,

now that SCR has been successfully applied and costs much less, some of these processes have lost their attractiveness and been abandoned.

6.1.1 Dry Processes

NO_x Removal Only

Next to SCR, selective noncatalytic reduction (SNR) has been used most widely. Several relatively large SNR units and about 20 smaller units have been constructed. SNR uses ammonia at 800–1,000°C without a catalyst to remove 30–50% of NO_x (Section 6.2). To increase the NO_x removal efficiency and to reduce the unreacted NH₃ associated with SNR, a combination of SNR and SCR using a small amount of catalyst has been tested with utility boilers (Section 6.3).

A second dry NO_x removal process is MACT in-furnace reduction, in which a small amount of fuel (about 10% of total fuel) is injected above the flame to remove about 50% of NO_x. Commercial application of the process has begun (Section 6.4).

A third process, molecular sieve adsorption, has been used with nitric acid plant tail gas (Section 6.9.3).

Simultaneous NO_x/SO_x Removal

The Unitika Company tested an activated carbon process to remove 80–90% of SO_x and NO_x simultaneously but abandoned the process because of its high carbon consumption. Tests of the activated carbon process also have been conducted by EPDC jointly with Sumitomo Heavy Industries (Section 6.5) and also by Mitsui Mining Company (Section 6.9.2).

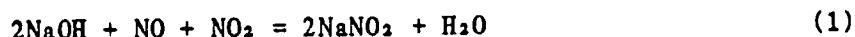
Ebara Corporation has developed an electron beam radiation process to remove 80–90% of SO_x and NO_x simultaneously (Section 6.6). The process is unique in that it converts SO_x and NO_x to ammonium sulfate and nitrate which can be used as fertilizer.

Another process, the Shell copper oxide process, has been applied to an industrial boiler where it removes about 90% of SO_x and about 40% of NO_x (Section 6.9.1).

6.1.2 Wet Processes

NO_x Removal Only

Essentially all of the NO_x in combustion gas is in the form of NO. NO is not easily absorbed in solutions. NO₂ or an equimolecular mixture of NO and NO₂ are fairly reactive with solutions although their reactivity is less than that of SO₂. The tail gas from a nitric acid plant contains both NO₂ and NO which can be absorbed by a sodium hydroxide solution to produce sodium nitrite by the following reaction:



This is the basis of the sodium scrubbing NO_x removal process.

However, the demand for by-product nitrite is small. There are several small commercial units which first oxidize NO to NO₂, then treat the gas with sodium scrubbing, and subject the resulting liquor to wastewater treatment. An oxidation absorption process such as this can not be applied on a large scale because it requires treatment of a large amount of wastewater containing nitrite and nitrate. Such treatment is very difficult.

Simultaneous Removal

Since 1973, many wet simultaneous removal processes have been developed. The processes can be classified into two groups: oxidation reduction and complex absorption, and are listed in Tables 6-2 and 6-3.

TABLE 6-2. OXIDATION REDUCTION PROCESSES AND PLANTS

Process Developer	Oxidizing Agent	Absorbent	By-Product	Capacity (Nm ³ /hr)
Sumitomo-Fujikasui	ClO ₂	NaOH	(NaNO ₃ , NaCl, Na ₂ SO ₄)	62,000 39,000 100,000
Sumitomo-Fujikasui	ClO ₂	CaCO ₃	[Gypsum, CaCl ₂ , Ca(NO ₃) ₂]	25,000
IHI	O ₃	CaCO ₃	Gypsum, N ₂	5,000
MHI	O ₃	CaCO ₃	Gypsum, NH ₃	2,000
Chiyoda	O ₃	CaCO ₃	Gypsum, Ca(NO ₃) ₂	1,000

TABLE 6-3. COMPLEX ABSORPTION PROCESS (USING EDTA AND FeSO₄)

Process Developer	Absorbent	By-Product	Capacity (Nm ³ /hr)
Chisso Eng.	NH ₄ OH	(NH ₄) ₂ SO ₄	500
Asahi Chemical	NaOH, CaCO ₃	Gypsum, N ₂	600
Kureha Chemical	CH ₃ COONa CaCO ₃	Gypsum, N ₂	5,000
Kureha Chemical	KOH	Sulfur, N ₂	2,000
MKK - HZ	KOH	Sulfur, N ₂	Bench Scale

Using the oxidation reduction process, NO is first oxidized by chlorine dioxide or ozone to NO₂, which then is absorbed by a sodium salt solution or a calcium carbonate slurry. SO₂ is also absorbed to form sulfite. The NO₂ absorbed by the liquor is reduced by the sulfite to form N₂ or NH₃ while the sulfite is oxidized to sulfate.

The Sumitomo-Fujikasui process, which uses ClO₂ and sodium or limestone scrubbing, has been applied in four relatively small commercial units since 1973. However, its development has been halted because of the wastewater treatment problem associated with it (1). The similar IHI, MHI, and Chiyoda processes all use ozone to substantially reduce the wastewater treatment

problem. However, these processes are no longer being developed because of the high cost of ozone.

In order to oxidize NO to NO₂ economically, an NO oxidation catalyst has been studied (Section 6.8).

The complex absorption processes listed in Table 6-3 use a liquor containing EDTA and ferrous sulfate to absorb NO and form a complex compound. SO₂ is also absorbed to form sulfite, which in turn reduces the absorbed NO to N₂ or NH₃. Those processes do not require an oxidizing agent but have not been commercialized because of their complexity and the requirement for a large multi-stage absorber to remove NO at a high efficiency.

6.1.3 Gas Composition Appropriate for Simultaneous Removal Processes

In general, a flue gas with a relatively low SO_x/NO_x ratio is a good candidate for dry simultaneous removal. In the electron beam process, a high SO_x/NO_x ratio yields a byproduct which is rich in ammonium sulfate and lean in ammonium nitrate, and is therefore a low grade fertilizer. With the copper oxide process, a high SO_x content necessitates frequent regeneration of the cupric sulfate by-product and lowers the NO removal efficiency. Carbon consumption in the carbon process increases with the SO_x content of the gas.

On the other hand, a high SO₂/NO_x ratio is preferable for the wet NO_x removal processes because an excessive amount of sulfite is needed to attain a high NO_x removal efficiency (1).

6.2 SELECTIVE NONCATALYTIC REDUCTION (SNR)

6.2.1 Introduction

At about 900°C ammonia (NH₃) reacts with NO_x to form N₂ and H₂O:



Selective noncatalytic reduction (SNR) is based on this reaction. During the 1970s many organizations conducted pilot plant and demonstration tests using ammonia injection (at 500-1,100°C) for NO_x removal without a catalyst.

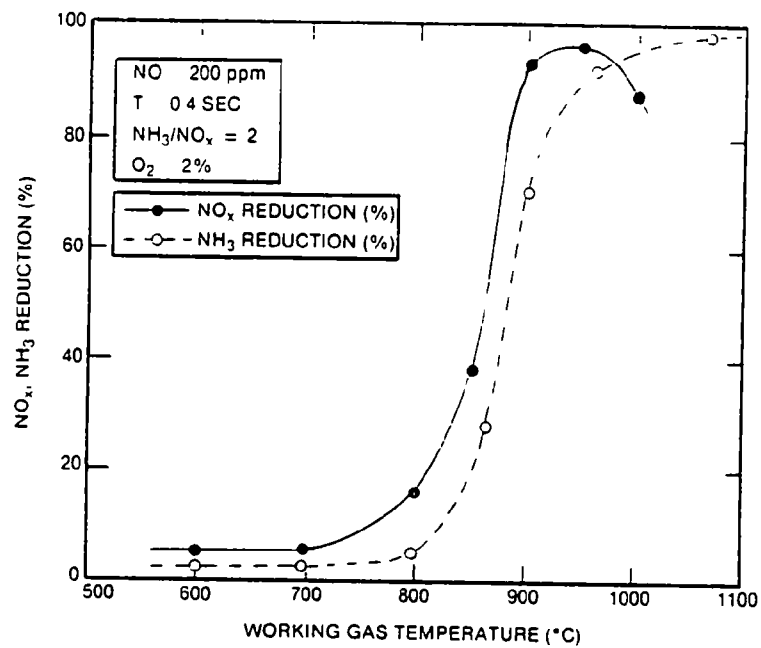
Mitsubishi Chemical Industries (MCI) and Mitsubishi Heavy Industries (MHI) conducted large-scale SNR tests using MCI's six industrial boilers. Based on the results of those tests, MHI constructed a large-scale SNR test plant for Chubu Electric at its Chita Station. The plant was designed to treat all the flue gas from a 375 MW existing oil-fired boiler. MHI also built a test plant to treat all the flue gas from an existing 375 MW oil-fired boiler at Tokyo Electric's Yokosuka Station. MCI submitted a patent application for its SNR process three months after a similar application by Exxon. Subsequently, MCI made a licensing agreement with Exxon although the patents have not been filed in Japan.

Tonen Technology also has made a licensing agreement with Exxon and has constructed 8 commercial SNR units to treat flue gases from industrial boilers and heating furnaces at oil refineries and petrochemical plants. Some of these units are specifically for use during photochemical emergency periods when more extensive NO_x reduction is temporarily required (Section 6.2.5).

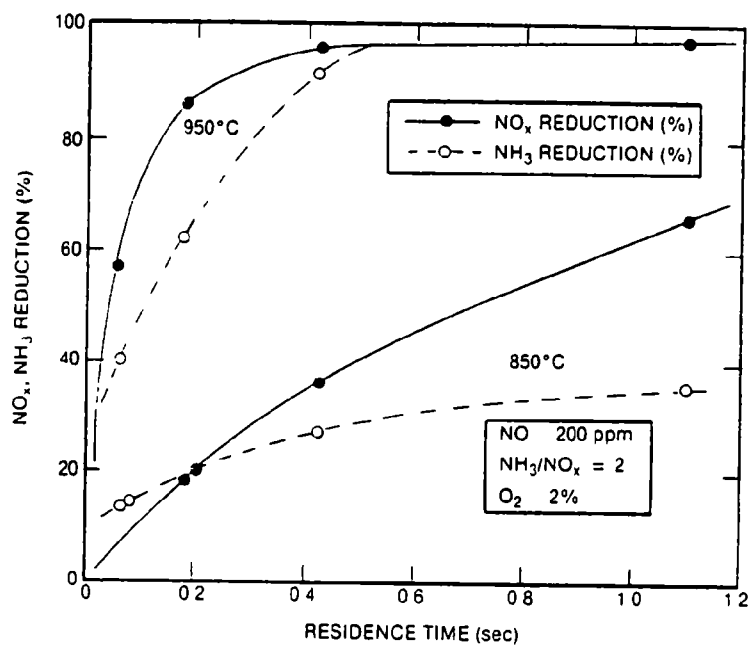
Mitsubishi Kakoki Kaisha (MKK) has developed its own SNR technology and has constructed many small commercial SNR units for a gas company (Section 6.2.6).

6.2.2 MHI's SNR Laboratory Studies (2)

MHI conducted laboratory tests to determine the effects of reaction temperature and residence time (reaction time) on NO_x removal efficiencies. The tests were conducted using a composite gas containing 200 ppm NO, 400 ppm NH₃, and 2% O₂ (Figure 6-1, A, B). At temperatures between 900 and 1,000°C the reaction was at an optimum level for NO_x removal and, in fact, produced a 90% NO_x removal efficiency in 0.4 seconds. The principal reactions are shown in equations (1) and (2) of Table 6-4. As can be seen in Figure 6-1, B



(A) EFFECT OF WORKING GAS TEMPERATURE



(B) EFFECT OF RESIDENCE TIME

Figure 6-1 MHI Laboratory Test Data

the reaction rate was low, below 850°C. Above 1,000°C the NO_x removal efficiency was lowered due to the partial conversion of NH₃ to NO, as shown in equation (6) of Table 6-4.

TABLE 6-4. THE MHI MECHANISM OF THE DE-NO_x REACTION

<u>Main Reaction</u>		
NH ₃ + 1/4 O ₂	----> NH ₃ + 1/2 H ₂ O	Eq. (1)
NH ₃ + NO	----> N ₂ + H ₂ O	Eq. (2)
<u>Sub Reaction</u>		
NH ₃ + 1/2 O ₂	----> 1/2 N ₂ + H ₂ O	Eq. (3)
NH ₃ + O ₂	----> NO + H ₂ O	Eq. (4)
<u>Overall De-NO Reaction</u>		
4NO + 4NH ₃ + O ₂	----> 4N ₂ + 6H ₂ O	Eq. (5)
4NH ₃ + 5O ₂	----> 4NO + 6H ₂ O	Eq. (6)
4NH ₃ + 3O ₂	----> 2N ₂ + 6H ₂ O	Eq. (7)
<u>Reaction Formula for NO₂</u>		
2NO ₂ + 4 NH ₃ + O ₂	----> 3N ₂ + 6H ₂ O	Eq. (8)

The NO_x removal efficiency at an actual plant may be much lower than the laboratory rate due to insufficient reaction times and the difficulty involved in obtaining a rapid uniform mix of ammonia and gas. In order to study these problems, the reaction constants K₁, K₂ and K₃ (as shown in Table 6-5) were determined empirically for different temperatures. This makes it possible for the NO/NH₃ reaction rate to be calculated using equations (12) and (13) of Table 6-5.

TABLE 6-5. BASIC FORMULAS FOR THE MHI PROCESS DE-NO_x REACTION AND RATE OF REACTIONS

4NO + 4NH ₃ + O ₂	$\xrightarrow{K_1}$	4N ₂ + 6H ₂ O	Eq. (9)
4NH ₃ + 5O ₂	$\xrightarrow{K_2}$	4NO + 6H ₂ O	Eq. (10)
4NH ₃ + 3O ₂	$\xrightarrow{K_3}$	2N ₂ + 6H ₂ O	Eq. (11)
$-\frac{d(NO)}{dt} = K_1[NO]^a[NH_3]^b[O_2]^{\gamma_1} - K_2[NH_3]^{\delta}[O_2]^{\gamma_2}$			
			Eq. (12)
$-\frac{d(NH_3)}{dt} = K_1[NO]^a[NH_3]^b[O_2]^{\gamma_1} + (K_2 + K_3)[NH_3]^{\delta}[O_2]^{\gamma_3}$			
			Eq. (13)

Computer simulation programs have been developed to predict the NO_x reduction in a large furnace. As shown in Figure 6-2, a cross section of the furnace gas passage is divided into small sections which take into account the number of ammonia injection nozzles. Each section is divided into smaller subsections both crosswise and in the direction of the gas flow so that differential equations for diffusion and mixing can be solved.

The results of one computer calculation are shown in Figure 6-3. The NO_x removal efficiency is shown along the gas flow axis. In this case, ammonia is injected into the flue gas at $1,050^\circ\text{C}$ and drives the gas temperature down to 900°C in 0.14 sec. over a distance of 1.8 meters. This results in an NO_x removal efficiency of more than 50 percent.

6.2.3 SNR Tests at MCI's Boilers (2)

Since 1974, SNR tests have been conducted with MCI's 6 existing oil-fired boilers (Table 6-6). All of the SNR units were constructed by MHI. The No. 3 and No. 4 boilers are the largest ones, each with a capacity of 180 MW equivalent.

As shown in Figure 6-4, ammonia injection nozzles, FF, FM, and FR with cooling water tubes were placed in three locations in the No. 3 boiler and also at the boiler wall (nozzle F). Figure 6-5, A shows the relationship between boiler load and NO_x removal efficiency when 2 mol NH_3 /mol NO_x is injected from each nozzle. The FM nozzle produced the highest efficiency (50%) at full load, while nozzles F and FF produced relatively high efficiencies at the lower load. As shown in the B portion of the figure, the NO_x removal efficiency reached 60% with 4 mol NH_3 /1 mol NO_x .

Because the nozzles used cooling water, low-temperature corrosion occurred due to the condensation of sulfuric acid derived from the SO_3 in the flue gas. As shown in Figure 6-6, the nozzles for the No. 4 boiler use boiler water for cooling and thus improve process economy and eliminate the possibility either of corrosion or of thermal damage.

TABLE 6-6. BOILERS USED FOR THE MHI APPLICATION TESTS

Unit Name	Capacity (Flue Gas Flow) Nm ³ /h	Boiler Type	Fuel	Firing	N/R	NH ₃ Injection Nozzle	Start of Tests
Mizushima I - #1, MCI.	175,000	OT	L.S. Oil	T	R	NCN	Aug. 1974
Mizushima I - #2, MCI.	194,000	OT	L.S. Oil	T	R	BWN	Apr. 1977
Mizushima I - #3, MCI.	540,000	OT	H.S. Oil	T	R	BWN	June 1975
Mizushima I - #4, MCI.	540,000	OT	H.S. Oil	T	R	BWN	Oct. 1974
Yokkaichi #1, MCI.	200,000	OT	H.S. Oil	T	R	SCN	May 1976
Yokkaichi, YD Boiler, MCI.	40,000	NC	H.S. Oil	H	R	SCN	Sept. 1975
Chita #2, Chubu Electric	1,000,000 (Unit Capacity 350 MW)	CC	L.S. Oil	H	R	BWN	Feb. 1976
Yokosuka #4 ^a Tokyo Electric	1,000,000 (Unit Capacity 350 MW)	CC	L.S. Oil	H	R	BWN	March 1978

^aThe Yokosuka plant uses also a catalyst (Section 6.3).

Remarks: Boiler Type: NC - Natural circulation
CC - Controlled circulation
OT - Once-through

Firing: T - Tangential, H - Horizontal

N/R: N - New unit, R - Retrofit

NH₃ Injection Nozzle:

BWN - Box-type water cooled nozzle
SCN - Steam cooled nozzle
NCN - Non-cooled nozzle

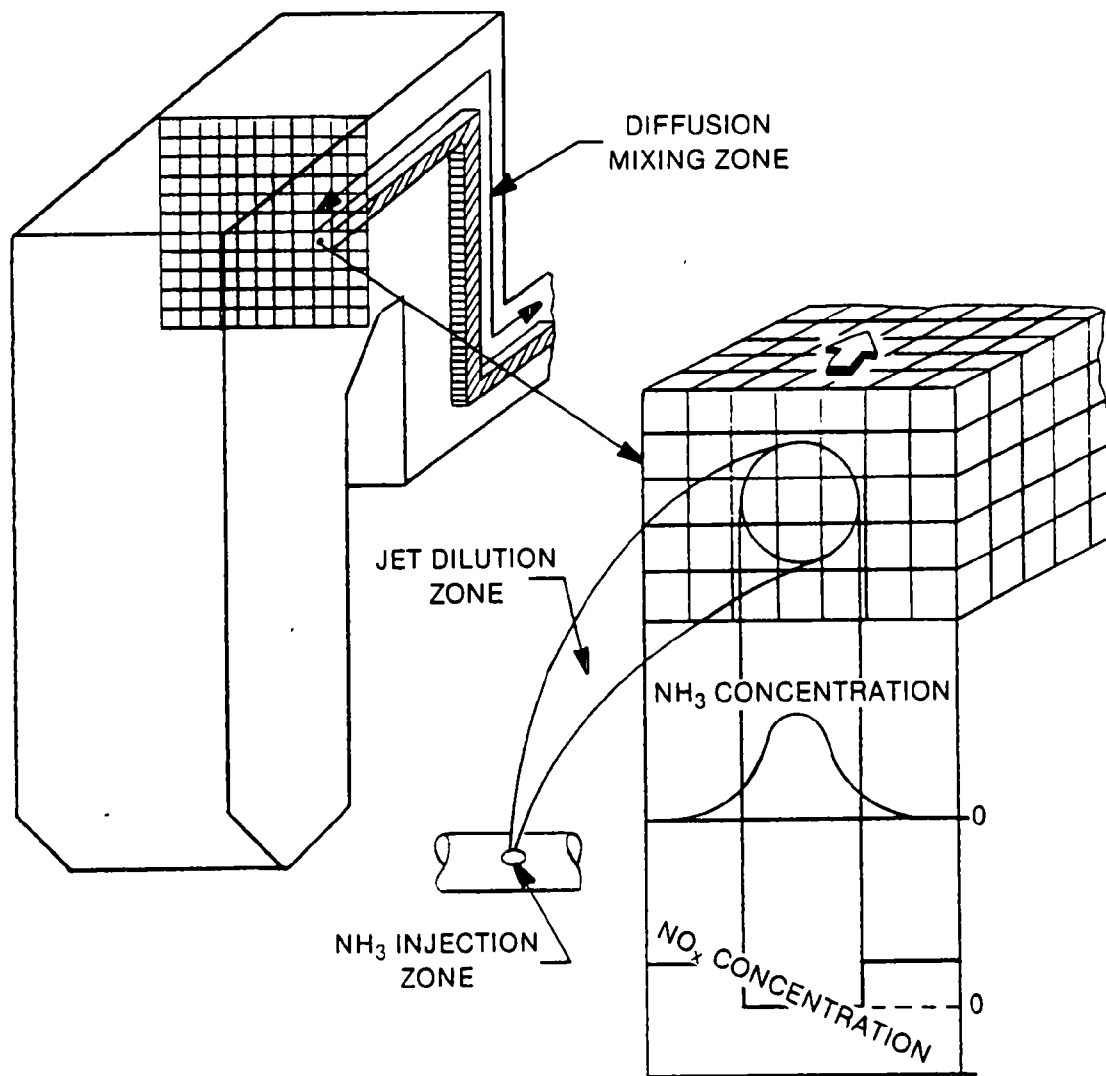


Figure 6-2 Calculation Procedure Used in the MHI Simulation Program.

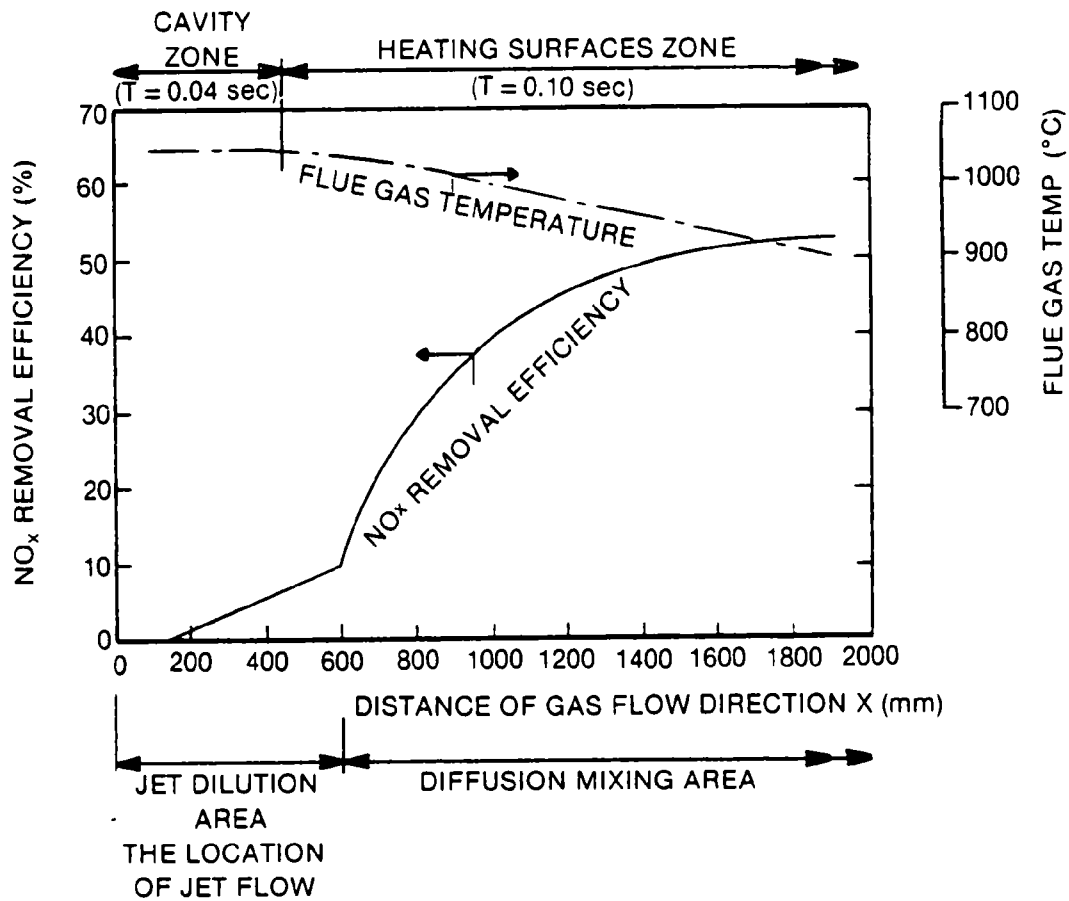


Figure 6-3 Results of a Computer Simulation of SNR DE-NO_x Performance.

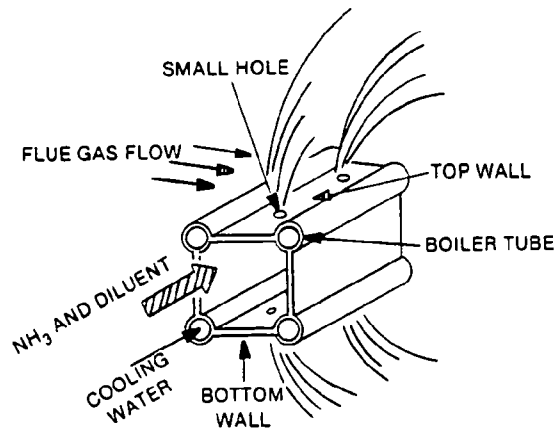
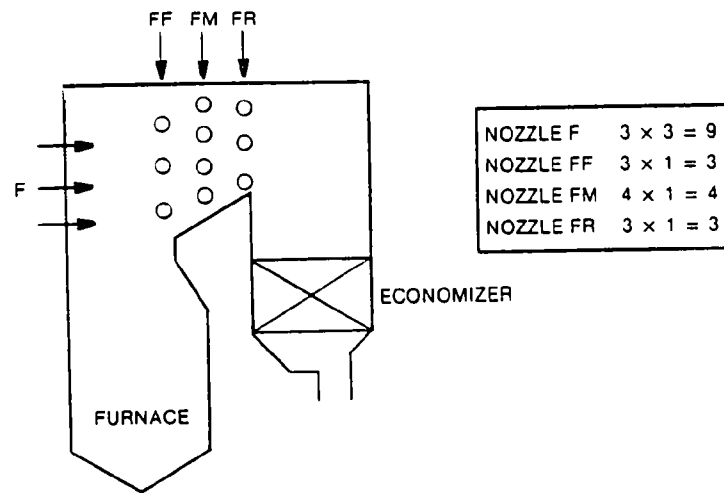


Figure 6-4 Ammonia Injection Nozzles for Mizushima Plant, Unit No. 3

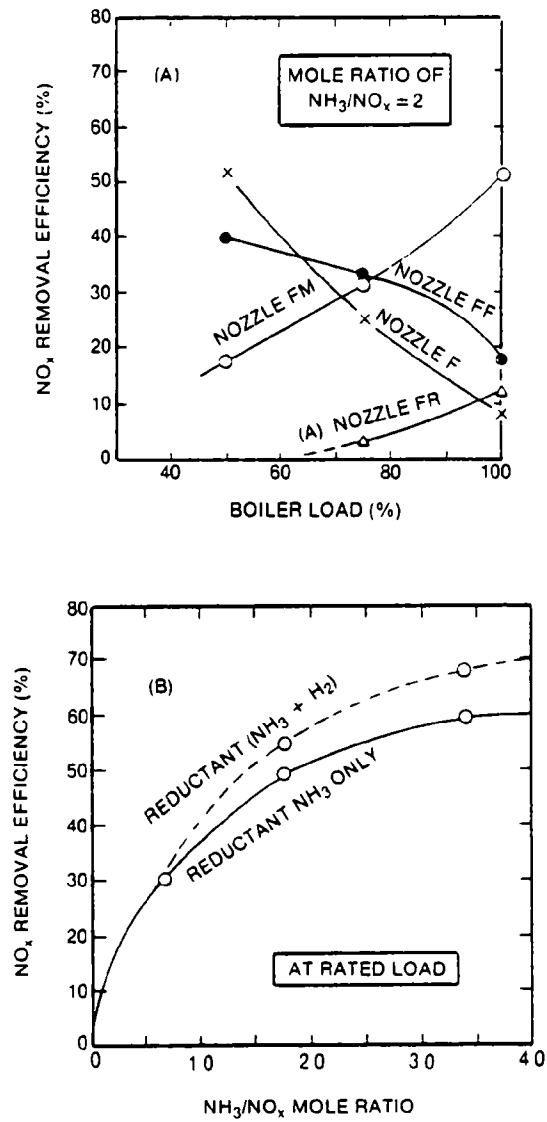


Figure 6-5 Test Results for Mizushima Plant's Unit No. 3

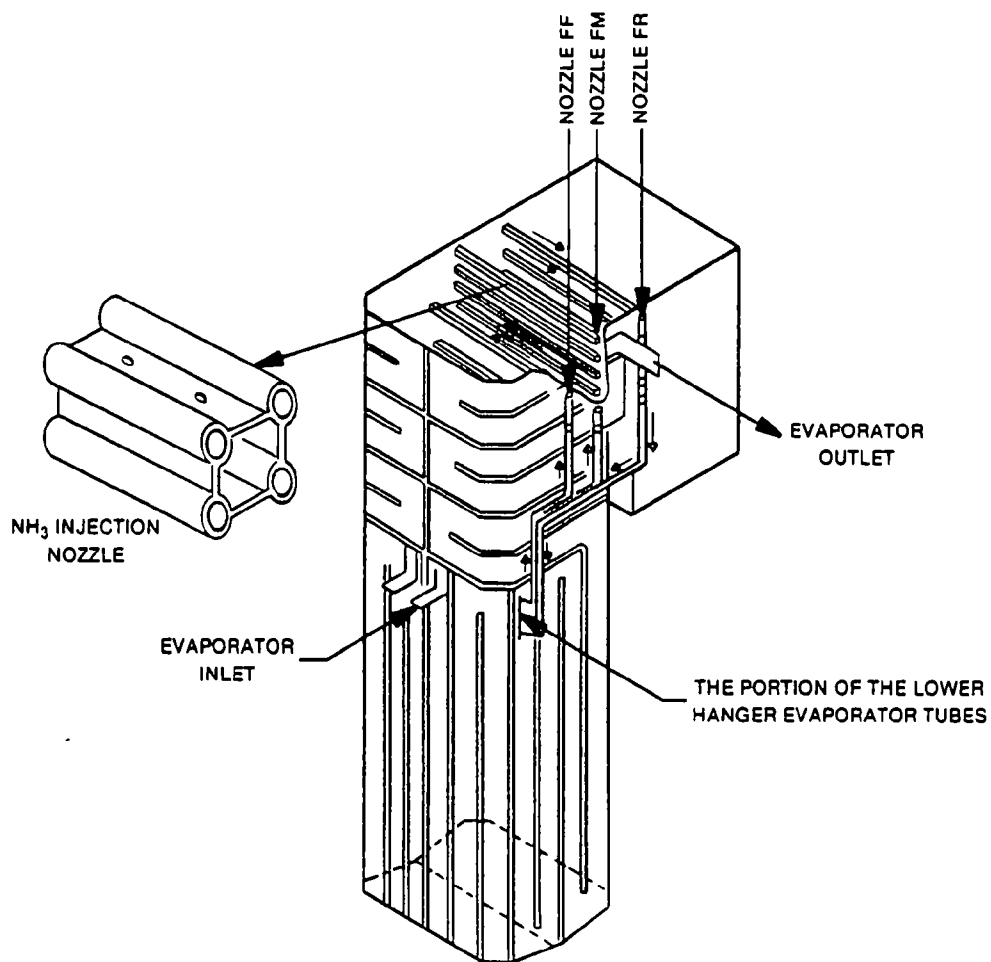


Figure 6-6 MHI Nozzle Cooling System for Unit No. 4, Mizushima Plant.

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6.2.4 Full-Scale SNR Test Unit at Chubu Electric's Chita Station (2,3)

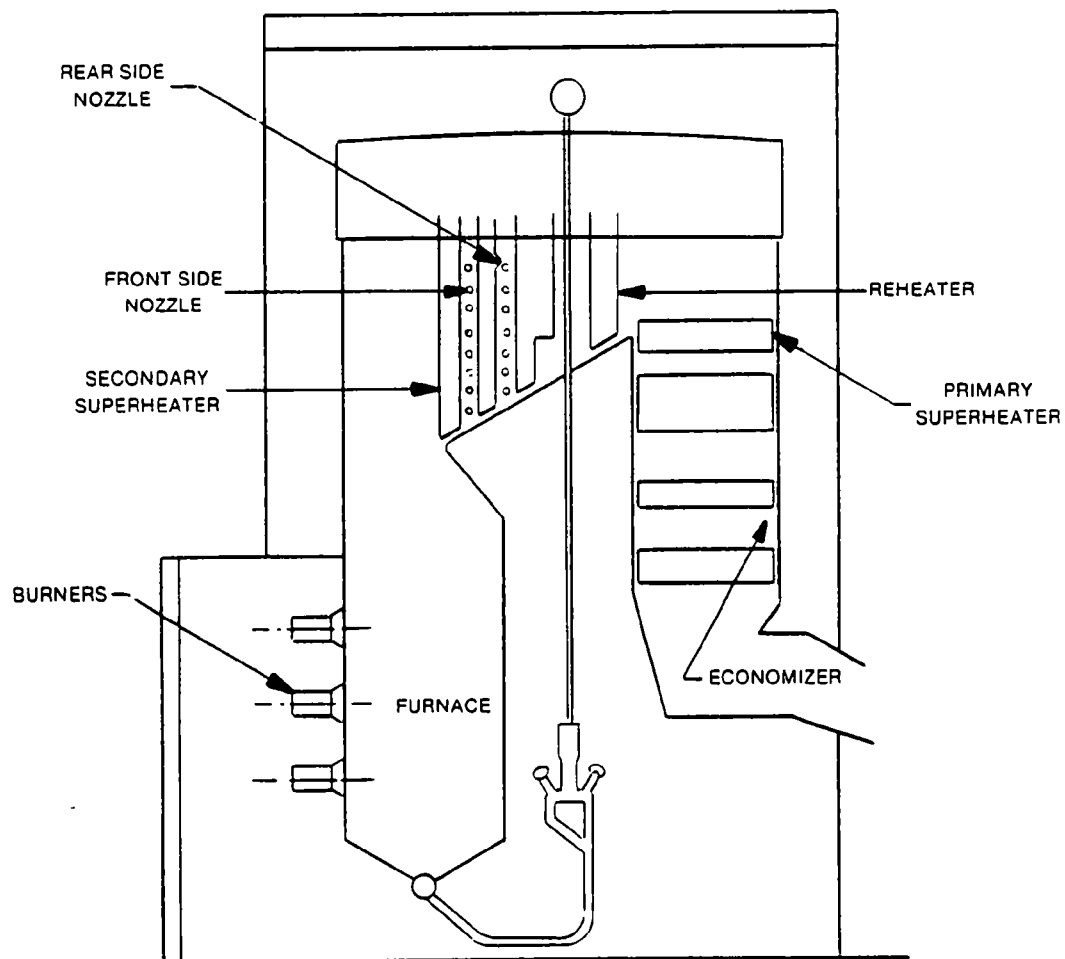
Boiler and SNR Unit

In 1976, Chubu Electric installed a full-scale SNR test unit for the existing No. 2 boiler at the Chita Station. The No. 2 boiler has a capacity of 375 MW and burns 0.2% sulfur oil. Among the four boilers which existed at Chita, the No. 2 boiler was chosen as being the most suited for SNR; it had space available for ammonia injection nozzles with adequate temperature ranges.

The specifications of the Chita SNR system are presented in Table 6-7. Since the boiler load fluctuates between 375 and 120 MW, a total of 15 nozzles were placed in two locations, front and rear, as shown in Figure 6-7.

TABLE 6-7. SNR SYSTEM SPECIFICATIONS, UNIT NO. 2, CHITA STATION, CHUBU ELECTRIC POWER COMPANY

BOILER:	
Unit Name	Unit No. 2 of Chita Station, Chubu Electric
Evaporation, t/h	1,225
Steam Pressure, kg/cm ² G	176
Steam Temperature, °C	571/541
SNR TEST FACILITY:	
Treated Gas Flow Rate, Nm ³ /h	1,000,000 (375 MW rating)
Retrofit Period	Aug. 1976 ~ Jan. 1977
NH ₃ Injection Nozzle (Fin-welded box type)	15 sets
Booster Air Fan for NH ₃ dilution and transport	1 set
NH ₃ storage and supply	1 set
SNR APPLICATION TEST START	Feb. 1977
PREDICTED DE-NO_x PERFORMANCE:	
Target NO _x Removal	40
Efficiency, %	



* Boiler Type Mitsubishi-CE Control, Radiant Reheat Divided
 Evaporation 1225 t/h, 375 MW
 Pressure 176 atg
 Temperature 571/540.6°C

Figure 6.7 Locations of Nozzles in the No. 2 Boiler Chita Station *

As shown in Figure 6-8, the rear nozzles (injection point 2) are used when the boiler load exceeds 290 MW, the front nozzles (point 1) are used with a boiler load below 220 MW, and both sets of nozzles are used with a load of between 220 and 290 MW. In this way, ammonia is always injected into the gas within a suitable temperature range--930-1,030°C. When the boiler load goes below 180 MW, ammonia injection is stopped. At this load level, the amount of NO_x produced is low enough to meet the regulations without control measures.

The SNR unit has operated almost continuously since February 1977 except for a period when the boiler was shut down. Figure 6-9 indicates the performance of the SNR system. By using 1.5 mol NH_3 /1 mol NO_x , 35-45% of NO_x is removed with 15-25 ppm of unreacted NH_3 . With a higher inlet NO_x concentration (about 150 ppm) the SNR unit produces a higher removal efficiency (45%). When the nozzles were modified to have more holes the result was better utilization of NH_3 . The same NO_x removal rate was obtained using 1.3 mol NH_3 with nozzle modification and 1.5 mol NH_3 without the modification. Recently at the plant about 1 mol NH_3 has been used to produce about 35% efficiency with 10 ppm unreacted NH_3 .

Evaluation/Economics

The operation of the SNR system at Chita Station has been virtually trouble-free except for problems associated with SO_x and NH_3 in the treated flue gas. The boiler flue gas contains about 100 ppm SO_2 and 1-2 ppm SO_3 which tend to combine with NH_3 and condense on cooling. This produces 2 problems. First, during the winter, when unreacted NH_3 exceeded 40 ppm, a plume was observed coming from the stack. Second, when the system began operation the pressure of the air preheater soot blower was too low. As a result, deposits in the preheater caused the pressure drop to increase from 100 to 140 mm H_2O in two months. Eventually, the boiler had to be shut down for washing of the preheater. The deposition has been reduced by using high-pressure soot blowing and less NH_3 to reduce unreacted NH_3 .

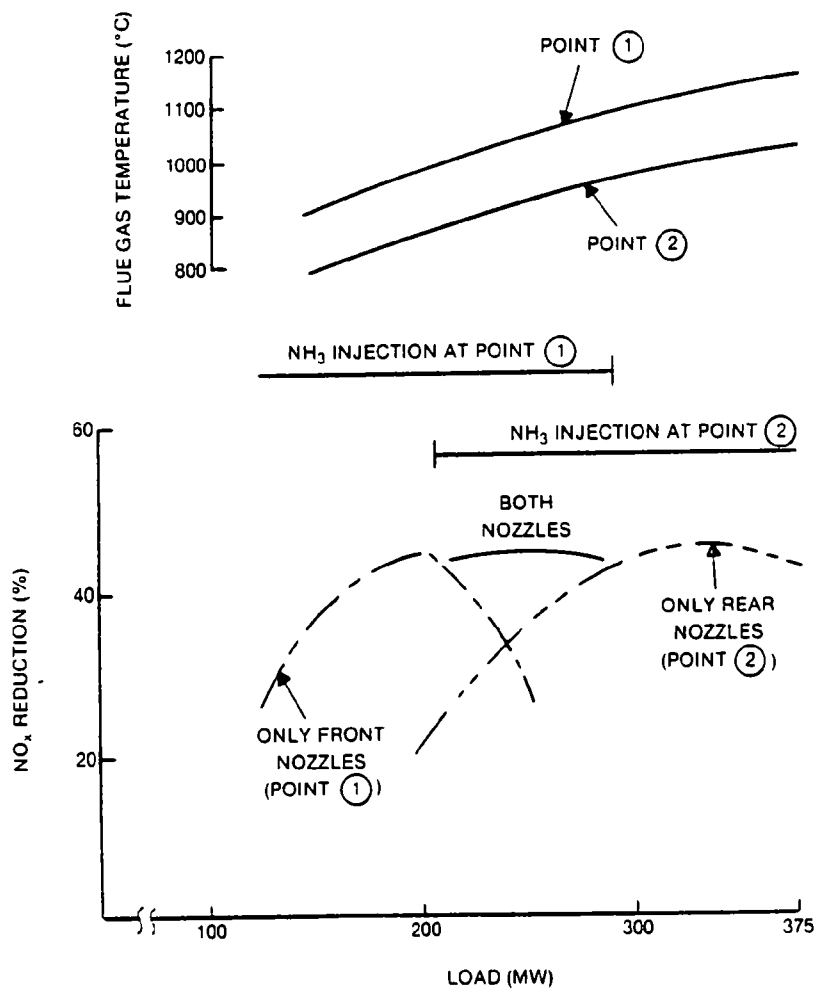


Figure 6-8 Effects of NH₃ Injection Position and Load on NO_x Reduction Rates During Operation of the No. 2 Boiler at the Chita Station

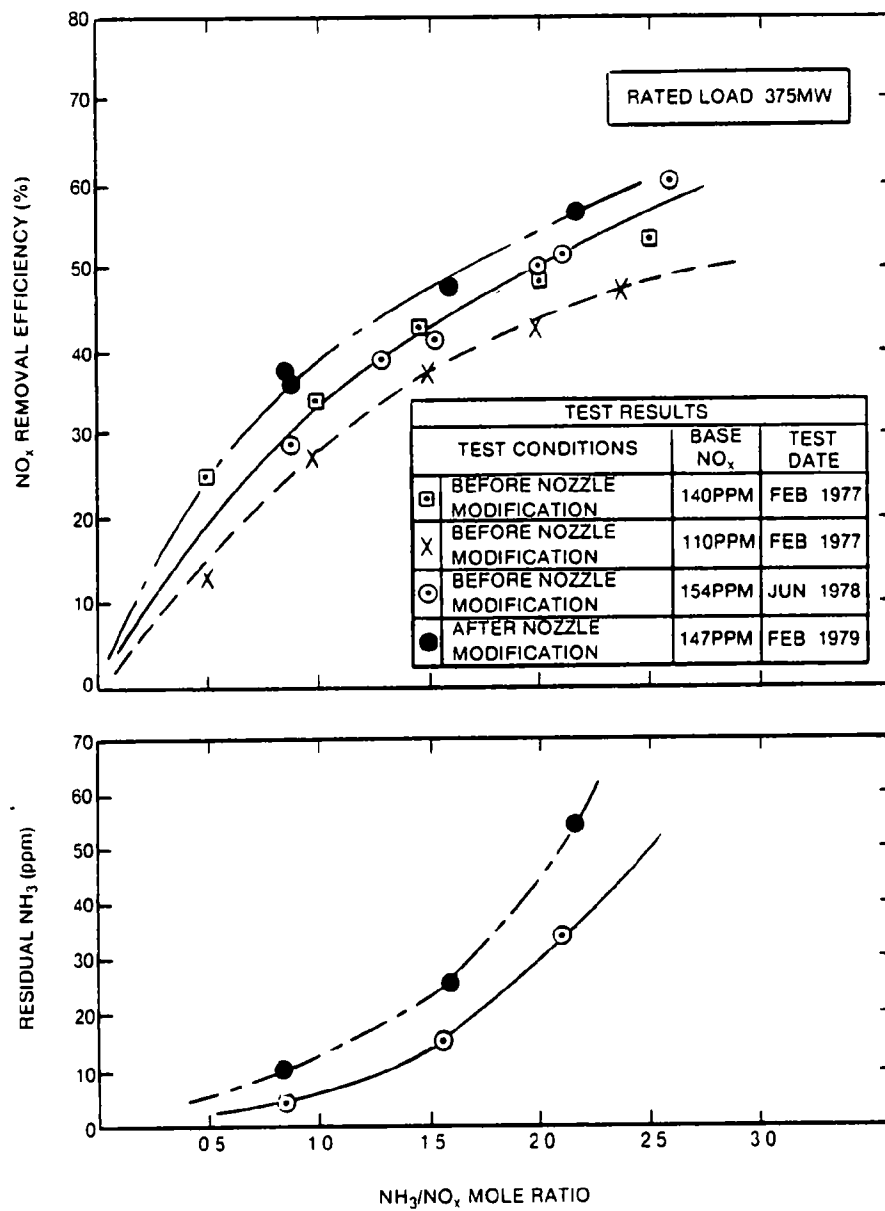


Figure 6-9 De NO_x Performance Test Results for Unit No.2 at the Chita Station

The SNR unit cost 600 million yen (1,600 yen/kW) in 1976. This cost is quite high due to the price of boiler modification for retrofitting of the SNR unit. In general, both the costs and the NO_x removal efficiency of SNR are slightly less than half of those for SCR.

6.2.5 Exxon Thermal De NO_x Systems

Eight thermal De NO_x SNR systems which use the technology developed by Exxon (Table 6-8) have been constructed at oil refineries and petrochemical plants. In most of the boilers and furnaces there was available space in which to install the ammonia injection nozzles at the optimum temperature of 900-1,000°C. The exception is at Mitsui Petrochemical's industrial boiler at Chiba. There the nozzles were installed where the temperature is 700-800°C and hydrogen is used with ammonia to increase NO_x removal efficiency. The ammonia and hydrogen are diluted with steam; air cannot be used for dilution because of the risk of explosion.

Mitsui Petrochemical's SNR unit has nozzles in three locations where the temperature is between 700 and 800°C. Two mol NH_3 and 1-2 mol H_2 to 1 mol NO_x are injected from the three locations according to the boiler load. As such, the unit removes 30-45% of inlet NO_x (100-150 ppm) with 10-15 ppm of unreacted NH_3 . When the unit began operation in late 1975, the boiler burned 0.8% sulfur fuel oil and the air preheater became clogged with deposits in about 700 hours. Since then either gas or cracked naphtha fuel containing 0.2% sulfur has been used to reduce the deposition. The unit was operated for about a year and then shut down for the following reasons: 1) low NO_x removal efficiency with high unreacted NH_3 , 2) high consumption of NH_3 and H_2 , and 3) the fact that combustion modification can reduce NO_x for a lower cost.

Tonen Sekiyu Kagaku (Tonen Petrochemical) and Toa Nenryo each operate two SNR systems (at Kawasaki and Wakayama, respectively) which meet current regulations and remove 10-20% of NO_x using 0.3-0.5 mol NH_3 to 1 mol NO_x . Unreacted NH_3 has been maintained at 5 ppm in all four units. The regulated NO_x limit is about 140 ppm at Kawasaki and 190 ppm at Wakayama.

TABLE 6-8. RIXION TECHNOLOGY THERMAL DENO_x PLANTS

User	Plant Site	Gas Source	Fuel	Gas Treated (Nm ³ /hr)	Inlet NO _x (ppm)	NH ₃ /NO _x mole ratio	Use of H ₂	Gas temp. (°C)	NO _x removal (%)	Date of Start	Status of operation
Mitsui Petrochemical	Chiba	Industrial boiler	Naphtha	120,000	130	1-2 ^a	Yes	700-800	30-40	Dec. 1975	No operation since 1977
Tonen Sekiyu Kagaku	Kawasaki	Industrial boiler	Low-S oil, Gas	468,000	~150	0.3-1 ^b	Yes ^c	700-1000	10-50	Oct. 1976	Occasional
Tonen Sekiyu Kagaku	Kawasaki	Industrial boiler	Low-S oil, Gas	468,000	~150	0.3-1 ^b	Yes ^c	700-1000	10-50	July 1977	Occasional
Kyokuto Petroleum	Chiba	Pipestill furnace	Low-S oil, Gas	160,000	80-100	2.0 ^b	Yes ^c	700-1000	50	Oct. 1977	For emergency
Toa Nenryo	Kawasaki	CO boiler	CO	314,000	200	1-2 ^b	Yes	700-1000	45-55	March 1978	For emergency
Toa Nenryo	Kawasaki	Pipestill furnace	Low-S oil, Gas	254,000	155	1-2 ^b	Yes ^c	700-1000	50-55	March 1978	For emergency
Toa Nenryo	Wakayama	Industrial boiler	Low-S oil	176,000	~200	0.3-0.5 ^b	No	850-900	10-20	Aug. 1978	Continuous
Toa Nenryo	Wakayama	Industrial boiler	Low-S oil	176,000	~200	0.3-0.5 ^b	No	850-900	10-20	Feb. 1981	Continuous

^aNH₃ is injected at three locations.^bNH₃ is injected at one location.^cH₂ is used at about 800°C or below.

The 3 other SNR units listed in Table 6-8 have been used for emergency purposes when total NO_x emissions from the plants exceed the regulation or when photochemical smog warnings require further NO_x reduction. The units each remove 45-55% of NO_x using hydrogen and 1-2 NH₃/mol NO_x.

Economics

Tonen Technology calculated the typical cost figures for an SNR system applied to an existing boiler and furnace; these are presented in Table 6-9.

TABLE 6-9. THERMAL DeNO_x COST FIGURES CALCULATED BY TONEN TECHNOLOGY

	Boiler	Furnace
Flue gas volume, Nm ³ /hr (MW equivalent)	500,000 165	200,000 65
Inlet NO _x , ppm	200	200
Outlet NO _x , ppm	100	100
Investment cost (10 ⁶ yen),	80	90
Utility consumption		
NH ₃ , kg/hr	80-120	30-45
Steam, t/hr ^a	2.5-3.0	1.0-1.2
H ₂ , Nm ³ /hr ^b	0-80	0-40

^a Air may be used when H₂ is not used.

^b H₂ is used when the gas temperature is below 850°C. H₂ costs 10-20 yen/Nm³.

The investment cost may be less for a new boiler and furnace. Most of the cost of SNR systems for existing boilers and furnaces is for retrofitting. These modifications differ considerably with each boiler and furnace. Mitsui Petrochemical's SNR unit cost 140 million yen in 1975, including the cost of

the NO_x analyzer, and control system and royalty fees. The cost is equivalent to 3,500 yen/kW (\$14/kW) and is fairly high due mainly to the installation of nozzles in 3 locations. The annual operating cost of the same unit was 150 million yen including 7 years depreciation, interest, overhead, and other similar costs. The annualized cost was 0.5 yen/kW_{hr}.

6.2.6 Toho Gas Company's SNR Units (4)

MKK constructed many small commercial SNR units for the Toho Gas Company at the Sorami and Chita plants near Nagoya City (Table 6-10). The units are for kerosene-fired boilers, naphtha-fired naphtha evaporation furnaces, and steam naphtha superheaters and each has a unit capacity of treating 3,200 - 10,700 Nm³/hr of flue gas.

The NO_x removal efficiencies of these units are relatively high and range from 54 to 62 percent for the boilers, 58 to 67 percent for the evaporators, and 44 to 56 percent for the superheaters. No other information regarding their operation is available.

It is presumed that the inlet NO_x concentrations are in the range of 100-200 ppm, and that the relatively high removal efficiencies may be due to the following: 1) the units' small size which enables rapid and uniform mixing of ammonia, 2) a relatively long reaction time in a suitable temperature range, in the case of the naphtha evaporator, 3) possible use of a large NH₃/NO_x mole ratio (2.0 or more), and 4) no ammonium bisulfate problem even with a large concentration of unreacted NH₃, since the fuel contains little sulfur.

6.2.7 Evaluation

SNR is the simplest method of flue gas treatment for NO_x abatement and is well suited to boilers and furnaces which require up to 50% NO_x reduction. In order to remove NO_x efficiently, ammonia must be mixed with the flue gas very rapidly and uniformly. The mixed gas then should be maintained for a certain time period, preferably more than 0.2 seconds, within a suitable

TABLE 6-10. TOHO GAS COMPANY'S SNR UNITS

Plant site	Gas Source	Fuel	Gas treated (Nm ³ /hr)	NO _x removal (%)	Startup date
Sorami	Boiler	Kerosene	3,490	62	Oct. 1976
"	SNS ^a	Naphtha	2,570	56	"
"	NE ^b	"	3,540	67	"
"	Boiler	Kerosene	3,840	54	Oct. 1977
"	SNS	Naphtha	4,362	44	"
"	NE	"	6,216	58	"
"	Boiler	Kerosene	3,870	54	Nov. 1977
"	SNS	Naphtha	4,762	44	"
"	NE	"	6,216	58	"
"	SNS	"	3,168	44	Dec. 1977
"	NE	"	4,166	58	"
"	Boiler	"	3,169	44	June 1978
"	NE	"	4,166	58	"
"	Boiler	Low-S oil	10,700	60	July 1978
"	SNS	"	3,800	62	"
"	NE	"	5,200	62	"
Chita	NH ^c	Kerosene	6,000	50	Oct. 1977
"	SNS	"	4,300	50	"
"	NH	"	3,200	50	"

^aSteam naphtha superheater^bNaphtha evaporator^cNaphtha heater

temperature range---900-1,030°C without H₂ and 700-900° with H₂. Hydrogen may be used at refineries and petrochemical plants but is not appropriate for use at power plants.

SNR also may be suitable for certain types of furnaces that have relatively long gas retention times at the appropriate temperatures. Over 60% NO_x reduction may be attained with these furnaces. On the other hand, a removal efficiency of 30-40 percent may be a practical limit for utility boilers which must maintain unreacted NH₃ at a low level even during load fluctuations.

SNR works well in an emergency situation when 40-50 percent removal of NO_x is needed temporarily. In this application, however, the maintenance of the ammonia injection nozzles may present a problem, since they must be kept cool at all times. MHI's cooling system which uses boiler water can be used to reduce the cooling costs.

SNR also may be useful for treating very dirty gas such as gas from a glass melting furnace or a municipal incinerator which contains particulates and gases capable of poisoning SCR catalysts.

A combined SNR/SCR system can be used to attain a higher NO_x removal efficiency (50-70 percent) than can be attained by SNR alone. This combination is described in the following section.

6.3 SNR/SCR COMBINED SYSTEMS

6.3.1 Introduction

Between 1978 and 1980, both Toyko Electric and Kamsai Electric conducted large-scale tests of combined SNR/SCR systems applied to existing oil-fired boilers. In the combined system, 1000°C ammonia is injected into the boiler for SNR; the 300-400°C gas leaving the boiler economizer is sent through a small amount of parallel-flow SCR catalyst (located in the existing duct) for further reduction of NO_x and NH₃. The combined system's advantage is that

it removes 50-60 percent of NO_x in flue gas from an existing boiler, requires neither an SCR reactor nor an additional fan, and produces less than 10 ppm of unreacted NH_3 .

6.3.2 Tokyo Electric's SNR/SCR Demonstration Plants

Tokyo Electric's three SNR/SCR demonstration plants are described in Table 6-11. All of the combined units were installed for existing oil-fired boilers which burn low-sulfur oil and produce a flue gas with 120-200 ppm NO_x .

The SNR/SCR system for the No. 2 oil-fired boiler (350 MW) at Tokyo Electric's Ohi Power Station is shown in Figure 6-10. Fifty ammonia injection nozzles, each with 40 holes, were installed at one location in the boiler where the gas temperature is about $1,000^\circ\text{C}$ at full load. A honeycomb catalyst, (87 m^3 ($\text{SV } 11,720 \text{ hr}^{-1}$)), was installed in the duct between the economizer and the air preheater. For test purposes, honeycomb catalysts with different compositions and channel diameters, ranging from 8 to 10 mm, were used. The pressure drop through the catalysts bed was less than 30 mm H_2O .

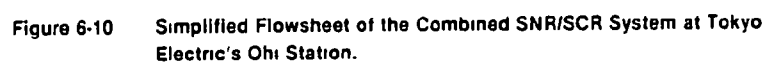
The combined system at Tokyo Electric's Yokosuka Station is shown in Figure 6-11. It has ammonia injection nozzles at two locations in order to compensate for changes in the gas temperature.

The demonstration plants operated for 7,900 - 10,700 hours as shown in Table 6-11. Similar results concerning NO_x removal efficiency and unreacted NH_3 were obtained at all three plants. A typical example of a test result is shown in Figures 6-12 and 6-13. By using 2.0-2.5 mol NH_3 to 1 mol NO_x , the NO_x removal efficiency was 50-60 percent with unreacted NH_3 below 10 ppm. Roughly 20 percent of the NO_x was removed by SNR; the rest was removed by SCR.

The NO_x removal efficiency was higher at the smaller boiler load as shown in the Figure 6-13. The reduced load was unfavorable for SNR because of the decrease in the gas temperature but increased the SCR efficiency because

TABLE 6-11. TOKYO ELECTRIC'S SNR/SCR DEMONSTRATION PLANTS (5)

Power Station and Unit No.	Yokosuka No.4	Ohi No.2	Yokohama No.1
Capacity in MW (m ³ N/H)	350 (1,076,000)	350 (1,020,000)	175 (531,000)
Fuel	Low sulfur oil	Low sulfur oil	Low sulfur oil
Sulfur content in fuel (wt %)	0.1 ~ 0.2	0.1	0.1 ~ 0.2
Dust in flue gas, mg/Nm ³ (at economizer outlet)	Approximately 50		
NO _x in flue gas, ppm	200 ~ 120		
NO _x reduction efficiency	More than 50 percent		
Residual ammonia	Less than 10 ppm		
Ammonia injection (NH ₃ /NO _x mole ratio)	1.5 ~ 2.5		
Type of catalyst	Honeycomb & plate	Honeycomb	Plate
Test Period	Apr. 1978 ~ Aug. 1980	June 1978 ~ Sep. 1980	Aug. 1978 ~ Sep. 1980
Operating Hours	7,900	10,700	10,500
Manufacturer	Mitsubishi Heavy Industries	Ishikawajima Harima Heavy Industries	Babcock Hitachi



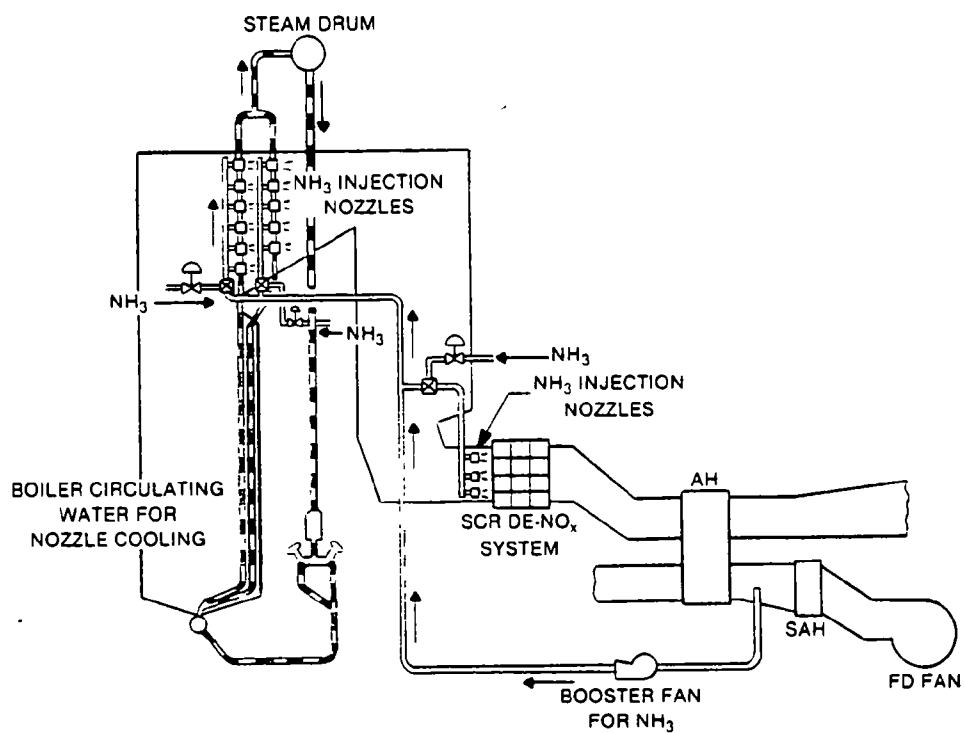


Figure 6-11 Schematic Diagram of the Combined SNR/SCR System at Tokyo Electric's Yokosuka Station (2)

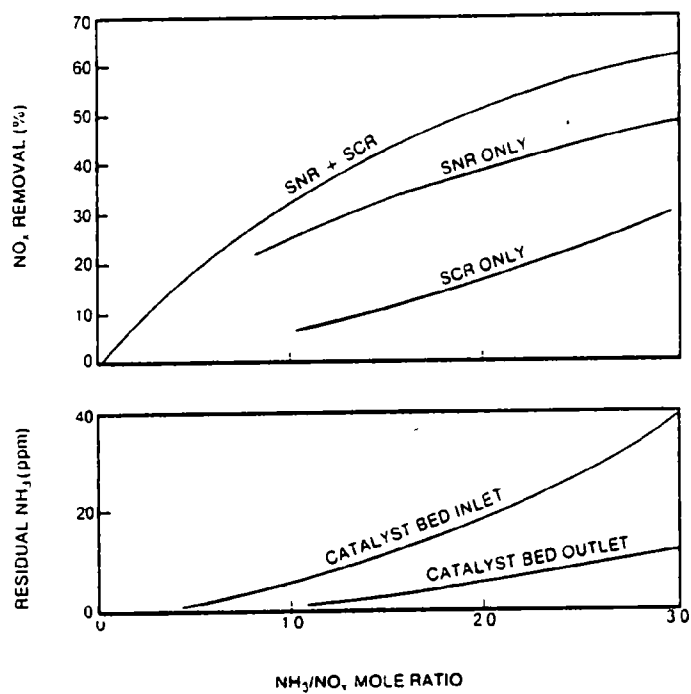


Figure 6-12 Typical Operation Data for Tokyo Electric's Combined SNR/SCR System. (2)

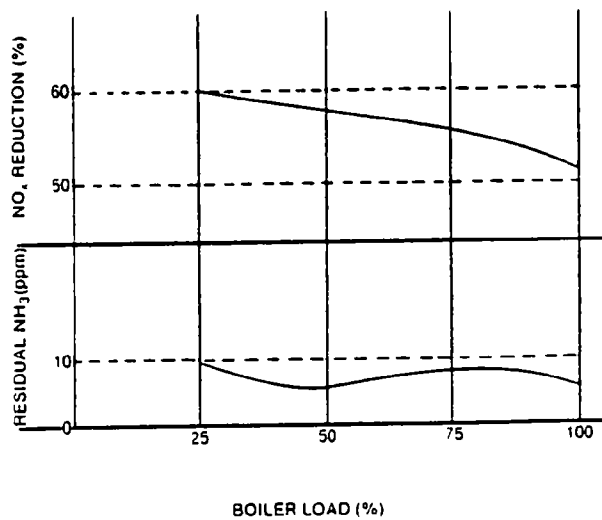


Figure 6-13 Tokyo Electric's Test Data: Effect of Boiler Load on the SNR/SCR Combined System (5)

of the smaller SV (longer reaction time through the catalyst bed). The increased SCR efficiency was more than sufficient to compensate for the decrease in SNR efficiency.

The catalyst was effective not only for increasing NO_x removal efficiency but also for reducing unreacted NH_3 below 10 ppm. Unfortunately, the air preheaters experienced ammonium bisulfate plugging. The only exception was at the Ohi plant which only had a slight bisulfate problem probably because of the low sulfur content of its fuel. The air preheaters at the other stations required water washing once every 3 or 4 months.

The demonstration tests were completed in September 1980. At that time the SNR ammonia injection nozzles were removed. Since that time, at the Ohi plant a small amount of ammonia ($0.15 - 0.2 \text{ mol NH}_3/\text{mol NO}_x$) has been injected through the nozzles for SCR to remove 15-20% of NO_x with 2-3 ppm of unreacted NH_3 .

Use of the SNR systems was discontinued for several reasons. First, the local NO_x regulation can be met using combustion modification. For example, the NO_x regulation for the Ohi No. 2 boiler is 140 ppm. This level can be achieved by using combustion modification, including staged combustion, flue gas recirculation and a low- NO_x burner. For safety reasons, 15-20% of NO_x from the boiler is removed by SCR. Second, because of the high temperatures in which they were used, the SNR ammonia injection nozzles caused maintenance problems. Another reason was that in the SNR system the ammonia consumption is high and the unreacted NH_3 is higher than it would be in a standard SCR plant. This caused ammonium bisulfate deposition problems in two plants.

6.3.3 Kansai Electric's Full-Scale SNR Test

In October 1977, Kansai Electric installed a full-scale SNR test unit for an existing 156 MW oil-fired boiler at the Himeji No. 1 Station. In July 1978, a small amount of SCR catalyst was placed in the duct between the boiler economizer and air preheater to increase NO_x removal efficiency to 50-70% and to reduce unreacted NH_3 .

In 1979, the SNR unit was removed primarily because of the maintenance problems associated with the ammonia injection nozzles. Since that time, the SCR catalyst successfully has removed about 30% of the NO_x with little catalytic degradation.

6.3.4 Evaluation

A combined SNR/SCR system was once considered ideal for removal of 50-60% of NO_x in flue gas from existing boilers. However, maintenance of the system's ammonia injection nozzles proved to be a serious drawback. For most existing utility boilers, a standard SCR reactor can be retrofitted between the boiler economizer and the air preheater to remove over 80% of NO_x. Alternatively, a parallel flow catalyst placed in the existing duct can remove 30-40% of NO_x.

The combination system still may be valuable for removing 50-60% of NO_x from existing furnaces and boilers that have no space for installation of SCR reactors.

6.4 MITSUBISHI ADVANCED COMBUSTION TECHNOLOGY (MACT) IN-FURNACE NO_x REMOVAL PROCESS

6.4.1 Introduction

MHI developed the Mitsubishi Advanced Combustion Technology (MACT) in-furnace process to remove about 50% of NO_x from a boiler. In the process the secondary fuel--about 10% of the fuel for the boiler--is used as a reducing agent. At temperatures above 1200°C the secondary fuel is injected into the boiler combustion gas to create a reducing atmosphere. In this atmosphere 70-90% of NO_x is converted to N₂ and H₂O and additional air is injected for complete combustion (Figure 6-14). Since a small amount of NO_x is formed during the complete combustion stage, the overall NO_x removal efficiency of the process is usually about 50%.

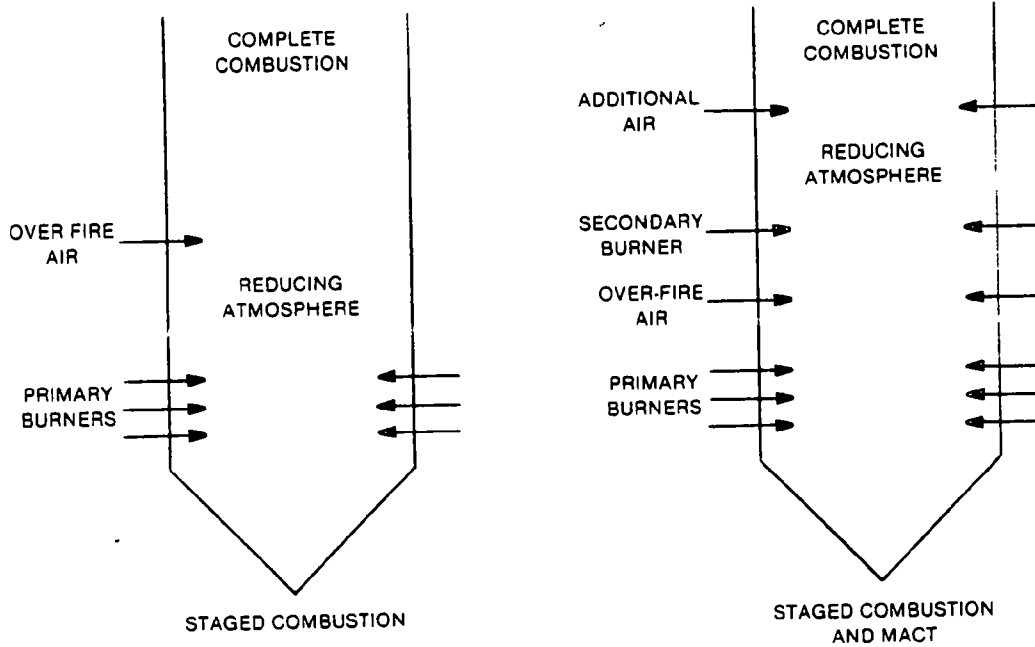


Figure 6-14 Staged Combustion and Staged Combustion/MACT Processes.

After completing small-scale tests, MHI joined with Tokyo Electric to conduct pilot plant tests using corner-firing furnaces. With a combination of combustion modification and MACT, NO_x concentrations were lowered to about 60 ppm for coal, 30 ppm for oil and 10 ppm for gas fuels. Tokyo Electric has been using the MACT/staged combustion system commercially for two small oil-fired boilers (125 MW each) which were originally designed to burn coal. The system has reduced NO_x to 30-40 ppm.

6.4.2 Small-Scale Tests (6,7)

Figure 6-15 and Table 6-12 provide a description of the small MACT test furnace. The compositions of the domestic low-sulfur coals which were used for the test are shown in Table 6-13.

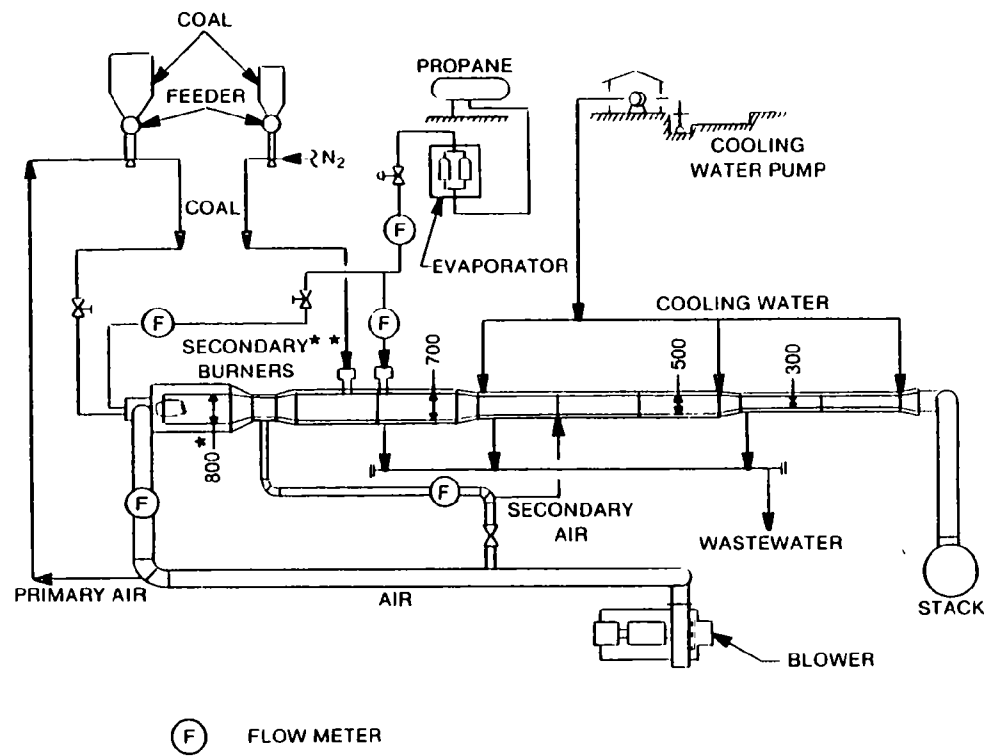
TABLE 6-12. SMALL TEST FURNACE SPECIFICATIONS

Furnace	Diameter 0.8 m Length 2.2 m Castable refractory-lined cylindrical furnace
Primary burner	Propane (10 kg/hr) or pulverized coal (100 kg/hr) Air at room temperature
Secondary burner	Propane or pulverized coal 10 kg/hr Air at room temperature is used for combustion. Pulverized coal is carried by nitrogen gas.

TABLE 6-13. COMPOSITION AND HEAT VALUE OF COALS (200 mesh 90% pass)

	Ash (%)	Volatile (%)	Fixed Carbon (%)	Moisture (%)	N (%)	S (%)	Heat Value (kcal/kg)
Small scale tests	13.2	42.2	38.4	6.2	1.0	0.28	6220
Pilot plant tests	10.1	42.6	40.8	6.5	1.0	0.20	6400

Figure 6-16 illustrates test results when propane fuel was used. Propane was burned in the primary burner producing a flue gas containing 140 ppm NO and 1% O₂. A reducing gas formed by the partial combustion of the propane (10% of primary fuel) was introduced into the flue gas at 1,200°C; this



*Dimensions are in mm

**Location of the secondary burner is changeable

Figure 6 15 Flowsheet of a Small-Scale MACT Test Plant

reduced NO to 25 ppm. For complete combustion, additional air was introduced. This had the effect of increasing NO to 70 ppm, resulting in an overall NO_x removal efficiency of 50%.

Figure 6-17 shows that NO_x was reduced when the secondary fuel was injected above 750°C and that the NO_x removal efficiency was higher when the flue gas contained a lower O₂ concentration before the secondary fuel injection.

Figure 6-18 shows the results of a test using a low-NO_x burner with pulverized coal fuel. The NO concentration ranged from 100 to 150 ppm before the secondary fuel was injected, and was reduced to 50 to 60 ppm by the MACT. The gas at the stack contained 10 ppm CO, but no hazardous gases such as HCN.

6.4.3 Fundamental MACT Studies (6)

Figures 6-19 and 6-20 show the NO_x decomposition ratio that occurred with propane fuel before the introduction of the additional air for complete combustion. The decomposition ratio was influenced by λ , which is defined by the following equation:

$$\lambda = \frac{\text{Inlet O}_2 \text{ (O}_2 \text{ in flue gas before secondary fuel was added)}}{\text{O}_2 \text{ required for complete combustion of the secondary fuel}}$$

About 90% of NO was decomposed at 1,150 - 1,300°C when λ was 0.18 and 0.53, while the decomposition ratio was only about 10% when λ was 2.2. At 1,300°C a reaction time of 0.1 second was sufficient for decomposition when λ was 0.53. Figure 6-20 shows that the decomposition ratio was not influenced by the inlet NO concentration, which ranged from 30 to 1,000 ppm.

Figure 6-21 shows test results with different fuels. When λ was between 0.15 and 0.9, 80-95% of NO was decomposed for all fuels including gas, oil, and coal. The decomposition ratio was considerably lower when λ was below 0.1 and above 1.0. This indicates that a small amount of O₂ is needed for the reaction and that excessive O₂ prevents decomposition.

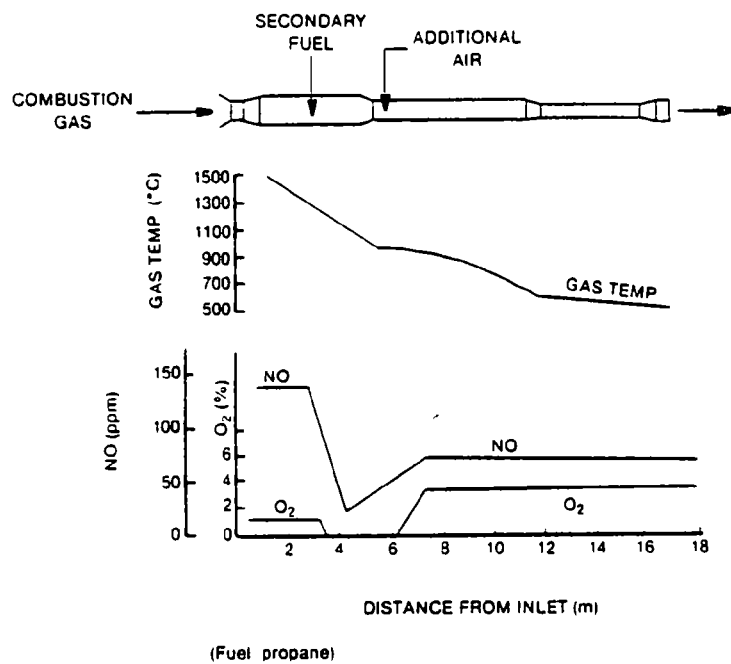


Figure 6-18 Change in NO Concentration Caused by MACT

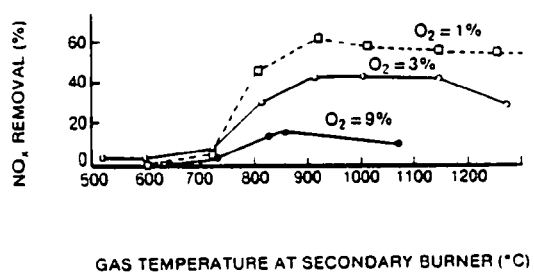


Figure 6-17 Gas Temperature, O₂ Percentage, and NO_x Removal During MACT Treatment

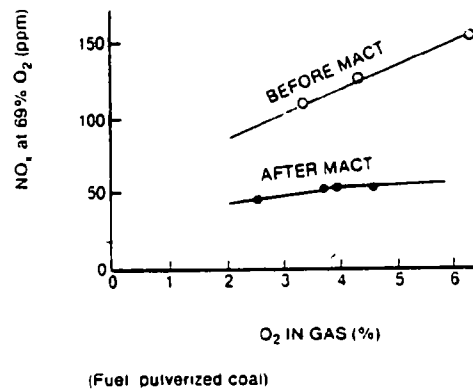
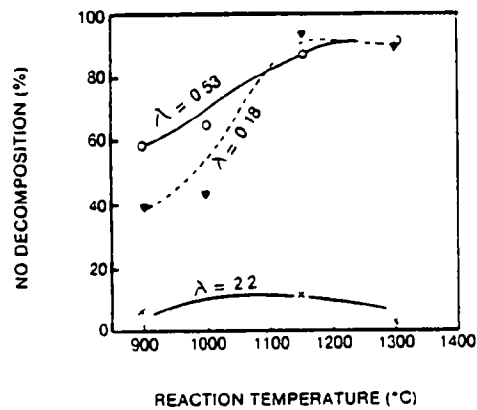
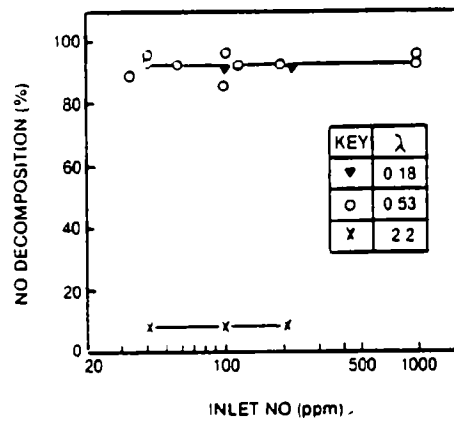


Figure 6-18 NO_x Concentration Before and After MACT Treatment



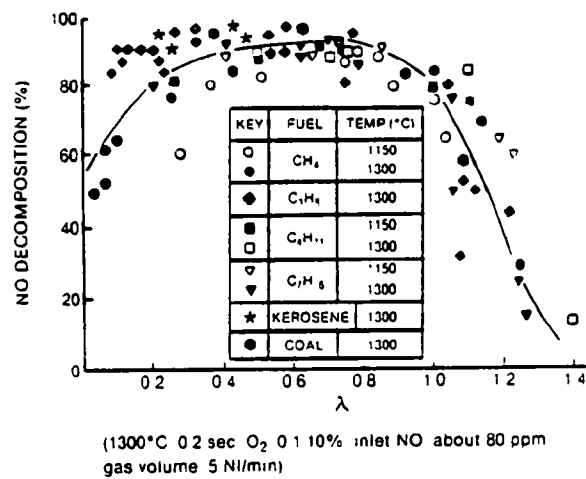
(Inlet O_2 1% inlet NO 92-103 ppm, reaction time 0.2 sec
gas volume 5 Nl/min fuel propane)

Figure 6-19 NO Decomposition Ratio at Different Temperatures and O_2 Concentrations



(Fuel: propane 1300°C, reaction time 0.2 sec
inlet O₂ 1% gas volume 5 Nl/min)

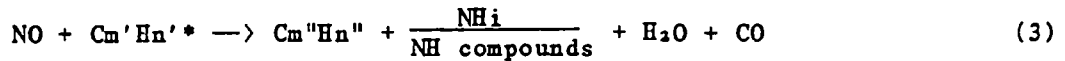
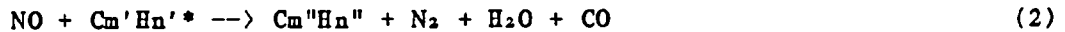
Figure 6-20 Inlet NO and Decomposition Ratio.



(1300°C 0.2 sec O₂ 0.1-10% inlet NO about 80 ppm
gas volume 5 Nl/min)

Figure 6-21 Relationship Between λ and NO Decomposition for Various Fuels.

The decomposition reactions are assumed to be these:



*indicates radical

Hydrocarbon (secondary fuel) is decomposed by O_2 to form hydrocarbon radical (1), which reacts with NO to form N_2 (2) and NH_i or nitrogen hydrogen compounds such as NH_3 and NH_2 (3).

Figure 6-22 shows the relationship between the amount of NO decomposed and the amount of NH_i formed from the NO. When less than 40 ppm NO was decomposed, nearly all of the NO was converted to NH_i ; the conversion ratio decreased as the amount of decomposed NO increased. This indicates that the MACT process may work more efficiently with flue gas richer in NO.

The reactions which take place during complete combustion by air addition are shown below:



The nitrogen hydrides, NH_3 and NH_2 , shown as NH_i , may be converted to both N_2 and NO. The conversion of NH_i to NO occurs at temperatures above 700°C as shown in Figure 6-23; the conversion ratio is higher with a higher O_2 concentration in the gas.

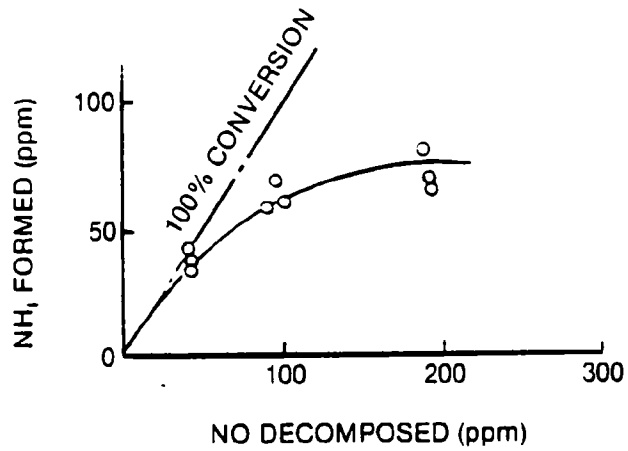


Figure 6-22 Conversion of NO to NH₃ by Secondary Fuel Addition.

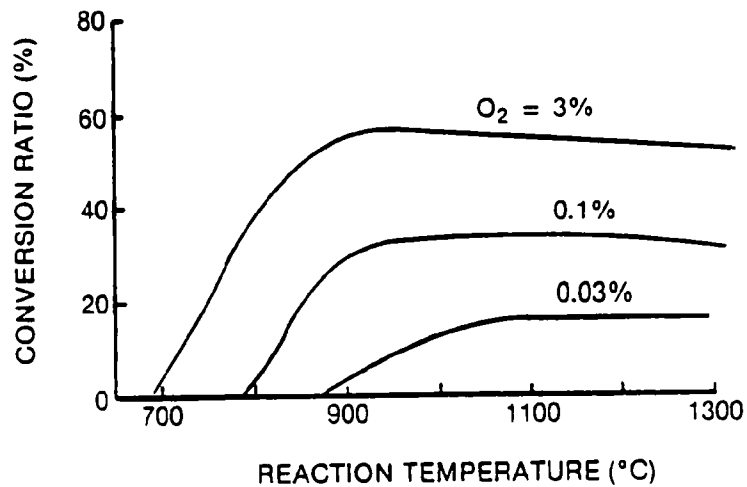


Figure 6-23 Conversion of NH₃ to NO_x by Air Addition for Complete Combustion.

6.4.4 Pilot Plant Tests with Corner-firing Furnaces(7)

As shown in Table 6-14, pilot plant tests of MACT were conducted with two corner-firing furnaces. The operating conditions and the coals used for the pilot plant tests are shown in Tables 6-15 and 6-13, respectively.

TABLE 6-14. FURNACE SPECIFICATIONS

Fuel	Gas and Oil	Coal
Heat capacity (10^7 Kcal/hr)	1.5	2.0
Number of burners	12 (gas), 8 (oil)	12
Forced draft fan (m^3/min) (mmH ₂ O)	450 (20°C) 800	920 (20°C) 800
Induced fan (m^3/min) (mmH ₂ O)	650 (300°C) 200	1140 (100°C) 800
Gas recirculation fan (m^3/min) (mmH ₂ O)	427 (500°C) 400	760 (350°C) 600
Air preheater (Nm ³ /min)	430 (288°C)	750 (350°C)

TABLE 6-15. MACT PILOT PLANT TEST CONDITIONS

Fuel	Gas	Oil	Coal
Main burner			
Type	PM	PM	SGR
Fuel (kg/hr)	240-800	200-800	600-1200
Gas recirculation (%)	0-30	0-20	0-10
Over fire air (%)	0-20	0-20	0-20
Secondary burner			
Fuel (kg/hr)	0-150	0-150	0-150
Gas recirculation (%)	0-15	0-15	5-15
Additional air (%)	0-20	0-20	0-20
O ₂ at furnace outlet (%)	1-3	1-3	2-4

The furnace was operated manually. As shown in Figure 6-24, furnace operation stabilized three to five minutes after the use of MACT began.

Figures 6-25 to 6-27 show the relationship between O_2 concentrations in the flue gas (prior to the injection of the secondary fuel) and NO_x concentrations with and without MACT. Using a combination of combustion modification and MACT, NO was reduced to 7-10 ppm for gas, 40-50 ppm for oil, and 50-70 ppm for coal. Figure 6-28 shows the effect of MACT for oil-burning when the nitrogen content of the oil was increased to 0.9% by adding pyridine. NO was maintained at 70 ppm even for oil containing 0.9% N.

An analysis of both the flue gas and the fly ash leaving the MACT system indicated that MACT did not cause any degradation in their composition and properties.

6.4.5 Evaluation

The MACT in-furnace process requires the same investment and operation expenditures as the process of combustion modification by staged combustion. By combining combustion modification and MACT, NO_x in flue gas from a large utility boiler may be reduced to about 100 ppm for coal, 40 ppm for oil, and 20 ppm for gas. Process operation appears to be problem-free.

A disadvantage associated with MACT is that it requires a furnace that is about 10% taller than most conventional furnaces. For this reason, MACT may not be applied to most existing boilers without a reduction in boiler capacity. An exception to this is the type of the boiler used commercially by Tokyo Electric. This boiler was originally designed for burning coal and oil and has a very large furnace for oil-firing.

The MACT process may be useful for a new boiler, especially for a coal-fired boiler in which NO_x reduction to 100 ppm is needed. For 50% NO_x reduction, the MACT may be more advantageous than selective noncatalytic

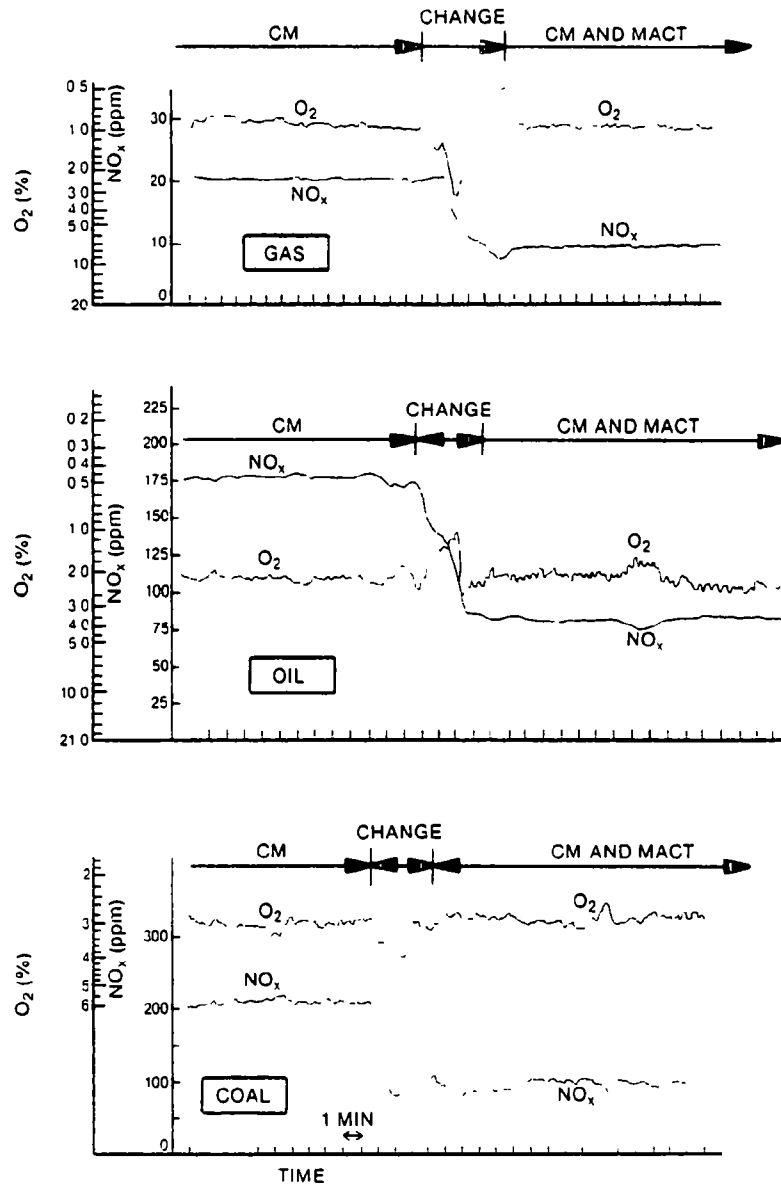


Figure 6-24 O₂ Percentage and NO_x Concentration After Combustion Modification (CM) and CM Plus MACT in a Corner-Firing Furnace Using Three Fuels

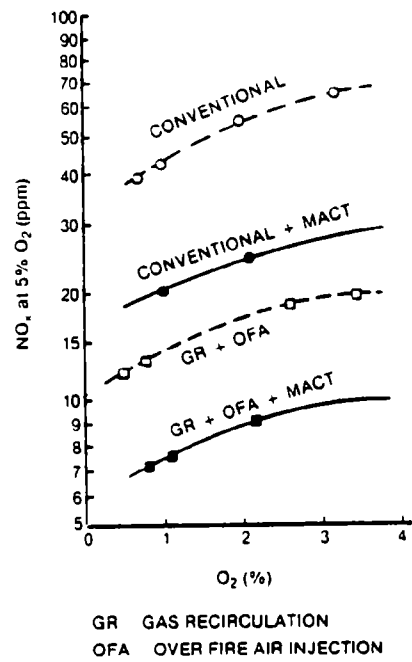


Figure 6-25 Results of MACT Pilot Plant Tests with Propane Fuel. (624 kg/hr)

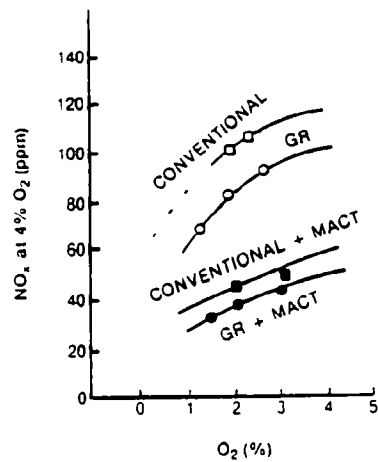


Figure 6-26 Results of MACT Pilot Plant Test with Heavy B Oil Fuel. (N 0.12%, 800 l/hr)

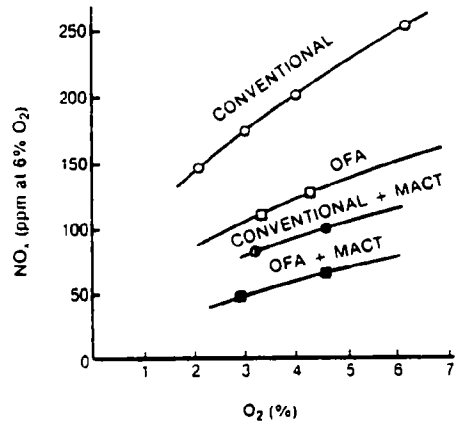
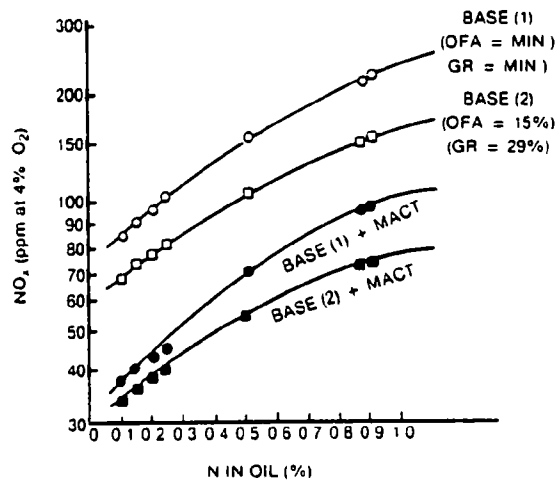


Figure 6-27 Results of MACT Pilot Plant Tests with Coal Fuel (1150 kg/hr)



* O₂ was 2% before the addition of the secondary fuel

Figure 6-28 Results of MACT Pilot Plant Tests with Oil Containing Pyridine*

reduction (Thermal DeNO_x) because MACT does not require ammonia and therefore does not have an ammonium bisulfate problem. For additional NO_x abatement, selective catalytic reduction (SCR) must be used with MACT.

IHI, Babcock Hitachi (BH), and Tokyo Electric have tested a process similar to MACT and have obtained about 50% NO_x removal. In addition, Hitachi Zosen has developed a similar process for industrial boilers (Section 6.9.5) (8). The MACT process may be best suited to corner-firing (tangential firing) boilers. It is based on rapid uniform mixing of the secondary fuel with combustion gas which can be attained easily in that type of boiler.

6.5 ACTIVATED CARBON PROCESS (EPDC - SHI PROCESS)

6.5.1 Introduction

EPDC and Sumitomo Heavy Industries (SHI) have conducted tests of the activated carbon process with the objective of removing 95% of SO_x and 40% of NO_x in flue gas from a coal-fired boiler. They have operated a pilot plant with a capacity of treating 10,000 Nm³/hr of flue gas from a coal-fired boiler at EPDC's Takehara Station since November 1978.

In the activated carbon process, the SO₂ adsorbed by the carbon is regenerated by heating and converted to elemental sulfur by the RECLAUS process. In the RECLAUS process, SO₂ is reduced to H₂S and S using coal, and then the H₂S and the SO₂ react in the Claus furnace to form byproduct elemental sulfur. Ammonia is added to the flue gas to: 1) increase SO_x removal efficiency, 2) reduce carbon consumption by thermal regeneration, and 3) remove a portion of the NO_x.

An activated carbon process demonstration plant sponsored by the Ministry of International Trade and Industry will be completed in 1983. The plant will be located at EPDC's Matsushima Station and will have a capacity of treating 300,000 Nm³/hr of flue gas from a coal-fired boiler.

6.5.2 Pilot Plant Test of the Activated Carbon Process (9)

The composition of the flue gas and the pilot plant test conditions at EPDC's Takehara Station are shown in Tables 6-16 and 6-17.

TABLE 6-16. FLUE GAS COMPOSITION DURING PILOT PLANT TEST

	Range	Average
SO ₂ , ppm	600-1000	900
NO _x , ppm	200-400	250
O ₂ , %	5.0-8.9	6.6
CO ₂ , %	12.0	12.0
H ₂ O, %	8.1-9.0	8.4
Dust, mg/Nm ³	140-310	250

TABLE 6-17. TEST CONDITIONS

SO ₂ , ppm	600-1000
NO, ppm	200-350
Gas temperature, °C	120-150
Space velocity (SV), hr ⁻¹	500-900

A flowsheet of the pilot plant is presented in Figure 6-29. Ammonia is added to the flue gas in the ratio of 0.5 mol ammonia/mol SO_x and the gas is sent horizontally through a moving bed in which granular activated carbon moves downward. The SO_x in the gas is adsorbed by the carbon to form sulfuric acid:



A portion of the ammonia reacts with the sulfuric acid to form ammonium bisulfate while the rest of it is reacted with NO by the catalytic action of the carbon:

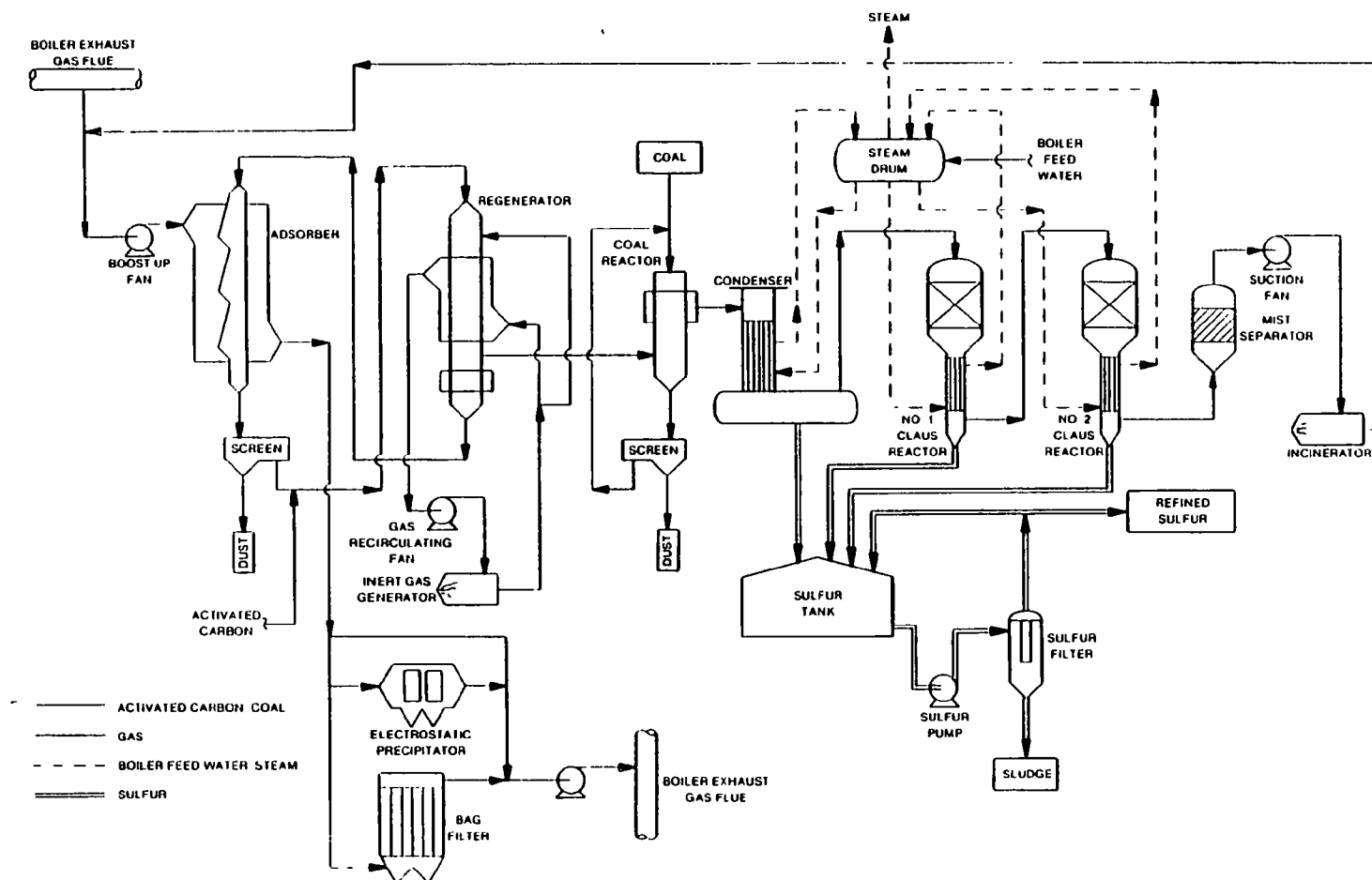


Figure 6 29 Flowsheet for the Activated Carbon Process Pilot Plant at EPDC's Takehara Station (9)



The relationship of reaction temperature to removal efficiency in the system is shown in Figure 6-30. The flue gas is then sent through an ESP or a baghouse and on to the stack. Loaded with ammonium bisulfate and sulfuric acid, the carbon is discharged from the bed and sent into another moving bed reactor (regenerator). There it is heated above 350°C by an inert gas produced by the incomplete combustion of fuel. The treated carbon is returned to the adsorber and the SO₂ is regenerated by the following reactions:



The SO₂-rich gas leaving the regenerator is mixed with a small amount of air and sent to the bottom of the coal reactor, a shaft furnace charged with coal. As a result of the partial combustion of the coal, the gas temperature in the reactor reaches about 900°C. This causes the following reactions:



About 80% of the SO₂ is reacted in the furnace; about 40% forms sulfur, 30% forms H₂S, and 10% forms COS. The gas is then cooled to allow condensation of elemental sulfur, and is sent into two Claus furnaces in series. In the furnaces, nearly all of the sulfur compounds are converted to elemental sulfur:



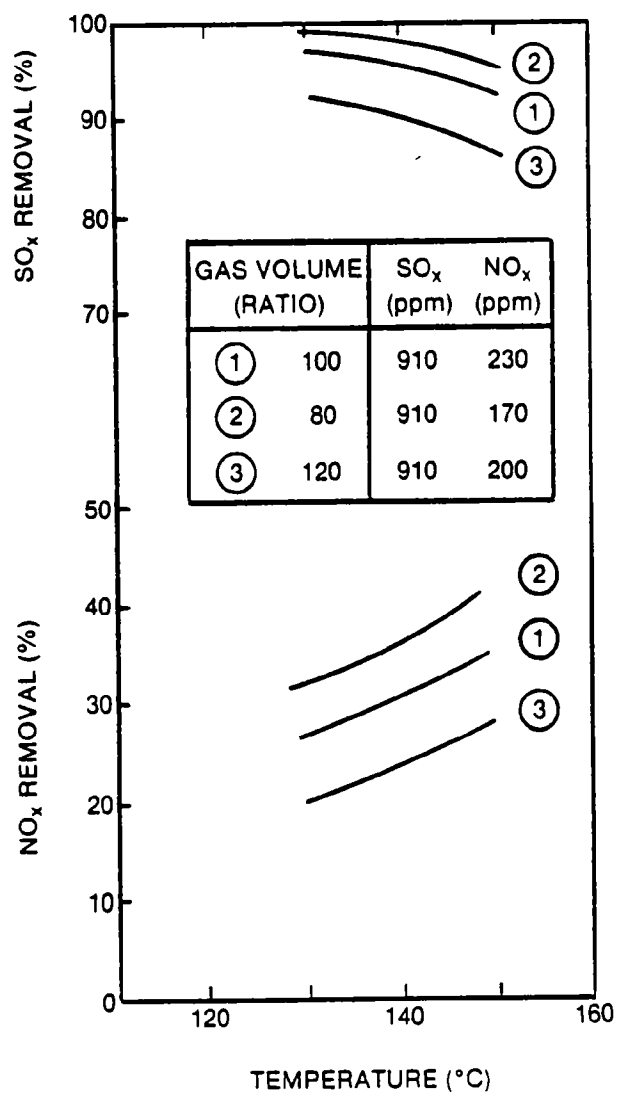


Figure 6-30 Effect of Temperature and Gas Volume on SO_x and NO_x Removal Efficiencies. (NH₃/SO_x = 0.5) (10)

In actuality, a small amount of air is added to the gas leaving the coal reactor in order to adjust the $\text{H}_2\text{S}/\text{SO}_2$ ratio to 2. The gas leaving the Claus furnace (containing small amounts of H_2S , SO_2 and COS) is incinerated to convert H_2S and COS to SO_2 and is returned to the adsorber.

Figure 6-31 shows the SO_2 and NO_x removal efficiencies during an 8,000-hour continuous test cycle at the pilot plant. The SO_x removal efficiency ranged from 80 to 99% (90-95% removal for most of the time) while the NO_x removal efficiency ranged from 20-40% (30% average). The activated carbon was consumed at a rate of 0.5-1% per day. Ammonia was not detected in the flue gas leaving the adsorber as long as the NH_3/SO_x mole ratio was kept below 0.5. The recovered sulfur contained a very small amount (less than 0.5%) of impurities such as NH_4HSO_4 and NH_4Cl ; the impurities subsequently were removed by filtration to yield a byproduct sulfur with over 99.9% impurity.

6.5.3 Evaluation

The activated carbon process is advantageous in that it does not require either water or gas reheating, while it simultaneously removes over 90% of SO_x and about 30% of NO_x , and produces elemental sulfur. On the other hand, the process does consume a large amount of carbon even with the addition of ammonia. The cost of carbon may be one of the important factors to consider in determining the commercial applicability of the process.

The NO_x removal efficiency of the process can be increased to 80-90% by using a much larger amount of ammonia and a high quality carbon at 230°C . This was demonstrated by the Unitika process pilot plant. The Unitika process, however, was abandoned because of its large consumption of costly carbon and ammonia. It may be possible to use less costly carbon and smaller amounts of ammonia for about 30% NO_x removal at a lower temperature.

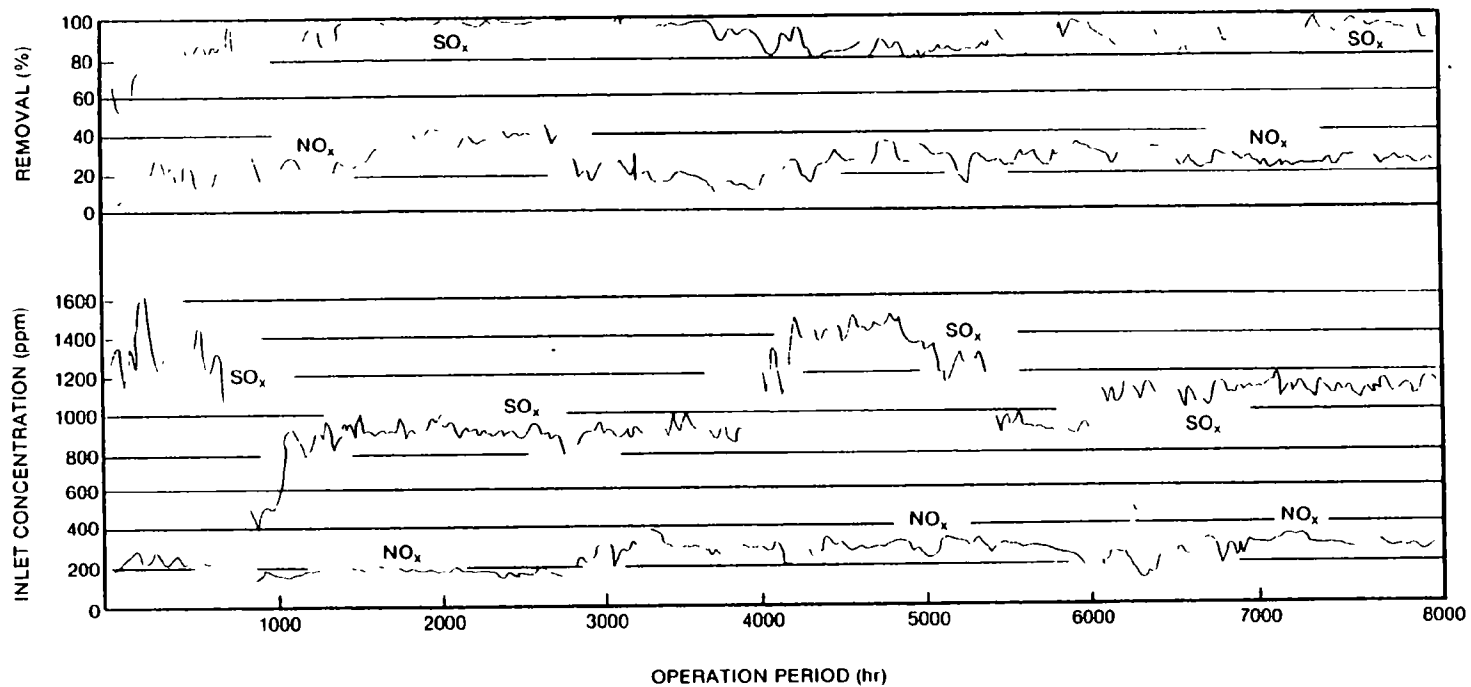


Figure 6-31 SO_x and NO_x Concentrations and Removal Efficiencies During an 8000 Hour Continuous Test Cycle (9)

The activated carbon process may not be suitable for flue gas with a high SO_x content because both ammonia and carbon consumption increase with SO_x concentration; it may be well suited for flue gas from coal or oil with less than about 1% sulfur. The operation of the demonstration plant now under construction at Matsushima should provide more valuable information on the process. SHI also conducted tests on the feasibility of using 2 absorbers to remove about 80% of NO_x and 90% of SO_2 . Further study is needed to evaluate this process.

6.6 EBARA ELECTRON BEAM IRRADIATION PROCESS

6.6.1 Introduction

Ebara Corporation, and the Japan Atomic Energy Research Institute, have developed a process which simultaneously removes SO_x and NO_x from flue gas by irradiating the gas with an electron beam and then collecting the resulting particulates with an ESP. From 1974-1977, Ebara operated a pilot plant with a capacity of treating 1,000 Nm^3/hr of flue gas from an oil-fired boiler. Tests at this early stage of development were not very successful. Later Ebara began using ammonia, which substantially improved the process.

By irradiating the gas containing ammonia, over 90% of SO_x and 80% of NO_x can be removed, and converted to fine crystals of ammonium sulfate nitrate (double salt) which can be used for fertilizer. A larger pilot plant with a capacity of treating 3,000 to 10,000 Nm^3/hr of flue gas from an iron-ore sintering machine was operated from July 1977 through June 1978 at Nippon Steel's Yawata Works. The Ebara electron beam irradiation process has been licensed to AVCO, USA.

6.6.2 Ebara Process Pilot Plant Tests (11, 12)

A flowsheet of the larger Ebara process pilot plant is shown in Figure 6-32. The most important pieces of equipment in the plant are: gas coolers for indirect cooling (heat exchanger) and direct cooling (water spray), an ammonia injection facility, an electron beam reactor surrounded by a concrete

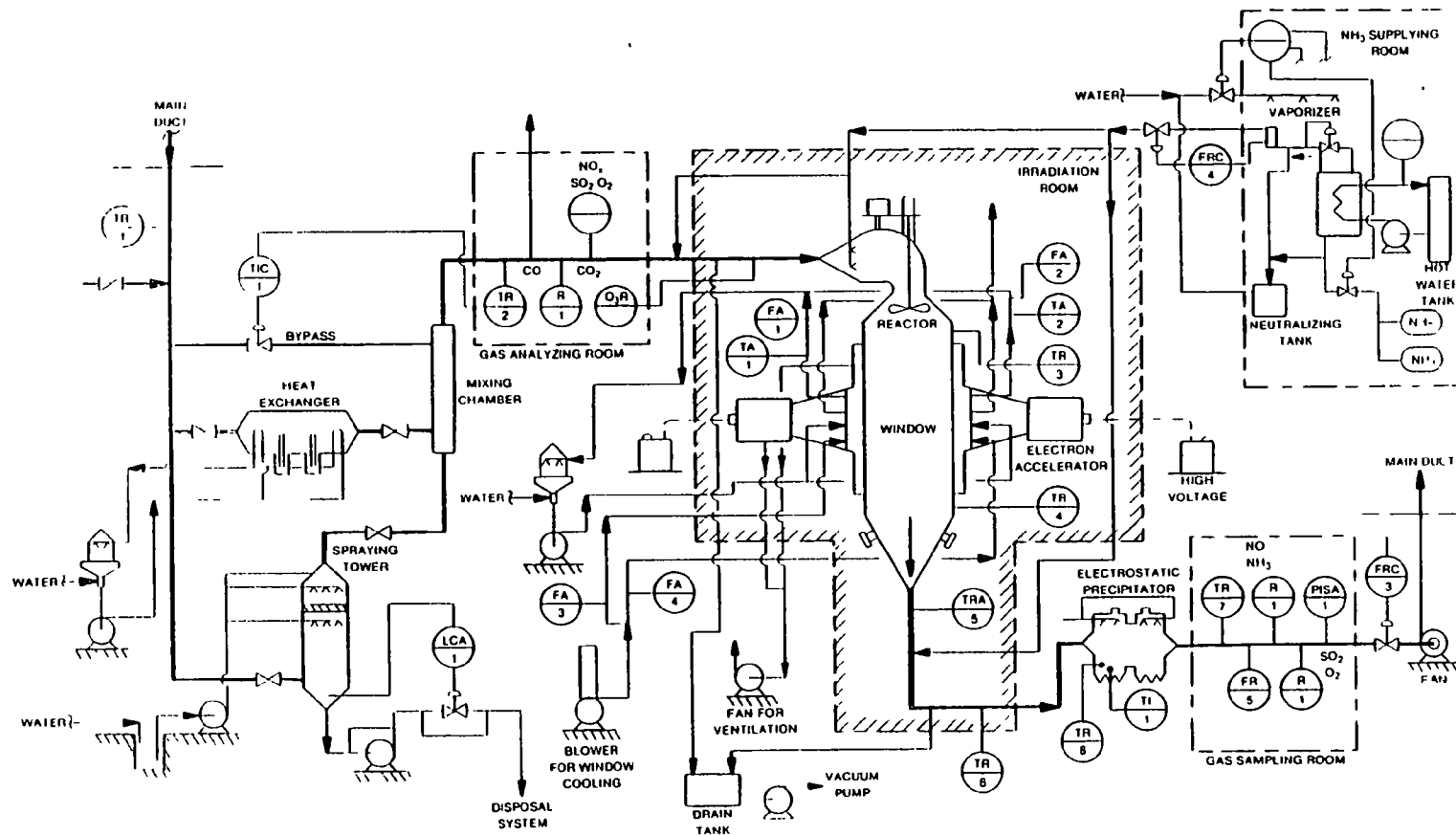


Figure 6 32 Flowsheet of an Ebara Electron Beam Process Pilot Plant
(3,000 10,000 Nm³/hr)

wall to prevent x-ray emissions, an ESP, and a control system. As shown in Figures 6-32 and 6-33, two electron beam accelerators with a unit capacity of 750 kV, 60 mA were placed at opposite ends of a cylindrical reactor with a diameter of 2.6 m. The distribution of the dose rate in the reactor is shown in Figure 6-33.

Since the dose rate was not uniform throughout the reactor, an impeller was placed at the reactor inlet to rotate the gas and homogenize the reaction. A side stream of the gas from an iron-ore sintering furnace was treated in the reactor. The gas contained about 200 ppm each of SO₂ and NO_x (mainly NO), 40 mg/Nm³ of dust, 15.5% O₂, 10.3% H₂O, and 16.2% CO₂, and had a flow rate of 3,000-10,000 Nm³/hr. It was cooled to 70-90°C, injected with ammonia, and sent into the reactor. In some of the tests, SO₂, NO, and fly ash were added to the gas in order to simulate flue gas from coal. Ammonia was used at an average stoichiometry of 1.0 (2 mol NH₃/mol SO_x and 1 mol NH₃/mol NO_x). For some of the tests, this stoichiometry was changed.

The relationship between the gas rotation ratio and the NO_x and SO_x removal efficiencies is shown in Figure 6-34. The gas rotation ratio is defined as:

$$\frac{\text{revolutions of impeller (rpm)}}{\text{gas flow rate (Nm}^3\text{/hr)}}$$

A maximum efficiency--over 95% for SO_x and 80% for NO_x--was obtained at the ratio of about 1/60, with 1.8 Mrad at 90°C.

The effect of the dose on removal efficiency and unreacted NH₃ is shown in Figure 6-35. SO_x removal efficiency exceeded 90% at 1.3 Mrad at 70°C and at 2 Mrad at 90°C, while NO_x removal efficiency reached a maximum ---- about 80%--with 1.8 Mrad at 70°C or about 65% with 1.8 Mrad at 90°C. The decrease in NO_x removal efficiency at the higher dose level may be due to the formation of NO_x from N₂ and O₂. The amount of unreacted NH₃ decreased with an increasing dose and was almost zero above 1.8 Mrad at 70°C; there was a considerable amount of unreacted NH₃ at 90°C even with 2.4 Mrad. The tests shown in

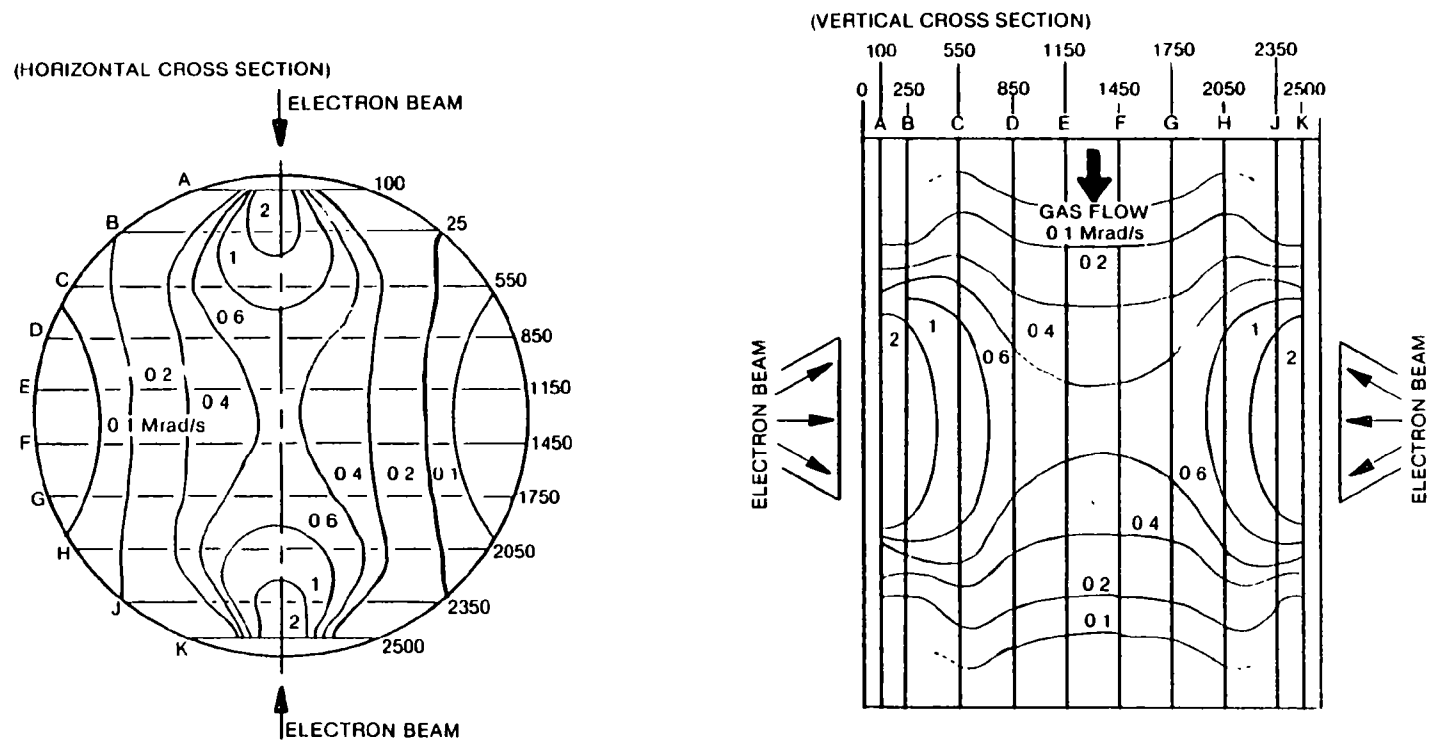


Figure 6 33 Dose Rate Distribution in Ebara Process Pilot Plant Reactor *

* accelerating voltage = 600 kV

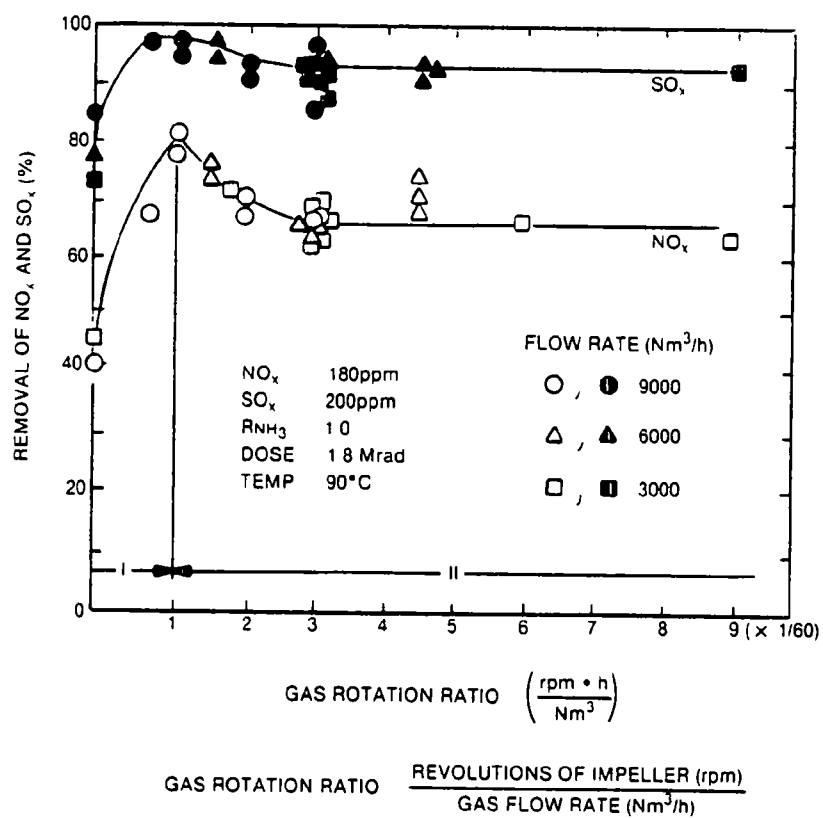


Figure 6-34 Relationship Between Gas Rotation Ratio and SO_x and NO_x Removal Efficiencies.

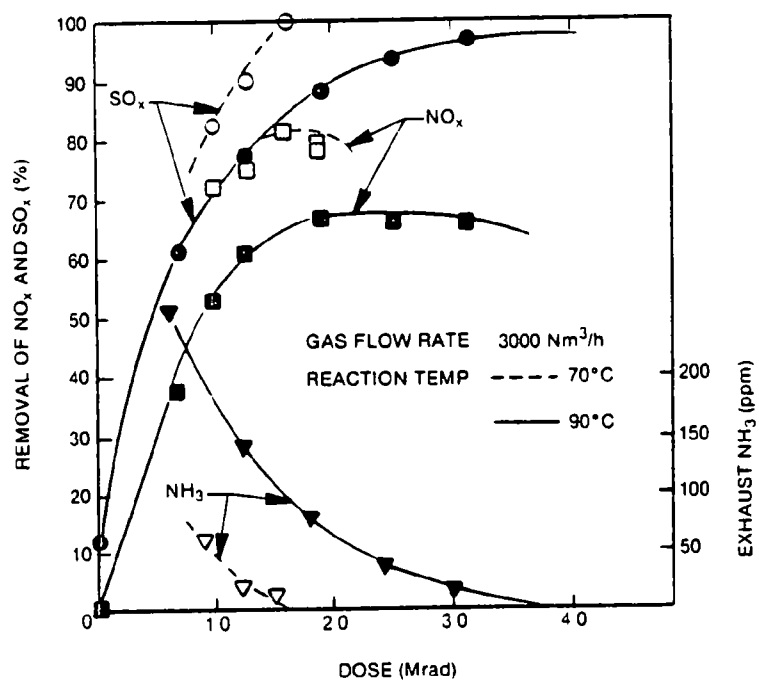


Figure 6-35 Effect of Dose on Removal Efficiencies and Exhaust NH_3 *

* gas rotation ratio 1/33

Figure 6-35 were conducted at a gas rotation ratio of 1/33 units. Better results may be obtained with a ratio of 1/60.

Figure 6-36 shows the results of 600 hours of pilot plant operation at 1.5 Mrad and 90°C with a gas rotation ratio of 1/33. During this test period the pilot plant was shut down twice due to the shutdown of the the sintering machine. The inlet SO_x concentration ranged from 180 to 250 ppm; the inlet NO_x concentration was in the range of 170 to 210 ppm. The SO_x and NO_x removal efficiencies ranged from 92 to 97% and 75 to 85% , respectively, while unreacted NH₃ leakage at the reactor outlet ranged from 10 to 50 ppm. This high level of unreacted ammonia was caused by the frequent fluctuations in inlet SO_x and NO_x concentrations and by problems with the ammonia flow meter.

The balance of NO_x, NH₃, and SO_x in three pilot plant test runs is shown in Table 6-18. Most of the NO_x, NH₃, and SO_x were reacted and caught by the ESP, but a large portion of the NH₃ and SO_x did deposit in the duct and a considerable amount of NO_x was emitted from the recovery system. The total amounts of NH₃ and SO_x were slightly larger than 100% presumably because of a sampling and analysis error. The NO_x totals were considerably larger than 100%, which indicated that irradiation was causing the formation of NO_x from N₂ and O₂. Chemical analysis of the exhaust gas revealed the presence of N₂O in concentrations ranging from 10 to 20 ppm.

TABLE 6-18. BALANCE OF NO_x, NH₃ AND SO_x (PERCENT OF INLET CONCENTRATION)

Run No.	Component	Caught by ESP	Deposit in Duct	Emitted	Total
1109	NO _x	81	6	49	136
	NH ₃	64	36	9	109
	SO _x	62	43	10	115
1111	NO _x	87	6	31	124
	NH ₃	65	36	10	111
	SO _x	64	40	8	112
1114	NO _x	78	6	38	132
	NH ₃	65	36	7	105
	SO _x	59	43	8	110

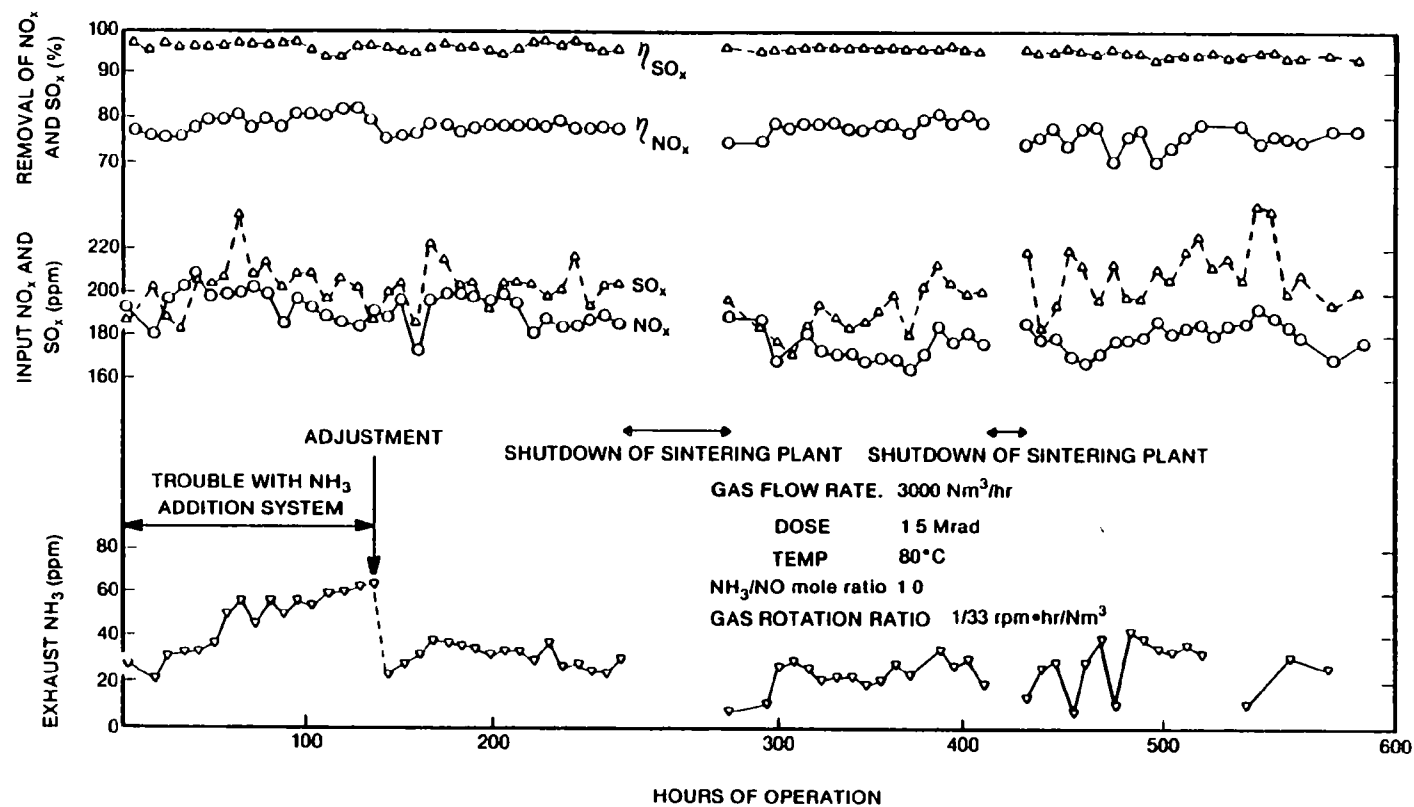


Figure 6-36 Results of 600 Hours of Continuous Ebara Process Pilot Plant Tests.

During the test period, the titanium foil at the reactor window was often broken. Later, a foil with a titanium alloy was used which lasted for over two months. Ebara has developed a method of changing the foil without stopping the operation of the accelerator.

An X-ray diffraction analysis of products caught by the ESP indicated that the major compounds present were $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$, $3\text{NH}_4\text{NO}_3 \cdot \text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$. Chemical analysis of a product obtained from a gas containing 220 ppm SO_2 and 235 ppm NO_x with 700 ppm NH_3 at 90°C revealed that the product contained 33.6% SO_4 , 29.4% NO_3 , 23.6% NH_3 , and 0.9% C.

The results of a pilot plant test using SO_x - and NO_x -rich gas are shown in Figure 6-37 (13). About 80% of both SO_x and NO_x were removed at 1.8 Mrad with an ammonia stoichiometry of 1.0. With these conditions unreacted ammonia was about 50 ppm; the gas rotation ratio was poor (1/17) because of a limited ammonia supply and a flue gas volume of only 1,500 Nm^3/hr . It is probable that about 90% of both SO_x and NO_x can be removed with a better rotation ratio, as shown in Figure 6-34.

For some of the tests, 0.1 - 0.5 g/ Nm^3 of fly ash (equivalent to 95-75% removal of fly ash from pulverized coal) were added to the system. The results indicated that the fly ash produced no adverse effect on the SO_x and NO_x removal efficiencies (13).

6.6.3 Reaction Mechanism

Fundamental tests also were conducted on the reaction mechanism of the Ebara process. Although the reactions are complex, the major one appears to be the formation of oxidant radicals such as OH caused by the radiation of water vapor. In this reaction SO_2 and NO are oxidized to form sulfuric acid and nitric acid mists; the mists react with ammonia to form fine crystals of sulfate and nitrate. Tests results also showed that the SO_2 removal efficiency is slightly higher when the gas is cooled by a water spray rather than by a heat exchanger; the NO_x removal was not significantly different with the

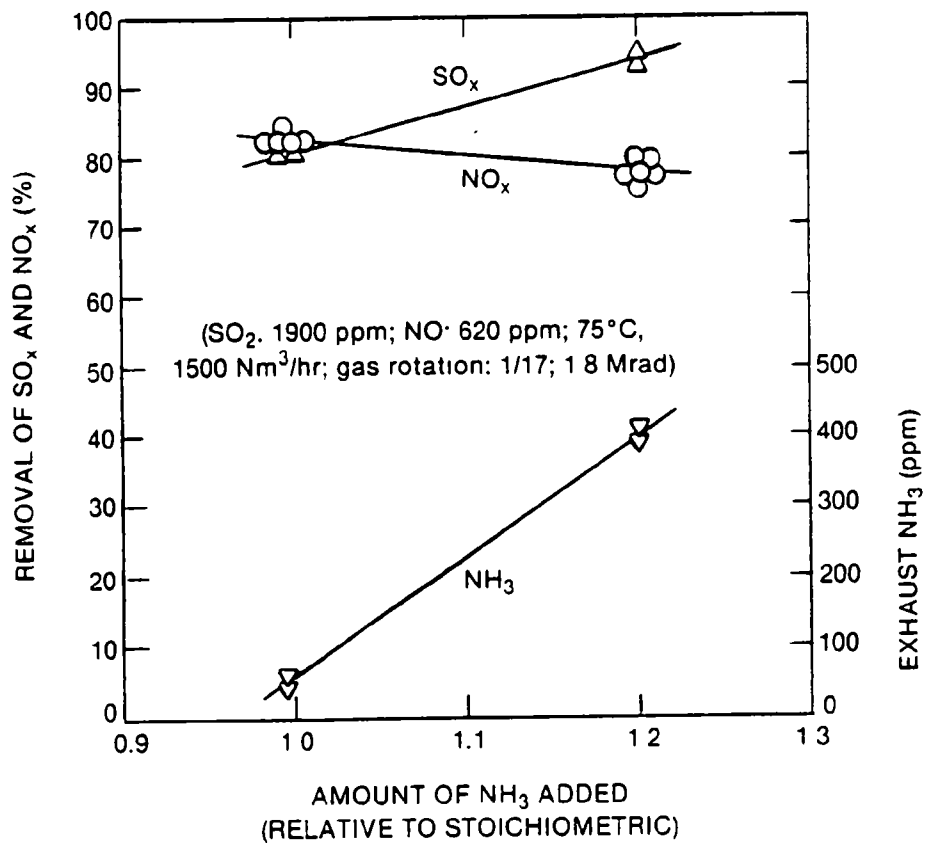


Figure 6-37 Removal of SO_x and NO_x vs. Amount of Ammonia Added.

two types of cooling. Presumably the fine water droplets in the spray combine with SO_3 to form sulfuric acid mists which promote the formation of SO_3 from SO_2 .

6.6.4 Ebara Process Commercial Plant Assumptions

Electron beam accelerators with capacities of 100 - 150 kW have been used commercially for various purposes without problems. A larger accelerator with a capacity of 500 kW will be commercialized in Japan in the near future. This 500 kW accelerator can treat 60,000 to 70,000 Nm^3/hr of flue gas. Since it is advantageous to use at least 2 accelerators with a reactor, an economical minimum capacity for a reactor may be 120,000 to 140,000 Nm^3/hr , which is equivalent to 35 to 50 MW.

Figure 6-38 shows a layout plan for a commercial Ebara process plant with a capacity of treating 1,000,000 Nm^3/hr of flue gas from a utility boiler (290 MW for coal and 350 MW for oil). The flue gas contains 60 ppm NO_x , 1,000 ppm SO_x , and 100 mg/Nm^3 of dust. In such a plant the 150°C flue gas is cooled by a heat exchanger to about 110°C and then indirectly cooled to 70°C with water tubes. The cooled gas is mixed with ammonia and treated by two reactors in parallel (diameter approximately 4 m), and sent through an ESP.

A total of 14-16 accelerators (500 kW each) may be used to remove 80% of NO_x and 90% of SO_x . The treated gas will probably contain 120 ppm NO_x , and 100 ppm SO_x , and less than 20 ppm unreacted NH_3 with about 15 mg/Nm^3 of dust.

Ebara estimated the investment cost of the electron beam process to be close to that of a conventional wet FGD system, provided that a large accelerator (500 kW) is available at a reasonable cost. The estimated utility requirements for the 1,000,000 Nm^3/hr plant are shown in Table 6-19. The electron beam system's total power consumption of 10,000 kWhr accounts for 2.9 to 3.4% of the power generated by the power plant. This power consumption is

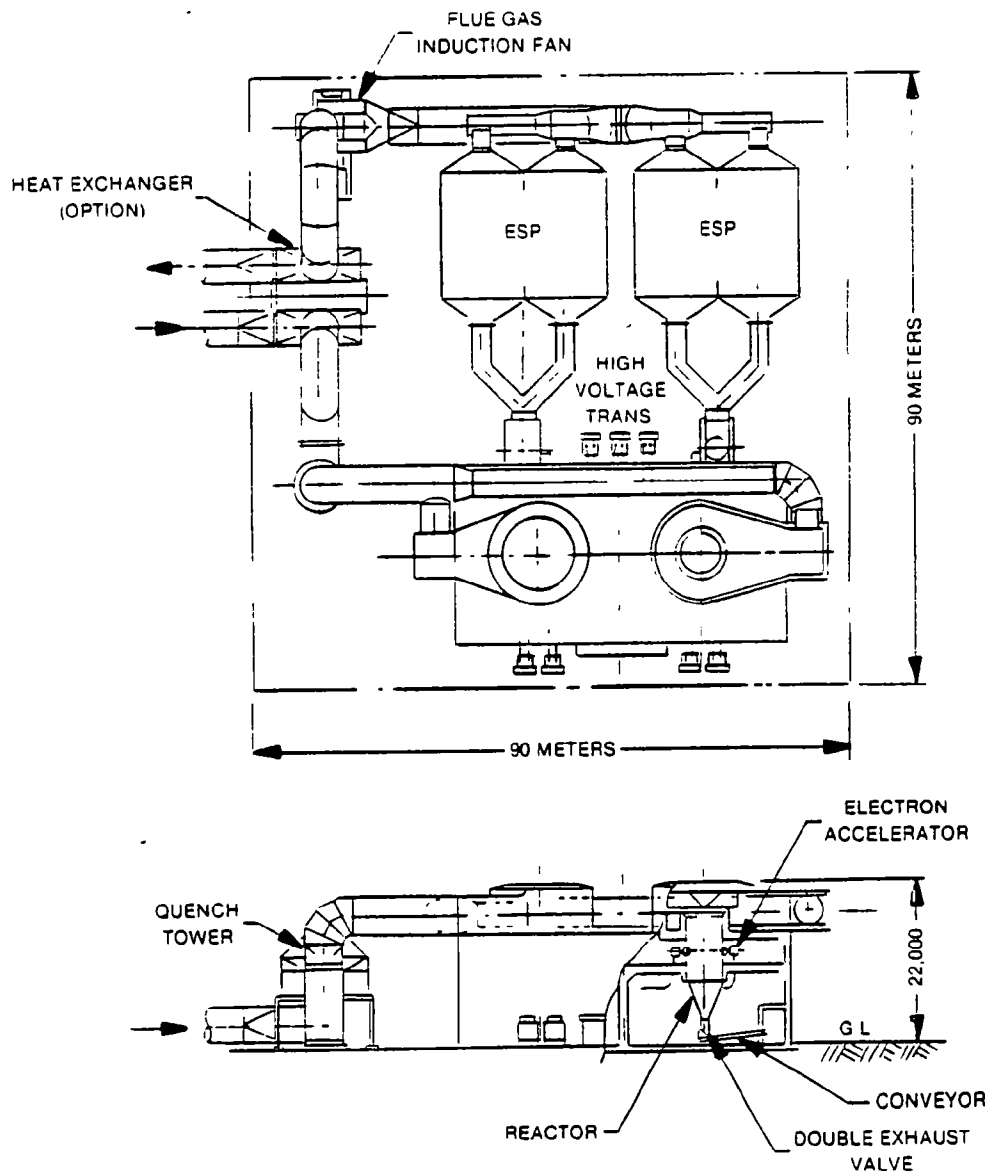


Figure 6-38 Layout Plan for a 1,000,000 Nm³/hr Commercial Ebara Process Plant

TABLE 6-19. ESTIMATED UTILITY REQUIREMENTS PER HOUR ESTIMATED FOR EBARA
PROCESS SYSTEM APPLIED TO A UTILITY BOILER
(FLUE GAS 1,000,000 Nm³/hr, 350 MW FOR OIL, 290 MW FOR COAL)

Power	Electron beam accelerator	6,900 kWhr
	Other	3,100 kWhr
	Total	10,000 kWhr
Steam	Ammonia vaporization	1 ton
	Soot blowing	1 ton
	Total	2 ton
Water	Gas cooling	33 ton
	Other	1 ton
	Total	34 ton
Ammonia	0.94 of stoichiometric amount	2 ton

TABLE 6-20. COST COMPARISON OF FLUE GAS TREATMENT PROCESSES (500 MWe) (13)
(Cost estimates established by Gibbs & Hill, Inc., New York. SO₂ = 1900 ppm,
90% removed; NO_x = 620 ppm, 90% removed; lime scrubber does not remove NO_x.)

	Avco/Ebara	Lime Scrubber
Total capital cost \$M	43	60
\$/kW	86	120
	(\$/MWh)	(\$/MWh)
Depreciation and overhead ^a	2.4	3.4
Variable operating cost ^b	2.5	2.8
Reheat cost	0	1.0
Total operating cost	4.9	7.2
Byproduct charge/(credit)	(0.6) ^c	0.4 ^d
Net operating cost	4.3	7.6
Total first year cost	\$14M	\$26M

^a 80% load factor; annual cost = 20% of total capital.

^b Ammonia at \$130/ton.

^c Sold as agricultural fertilizer at \$15/ton.

^d Does not include cost of disposal site and preparation.

slightly more than to that of a combination of SCR and wet FGD. SCR requires about 0.2% and FGD consumes 2 to 2.5% (excluding gas reheating) of the total power generated by the plant.

In Table 6-20 estimated costs for the AVCO/Ebara process are compared with the costs of lime scrubbing. The cost of the AVCO/Ebara process assumes the use of simple water spraying for gas cooling and is considerably lower than the cost of lime scrubbing.

6.6.5 Evaluation

The Ebara/AVCO electron beam irradiation process is unique and has the following advantages:

- (1) SO_x and NO_x are removed simultaneously.
- (2) Since it is a dry process, wastewater treatment is not necessary.
- (3) Ammonia, SO_x and NO_x are recovered as useful byproducts.
- (4) The process is simple; the only problem so far has been the need for occasional renewal of the foil at the accelerator window.

However, the process does have the following disadvantages:

- (1) For treating flue gas from coal, a dust removal facility is needed upstream of the reactor in order to obtain a useful byproduct.
- (2) Gas cooling to about 70°C is needed to obtain a high NO_x/SO_x removal efficiency.
- (3) Large amounts of NH_3 and N_2O may be emitted for high removal efficiencies from SO_x -rich gas.

Fly ash from coal has been used as fertilizer to supply micronutrients such as zinc and boron to certain soils. For this reason small amounts of fly ash in the Ebara process byproduct ammonium may be acceptable but large amounts decrease the compounds' fertilizer value.

Using a water spray for cooling is simpler and produces a higher SO_2 removal efficiency than indirect cooling. The gas can be cooled to 70°C without producing any wastewater. Unfortunately water spraying may cause the ammonium compounds to absorb moisture when a large amount of spray is used and the moisture content of the gas also exceeds the critical humidity for the compounds.

The amount of unreacted ammonia from the Ebara reactor may be reduced with improved control of ammonia addition. This can be achieved by measuring the concentration of outlet NH_3 as well as that of inlet SO_x and NO_x . The formation of N_2O may be also reduced, but cannot be prevented. A substantial concentration of N_2O occurs naturally, so the emission of a small additional amount will not produce any adverse environmental effect. Nonetheless, further study is necessary to determine ways of reducing N_2O formation.

Table 6-18 shows that a considerable portion of the byproducts deposited in the system ductwork. This deposition may be eliminated by increasing the gas velocity through the duct.

Although there are many simultaneous SO_x/NO_x removal processes, the Ebara process is the only one that may be commercially applicable for byproduct recovery of SO_x , NO_x , and NH_3 . Additional tests using a larger pilot plant with gases of various compositions will be necessary for definite proof of this commercial potential.

6.7 MKK POTASSIUM-EDTA WET SIMULTANEOUS SO_x/NO_x REMOVAL PROCESS

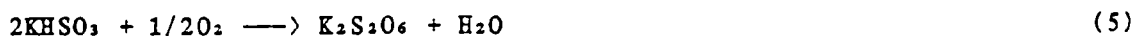
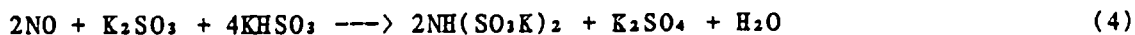
6.7.1 Introduction

The potassium-EDTA wet process simultaneously removes SO_x and NO_x from flue gas by using a solution containing potassium salts, ferrous sulfate, and EDTA (ethylenediamine tetraacetic acid). NO_x is converted to N₂ and SO_x to elemental sulfur. The process was developed by Mr. Y. Kobayashi who was associated with Mitsubishi Kakoki Kaisha (MKK) and is now with Hitachi Zosen (HZ). The process resembles the Kureha KDSN process which also uses potassium salts, ferrous sulfate, and EDTA to convert SO_x to elemental sulfur(4). Each process has been studied independently.

The MKK process is a combination of several commercially proven steps plus a few new steps; bench scale tests have been conducted on the new steps.

6.7.2 Process Description

Figure 6-39 presents a flowsheet of the MKK process. Flue gas is sent into an absorber and treated with a solution containing KHCO₃, K₂CO₃, FeSO₄, and EDTA. About 99% of SO_x and 90% of NO_x can be absorbed by the following reactions:



EDTA and FeSO₄ promote the absorption of NO by reaction (4) to form potassium imidodisulfonate (NH(SO₃K)₂). K₂SO₄, K₂S₂O₆ and NH(SO₃K)₂ are crystallized in the liquor, separated by a thickener and filter, and then heated in a two-stage flash dryer. The heater uses hot gas obtained by incineration of a portion of the H₂S that was produced by the reduction of the



potassium salts. The first stage of heating is for drying. During the second stage at 370°C, $K_2S_2O_6$ is decomposed to K_2SO_4 and SO_2 :

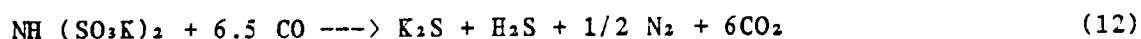
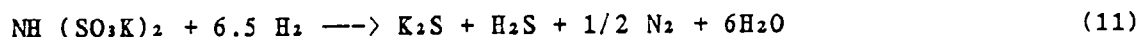


The SO_2 contained in the hot gas, as well as that released from the $K_2S_2O_6$, is absorbed by a solution containing K_2CO_3 and $KHCO_3$ (obtained by the carbonation of K_2S).



The liquor leaving the SO_2 absorber contains $KHCO_3$, K_2CO_3 and $KHSO_3$ and is mixed with EDTA, KOH, and $FeSO_4$, and sent into the main absorber. In the main absorber SO_x and NO_x are removed simultaneously by the 50-60°C liquor (pH 6.8-7.0). A large $(SO_2 + HSO_3)/NO$ ratio is needed in order to attain a high NO removal efficiency. Incineration of a portion of the recovered H_2S increases both the ratio and the NO removal efficiency.

The drying process produces a solid consisting of K_2SO_4 and $NH(SO_3K)_2$. The solid is caught by a cyclone, jet milled into a very fine powder of about 5 μ m, and then sent into a reduction furnace. In the furnace a 1,400-1,500°C hot gas instantaneously reduces the powder to K_2S at 800-900°C. The reducing gas is produced by the partial oxidation of fuel oil by oxygen and steam:



K_2S is dissolved in water and the solution is sent to the No. 1 carbonation tower where it is treated with CO_2 at 80-90°C (pH 9.5-12.5):



The resulting solution is carbonated at 40–60°C (pH of 8–9.5) in the No.2 tower:



In actual practice, 3 to 4 towers in series may be needed to attain a high carbonation efficiency.

As it leaves the tower, the liquor contains K_2CO_3 and KHCO_3 . Next it is sent into the SO_2 absorber; the gas (containing H_2S and CO_2) leaving the tower is sent into an H_2S absorber, where H_2S is selectively absorbed by an amine solution at 40°C.

The gas which leaves the H_2S absorber containing CO_2 is returned to the No. 2 tower. The liquor leaving the H_2S absorber is sent to the H_2S stripper, where steam is injected to vaporize H_2S . Most of the H_2S is sent to a Claus furnace where elemental sulfur is recovered and a portion of H_2S is incinerated. This produces a hot gas for the heating process. The amount of H_2S incinerated is adjusted according to the inlet O_2 , SO_2 , and NO_x concentrations and the required NO_x removal efficiency.

6.7.3 Requirements and Costs

Table 6-21 shows the amounts and costs of the estimated raw materials and utilities needed for an MKK system designed to treat 150°C flue gas from a 1,000 MW coal-fired boiler containing 4.5% O_2 , 900 ppm SO_x , 300 ppm NO_x , 50 ppm HCl , and 100 mg/ Nm^3 of fly ash. The system will remove 99% of SO_x and 80% of NO_x .

TABLE 6-21. UTILITY AND MATERIAL REQUIREMENTS AND COSTS OF AN MKK PROCESS SYSTEM FOR A MW COAL-FIRED BOILER (1980) (For 1000 MW hr)

	Consumption	Unit Cost	Cost (1000 Yen)
EDTA	282.9 kg	600 yen/kg	149.7
FeSO ₄	320 g	5 yen/kg	1.6
KOH	188 kg	150 yen/kg	29.0
High S oil (asphalt)	8690 l	50 yen/l	434.5
Low S oil	3450 l	57 yen/l	196.6
O ₂ (95%)	6400 Nm ³	yen/Nm ³	75.5
Power	29100 Kwhr	9 yen/Kwhr	261.9
Industrial Water	170 t	10 yen/t	1.7
Cooling water (sea water)	1250 t	2 yen/t	2.5
Others			8.0
TOTAL			1160.1
Recovered S	4280 kg	22 yen/kg	94.2

It is estimated that such a system produces 700 kg/hr of sludge containing fly ash as well as 2,030 kg/hr of wastewater. The wastewater is needed to prevent the accumulation of chlorine in the system.

The investment cost is estimated at 18.8 billion yen or 18,800 yen/kW. The annual cost for 7,000 hours full load operation is shown in Table 6-22.

The relationship between the annualized treatment cost and the inlet O₂ percentage, NO_x concentrations and NO_x removal efficiency is shown in Figure 6-40. The treatment cost increases sharply with an increase in the inlet concentrations and the removal ratio. An increase in the inlet SO₂ concentration, unlike a similar increase in the inlet NO_x concentration, does not have a significant effect on the cost. Over 99% of SO₂ is absorbed, even with 75% NO_x removal. Although an increase in SO₂ necessitates the treatment of a larger amount of potassium salts during the reduction and carbonation steps, a high SO₂/NO_x ratio favors NO_x removal and reduces the amount of H₂S needed to produce SO₂. It is also estimated that when the HCl concentration increases by 10 ppm, the cost subsequently increases by 0.037 yen/kWhr due to the larger amount of wastewater which must be treated.

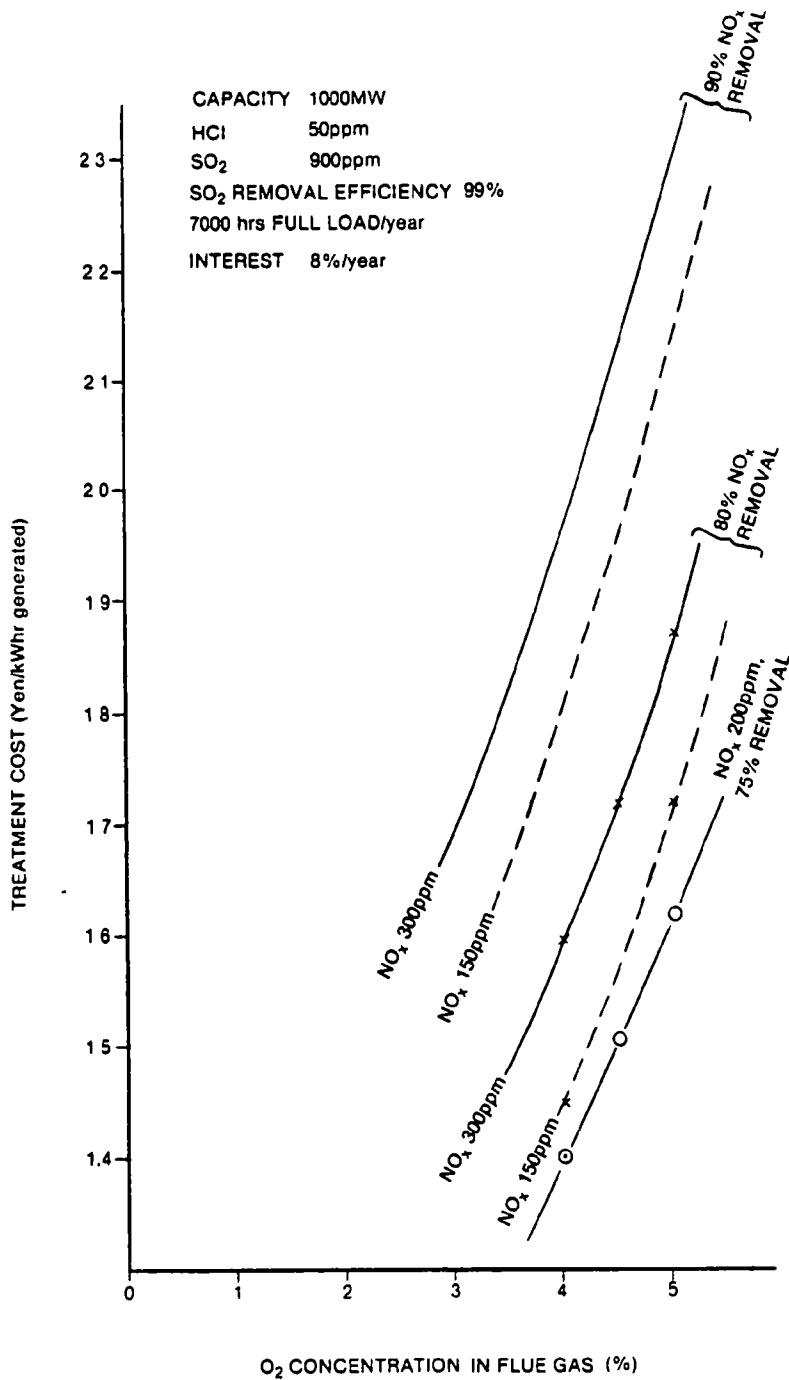


Figure 6-40 Annualized Cost for Various Operating Conditions in an MKK Process System.

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TABLE 6-22. ANNUAL COST OF AN MKK PROCESS SYSTEM
FOR A 1000 MW COAL-FIRED BOILER

Item	Calculation Basis	Cost (10 ⁶ yen)
(1) Capital Cost		
Depreciation	Investment Cost $\times 0.9 \times (1/7)$	2,417.1
Interest	" $\times 0.08 \times 0.55$	827.2
Tax	" $\times 0.014 \times 0.55$	144.8
Insurance	" $\times 0.4 \times 0.003$	22.6
Total		3,411.7
(2) Direct Cost		
Labor	8,000 \times 24 (person)	192.0
Maintenance	Investment cost $\times 0.015$	282.0
(3) Chemicals		
Utilities	1,116,100 \times 7000	8,120.7
(4) Related cost	(2) + (3) $\times 0.08$	687.6
(5) Total	(1) + (2) + (3) + (4)	12,694.0
(6) By-product S	94,200 \times 7,000	659.4
(7) Difference		12,034.5
ANNUALIZED COST	(7) 7,000,000,000 (kWhr)	1.719 yen/kWhr

6.7.4 Evaluation

The MKK system is a combination of several steps most of which have been proven to be feasible through commercial operation or pilot plant tests. One exception is the step in which K_2SO_4 and $NH(SO_3K)_2$ are instantaneously reduced to K_2S . Basic chemical and thermodynamic studies related to the process have been conducted, although the total system has not been tested yet at a pilot plant.

One advantage that potassium scrubbing has over sodium scrubbing is that K_2SO_4 , $NH(SO_3K)_2$, and $K_2S_2O_8$ are less soluble than the corresponding sodium salts, and can be separated from the mother liquor. On the other hand, for carbonation of K_2S , a larger CO_2/H_2S ratio is needed than for Na_2S , because $KHCO_3$ is more soluble than $NaHCO_3$ and cannot be crystallized out.

The use of oxygen instead of air in the MKK system substantially reduces fuel consumption, gas volume, and reactor size. Moreover, the loss of CO_2 is eliminated because it is not necessary to purge N_2 as it is when air is used. Thus, the overall cost may be reduced by using oxygen.

Simultaneous SO_x and NO_x removal and the conversion of SO_x to elemental sulfur are other advantages of the MKK process. However, the process does require complex equipment including an oxygen generator, Claus furnace, and wastewater treatment system in addition to the facilities shown in Figure 6-39. Pilot plant tests on the reduction and carbonation steps are needed to prove the feasibility of the process. Although the wastewater treatment system appears to be complex, it may not prove to be a serious problem because of the small quantity of wastewater produced.

The system has a silo for solids storage and a storage tank for the absorbing liquor. This allows the continuous operation of the absorber and reduction furnace even when other steps in the process must shut down.

The estimated investment and operation costs for an MKK system are slightly lower than those for a combined SCR/FGD system. For more accurate cost estimates, a pilot plant test of the entire system is necessary. Since 90% NO_x removal requires a large multi-stage absorber and a large pressure drop, 80% removal may be more practical. Because its cost increases sharply with increases in the inlet O_2 and NO_x concentrations, the MKK process may be best suited to flue gas from high-sulfur oil rather than from coal. An increase in the SO_2 content of flue gas does not significantly increase the operation cost since it aids in NO_x removal.

The MKK process, as well as the Kureha KDSN process, is sophisticated and probably will not be used commercially in the near future. The ability of both of these processes to byproduce elemental sulfur and to remove NO_x without using ammonia is an attractive feature. This type of NO_x/SO_x removal technology should be further studied as a possible alternative to the SCR/FGD combination. The latter may experience problems when widely used, due

to its ammonia consumption and the difficulty associated with disposal of its byproduct sulfur compounds.

6.8 NO OXIDATION CATALYST

6.8.1 Introduction

Almost all of the NO_x in combustion gases is present in the form of NO. NO is only slightly absorbed in most solutions except for those which contain a complexing agent such as EDTA with ferrous ion. NO_2 , on the other hand, is readily absorbed in solutions. The equimolecular mixture of NO_2 and NO is also fairly well absorbed. In several wet NO_x removal processes, most of the NO is first oxidized to NO_2 using chemicals such as ozone or chlorine dioxide. However, these chemicals are expensive or cause wastewater treatment problems.

In the air NO is oxidized slowly to NO_2 . As the temperature increases this reaction rate also increases, but a high temperature lowers the NO conversion ratio in equilibrium. The theoretical NO/ NO_2 conversion ratio in air is about 80% at 300°C and 20% at 500°C . Catalytic oxidation of NO at a relatively low temperature may cause the conversion of a considerable portion of NO in a short time period.

6.8.2 Catalytic Oxidation Tests

In Japan, H. Tominaga has conducted extensive studies of catalytic oxidation of NO to NO_2 (13). Tominagas' preliminary tests indicate that zeolite impregnated with heavy metals is effective as a catalyst. He used synthetic zeolite (molecular sieve) 13X and 13Y after the Na ion was exchanged with heavy metal ions. Heavy metal compounds of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were used for the ion exchange. The exchange ratio was 67% with Cu (II), 44% with Cr (III), 74% with Co (II), and 47% with Ni (II).

A pyrex glass tube (13 mm inner diameter and 500 mm long) was used for the fixed bed reactor. Mixtures of NO and O₂, diluted with He, were passed through the reactor after being preheated. In some of the tests, the effects of adding H₂O and SO₂ to the gas were studied. Two grams of catalyst between 10 mesh and 40 mesh were used for an SV of 30,000 hr⁻¹, four grams for an SV of 15,000 hr⁻¹. Results of tests using 13x catalysts are shown in Figure 6-41.

It is interesting to note that in some of the tests with the Cr (III) catalyst the conversion ratio exceeded 70% (above the theoretical value) at 400°C in the presence of water vapor.

6.8.3 Evaluation

At 400°C or below, the catalysts tested by Tominaga are poisoned by SO₂. Although the poisoning is not noticeable at 450°C, the conversion ratio at this temperature may be too low to be useful. For this reason, the process does not seem to be applicable to SO₂-rich gas.

The process may work well for gases which do not contain SO_x. With these gases it can be used to convert about 50% of NO to NO₂ at 350°-400°C, in order to achieve equimolecular absorption.

6.9 OTHER PROCESSES AND PLANTS

6.9.1 Copper Oxide Process for Simultaneous NO_x/SO_x Removal (Shell Process)

In 1973, Showa Yokkaichi Sekiyu Co. (SYS) installed at its Yokkaichi Refinery, a Shell Process FGD unit which uses copper oxide as the acceptor. In the process, SO_x absorption forms copper sulfate, which is treated with hydrogen to regenerate Cu and concentrated SO₂ gas. The latter is sent to a Claus furnace for production of elemental sulfur.

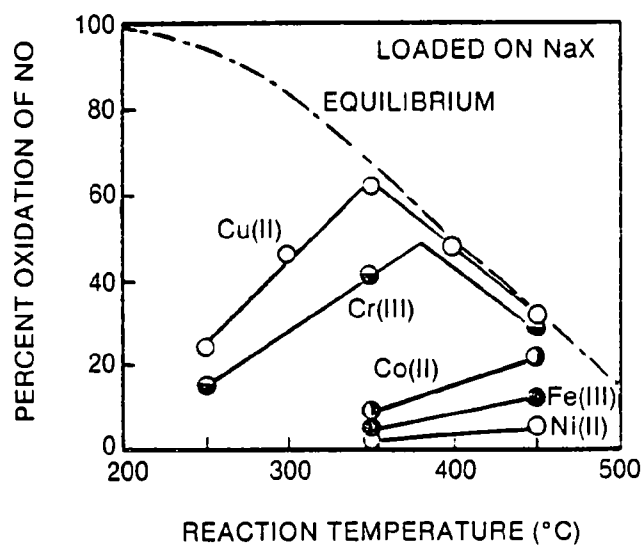


Figure 6-41 Oxidation Ratio vs. Catalyst Type and Temperature.

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Since copper sulfate is a catalyst for SCR of NO_x , ammonia has been added to flue gas since 1975 to remove about 40% of NO_x and about 90% of SO_x to meet the local regulation(1). The operability of the unit, however, has been low except that for one year of continuous operation in 1978. SYS does not plan to install a new unit.

6.9.2 Activated Coke Simultaneous Removal (Mitsui Mining Process)

Mitsui Mining Company has developed a simultaneous SO_x/NO_x removal process which uses activated coke produced by a special coal treatment. A pilot plant with a capacity of treating 1,000 Nm^3/hr of flue gas from an oil-fired boilers at 150°C has been operated to remove over 80% of the NO_x and about 98% of the SO_2 . Coal fly ash was added to the flue gas to study the effect of the ash. The pilot plant has two reactors in series; most of the SO_2 is absorbed in the first reactor by the coke. A small portion of ammonia is fed to the first reactor, but the major portion is fed to the second reactor where most of the NO_x is converted to N_2 and H_2O by reacting with the ammonia. SO_2 is further adsorbed in the second reactor.

The adsorbed SO_2 is regenerated by a hot gas. The recovered concentrated SO_2 may be used for sulfuric acid or liquid SO_2 production. Mitsui Mining has conducted some studies on a method of producing elemental sulfur from the SO_2 .

6.9.3 Molecular Sieve Process for NO Adsorption

Nissan Chemical Industries installed an NO_x recovery plant which uses a molecular sieve produced by Union Carbide Corp. USA, to treat 22,000 Nm^3/hr of tail gas from a nitric acid plant. The plant reduces the NO_x concentration in gas from 1,000 ppm to 50 ppm (1). The adsorbed NO_x eventually is thermally desorbed and returned to the nitric acid plant. The plant was commissioned in 1976 and has operated successfully for over five years without requiring any replacement of the original molecular sieve.

6.9.4 Sumitomo-Fujikasui Wet Simultaneous Removal Process

Sumitomo Metal and Fujikasui Engineering have developed a wet simultaneous removal process which uses ClO_2 as the oxidizing agent and NaOH as the absorbent. In 1973 and 1974 they constructed three medium-sized commercial plants, as shown in Table 6-2. The process can remove about 90% of both SO_x and NO_x but may not be suitable for large plants, because a large amount of NaOH is consumed and the waste liquor containing sodium chloride, nitrate, and sulfate must be treated (1).

Sumitomo and Fujikasui have also developed a modified process which uses ClO_2 as the oxidizing agent and CaCO_3 slurry containing a catalyst as the absorbent. In 1976 they built a demonstration plant which can treat 25,000 Nm^3/hr of flue gas from an iron ore sintering machine. The modified process is less costly than the sodium process but still produces waste liquor containing calcium chloride and nitrate which requires treatment (1). There has been no further development of either of the processes.

6.9.5 In-Furnace NO_x Removal (Three Stage Combustion - Hitachi Zosen) (15)

Hitachi Zosen has conducted tests of in-furnace NO_x removal, a process they call "three stage combustion". The process is similar to the MACT process described in Section 6.4. Figure 6-42 shows a horizontal cylindrical test furnace with a length of 7m and an inner diameter of 1.5m. The furnace has a capacity of burning 200 kg/hr of pulverized coal. Some of the three stage combustion test results are shown in Figure 6-43. The NO_x concentration was about 800 ppm with a conventional burner, 600 ppm with a staged-combustion burner, and about 100 ppm when 30% of the coal was injected as the secondary fuel, with air introduced for complete combustion. In all of the tests, the CO in the flue gas was below 100 ppm and the amount of combustible components in the fly ash was less than 5%.

Hitachi Zosen plans to conduct additional tests using a larger furnace which can burn 2,000 kg/hr of pulverized coal.

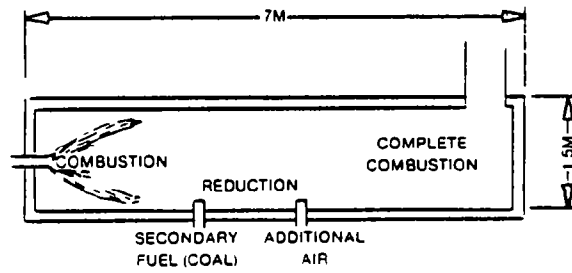


Figure 6-42 Hitachi Zosen's Three Stage Combustion Test Furnace

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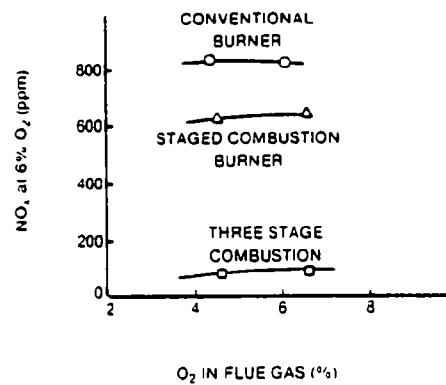


Figure 6-43 Results of Three Stage Combustion Tests (In furnace combustion)

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