

FEASIBILITY AND COSTS OF
APPLYING NO_x CONTROLS ON STATIONARY EMISSION
SOURCES IN CALIFORNIA

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ABSTRACT

The feasibility and costs of various NO_x control methods, i.e., ammonia-based reduction and low NO_x burners, were determined for potential application to eight selected stationary sources of nitric oxide (NO_x) emissions in California, primarily in the Los Angeles area. The applicability of selective ammonia-based reduction systems, both catalytic and noncatalytic, were studied for seven major NO_x sources: simple and combined cycle turbines used by electric utilities, an internal combustion engine used in compressing natural gas, an oil refinery process heater, an oil field steam generator used in thermally enhanced oil recovery, a cement kiln, and a glass melting furnace used in the manufacture of flat glass. Although the units selected were considered as representative either in terms of size, operation, or numbers in use, the results apply specifically to them.

A 90% NO_x reduction criterion was defined by the California Air Resources Board staff for these sources except for the oil field steam generator and refinery heater. For the refinery heater the criterion was 50% and for new and existing oil field steam generators was 70 and 50%, respectively. In addition, the potential reduction that could be expected by using low NO_x burners on utility boilers and other emission sources was also assessed.

The major feasibility emphasis in this study was on the applicability of existing control technology. Technical feasibility for NO_x control was evaluated on the basis of control technology developed in Japan and currently being considered for application in the United States. Other factors such as the compatibility of control measures with the emission source and power and exhaust gas reheat requirements were also addressed.

It was concluded that all NO_x emission sources studied could utilize selective catalytic reduction (SCR) to achieve the specified percent reduction in NO_x levels. Thermal denitrification (DeNO_x), i.e., selective noncatalytic reduction, was determined to be applicable in only those instances where reductions of 50 to 70% relative to current levels were specified but at significantly lower costs than for SCR installations. The use of thermal DeNO_x to achieve 90% reduction is not feasible for any of these sources.

The benefit for further reduction in NO_x emission rates resulting from the use of low NO_x burners in utility boilers in combination with combustion modifications currently in use, i.e., two-stage firing and off-stoichiometric combustion, appear somewhat limited. Further reductions of approximately 10% appear realistic, with additional reductions possible depending on specific boiler and burner characteristics.

Capital investment estimates for early 1979 reflecting estimated retrofit complexity factors for the various installations are provided. Annual control in terms of mills per kilowatt hour, dollars per pound NO_x removed, dollars per million Btu thermal input, and dollars per ton product, as appropriate, are reported.

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CONVERSION TABLE

British	Metric
1 inch	2.540 centimeters
1 foot	0.3048 meter
1 cubic foot	28,316 cubic centimeters; 0.028316 cubic meters
1 gallon	3.785 liters
1 pound	454 grams
1 ton (short)	0.9072 metric ton
1 pound per square inch	0.0703 kilogram per cubic centimeter
1 pound per square foot	0.1602 gram per cubic centimeter
1 British thermal unit (Btu)	252 calories
1 pound per million Btu	0.430 gram per million joules; 1.80 grams per million calories
1 Btu per pound	2.324 joules per gram; 0.555 calorie per gram
1 grain	64.8 milligrams
1 grain/SCF	2.29×10^3 milligrams/Nm ³

GLOSSARY

ACFM	actual cubic feet per minute
AIG	altered fuel injection geometry
AV	area velocity
BBF	biased burner firing
BOOS	burners out of service
bbl	barrel
CM	combustion modification
COG	coke oven gas
CPCC	California Portland Cement Company
CRIEPI	Central Research Institute for Electric Power Industry (Japan)
DeNO _x	denitrification
DWP	Los Angeles Department of Water and Power
EER	Energy and Environmental Research, Inc.
ERE	Exxon Research and Engineering Company
ESP	electrostatic precipitator
FB	fixed bed
FGR	flue gas recirculation
GPH	gallons per hour
GPM	gallons per minute
IC	internal combustion
IHI	Ishikawajima-Harima Heavy Industries, Co., Ltd.
JGC	JGC Corporation
KHI	Kawasaki Heavy Industries, Ltd.

1. INTRODUCTION AND SUMMARY

The State of California Air Resources Board is evaluating the potential for reducing nitric oxide (NO_x) emissions from utility power plants and other stationary sources, primarily in the Los Angeles area.

This study examines the feasibility and costs of installing ammonia-based reduction systems, both catalytic and noncatalytic for seven specific sources of NO_x : simple and combined cycle turbines used by electric utilities, an internal combustion engine used in compressing natural gas, an oil refinery process heater, an oil field steam generator used in thermally enhanced oil recovery, a cement kiln, and a glass melting furnace used in the manufacture of flat glass. It also examines the potential application of low NO_x burners to utility boilers and the other seven NO_x emission sources. Although the units selected (Table 1-1) were considered as representative either in terms of size, operation, or numbers in use, the assessments apply specifically to them.

A 90% NO_x reduction criterion was defined by the California Air Resources Board staff for these sources except for the oil field steam generator and refinery heater (Table 1-2). For the refinery heater the criterion was 50%, and for new and existing oil field steam generators the criteria were 70 and 55%, respectively (Table 1-3). In addition, the potential reduction that could be expected by using low NO_x burners (LNB) on utility boilers and other emission sources was also assessed.

The study involved a number of considerations including the following:

- a. Characterization of the selected NO_x emitting equipment.
- b. Assessment of LNB, selective catalytic reduction (SCR), and thermal denitrification (DeNO_x) technology.
- c. Evaluation of applicability of NO_x control systems to the various emission sources.
- d. Determination of control system applicability and control costs.

TABLE 1-1. EMISSION SOURCES STUDIED

NO _X EMISSION SOURCE	EQUIPMENT CHARACTERISTICS
Utility Boiler	175 MW boiler with existing combustion modifications, operated by Southern California Edison (SCE)
Simple Turbine	121 MW installation, 8 JP5-fired gas turbines, operated by SCE
Combined Cycle Turbine	236 MW installation, 2 oil-fired gas turbines and associated waste heat boilers, operated by SCE
Internal Combustion Engine	2000 HP two-cycle turbocharged, natural gas-fired engine, operated by Southern California Gas Company
Oil Field Steam Generator	50 million Btu/hr crude oil-fired unit, operated by various oil producers in Kern County, California
Refinery Heater	65 million Btu/hr, refinery gas-fired unit operated by Chevron, USA, El Segundo, CA
Cement Kiln	45 ton/hr coal-fired kiln operated by California Portland Cement Company, Colton, CA
Glass Melting Furnace	Natural gas-fired furnace for producing flat glass operated by PPG Industries, Fresno, California

TABLE 1-2. NO_x REDUCTION CRITERIA

EMISSION SOURCE	NO _x REDUCTION CRITERIA
1. Utility boiler- 175 MW with existing combustion modifications	Potential reduction based on state-of-the-art application of low NO _x burners
2. Simple turbine-electric utility application	90% reduction
3. Combined cycle turbine-electric utility application	90% reduction
4. Internal combustion engine-natural gas storage field application	90% reduction
5. Oil field steam generator thermally enhanced oil recovery (TEOR) application	a) 100 ppm (approximately 70% reduction) for new units b) 150 ppm (approximately 55% reduction) for existing units
6. Oil refinery process heater	50% reduction
7. Cement kiln	90% reduction
8. Glass melting furnace-flat glass	90% reduction

TABLE 1-3. NO_x REDUCTION CRITERIA AND CONTROL METHODS STUDIED

Emission Source ^a	NO _x Reduction Criteria	Feasibility of NO _x Control Assessed ^{b, c}		
		Low NO _x Burner	Thermal DeNO _x	SCR
Utility Boiler	State-of-the-Art	X	- ^d	- ^d
Turbine (Simple)	90%	X	X	X
Turbine (Combined Cycle)	90%	X	X	X
I. C. Engine	90%	X	X	X
Oil Field Steam Generator	70% (New) 55% (Existing)	X	X	X
Refinery Heater	50%	X	X	X
Cement Kiln	90%	X	X	X
Glass Furnace	90%	X	X	X

^aSee Table 1-1 for identification of specific sources

^bApplication of only individual control methods assessed per study ground rules

^cSee Table 1-7 for applicability

^dNot part of study

For the data needed to characterize an emission source, information was derived from conferences with cognizant technical personnel from the various companies involved in its operation. The responses of various organizations to questionnaires developed by The Aerospace Corporation also were used.

The major feasibility emphasis in this study was on the applicability of existing control technology. Technical feasibility for NO_x control was evaluated on the basis of control technology developed in Japan and currently being considered for application in the United States. Information developed through discussions with personnel knowledgeable of the details of the Japanese NO_x control processes and applications and those familiar with U.S. technology was used to augment published data.

The applicability of a control system and its potential for meeting the NO_x reduction criterion when installed on a specific emission source was then determined.

Based on budget-type information from a number of sources, capital investment estimates were prepared for retrofitting controls on the NO_x emitting equipment. Levels of installation complexity and equipment redundancy, as appropriate, were defined. Annual costs were defined which included capital charges and operating and maintenance costs. Costs associated with plant or unit shutdown for installation of control equipment were not included.

1.1 NO_x EMISSION SOURCE CHARACTERIZATION

The characteristics of each of the eight stationary sources; i.e., size, fuel, operation, and thermal input are summarized in Table 1-4. The thermal input of the various equipment ranges from 12.6 million Btu/hr for the internal combustion (IC) engine to 1645 million Btu/hr for the utility boiler, corresponding to 1.3 and 175 MW_e (electrical equivalent), respectively.

NO_x emissions range from 6.7 lb/hr NO_x as NO_2 ($3.2 \text{ lb}/10^6$ Btu input) for the IC engine to 627 lb/hr ($0.38 \text{ lb}/10^6$ Btu) for the utility boiler (Table 1-5).

TABLE 1-4. EMISSION SOURCE CHARACTERISTICS OF SOURCES STUDIED

EMISSION SOURCE ^a	SIZE	FUEL	THERMAL INPUT		MW ^e	OTHER
			BTU/HR	(000,000)		
UTILITY BOILER	175 MW	NO. 6 OIL	1645		175	WITH EXISTING TWO-STAGE COMBUSTION OR OFF-STOICHIOMETRIC FIRING
TURBINE (SIMPLE)	121 MW	JP-5	1720		121	8 TURBINES
TURBINE (COMBINED CYCLE)	236 MW	NO. 2 OIL	1480		236	2 TURBINES, 2 WASTE HEAT BOILERS
I. C. ENGINE	2000 HP	NATURAL GAS	12.6		1.3 ^b	2 CYCLE, SUPERCHARGED
OIL FIELD STEAM GENERATOR	50 MMBTU/HR OUTPUT	RECOVERED CRUDE OIL	62.5		6.6 ^b	FORCED DRAFT
REFINERY HEATER	65 MMBTU/HR INPUT	REFINERY GAS	65		6.8 ^b	NATURAL DRAFT
CEMENT KILN	45 TPH	COAL	180		18.9 ^b	DRY PROCESS
GLASS MELTING FURNACE	-- ^c	NATURAL GAS	146		15.4 ^b	FLAT GLASS (FLOAT PROCESS)

^a See Table 1-1 for identification of specific sources

^b Electrical output equivalent based on 9400 Btu/kW

^c Capacity not disclosed

TABLE 1-5. NO_x EMISSIONS FROM STATIONARY SOURCES STUDIED

EMISSIONS SOURCE ^a	CURRENT NO _x EMISSIONS		
	ppm, Dry, 3% O ₂	lb/hr as NO ₂	lb/10 ⁶ BTU Input
UTILITY BOILER	288	627	0.38
TURBINE (SIMPLE)	415	588	0.34
TURBINE (COMBINE CYCLE)	76	140	0.09
I. C. ENGINE	3365	40.2	3.19
OIL FIELD STEAM GENERATOR	335	22.2	0.39
REFINERY HEATER	77	6.7	0.10
CEMENT KILN	274	146	0.81
GLASS FURNACE	834	220	1.51

^aSee Table 1-1 for identification of specific sources

1.2 CONTROL SYSTEM TECHNOLOGY AND APPLICABILITY TO EMISSION SOURCES

Control technology and its application in Japan and the U.S. were examined. This was based on the reduction criteria for the various sources defined for the study by the research staff of the California Air Resources Board and on the use of LNB, thermal DeNO_x, and SCR (Table 1-3).

1.2.1 Low NO_x Burners

Low NO_x burners are widely used in Japan on utility and industrial boilers and on other industrial processes. The NO_x reduction is influenced by the burner configuration, size, type of fuel burned (oil, gas, coal, and fuel nitrogen content), and type of combustion modifications (CM) implemented prior to the use of LNB; in no instance did it approach 90%. As an example for one type of LNB with heavy oil, NO_x was reduced from 18 to 42% when operated without other CM techniques in use. When 40% reduction was achieved by other types of CM, such as flue gas recirculation (FGR), staged combustion, water injection, or a combination of these, further reductions of 10 to 20% were achieved by the addition of an LNB, for a total removal of 50 to 60% (Ref. 1-1).

The potential for further reduction in NO_x emission rates resulting from the use of LNB in combination with CM currently in use on oil-fired utility boilers in the Los Angeles basin, i.e., two-stage firing (TSC) and off-stoichiometric combustion (OSC), appears somewhat limited. On the basis of average conditions, further reductions of approximately 10% appear realistic with the addition of LNB, bringing the total to 27 and 41% for the boilers with existing TSC and OSC, respectively (Table 1-6).

The potential for meeting the NO_x reduction criteria defined in this study for the other emission sources with LNB was not evident and is reflected in the summary presented in Table 1-7.

1.2.2 Selective Catalytic Reduction

NO_x, which is virtually all nitric oxide (NO), is reduced to N₂ and H₂O by ammonia in the presence of certain base metal catalysts. In order to achieve a 90% reduction, temperatures in the range of 340 to 380°C (645 to

TABLE 1-6. EFFECT OF ADDING LOW NO_x BURNER TO 175 MW OIL-FIRED UTILITY BOILERS

	AVG. RED, %	EMISSIONS AT MAX LOAD				LNB NO _x REDUCTION
		FROM		TO		
		PPM	LB/HR	PPM	LB/HR	
LNB*	55(MAX)	360	790	162	355	435
LNB*	27	360	790	263	577	213
TSC**+LNB	27	288*	632	263	577	55
OSC***+LNB	41	238**	522	213	467	55

* Low NO_x burner, Japanese data (Ref. 1-1).

** 20% for two stage combustion (TSC)

*** 34% for off-stoichiometric combustion (OSC)

TABLE 1-7. FEASIBILITY OF NO_x CONTROL METHODS FOR UNITS STUDIED

STATIONARY SOURCE ^a	STUDY CRITERIA, % REDUCTION	NO _x CONTROL METHODS		
		LNB	THERMAL DENO _x	SCR
UTILITY BOILER	STATE-OF-THE-ART	YES	N/S ^b	N/S
STATIONARY TURBINE	90	N/I ^c	NO	YES
COMBINED CYCLE TURBINE	90	N/I	NO	YES ^d
I. C. ENGINE	90	N/I	NO	YES
OIL FIELD STEAM GENERATOR	70 (NEW) 55 (EXISTING)	NO	YES	YES ^e
REFINERY HEATER	50	NO	YES	YES
CEMENT KILN	90	NO	NO	YES ^f
GLASS FURNACE	90	NO	NO ^g	YES

^aSee Table 1-1.

^bN/S = Not specified as part of study.

^cN/I = Not implementable

^dReheat of exhaust gas, 41.4 bbl/hr required. Equivalent 108% of fuel burned for waste heat boiler.

^eReheat of exhaust gas, 0.5 bbl/hr required. Equivalent 0.13% of fuel burned in steam generator.

^fReheat of exhaust gas, 4.6 bbl/hr required. Equivalent 14.4% of thermal input to kiln.

^gPotential for 50% reduction without major modification may be feasible.

715°F) are required in the reactor with an NH_3 to NO_x ratio of 0.9 to 1.1. Small quantities of oxygen in amounts normally present in the emissions as a result of excess air in the combustion process are needed. Exhaust gas characteristics of the units studied are summarized in Table 1-8.

In all cases SCR is capable of meeting the NO_x reduction criteria (Table 1-7). For the IC engine and refinery heater studied, the exhaust gas temperatures are appropriate for SCR. However, in some situations, such as the combined cycle turbine, oil field steam generator, and cement kiln, heating of the exhaust gas is necessary to achieve the required temperature levels; for the simple turbine and glass furnace, cooling (such as by air dilution) is required. Although development of a low-temperature catalyst of 225 to 325°C has been conducted in Japan, use of such catalysts was not considered for this study because they are not as well developed as those operating in the 300 to 400°C range. Catalysts capable of operating at high temperatures, approximately 650°C, are being developed in Japan; however, their use was not considered current technology.

Catalyst life and reactivity are affected by catalyst configuration, sulfur dioxide, particulates, and other constituents in the gas such as alkalis. In most cases the exhaust gases from the sources studied were relatively clean, except for the oil field steam generator, which contains SO_2 and particulates, and for the cement kiln and glass furnace, which involve high exhaust gas particulate content and alkalinity. Although SO_2 -resistant catalysts are available, existing rules limiting SO_2 emissions from oil field steam generators will result in approximately 90% reduction in SO_2 , thereby appreciably reducing the SO_2 content in the exhaust gas. Use of wet scrubbers to accomplish this would also reduce particulate levels wherein they would not be a significant factor. The cement kiln studied has a particulate removal system (baghouse), and the particulate concentrations exiting are such that they are not expected to present severe problems for catalysts with parallel flow-type catalyst configurations such as those with honeycomb, tubular, or parallel plate shapes. Vendor recommendations indicate the need for an electrostatic precipitator on the glass furnace installation.

TABLE 1-8. STATIONARY SOURCE EMISSIONS NO_x REMOVAL CRITERIA

Emission Source ^a	Current Emissions		Exhaust Gas Temp, °F (°C)	Other Emissions (Uncontrolled) Affecting NO _x Controls		
	NO _x , lb/hr ^b	% O ₂ at Stack Exit		SO ₂	Particulates	Offsetting Factors
Utility boiler	627 ^c	2-3	155(69)	NA ^d	NA	--
Turbine (Simple)	588	15	300(149) ^e	NA	NA	--
Turbine (Combined) Cycle	140	14	300(149)	NA	NA	--
I. C. Engine	40.2	18	650(343)	NA	NA	--
Oil Field Steam Generator	22.2	4	450(232)	885 ppm (80.3 lb/hr)	0.064 gr/SCF (147 mg/Nm ³)	Regulatory Requirements - 90% SO ₂ Removal ^f
Refinery Heater	6.7	4	770(410)	NA	NA	--
Cement Kiln	146	14	390(199)	NA	0.01 gr/SCF (23 mg/Nm ³)	Periodic Water Wash of Catalyst
Glass Furnace	220	5	450(230) ^g	NA	0.023 gr/SCF (54 mg/Nm ³)	Electrostatic Precipitator

^aSee Table 1-1 for identification of specific sources

^bAs NO₂

^cAt full load

^dNot affected

^eTemperature at turbine exit: 900°F (482°).

^fSO₂ removal by wet scrubbing reduces particulates

^gTemperature at second regenerator exit: 1000°F (540°C)

Unreacted NH_3 concentrations in the exhaust gas of approximately 10 ppm are typical with NH_3/NO_x ratios of 1.0 and 90% removal. Limits on NH_3 emissions have not been established either in the U.S. or Japan. In general the control systems in Japan are designed to limit the NH_3 concentration to 10 ppm or less. Under certain conditions unreacted ammonia tends to be a problem. At low exhaust gas temperatures in those systems containing SO_x in the exhaust, SO_3 combines with NH_3 to form NH_4HSO_4 , which at temperatures below 250 to 300°C tends to condense on the catalyst, thereby reducing its activity. In installations with air preheaters downstream of the SCR reactor, the bisulfate may tend to plug passages. Intermittent heating of the catalyst or equipment surfaces to temperatures above 350°C will remove the sulfate and, in the case of the catalyst, restore its activity.

Considering all these factors, it was concluded that SCR is applicable to the emission sources studied. The catalyst bed sizes to achieve the reduction criteria are shown in Table 1-9.

The catalyst volume is based on the space velocity (hr^{-1}) and superficial velocity correlations for honeycomb-type catalysts to remove the specified levels of NO_x . For example, 50% removal requires a catalyst volume of approximately 30% of that for 90% removal from a gas with the same conditions.

1.2.3 Thermal Denitrification (Selective Noncatalytic Reduction)

Ammonia reacts selectively with NO at approximately 1000°C (1830°F), forming N_2 and H_2O . As in the case of SCR, DeNO_x requires the presence of a small amount of O_2 for the reaction to occur. Exxon Research and Engineering Company has patented the noncatalytic reduction process as well as the introduction of hydrogen, which reduces the temperature window at which the reaction occurs.

Tests have shown that the temperature range over which appreciable NO reduction occurs is approximately 100°C (180°F) and the reduction levels are a function of the NH_3 to NO ratio and the time during which the reactants are at the appropriate temperature. Introducing hydrogen maintains the selectivity of the NO reduction reaction, and depending on the amount of H_2 introduced (up to H_2 to NH_3 ratios of 2) the location of the temperature

TABLE 1-9. ESTIMATED CATALYST BED SIZE FOR SELECTIVE CATALYTIC REDUCTION REACTORS

Emission Source ^a	NO Reduction x Criteria, %	Estimated Catalyst Bed Size	
		Volume (ft ³)	X x X x L(ft) x n ^b
Simple Turbine	90	2,916	9 x 9 x 9 x 4
Combined Cycle Turbine	90	3,450	15 x 15 x 7.7 x 2
Internal Combustion Engine	90	27	3 x 3 x 3 x 1
Oil Field Steam Generator	70 (New) 55 (Existing)	47 31	2.6 x 2.6 x 7 x 1 2.6 x 2.6 x 4.6 x 1
Refinery Heater	50	33	3.7 x 3.7 x 2.4 x 1
Cement Kiln	90	16,632	21 x 22 x 36 x 1
Glass Melting Furnace	90	3,120	11.6 x 11.6 x 11.6 x 1

^aFor sources identified in Table 1-1.

^bX = Cross sectional flow dimension; L = length dimension; n = number of beds in parallel.

window can be lowered by approximately 250°C (450°F) from the needed 1000°C (1830°F).

Laboratory tests have shown that 80 to 90% NO_x reduction can be achieved with ammonia injection rates of 1.1 to 1.6 NH₃/NO mole ratios. However, for full-scale applications the removal rate appears to be limited to approximately 65%, with 50% being a typical value for a constant load source and perhaps 40% for a source with a variable load and hence fluctuating temperature conditions occurring at fixed NH₃ injection sites.

By-product emissions include unreacted NH₃, which may be from 30 to 50 ppm, resulting from the 1.5 NH₃/NO mole ratio required to achieve 50% reduction. The NH₃ has the potential for forming NH₄HSO₄ where SO₃ is present and condensing at temperatures of approximately 215°C (425°F). Other emissions such as cyanides and nitrates have been reported, averaging 2 and 10 ppm, respectively (Ref. 1-2). However, no correlation was observed between the amount of ammonia injected and the emission levels of these pollutants, thereby suggesting that the cyanide and nitrates are not a by-product of the NH₃ injection process.

Full-scale use of thermal DeNO_x has been applied in Japan, with approximately 11 units being reported, ranging from 190 to 1320 MMBtu/hr thermal input. Five are operated during pollution alerts only; two were demonstration units; and the remainder are operated continuously. A full-scale demonstration tested in the U.S. on a 50 MMBtu/hr oil field steam generator has been reported, with up to 65% removal at a mole ratio (NH₃/NO) of 1.5.

On the basis of the performance reported above for similar units, the feasibility for thermal DeNO_x achieving a 50 and 55% reduction has been shown for the refinery heater and for the oil field steam generator retrofit, respectively. For the new oil field steam generator installation requiring 70% removal, the potential appears marginally feasible with an NH₃ to NO mole ratio of 2.0 and with NH₃ emissions of 30 to 50 ppm.

1.3 CONTROL SYSTEM COSTS

Costs were defined for the application of control systems capable of meeting the NO_x reduction criteria (Table 1-9). Capital investment and annual costs for those applications are summarized in Table 1-10. Total capital investment estimates for SCR range from \$33/kW for a simple turbine installation to \$372/kW_e for a flat glass melting furnace. The range of operating costs are similar, i.e., from \$1.04/lb of NO_x removed for the IC engines to \$57.78/lb of NO_x removed for the combined cycle turbine, the latter being very high because of the large amount of reheat required and the relatively low mass of NO_x removed in meeting the 90% criterion.

The total capital investment for the SCR installations included an estimate of the level of complexity of the retrofit and was included as an incremental factor of 10 to 25%, as appropriate on the facility investment costs. The glass furnace required a particulate removal device and that item, \$224/kW_e for an electrostatic precipitator, is reflected in the capital investment for that installation.

Operating and maintenance (O&M) costs were typically 25% of the control costs, the remainder being the annual charge on capital. Some installations such as the combined cycle turbine, oil field steam generator, and cement kiln required heating of the exhaust gas to achieve SCR operating temperature. This affected the O&M costs. In the case of the cement kiln, the fuel cost for reheat represented about 30% of the annual cost.

In several instances where the NO_x reduction criterion was less than 90%, i.e., oil field steam generator retrofit (55%) and refinery heaters (50%), thermal De NO_x is applicable, and its capital investment was determined to be \$16/kW_e for each, and 0.36 and \$1.58/lb NO_x removed, respectively.

The investment for retrofitting LNB on utility boilers is approximately \$3.20/kW_e. For the single LNB and combined LNB with CM installations, the costs were 0.19 mills/kWh, or \$0.020/10⁶ Btu thermal input, in

TABLE 1-10. SUMMARY OF NO_x REMOVAL COSTS FOR SELECTED STATIONARY SOURCES

Stationary Source ^a	MW ^b _c	HRS/ YR ^c	Control Method	NO _x Reduction Criterion, %	Total Capital Investment, \$/kW ^{d,e}	Control Costs ^f		
						Unit Costs	\$/lb NO _x Removed ^x	\$/MMBtu Input
Utility Boiler	175	0.45 ^g	LNB only ^h	27-55	3.18	0.19 $\frac{\text{mills}}{\text{kWh}}$	0.076-0.155	0.020
			LNB+exist CM ^{h,i}	7 ^j	3.18	0.19 $\frac{\text{mills}}{\text{kWh}}$	0.60	0.020
Stationary Turbine	121	100	SCR	90	33	76 $\frac{\text{mills}}{\text{kWh}}$	17.28	5.03
Combined Cycle Turbine	236	1300	SCR	90	162	29.5 $\frac{\text{mills}}{\text{kWh}}$	57.78	5.24
Internal Combustion Engine	1.4	1800	SCR	90	183	\$0.019/hp-hr	1.04	2.98
Oil Field Steam Generator	6.6	7900	Thermal	70 N ^k	15 ^l	\$0.29/bbl ^m	0.30	0.096
				55 E ^k	16 ^l	\$0.27/bbl ^m	0.36	0.091
			SCR	70 N	335	\$4.03/bbl ^m	4.03	1.30
				55 E	313	\$3.78/bbl ^m	3.78	1.22
Refinery Heater	6.8	7900	Thermal ⁿ	50	16 ^l	-- ^o	1.58	0.092
			SCR	50	74	--	5.19	0.30
Cement Kiln	18.9	7900	SCR	90	324	\$6.42/ton	2.40	1.75
Glass Furnace	15.4	8760	SCR	90	372 ^p	-- ^o	0.91	1.38

^aFor specific units identified in Tables 1-1 and 1-5.

^bMW equivalent to an electric power plant (based on thermal input to generate 1 MW of electricity).

^cEquivalent hours at rated capacity.

^dRounded off to nearest dollar except for low NO_x burner.

^eIncludes retrofit cost on plant facility investment, see Tables 4-2, 4-6, and 4-8.

^fCost related to facility; downtime (if any) not included.

^gCapacity factor.

^hBurner replacement only; O₂ control costs not included.

ⁱExisting combustion modifications.

^jIncremental removal relative to unmodified levels (25 ppm, or 55/hr).

^kN = new installation, E = existing installation.

^lIncludes Exxon licensing fee, \$3.00/kW.

^mPer net barrel of oil recovered (2 bbl net per bbl consumed).

ⁿAssuming conditions in furnace are applicable for thermal DENO_x (must be determined experimentally for the unit).

^oProduct rate not available.

^pIncludes \$224/kW for an electrostatic precipitator (ESP).

either instance. However, on the basis of dollars per pound of NO_x removed, a different perspective is gained, with the costs for an individual LNB installation being \$0.076 to 0.155/lb NO_x relative to \$0.60/lb for the combined LNB with CM.

1.4 CONCLUSIONS AND RECOMMENDATIONS

The results of this study have shown the feasibility of using SCR as a NO_x control method for removing 90% from the various emission sources studied. In many instances, its use tended to be expensive because of varying degrees of complexity in retrofitting existing installations due to equipment size, additional fan capacity, or the need for exhaust gas reheating. In general, thermal DeNO_x systems can be expected under favorable exhaust gas temperatures to reduce NO_x by about 50% and are expected to meet the NO_x reduction criteria for the refinery heater and existing oil field steam generators. Also, because of the potential simplicity and relatively low cost of this method, it may be possible that the simultaneous application of thermal and SCR (at a reduced capacity, size, and resultant cost) may achieve nearly 90% NO_x removal, where required, at a cost less than catalytic reduction alone. Furthermore, the addition of LNB in some applications together with either thermal or catalytic control devices, or both, may be even more energy efficient and cost effective. Also, because unreacted ammonia emissions in some instances involving thermal reduction may be unacceptably high, its combination with SCR may also be advantageous as a means of reducing ammonia emissions. Therefore, a study to evaluate NO_x reduction potential and costs, as well as the operating impact of the simultaneous use of LNB, thermal DeNO_x, and SCR, is recommended.

1.5 REFERENCES

- 1-1. Jumpei Ando, NO_x Abatement for Stationary Sources in Japan, EPA-600/7-79-205, U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., August 1979.
- 1-2. C. Castaldini, et al., Technical Assessment of Thermal DeNO_x Process, EPA-600/7-79-117, U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., May 1979.

2. TECHNOLOGY ASSESSMENT OF NO_x ABATEMENT ALTERNATIVES

2.1 NO_x FORMATION

NO_x is formed in combustion processes as the result of the oxidation of nitrogen from two different sources; i.e., fixation of atmospheric air at high temperatures (thermal NO_x^{*}) and organically bound to the fuel (fuel NO_x^{*}). NO_x produced from atmospheric nitrogen increases with increasing temperature and oxygen concentration.

In either very fuel-rich or very air-rich mixtures, the NO formation rate is very low. Even under stoichiometric combustion conditions, the NO formation rate will be very low if the temperature of the combustion products is less than about 2400 to 2800°F (1600 to 1800 K). Total NO_x formed by the thermal mechanism can be further minimized, in most cases, by minimizing the total time that the combustion products spend in the combustion process under conditions of high NO formation rates. The NO formation rate, however, is exponential in temperature and under near-stoichiometric conditions. With average combustion temperatures of about 3900°F (2400 K) or higher, the NO formation rate increases rapidly. Conversely, small reductions away from high combustion temperatures can result in large reductions in NO_x emissions.

The hydrocarbon molecules in liquid and solid fossil fuels are complex. Among a wide variety of elements that are often found chemically bound to the C-H molecules, there are usually significant quantities of nitrogen, sulfur, and oxygen. The fate of the chemically bound nitrogen is determined during the early stages of combustion where vaporization (or gasification), oxidative pyrolysis, and heterogeneous combustion are occurring. It appears that, as the initial hydrocarbon oxidation reactions are being completed, the nitrogen atoms are released. If oxidation of the nitrogen atoms to NO is to

*Although once formed there is no difference in the chemistry, for ease of identifying the origin of the nitrogen and mechanism of NO formation reference will be made to thermal and fuel NO_x.

occur, it takes place at approximately the same time and in the same place as the initial hydrocarbon reactions.

Currently, the mechanism by which this chemically bound nitrogen is converted to NO_x , to molecular N_2 , and to other nitrogen compounds such as HCN is not understood. However, some empirical observations are well established and can be used as guidelines to minimize NO_x formed from this source. High excess air favors conversion of organic fuel nitrogen to NO, but the conversion rate is only affected slightly by temperature.

2.2 NO_x CONTROL METHODS

Control of NO_x can be accomplished by combustion modifications (CM) that affect the oxidation of nitrogen to NO or by treatment of the flue gas after combustion to chemically reduce the NO to molecular nitrogen at temperatures below those required for the oxidation reaction to occur.

Combustion modifications to reduce thermal NO_x are based on reducing (1) peak temperatures during combustion, (2) residence time of the combustion gases in high temperature zones, and (3) reducing the availability of oxygen in the primary, high-temperature combustion regions. Fuel NO_x can be reduced by decreasing the availability of oxygen in the combustion reaction zone or by utilizing a fuel with a lower organic nitrogen content.

2.3 NO_x CONTROL ALTERNATIVES

The NO_x control alternatives examined in this study included the use of (1) CM, primarily as implemented by low NO_x burners (LNB) and (2) two types of flue gas treatment, one with ammonia in the presence of a catalyst, selective catalytic reduction (SCR), and the other selective gas-phase decomposition of NO by ammonia at the appropriate temperature and referred to as thermal denitrification (DeNO_x), selective noncatalytic reduction (SNR) or thermal DeNO_x .

The purpose of the study was to assess the feasibility and applicability of applying these alternatives to reduce NO_x emissions from eight selected stationary sources, viz., utility boilers, simple and combined cycle gas turbines, an internal combustion (IC) engine, oil field steam generator, refinery heater, cement kiln, and glass melting furnace (Tables 2-1 and 2-2).

TABLE 2-1. EMISSION SOURCES STUDIED

NO _x EMISSION SOURCE	EQUIPMENT CHARACTERISTICS
Utility Boiler	175 MW boiler with existing combustion modifications, operated by Southern California Edison (SCE)
Simple Turbine	121 MW installation, 8 JP5-fired gas turbines, operated by SCE
Combined Cycle Turbine	236 MW installation, 2 oil-fired gas turbines and associated waste heat boilers, operated by SCE
Internal Combustion Engine	2000 HP two-cycle turbocharged, natural gas-fired engine, operated by Southern California Gas Company
Oil Field Steam Generator	50 million Btu/hr crude oil-fired unit, operated by various oil producers in Kern County, California
Refinery Heater	65 million Btu/hr, refinery gas-fired unit operated by Chevron, USA, El Segundo, CA
Cement Kiln	45 ton/hr coal-fired kiln operated by California Portland Cement Company, Colton, CA
Glass Melting Furnace	Natural gas-fired furnace for producing flat glass operated by PPG Industries, Fresno, California

TABLE 2-2. NO_x REDUCTION CRITERIA

EMISSION SOURCE	NO _x REDUCTION CRITERIA
1. Utility boiler- 175 MW with existing combustion modifications	Potential reduction based on state-of-the-art application of low NO _x burners
2. Simple turbine-electric utility application	90% reduction
3. Combined cycle turbine-electric utility application	90% reduction
4. Internal combustion engine-natural gas storage field application	90% reduction
5. Oil field steam generator thermally enhanced oil recovery (TEOR) application	a) 100 ppm (approximately 70% reduction) for new units b) 150 ppm (approximately 55% reduction) for existing units
6. Oil refinery process heater	50% reduction
7. Cement kiln	90% reduction
8. Glass melting furnace-flat glass	90% reduction

2.3.1 Combustion Modifications

Combustion modifications can be classified into four separate categories:

- a. Change of operating conditions
- b. Modification of combustion system design
- c. Modification of burner design
- d. Other

Examples of the various methods in use are summarized in Table 2.3, as well as their overall effectiveness and the operational impact of implementation. Although the intent of this study is to concentrate on the assessment of burner design modifications (LNB), a brief description of the other more widely used CM is included. An appreciation of the other CM methods is important because existing stationary sources that are being studied for LNB retrofit applications, especially utility boilers, may already employ the other methods, and the LNB incorporates some of the principles used in various types of modifications.

2.3.1.1 Change in Operating Conditions

Low-Excess-Air Combustion (LEA)

In this technique combustion air is reduced to the minimum amount required for complete combustion while maintaining acceptable furnace cleanliness and steam temperature. It is also a known means of preventing low-temperature corrosion caused by SO_3 in large boilers. It reduces thermal and fuel NO_x by decreasing the oxygen concentration in the combustion region. In addition, the quantity of flue gas is reduced, resulting in an improvement in boiler efficiency.

Reduced Heat Release Rate (Reduced Power Output)

Thermal NO_x formation generally decreases as the volumetric heat release rate or combustion intensity decreases. Therefore, NO_x emissions can be lowered by reducing combustion intensity by load reduction, e.g., derating in existing units or enlarging the firebox in new units. The reduced heat

TABLE 2-3. OVERVIEW OF COMBUSTION MODIFICATIONS (Ref. 2-1)

Control Technique	Existing Applications	Effectiveness	Operational Impact
Low Excess Air (LEA)	Retrofit and new utility boilers; some use in industrial boilers	10 to 30% for thermal and fuel NO _x	Increase in efficiency; amount limited by smoke or CO at very low EA
Load Reduction	Some retrofit use on gas and oil utility boilers; enlarged fireboxes on new coal units	0 to 40% for thermal NO _x	Decrease in efficiency and power output; limited by spare capacity and smoke formation
Reduced Air Preheat (RAP)	Widespread use in large turbo-charged IC engines	10 to 40% for thermal NO _x	Slight decrease in efficiency, increase power output
Off-Stoichiometric Combustion (OSC), including OFA, BOOS, BBF	New and retrofit use on many utility boilers; demonstrated on industrial boilers	20 to 50% for thermal and fuel NO _x	No major impact with new design; potential for flame instability, efficiency decrease, increased corrosion (coal-fired) with retrofit
Flue Gas Recirculation (FGR)	Retrofit use on many gas- and oil-fired utility boilers; demonstrated on industrial boilers	20 to 50% for thermal NO _x ; effect on fuel NO _x	Possible flame instability; increased vibration
Water, Steam Injection	Widely used for gas turbines	30 to 70% for thermal NO _x	Slight decrease in efficiency; limited by CO formation; power output increases
Burner Modifications	New and retrofit use on utility boilers; demonstrated on residential furnaces	30 to 60% for thermal and fuel NO _x	No major impact with new design; retrofit use constrained by firebox characteristics

release rate lowers the bulk temperature, which then reduces the amount of thermal NO_x formed.

Generally, the overall heat release rate per unit volume is independent of the unit rated power output (Ref. 2-2). However, the ratio of primary flame zone heat release to heat removal often increases as the unit capacity is increased. This causes NO_x emissions from large units to be greater than for small units of similar design, firing characteristics, and fuel.

An average of 30% reduction in NO_x is reported for a 42% reduction in firing rate of oil-fired boilers and an average 44% reduction for gas-fired units with a 44% load reduction (Ref. 2-5). The influence of firing rate in gas-fired boilers is especially evident because NO_x emissions are solely the result of thermal effects. The effect on oil-fired units is less noticeable because the conversion of fuel nitrogen to NO_x generally represents a significant portion of the total NO_x formed. However, a reduction in firing rate will affect firebox aerodynamics, thereby affecting fuel NO_x emissions to a lesser degree.

A reduced firing rate may lead to several operating problems. Aside from the limiting of capacity, low-load operating usually requires higher levels of excess air to maintain steam temperature and to control smoke and CO emissions. The steam temperature control range is also reduced substantially, thereby reducing operating flexibility and response to changes in load. The combined results are reduced operating efficiency (due to high excess air) and reduced load following capability (due to a reduction in control range).

When the unit is designed for a reduced heat release rate, the problems associated with derating are largely avoided. The use of an enlarged firebox produces reductions in NO_x emissions similar to load reduction on existing units.

Reduced Air Preheat (RAP)

This reduces the flame temperature and therefore thermal NO_x. However, it also reduces fuel efficiency and is not considered a practical control technique.

2.3.1.2 Modification of Combustion System Design

Two major categories of staged combustion are generally used: off-stoichiometric combustion (OSC) and two-stage combustion (TSC).

Off-Stoichiometric Combustion

This technique depends on the combined effects of spacing fuel-rich and air-rich burners. The primary, fuel-rich regions reduce oxygen concentration, and the secondary, air-rich regions reduce temperatures. Combustion of the unburned fuel from the fuel-rich burners is completed at lower temperatures with the excess air from fuel-lean burners.

In practice, OSC is implemented by biased burner firing (BBF), burners out of service (BOOS), or overfire air injection (OFA).

The BBF technique consists of firing the lower rows of burners. This may be accomplished by maintaining normal air distribution to the burners while adjusting fuel flow so that a greater amount of fuel enters the furnace through the lower rows of burners than through the upper rows.

In the BOOS mode, individual burners, or rows of burners, admit air only. This reduces the airflow through the fuel-admitting or active burners. Thus, the burners are firing more fuel-rich than normal, with the remaining air required for combustion being admitted through the inactive burners.

These methods reduce NO_x emissions by reducing the excess air available in the active burner zone. This reduces fuel and thermal NO_x formation. These techniques are applicable to all fuels and are particularly attractive as control methods for existing units since few, if any, equipment modifications are required. Average NO_x reductions of 30 to 50% can be expected (Ref. 2-2).

Location of fuel- and air-rich burners require systematic testing. Often it is effective to place the air-rich burners or air ports in the central upper parts of the furnace walls or in the region of highest heat release. Flame stability and vibration may be problems. It was reported that these problems were avoided if the burners taken out of service did not exceed

25% for 335 MW tangential fired and 480 and 750 MW opposed-fired units (Ref. 2-3).

The OFA technique for NO_x control involves firing the burners more fuel rich than normal while admitting the remaining combustion air through overfire air ports. The method is effective in reducing NO_x and may be used with all fuels. Reduction in NO_x of 30 to 50% can be expected. However, there is an increased potential for furnace tube wastage due to local reducing conditions when firing coal or high-sulfur oil. There is also a greater tendency for slag accumulation in the furnace when firing coal. In addition, with reduced airflow to the burners, there may be reduced mixing of the fuel and air. Thus, additional excess air may be required to ensure complete combustion. This may result in a decrease in efficiency.

The OFA technique is more attractive in original designs than in retrofit applications for cost considerations. Additional duct work, furnace penetrations, and extra fan capacity may be required. Physical obstructions outside of the boiler may make installation more costly, or insufficient height between the top row of burners and the furnace exit may not permit the installation of OFA ports and the enlarged combustion zone required by the OSC technique.

Two-Stage Combustion

In TSC approximately 70 to 90% of the stoichiometric air is introduced into the first stage. Additional air to complete the combustion is admitted downstream. Because of the low oxygen concentration and temperature in the first stage, formation of thermal and fuel NO_x are reduced.

The size and characteristics of the combustor tend to dictate the location of the secondary air ports. The TSC technique cannot be applied to installations with dimensions that cannot accommodate greater flame lengths. With TSC the amount of unburned products tends to increase, thereby necessitating an increase in total excess air requirements. However, with suitable location of the second-stage ports, NO_x reductions are obtained. Depending on the location of the second-stage ports, TSC is further classified into four types:

- a. On the furnace wall above the burners
- b. Top burners using air only
- c. Side or rear walls of the furnace
- d. On the periphery of the burners

Large power plant boilers usually employ type (a) or (b). Type (b) is used in units where (a) cannot be accommodated. Types (c) and (d) are used in medium and small capacity boilers. Type (c) is not readily adaptable to water tube boilers as it requires considerable remodelling. Small installations with single burners generally can be readily adapted to type (d).

Flue Gas Recirculation

In flue gas recirculation (FGR), a portion of the flue gas from the economizer outlet is returned to the boiler via the furnace hopper or through the burner windbox or both to mix with the combustion air. The NO_x reduction is achieved primarily through a decrease in flame temperature.

Flue gas recirculation through the furnace hopper and near the furnace exit has been used for a long time for steam temperature control. However, FGR through the windbox is very effective for NO_x control on gas- and oil-fired units and, to a lesser degree, through the furnace hopper. However, it has been shown to be relatively ineffective on coal-fired units (Ref 2-2).

Recirculation ratios are limited to 30 to 40% to prevent unstable firing. In larger units, this limit is usually less. Maintaining recirculation ratios in appropriate units may improve combustion conditions and reduce soot formation. The decrease in flame temperature alters the distribution of heat to furnace walls and lowers the fuel efficiency of existing installations.

Flue gas recirculation for NO_x control is more adaptable to new designs than as a retrofit application. Retrofit installation for FGR requires a fan, flues, dampers, and controls and may result in the possibility of increasing existing fan capacity to compensate for increased draft loss. In addition, the FGR system itself may require a substantial maintenance program because of the high-temperature environment experienced and potential

erosion from entrained ash in the case of coal-fired units. Thus, the cost effectiveness of this method of NO_x control has to be examined carefully when comparing it to other control techniques.

As a new design feature, the furnace and convective surfaces can be sized for the increase in mass flow and change the furnace temperatures. However, in retrofits the increased mass flow increases turbulence and mixing in the burner zone and alters the convective heat absorption. Erosion and vibration problems may result. Flame detection can also be difficult with FGR through the windbox. In addition, controls must be employed to regulate the proportion of flue gas to air so that sufficient concentration of oxygen is available for combustion. Vibration and furnace rumble has been reported in implementing FGR with 480 and 750 MW units. The problems were corrected on the 480 MW unit by modifying the design of the oil gun diffusers (Ref. 2-3).

Limited data indicate that FGR alone reduces NO_x by about 15% for coal, 20 to 30% for oil, and 30 to 60% for gas. For oil and gas firing, FGR is more effective when combined with OFC.

Water or Steam Injection

Injection of water or steam is an effective method of reducing flame temperature and suppressing NO_x formation. However, boiler efficiency losses of about 10% have been reported. Two techniques may be used: injection into the combustion chamber (including the use of increased steam flow rate in the atomizer) and mixing (emulsification) of water with fuel. Injection ports close to the burners are effective for steam injection into the chamber. The water injection rate upper limit is approximately 278 lb/10⁶ Btu (5 kg/10⁴ kcal) (Ref. 2-4).

Formation of soot decreases with the use of steam injection, so that excess air may be reduced. In addition to decreased efficiency, higher corrosion rates may be experienced.

Reduced Heat Release in the Combustion Chamber

(Increase in Furnace Volume)

Reducing burner volumetric heat release rates by about 10 to 20% compared to conventional units by increasing firebox volume results in large boilers and furnaces that more easily adapt to various CM.

Increasing burner spacing also is a means of reducing flame temperatures and NO_x emissions especially in the center of closely spaced burners.

2.3.1.3 Modification of Burner Design

This approach achieves NO_x reduction by the use of an improved burner, generally referred to as an LNB. Most LNB designed for utility boilers control NO_x by reducing flame turbulence, delaying fuel air mixing, and establishing fuel-rich zones where combustion initially takes place. This represents a departure from the usual burner design procedures, which promote high turbulence, high intensity, and rapid combustion flames. The longer, less intense flames produced with LNB result in lower flame temperatures, which reduce thermal NO_x generation. Moreover, the reduced availability of oxygen in the initial combustion zone inhibits fuel NO_x conversion. Therefore, both thermal and fuel NO_x are controlled by the LNB.

Low NO_x burners, as applied to boilers and various types of furnaces, may be classified into five types (Ref. 2-4):

- a. Good mixing
- b. Divided flame
- c. Self-recirculation
- d. Staged combustion
- e. Combination

Much of the development and use of LNB, for oil and gaseous fuels has been in Japan, including large burners with capacities of up to 20×10^7 Btu/hr (5×10^7 kcal/hr) for boilers and 8×10^7 Btu/hr (2×10^7 kcal/hr) for furnaces.

Good Mixing Type

Good mixing type LNBs are useful in reducing thermal NO_x formation by shortening the high-temperature residence time of the combustion gases.

Generally, they have no effect in reducing fuel NO_x because of the high oxygen concentration in the initial combustion stage.

Divided Flame Type

In this type of burner, the flame temperature and residence time are reduced by means of dividing the burner into several independent small flame zones. NO_x reduction by this method decreases with an increase in the effectiveness of other control techniques. For example, without other techniques the reduction ratio from this burner ranges from 18 to 42%, and about 10 to 30% when 40% reduction is achieved by other techniques.

Self-Recirculation Type

The self-recirculation type reduces both thermal and fuel NO_x formation in such a manner that combusted hot gases from the periphery of the flame are aspirated by the action of the fuel jet and atomizing air or steam into the initial combustion stage. Thus gasification of the fuel and combustion occurs in a reduced oxygen zone.

This type of burner is effective not only for NO_x reduction but also for soot suppression because of the hot gas recirculation, and is used in metal heating furnaces.

Staged Combustion Type

Staged combustion burners are divided into two different types: TSC and OSC LNB. In addition, the TSC burners are classified by the first stage equivalence ratio, i.e., fuel-rich and air-rich.

Staged combustion-type burners are being developed by numerous manufacturers in Japan and are described in Section 2.4.2.4.

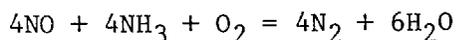
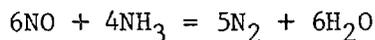
Combination Types

Several LNB combine the methods described above. An example of this is a burner combining TSC and self-recirculation features.

2.3.2 Thermal Denitrification

A method for removal of the oxides of nitrogen downstream of the combustion region of stationary sources involves selective gas-phase decomposition of nitric oxide by ammonia (Ref. 2-5).

If ammonia is mixed into the combustion products with temperatures in the range of 1300 to 2000°F (650 to 1095°C), it will selectively react with the nitric oxide in the presence of oxygen to form molecular nitrogen water:



Although under laboratory conditions NO conversion rates in excess of 85% have been observed, in practice reduction of nitrogen oxide occurs on the order of 50% in the temperature range of 1750°F ±100 (955°C ± 55°) for oil and gaseous fuels.

Mixing of NH₃ with the combustion products and residence time at temperature are important parameters. By introducing a readily oxidizable gas such as hydrogen in conjunction with ammonia, the temperature range at which the selective NO reduction occurs can be lowered to about 1300 to 1400°F (704 to 760°C).

Results which were obtained in a gas-fired combustion tunnel illustrating the effect of temperature and ammonia concentration are shown in Figure 2-1. It can be seen that the reaction occurs over a narrow temperature range and, under these laboratory conditions, approximately 75% of the NO_x is removed when one mole of NH₃ is injected for every mole of NO_x initially present. The amount of unreacted NH₃ (NH₃ breakthrough) for laboratory tests for 85% NO removal (at NH₃/NO mole ratio of 1.7 and 1000) is approximately 100 ppm (Figure 2-2). A more detailed discussion of thermal DeNO_x applications will be provided in Section 2.4.3.

It has been reported (Refs. 2-6 and 2-7) that at conditions wherein NO is reduced there is no reduction of CO₂ to CO. However, oxidations of CO to CO₂ is inhibited so that unburned CO will remain as such when the NO is

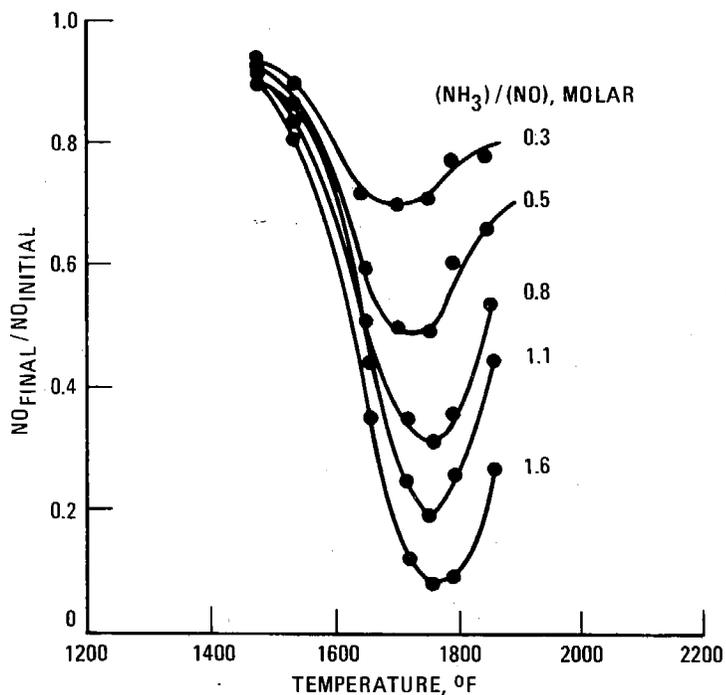


Figure 2-1. Effect of temperature on NO reductions with ammonia injection (excess oxygen, 4%; initial NO, 300 ppm) (Ref. 2-5)

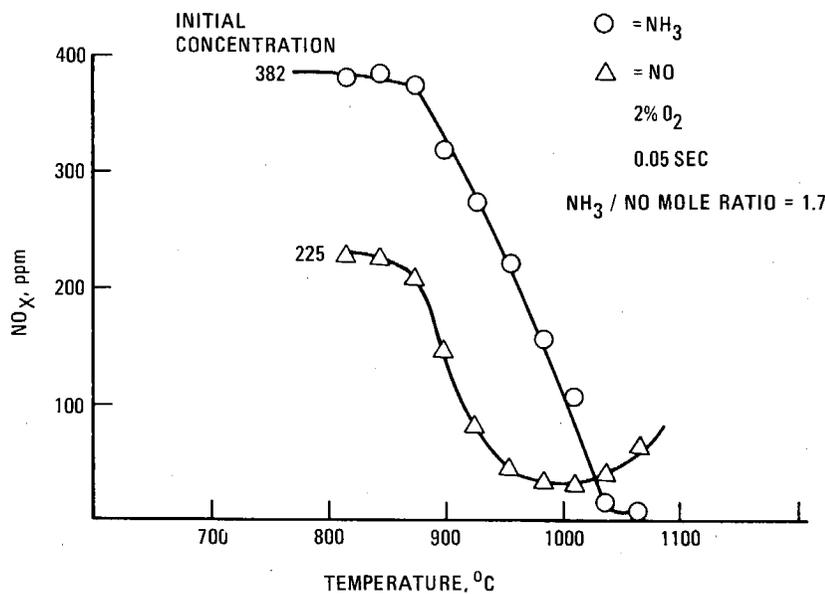


Figure 2-2. Thermal DeNO_x performance as a function of temperature (laboratory data) (Ref. 2-7)

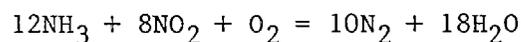
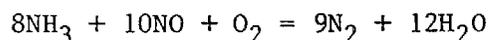
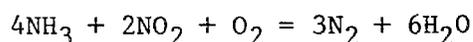
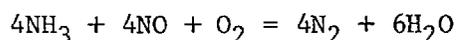
reduced. For normally operating gas- and oil-fired units, CO oxidation is usually complete prior to reaching the ammonia injection point. Also, no increases in the concentration of particulate nitrates, SO₃, and HCN relative to installations without thermal DeNO_x have been reported.

Although there is no increase in the amount of SO₃, unreacted NH₃ reacts with SO₃ and H₂O in the cooler downstream sections where ammonium bisulfate is formed.

2.3.3 Selective Catalytic Reduction

Ammonia selectively reacts with NO without the presence of a catalyst at elevated temperatures. The optimum temperature for the thermal DeNO_x reaction is 950 to 1000°C (Section 2.3.2). In the presence of a catalyst, the temperature of the NO reduction reaction in the presence of ammonia is lowered.

Currently, numerous catalysts (Figure 2-3) have been developed with an optimum reaction temperature of 300 to 400°C (570 to 750°F) (Ref. 2-4), with NO conversion rates of 90% or greater. The presence of small quantities of oxygen in the gas to be treated is necessary for the reduction of NO to occur. This effect is illustrated in Figure 2-4. The reactions that are generally considered to occur are:



At lower temperatures the reaction rate is low, and at higher temperatures the ammonia is oxidized to NO and N₂O.

Emphasis has been placed on nonnoble catalysts. Although they are less efficient and require higher temperatures than noble catalysts, they are less expensive, more resistant to SO_x poisoning, and do not promote formation of N₂O as has been reported for some noble catalysts (Ref. 2-8).

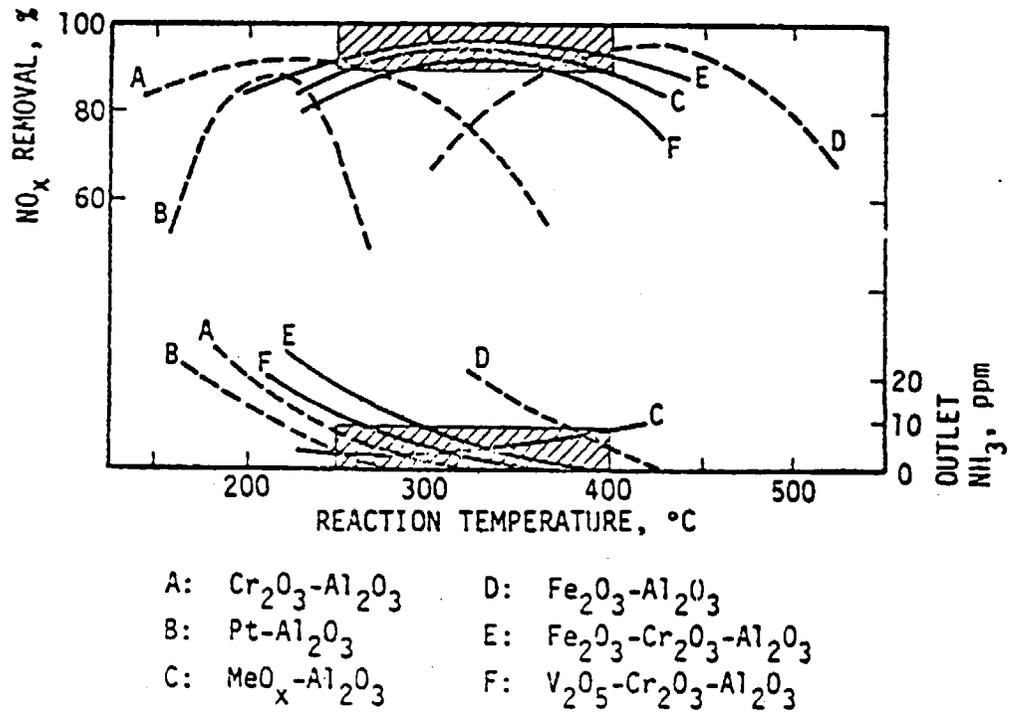


Figure 2-3. Catalyst performance (Ref. 2-4)

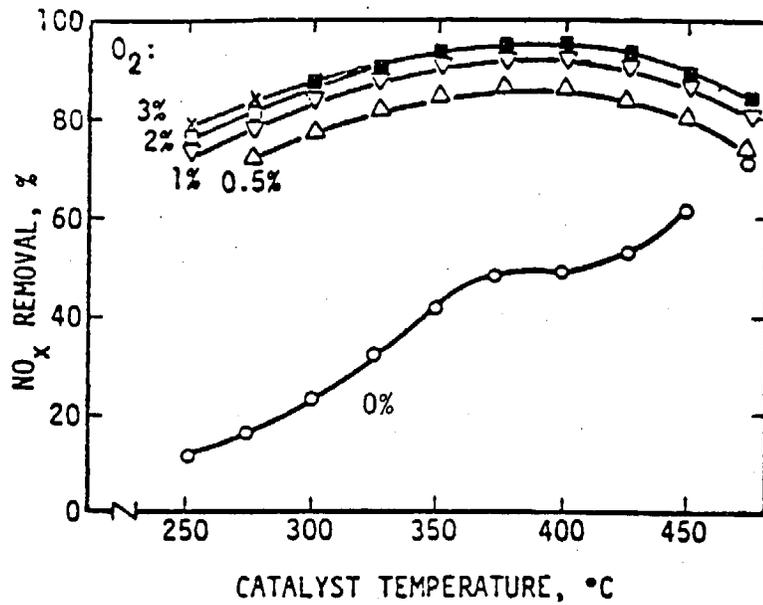
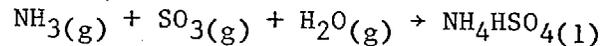


Figure 2-4. Effect of oxygen concentration on NO_x removal (Ref. 2-4)

SO_x may attack the catalyst carrier. For example, SO_x (especially SO₃) tends to react with Al₂O₃ to form an Al₂(SO₄)₃, thus decreasing the available surface area and catalyst activity. Base-metal oxide catalysts also react with SO_x to varying extents; however, these base metal sulfates are still reactive.

Other problems associated with the use of SCR processes are the decrease in catalyst activity and the increase in pressure drop, which are created from particulate pluggage of the reactor. Methods used to minimize these problems are parallel passage reactors, moving-bed reactors, regeneration steps, and specially shaped catalysts.

The formation of NH₄HSO₄ in the presence of SO₃ and unreacted ammonia presents another concern with the use of SCR processes. The unreacted ammonia is a function of the NH₃ to NO_x ratio that is defined by the NO_x reduction characteristics of the catalyst. It is usually formed downstream from the catalytic reactor as the flue gases are cooled in heat exchange equipment according to the following reaction:



The conditions at which it is formed are shown in Figure 2-5. For example, NH₄HSO₄ forms at approximately 210°C if the concentration of both SO₃ and NH₃ are 10 ppm. NH₄HSO₄ is corrosive and also interferes with heat transfer in the heat exchange equipment. At lower temperatures, it may solidify and form (NH₄)₂SO₄. When formed, occasional steam blowing or washing with water are needed for removal of these compounds.

A discussion of the application of the various SCR catalysts is provided in Section 2.4.4. They differ primarily in catalyst characteristics such as composition and shape. Denitrification efficiencies in excess of 90% have been reported in industrial applications. Factors affecting efficiencies in addition to catalyst composition and design include operating temperature, NH₃ to NO_x ratio, and resistance to contaminants such as particulates, SO_x, and others.

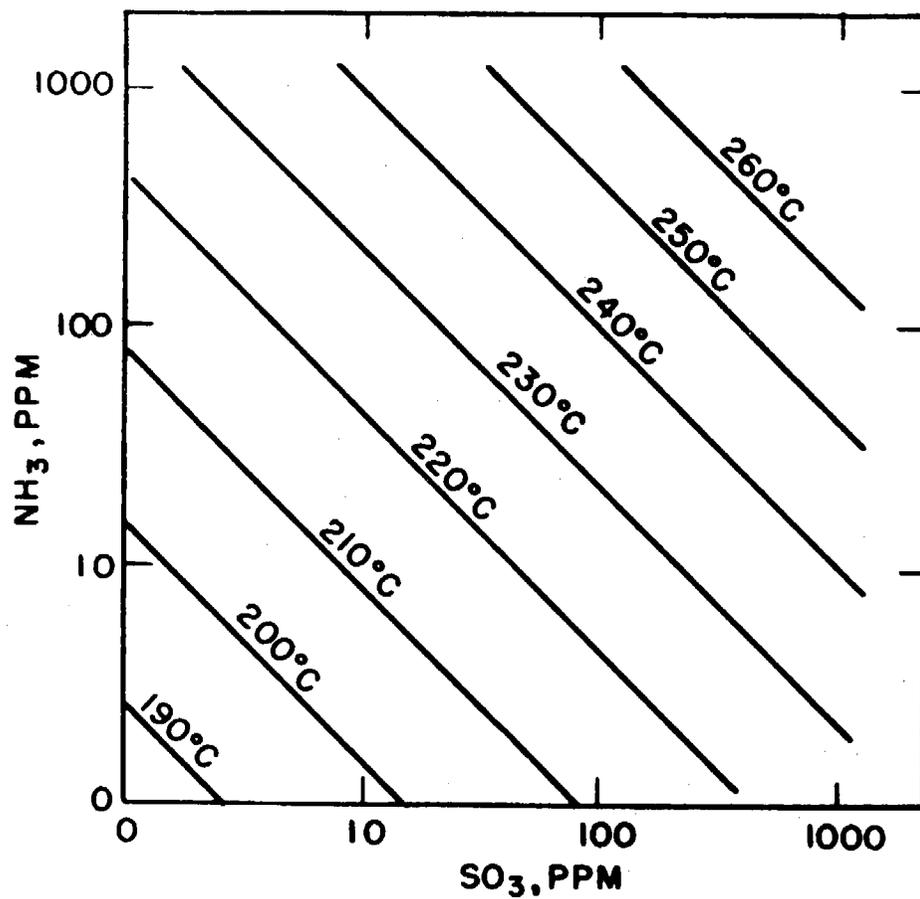


Figure 2-5. Conditions required to form NO₄HSO₄
(Refs. 2-4 and 2-8)

2.4 APPLICABILITY AND EFFECTIVENESS OF NO_x CONTROLS

The state of development and application of the various NO_x controls in this country and in Japan are discussed in this section. The applicability of installing the sources included in this study is discussed in Section 3.

2.4.1 Combustion Modifications

A number of effective CM for controlling NO_x emissions are being used, singly or in combination, on utility boilers and other furnaces. The effect of tests on 61 units in the U.S. and average NO_x reduction on 358 units in Japan are summarized in Table 2-4. The applicability of various CM to reduce NO_x emissions originating from nitrogen in the fuel and combustion air is shown in Table 2-5.

The common techniques applied to oil-fired boilers are low excess air (LEA) firing, OSC, and FGR (Ref. 2-2). Other techniques that have been tested are water injection (WI) and reduced air preheat (RAP). However, these latter have found little application due to attendant efficiency losses. Other techniques used include BBF, BOOS, OFA, and reduced firing rate (Refs. 2-2 and 2-4). These methods may be used on existing boilers although modifications to the unit may be necessary. A summary of the various control methods and their operational impact is provided in Table 2-3.

The major concerns regarding low NO_x operation employing CM are the effects on boiler efficiency, vibration and flame stability, and steam and tube temperature.

Before NO_x control techniques are applied to an existing boiler, it is important to assure that it is in good operating condition. Uniform burner air and fuel flows are essential for optimal NO_x control. Retrofit NO_x control systems must be designed and installed properly to minimize potentially adverse effects. In the event more problems occur, additional hardware modifications may be required, increased vigilance by the boiler operator, or an accelerated maintenance and overhaul schedule. As more background and hindsight is gained from problems experienced in the past, retrofit systems can be designed and installed with care to avoid potential adverse effects (Ref. 2-2).

TABLE 2-4. EFFECT OF COMBUSTION MODIFICATIONS ON NO_x EMISSIONS

Control Method	NO _x Reduction, %		
	U.S. ^{b, c}	Japan ^{d, e}	
		(Average)	No. of Units
Low Excess Air (LEA)	10 - 20	N/A ^f	-
Off-stoichiometric Combustion (OSC)	30 - 50	18	24
Two-stage Combustion (TSC)	30	27	72
Flue Gas Recirculation (FGR)	20 - 30	32	25
OSC + FGR	30 - 75	N/A	-
TSC + FGR	N/A	42	92
Low NO _x Burner (LNB)	40 - 60 ^g	27	80
LNB + OSC	N/A	25	17
LNB + TSC	N/A	34	32
LNB + TSC + FGR	N/A	44	16

a
Oil fired boilers (utility)

b
Ref. 2-2

c
Total of 61 utility boilers; 29 coal, 16 oil, and 16 gas

d
Ref. 2-4

e
Utility and industrial boilers

f
Not available

g
Coal-fired projections. Coal not included in d.

TABLE 2-5. APPLICABILITY OF COMBUSTION MODIFICATIONS TO
REDUCE NO_x EMISSIONS

Modification	Applicability to Reduce NO _x Originating from	
	Thermal	Fuel
Low Excess Air	Yes	Some
Reduced Power Output	Yes	Minimal
Reduced Air Preheat	Yes	No
Off-stoichiometric Combustion	Yes	Some
Two-stage Combustion	Yes	Yes
Flue Gas Recirculation	Yes	Minimal
Steam/Water Injection	Yes	No
Low NO _x Burner	a	a

a

Different designs embody modifications itemized above in varying degrees. Therefore their potential applicability will be based on the type of combustion modification(s) incorporated in the burner.

Low NO_x burners are being installed, especially in Japan, to reduce NO_x emissions from oil- and gas-fired units (Tables 2-6 and 2-7) (Ref. 2-4). These burners are being installed in many new and existing units as the primary NO_x control device or for use in conjunction with other NO_x reduction methods.

NO_x emission levels for boilers before and after the use of CM are shown in Table 2-8. The NO_x reduction ratio ranges from 20 to 50% with different fuels. New boilers tend to give lower NO_x emissions than do existing boilers.

The discussion that follows for LEA, OSC, and FGR pertains primarily to oil-fired boilers; characteristics of installation in California are summarized in Table 2-9.

The low NO_x techniques used for gas-fired boilers and their effects are similar to those for oil-fired boilers. Usually, there is no distinction between oil- and gas-fired boilers as they are designed to switch from one fuel to the other according to fuel availability. Since boiler design details, NO_x control methods, and the effects of low NO_x operation are similar for gas- and oil-fired units, most of the discussion of applicable NO_x control measures to oil-fired boilers and potential problems applies. After switching from oil to gas firing, NO_x emissions may be difficult to control. Burning of the residual oil tends to foul the furnace because of its oil ash content. Therefore, NO_x control measures which have been tested on a clean furnace with gas may be affected after oil firing as a result of the fuel change. These problems can be resolved by complete water washing of the furnace after burning oil (Ref. 2-2).

2.4.1.1 Low Excess Air Combustion

With LEA, reductions in NO_x emissions of 10 to 20% can be expected (Ref. 2-2). It may be used with virtually all fuels and firing methods. However, furnace slagging and tube wastages may limit the degree of application. LEA may be used in conjunction with other NO_x control methods. Care in operation is required to avoid carbon monoxide, smoke, and unburned fuel emissions. The effect of LEA operation on NO_x emissions from oil-fired

TABLE 2-6. NUMBER OF ALL BOILERS AND BOILERS WITH COMBUSTION MODIFICATION IN JAPAN (Ref. 2-4)

Capacity (1,000 Nm ³ /hr) ^d	Existing Boilers ^a			New Boilers with CM ^b	Total Boilers with CM
	Total (A)	With CM (B)	B/A (%) ^c		
Above 500	154	153	99.3	22	175
100-500	331	155	46.8	30	185
40-100	407	72	17.7	9	81
10-40	2,683	41	1.5	24	65
5-10	3,696	18	0.02	11	29
Below 5	72,313				
Total	79,584	439	0.6	96	535

^a Boilers installed by 1974.

^b Boilers installed between 1975 and 1977.

^c NO_x emission standards were first applied to large stationary sources and have gradually been extended to smaller ones. As a result, the CM application ratio (B/A) is larger for boiler with larger capacities.

^d 500,000 Nm³/hr approximately equal to a 167 MW electrical utility boiler.

TABLE 2-7. BOILERS IN JAPAN WITH COMBUSTION MODIFICATIONS (Ref. 2-4)

Capacity, 1000 Nm ³ /hr ^a	TSC ^{b,c}		OSC ^d		FGR ^e		LNB ^f		TSC+FGR		LNB+TSC		LNB+OSC		LNB+FGR		SI ^g		Other		Total		
	E	N	E	N	E	N	E	N	E	N	E	N	E	N	E	N	E	N	E	N	E	N	
>500	35	6	0	1	21	0	4	0	73	12	4	0	2	0	0	0	0	0	7	3	153	22	
100 to 500	21	5	12	1	8	2	38	1	15	0	25	1	18	0	6	0	1	0	8	4	155	30	
40 to 100	4	1	13	0	3	1	33	2	2	3	3	0	0	0	2	1	1	0	11	0	72	9	
10 to 40	10	4	1	0	2	5	11	7	2	5	2	0	2	0	0	0	3	0	8	3	41	24	
<10	5	0	0	0	2	0	5	9	1	0	1	1	0	0	1	1	1	0	7	0	18	11	
Total	70	16	26	2	36	8	91	19	93	20	35	2	17	0	9	2	6	0	41	10	439	96	
TOTAL of E and N																						535	

^a One megawatt equals ~3000 Nm³/hr

^b TSC = two stage combustion

^c E = existing installation; N = new installation

^d OSC = off-stoichiometric combustion

^e FGR = flue gas recirculation

^f LNB = low NO_x burner

^g SI = steam injection

TABLE 2-8. BOILER NO_x EMISSION LEVELS BEFORE AND AFTER COMBUSTION MODIFICATION

Fuel	Existing boilers						New boilers (with CM)		
	Before CM			After CM					
	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean
Coal	800	250	560	650	200	446	--	--	--
Grade C oil and crude oil	600	100	273	320	80	176	240	60	162
Naphtha, kerosene and by-product oil	310	70	233	230	30	117	110	30	87
Gaseous fuel	250	50	153	170	20	101	130	50	75
									Reduction ratio ^b
									20.4
									35.5
									49.8
									34.0

^a ppm, corrected to 4% O₂ for oil, 5% O₂ for gas, and 6% O₂ for coal

^b Reduction ratio = 100 x (mean before CM - mean after CM) / mean before CM

TABLE 2-9. EFFECT OF LOW NO_x OPERATION ON OIL-FIRED BOILERS (Ref. 2-2)

Boiler	Low NO _x Technique	Efficiency	Load Capacity	Vibration and Flame Instability	Steam and Tube Temperatures	Other Effects, Comments	
Tangential South Bay No. 4	LEA	5% increase	--	--	--	No adverse effects reported. Fan power consumption reduced.	
	BOOS	Decrease in efficiency compared to LEA due to increased excess air requirements	--	--	--	No other adverse effects reported	
	RAP	Unaffected due to special preheater design	--	--	--	Limited tests. NO _x control effectiveness not demonstrated.	
	OFA and FGR BOOS and FGR	-- --	Slower startups and load changes	FGR fan vibration problems	High water wall tube temperatures	No adverse effects reported	
Opposed Wall	Moss Landing Nos. 6 and 7	Increased excess air requirements resulting in decreased efficiency	--	FGR fan and duct vibration, furnace associated flame instability	--	High furnace pressures. Increased FGR and forced draft fan power consumption.	
	Ormond Beach Nos. 1 and 2	Increased excess air requirements resulting in decreased efficiency Increased sensible and latent stack losses	10 to 15% derate due to maxed FD fan capacity	Flame instability and associated furnace vibration	--	Flame detection problems due to change characteristics Limited tests carried out with WI at partial loads. Excess air requirements increased	
	SCE B&W Units	FGR reduced minimum excess air requirements increasing unit efficiency	--	Boiler vibration problems	--	Flame detection problems due to change in flame characteristics	
	Sewaren Station No. 5	LEA, BOOS	--	--	--	--	Tests carried out at partial loads. No adverse effects reported. Particulate loading and size distribution unaffected.

TABLE 2-9. EFFECT OF LOW NO_x OPERATION ON OIL-FIRED BOILERS (Ref. 2-2) (Continued)

Boiler	Low NO _x Technique	Efficiency	Load Capacity	Vibration and Flame Instability	Steam and Tube Temperatures	Other Effects, Comments
Single Wall Encina Nos. 1, 2, and 3	LEA and BOOS (2 burners on air only)	Increased unit efficiency. Some adverse effect on cycle efficiency due to lower steam temperatures	--	--	Decrease in SH & RH steam temperature	No other adverse effects reported
	BOOS (3 burners on air only)	Increased excess air requirements resulting in reduced efficiency	5% derate due to maxed ID fan capacity	In most tests no flame instability or blowoff noted	Intermittent flame carryover to SH inlet but tube temperature limits not exceeded	No abnormal tube fouling, corrosion or erosion noted. Increased tendency to smoke and obscure flame zone.
Turbo South Bay No. 3	Airflow adjustments	Slight reduction in EA resulting in slight increase in efficiency	--	--	--	No adverse effects reported
	Water injection	6% decrease at full load	--	No flame instability noted even at high rates of WI	--	No other adverse effects reported
	Reduced air preheat	Reduction in efficiency greater than that with water injection	--	--	--	Limited tests
Potrero No. 3-1	OFA and FGR	Higher excess air requirements, but addition of economizer surface expected to improve efficiency	5% derate due to excessive tube temperatures	Side to side windbox oxygen cycling	Tube and steam temperature limits approached, increased SH tube failures.	Increased tendency to smoke. Required higher minimum excess O ₂ levels. RH surface removed to avoid excessive RH steam attemperation. Larger economizer installed to compensate for RH surface removal.

burners is shown in Figure 2-6 (Ref. 2-9). A reduction of 23% was achieved in reducing the excess oxygen from 3 to 2% and 36% with reduction of O_2 from 3 to 1.5%.

In Japan, LEA has been applied to large boilers burning high-nitrogen fuels such as grade B (0.08 to 0.35% N) or grade C (0.20 to 0.35% N) heavy oils. This method has not been used to any extent on small boilers or furnaces because they generally burn low nitrogen fuels such as kerosene, grade A heavy oil (0.005 to 0.8% N), or gas and no specific attempt is made to reduce NO_x emissions. Small units are generally unmanned and their operation not well controlled; in these instances, LEA tends to cause incomplete combustion.

2.4.1.2 Off-Stoichiometric Combustion

An average NO_x reduction of approximately 20% in Japan and within a range of 30 to 50% for the U.S. is reported for OSC applications (Table 2-4). The influence of the amount of air at the burner on the formation of fuel NO_x with OSC combustion of oil is shown in Figure 2-7 (Ref. 2-10). Generally, when nitric oxide control is being implemented, operation is in the reducing region, i.e., the left side of 100% air (Figure 2-7). With these burner throat fuel-air ratios, the conversion of the fuel nitrogen to nitric oxide results in a low additional increment of 50 ppm or less.

An OSC operation generally increases the minimum excess air requirements of the boiler, which may result in a loss in boiler efficiency. In extreme cases when the boiler is operating close to the limits of its fan capacity, boiler derating may be required. Derating of as much as 15% has been reported in some instances because of inability to meet the increased airflow requirements at full load (Ref. 2-2).

Other potential problems attendant with the application of OSC in oil-fired boilers have included flame instabilities, boiler vibrations, and excessive temperatures of convective section tubes. However, on the basis of past experience, none of these problems have been considered significant.

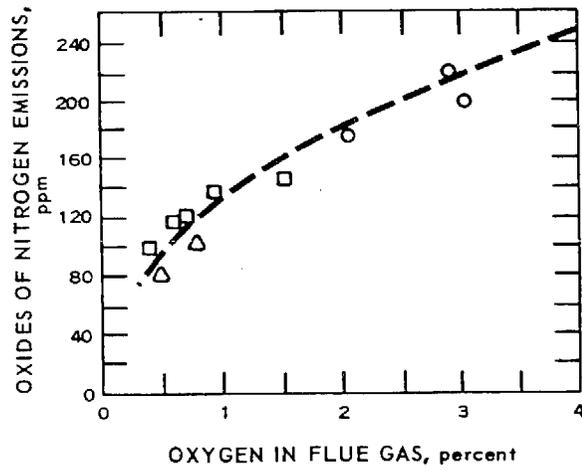


Figure 2-6. Oxides of nitrogen emissions from oil-fired boilers at low excess air (Ref. 2-9)

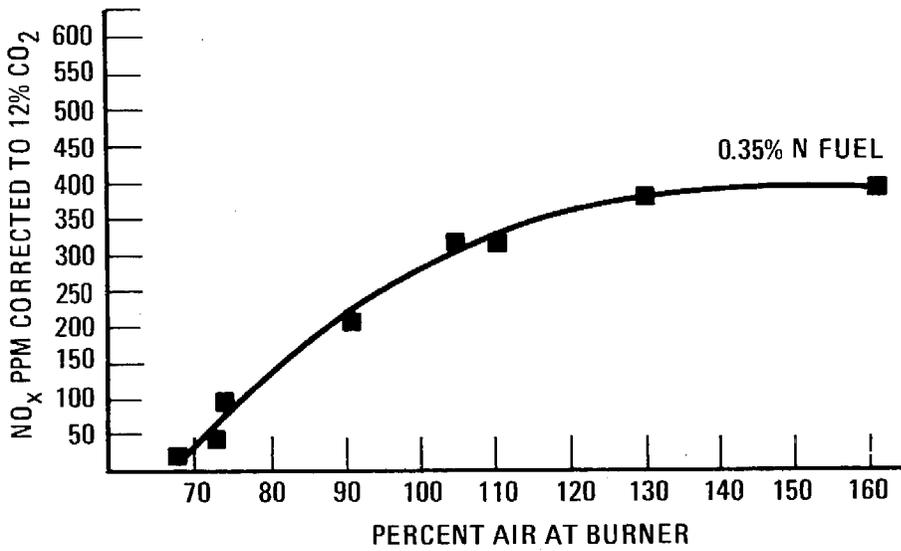


Figure 2-7. Effect of air at burner on NO_x formation in off-stoichiometric, fuel-rich combustion (Ref. 2-10)

Staged operation usually results in hazy flames and obscure flame zones. Therefore, new flame scanners and detectors are often required in retrofit applications. In addition, because OSC produces an extended flame zone, flame carryover to the convective section may occasionally occur. However, in one case where intermittent flame carryover occurred, no excessive tube temperatures were recorded.

2.4.1.3 Flue Gas Recirculation

The use of FGR is a process in which a portion of the flue gas, comprising approximately 10 to 20% of the air fed to the furnace is recirculated into the combustion zone.

Gas recirculation as practiced in utility plants for boiler tube temperature control is not the same as FGR for NO_x control because the recirculated gases are injected downstream of the burner. The flue gas must enter directly into the combustion zone if it is to be effective in lowering the flame temperature and reducing NO_x formation.

The effect of FGR theoretically may be treated as purely an enthalpy effect, the recirculated flue gas decreasing the flame temperature. The nitric oxide formed for the characteristic time in the adiabatic regions of the flame zone can be calculated theoretically (Figure 2-8).

For a typical recirculation rate of about 15%, the nitric oxide would theoretically be reduced by 80% or more. On gaseous fuel, the results shown are very close to what is predicted theoretically. The actual data spread shown in Figure 2-8 demonstrates that reduction of from 2.5 to 4.5 have been obtained (Ref. 2-10). However, with fuel oil the reductions are not as dramatic, with typical levels of approximately 30% reported in this country and Japan.

Gas recirculation has also been employed in low-temperature heating furnaces in industrial applications to achieve greater and more uniform heat transfer into the product. Vertical shaft lime kilns often use recirculation to control calcining temperatures more effectively. The effect on NO_x emissions in the latter cases, however, is not known (Ref. 2-9).

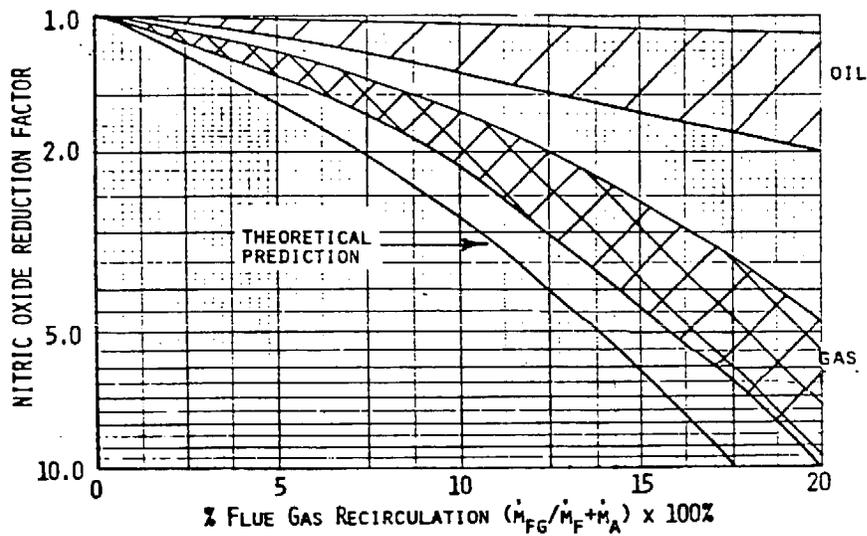


Figure 2-8. Effect of gas recirculation into windowbox on formation of nitric oxide for liquid and gaseous fuels (Ref. 2-10)

There are a number of potential problems which can occur in retrofit FGR applications. The most common problems, such as FGR fan and duct vibrations, can usually be avoided by good design. Other problems such as flame instability, which can lead to furnace vibration, are caused by the increased gas velocity at the burner throats. Modifications to the burner geometry and design, such as enlarging the throat, altering the burner tips, or adding diffuser plates or flame retainers, may then be required. These modifications are usually made by trial and error for each boiler and are often time consuming. If the problems of excessive boiler vibration and flame instabilities persist at high loads, boiler derating may be required.

Another potential problem associated with FGR is high tube and steam temperatures in the convective section. The increased mass velocities which occur with FGR cause the convective heat transfer coefficient to rise. This, coupled with reduced furnace heat absorption, can give rise to high convective section temperatures leading to tube failures. Increased mass flowrates in the furnace may also cause furnace pressures to increase beyond safe limits. Usually, however, FGR has an advantage of not increasing minimum excess air

levels. Boiler efficiency therefore is unaffected, except for the power consumed by the FGR or booster fans.

Boilers fired with gas usually have higher gas temperatures at the furnace outlet than when fired with oil. Gas flames are less luminous and therefore radiate less energy to the furnace walls than oil flames. The upper furnace and convective section inlet surfaces are thus subject to higher temperatures with gas firing. These temperatures may increase further when the combustion zone is extended due to OSC.

2.4.1.4 Combinations

The combination of OSC and FGR is found to be very effective in reducing NO_x emissions, i.e., 30 to 75% (Table 2-4). However, the problems associated with each technique are also combined. Tube and steam temperature problems in the upper furnace are particularly exacerbated, as both OSC and FGR tend to increase upper furnace temperatures and convective section heat transfer rates. In addition, boiler efficiencies usually decline slightly with combined OSC and FGR firing due to higher excess air requirements and greater fan power consumption.

2.4.2 Low NO_x Burners

A number of improvements in burner design for liquid and gaseous fuels have been developed in Japan to reduce the formation of NO_x . These have been applied to boilers and various kinds of furnaces and are clarified into five types:

- a. Good mixing
- b. Divided flame
- c. Self recirculation
- d. Staged combustion
- e. Combination.

Low NO_x burners have been developed in Japan with capacities of 20×10^7 Btu/hr (5×10^7 kcal/hr) for boilers and 8×10^7 Btu/hr (2×10^7 kcal/hr) for furnaces.

2.4.2.1 Good Mixing Type

These furnaces reduce the formation of thermal NO_x by shortening the residence time of the combustion gases in high-temperature regions, but have little effect in reducing fuel NO_x because of a high oxygen concentration in the initial stages of combustion.

An example of a good mixing type LNB is shown in Figure 2-9 (Ref. 2-11). This burner has been commercialized by Nippon Furnace Kogyo Kaisah, Ltd (NFK), based on a TRW design, and is designated as the NFK-TRW burner.

The basic burner has a single control configuration aligned with the centerline of the air venturi whereby the air is injected as a continuous cylindrical stream. Jets of fuel are mixed with either atomized steam or air injected radially outward through a large number of shaped ports. The air and fuel are then further mixed by means of a deflector, which functions as a flame holder. The mixture of fuel and air produces a thin, conical-shape flame according to the flow pattern. As a result of the flame shape, a maximum radiation surface is produced, and heat from the flame is rapidly removed. Therefore, the residence time of combustion gas in the high-temperature regions is shortened and reduction of thermal NO_x is accomplished. Relative to a conventional burner, NO_x reductions of approximately 40% have been achieved when burning type C fuel oil (0.29% nitrogen fuel) (Figure 2-10). A total of 120 boilers in Japan have these types of burners installed (Ref. 2-12). Burners which can burn either oil or gas have been commercialized. The burner reduces not only NO_x but also soot emissions. In addition, it allows the heat load in the combustion chamber to be maintained as high as before and serves to increase the fuel efficiency. Generally, this burner is considered applicable only to boilers because of its flame shape.

2.4.2.2 Divided Flame Type

In the divided flame type LNB, the fuel spray is divided into several independent streams. NO_x reduction occurs due to several factors. Flame temperatures are lowered and high-temperature residence times are shortened as a result of the formation of fuel-rich and lean zones in the fuel spray (Ref. 2-13). A split flame burner has been developed by Ishikawajima-Harima Heavy Industries, Ltd, (IHI) utilizing a liquid fuel atomizing tip in which the

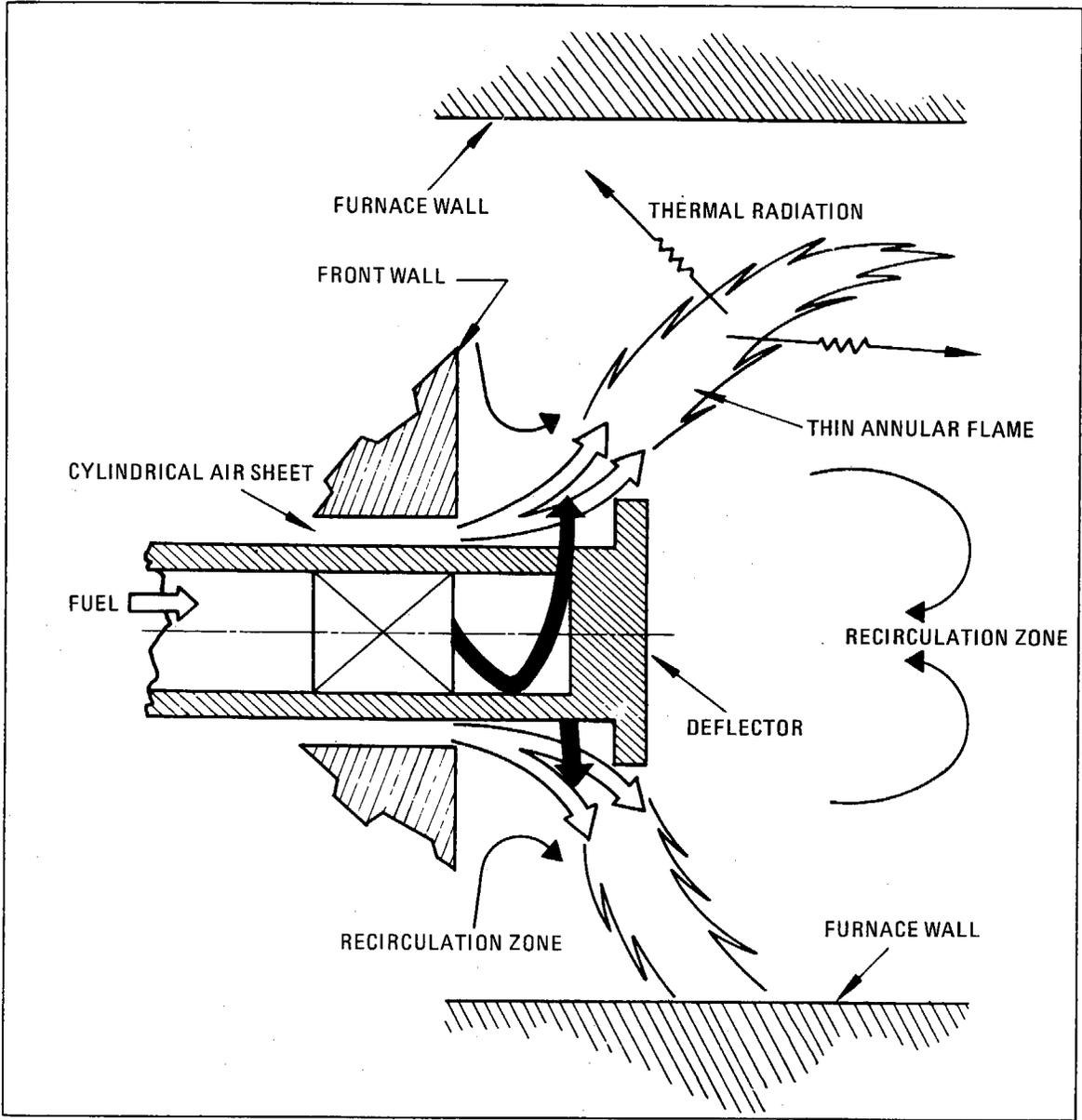
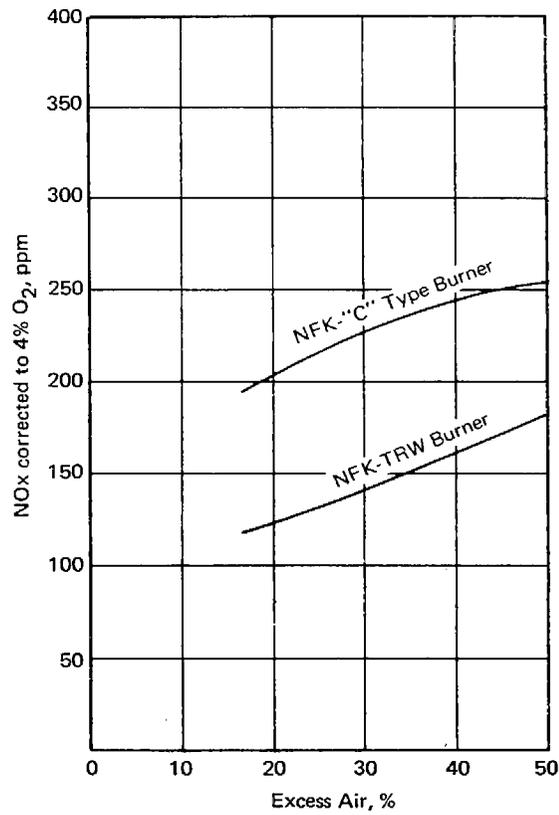


Figure 2-9. NFK-TRW burner: good mixing type (Ref. 2-11)



FUEL: C OIL (Fuel N = 0.29%)
 COMBUSTION AIR TEMPERATURE:
 100°C (212°F)
 CAPACITY: 1050 l/hr (4.6 gpm)
 FIRING RATE: 9.7 x 10⁶ kcal/hr
 (38.5 x 10⁶ Btu/hr)

Figure 2-10. NO_x emission characteristics of NFK-TRW and conventional burner (Ref. 2-11)

pressure atomizing tip divides a hollow, conical, conventional fuel jet into four groups. The steam atomizing tip divides the multiple fuel jets into two or three clusters of uniformly scattered, conventional fuel jets (Figure 2-11). For the split flame steam atomizing burner (Mark II model), the NO_x has been reduced 30 to 40%. The effect of this type of burner combined with other NO_x control methods such as FGR, staged combustion, and water injection for a pressure atomizing burner are shown in Figure 2-12.

2.4.2.3 Self-Recirculation Type

The self-recirculation type has the potential of reducing both thermal and fuel NO_x formation. Hot combustion gases are entrained by the action of the fuel jet and atomizing air or steam and introduced into the initial combustion stage. Both gasification of fuel and burning in a low-oxygen-concentration zone are achieved in an initial combustion stage.

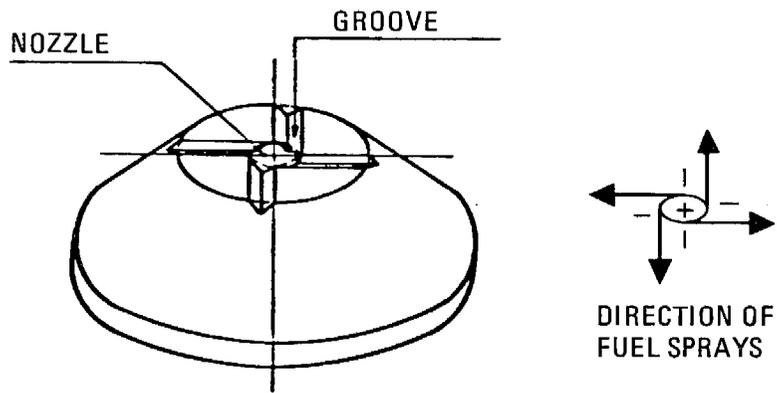
An example of the self-recirculation type burner is shown in Figure 2-13. This burner has been developed by Daido Tokushuko Company under a technical license agreement with Caloric Gesellschaft fur Apparate Bau, West Germany (Ref. 2-4). It can be applied to either gaseous or liquid fuels. The formation of NO_x has been reported to be reduced by over 50% (Figure 2-14). This type of burner is effective not only for NO_x reduction but also for soot suppression by hot combustion gas recirculation, and is used in metal heating furnaces.

A burner designed exclusively for gas firing, developed by Sanray Reinetsu Company, Ltd., is called the XB burner. Several fuel gas injection nozzles are positioned in a circular pattern in order to shorten the flame. The recirculated combustion gas is aspirated into an annular region in the vicinity of the fuel injection nozzles. NO_x levels are shown in Figure 2-15. A similar type of burner has been developed by Chugai Ro Kogyo Company, Ltd.

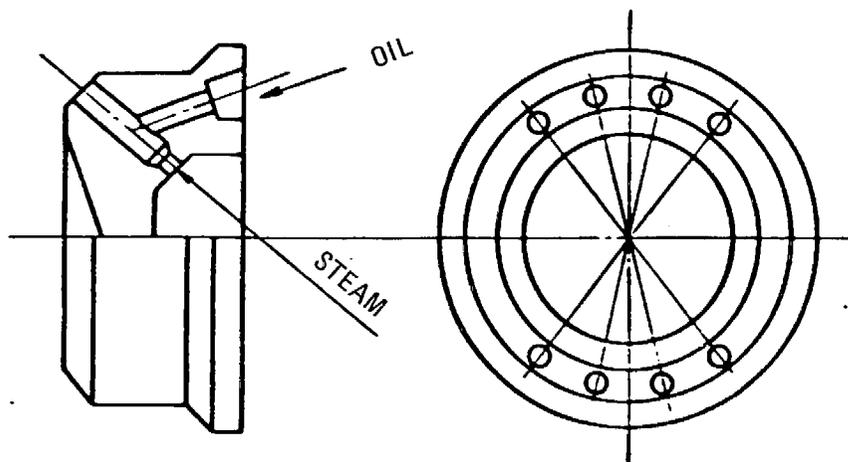
2.4.2.4 Staged Combustion Type

These may be divided into two general groups: the two-stage combustion (TSC) and off-stoichiometric (OSC) types.

The TSC burners employ a fuel-rich first stage, with air added in the second stage. An example of such a burner for gaseous fuel application is the



(1) PRESSURE ATOMIZING BURNER TIP WITH V SHAPED GROOVES



(2) STEAM ATOMIZING BURNER TIP (MARK II MODEL)

Figure 2-11. Split flame burner (Ref. 2-13)

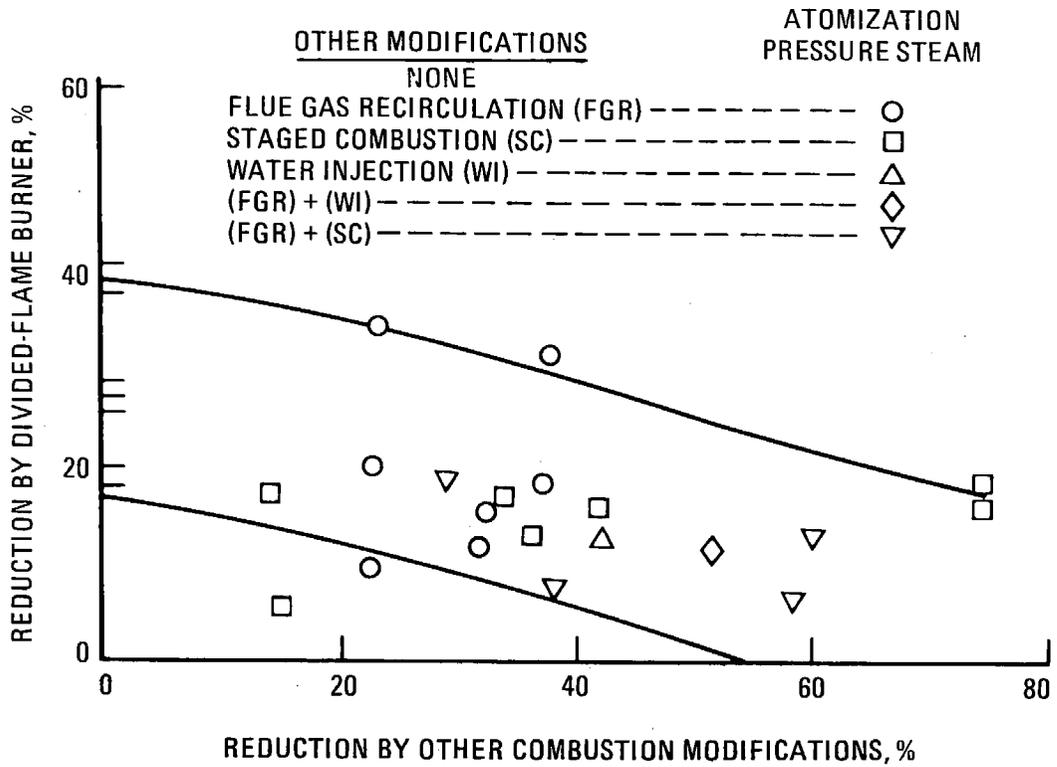


Figure 2-12. NO_x reduction on split flame low NO_x burner combined with other combustion modifications (Ref. 2-4)

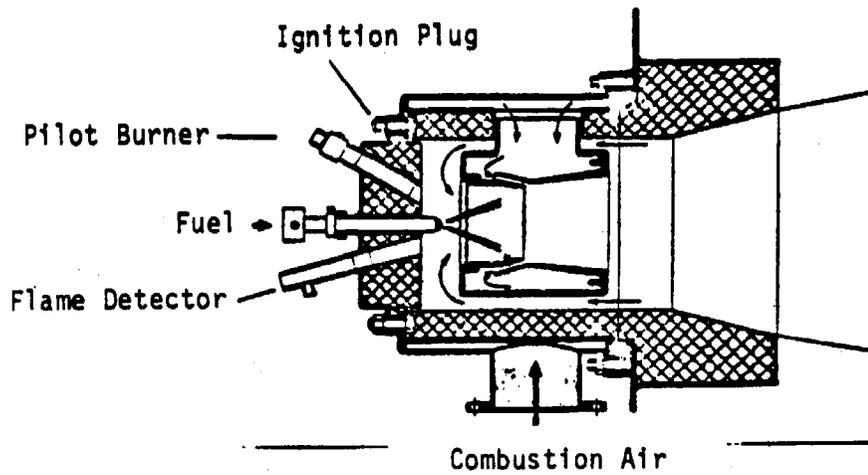


Figure 2-13. Self-recirculation type burner (Ref. 2-4)

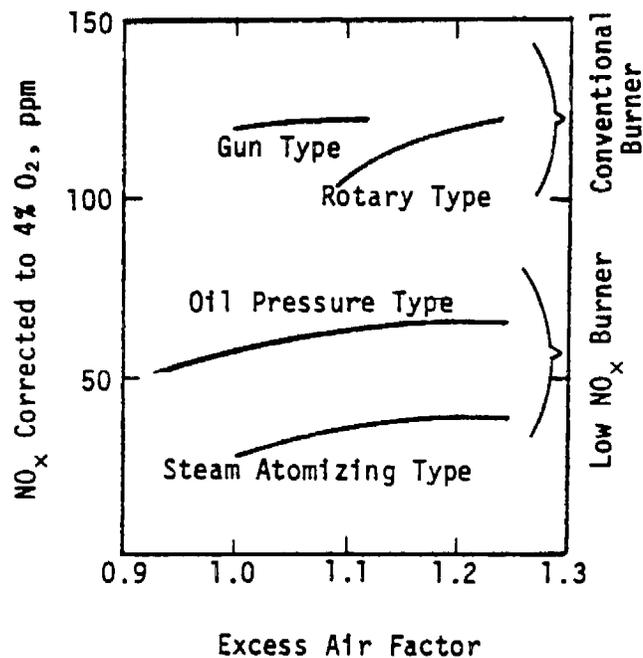


Figure 2-14. Effect of self-recirculation type burner [fuel, grade A oil; fuel flow rate, 100 liters/hr (0.44 gpm); firing rate, 0.9×10^6 kcal/hr (3.6 Btu/hr)] (Ref. 2-4)

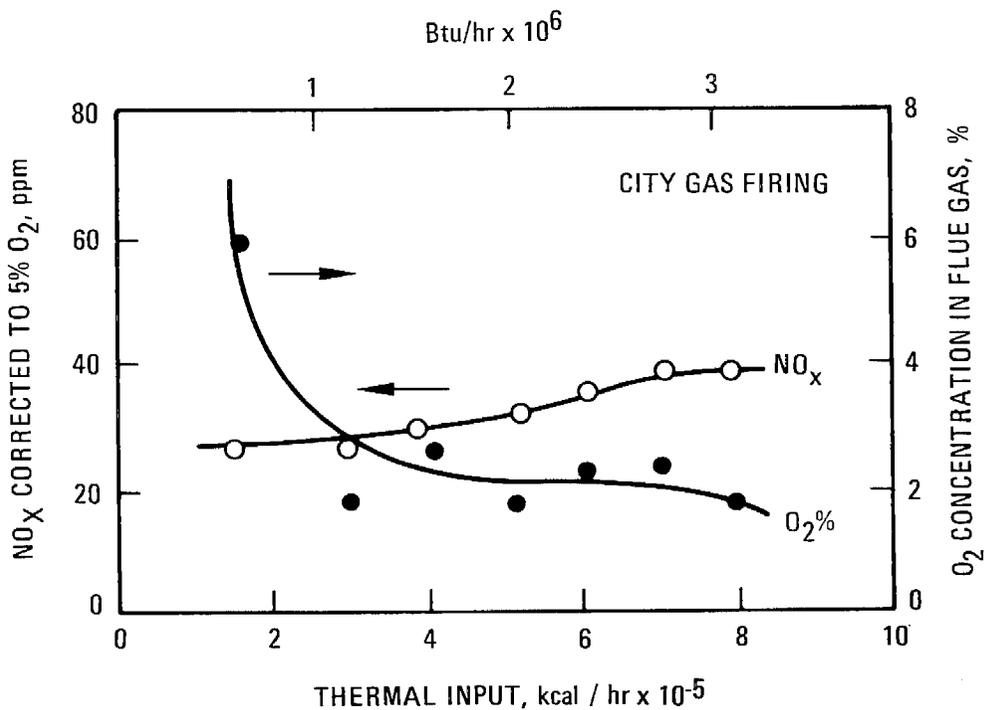


Figure 2-15. Characteristics of XB burner firing city gas (Ref. 2-4)

FH burner (Figure 2-16). The NO_x reduction characteristics are shown in Figure 2-17. It has been developed by Chugao Ro Kogyo Company, Ltd., and is used in heating furnaces. This type of burner has the advantages of a relatively simple configuration with the capability of fuel NO_x reduction. Similar types of burners have been developed by other burner manufacturers, viz., Mitsubishi Heavy Industries, Ltd. (MHI); Kawasaki Reinetsu Company, Ltd.; Osaka Gas Company; Sanray Reinetsu Company, Ltd.; and Rozai Kogyo Company, Ltd.

Results of LNB performance in a 125 MW boiler reported by Kawasaki (Ref. 2-14) are shown in Figure 2-18 for fuel oil containing 0.15% fuel-bound nitrogen. Combined with FGR, an overall 80% reduction to 63 ppm was achieved with its IS-2 burner relative to its conventional burner that produced 326 ppm. By adapting the IS-1 conventional burner to staged combustion and with 13% of the air in the second stage, the burner produced 176 ppm. With the Kawasaki LNB, designated as IS-2 and commercialized in 1978, emissions were further reduced to 63 ppm by staging 20% of secondary air and by recirculating 20% of the flue gas.

The effect of boiler output on NO_x emissions is shown in Figure 2-19 for the IS-2 burner, which exhibited slightly higher emissions at reduced levels. In Figure 2-20, the effect of combustion staging and FGR are shown. Emissions of 69 ppm are reported for 20% FGR and staging.

An LNB designed for use with liquefied natural gas (LNG) (containing 88% CH_4) has exhibited emissions as low as 28 ppm (Figure 2-21) at 156 MW. At 75, 50, and 40% loads, emissions were 30, 30, and 26 ppm, respectively, with FGR and second stage air in the range of 20 to 25%.

A basic configuration for an off-stoichiometric burner is illustrated in Figure 2-22. This burner has been developed by MHI for boilers using grade A oil or kerosene and has been designated as a spray premix T-burner. The fuel sprayed in the upper and lower compartments is evaporated by preheated air and premixed with air to generate air-rich premixed flames. The middle compartment forms a fuel-rich flame. Thus, OSC is realized. To reduce NO_x further, recirculated flue gas is mixed into the air. NO_x levels with this burner are shown in Figure 2-23.

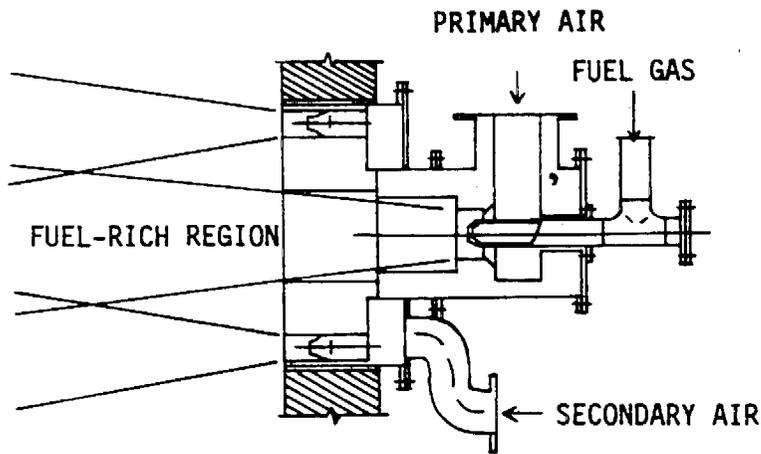


Figure 2-16. FH two-stage combustion type burner (Ref. 2-4)

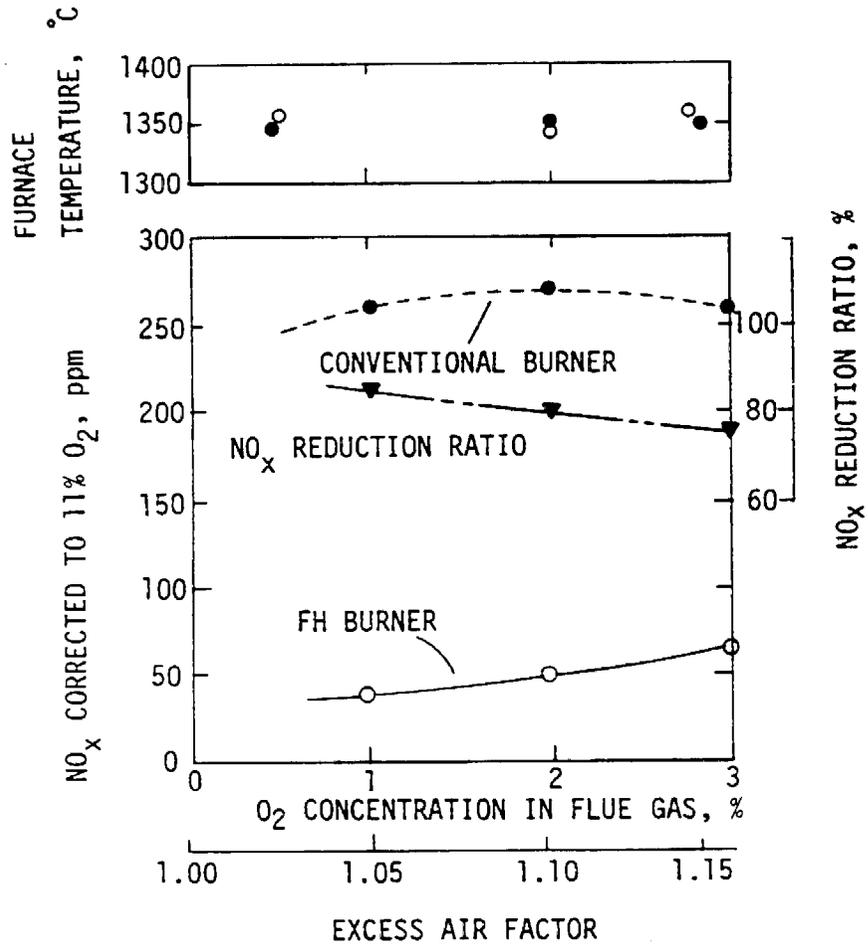


Figure 2-17. Characteristics of the FH burner (Ref. 2-4)

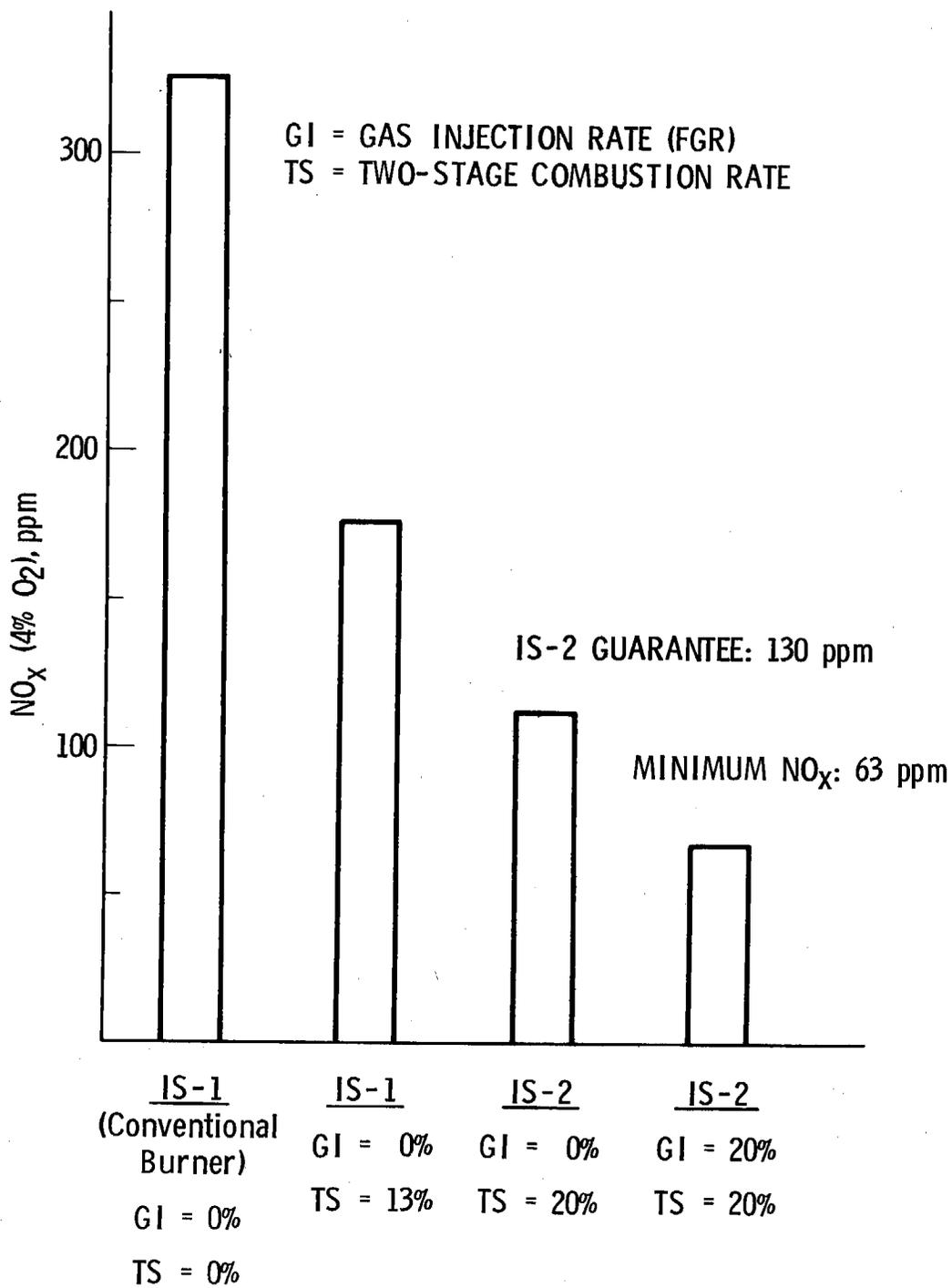


Figure 2-18. Low NO_x burner performance (Ref. 2-14)

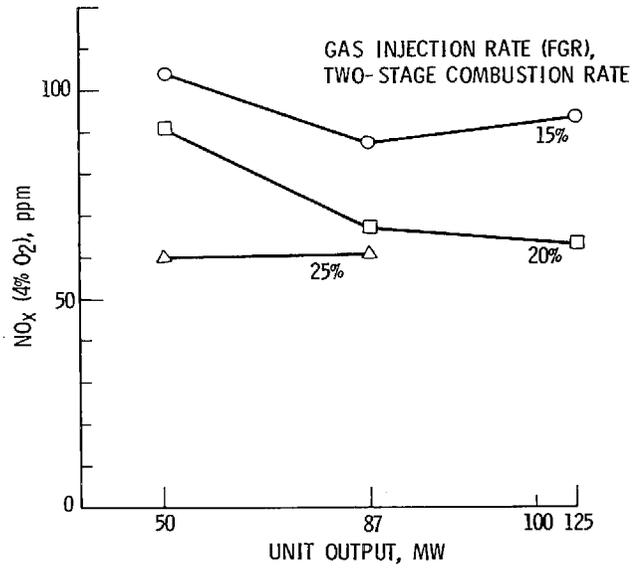


Figure 2-19. Effect of output load on NO_x emissions with IS-2 low NO_x burner (Ref. 2-14)

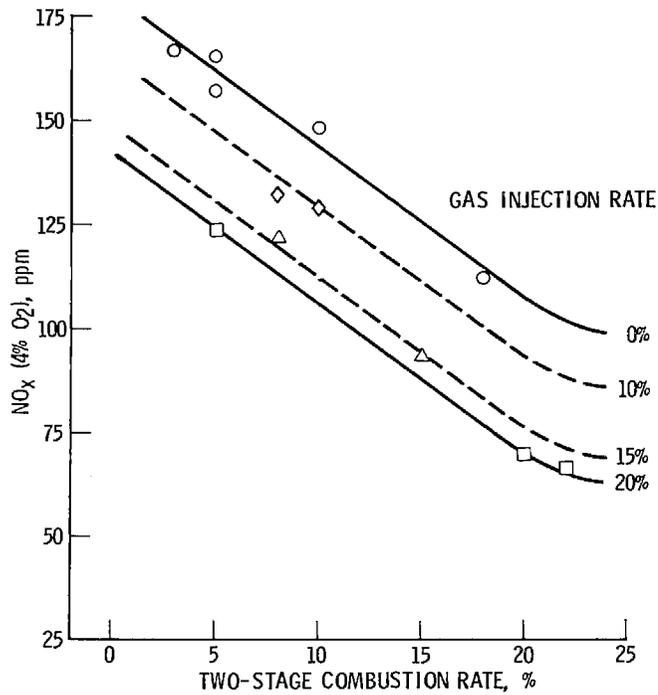


Figure 2-20. Effect of staged combustion and flue gas recirculation of NO_x emissions for IS-2 burner at full load (Ref. 2-14)

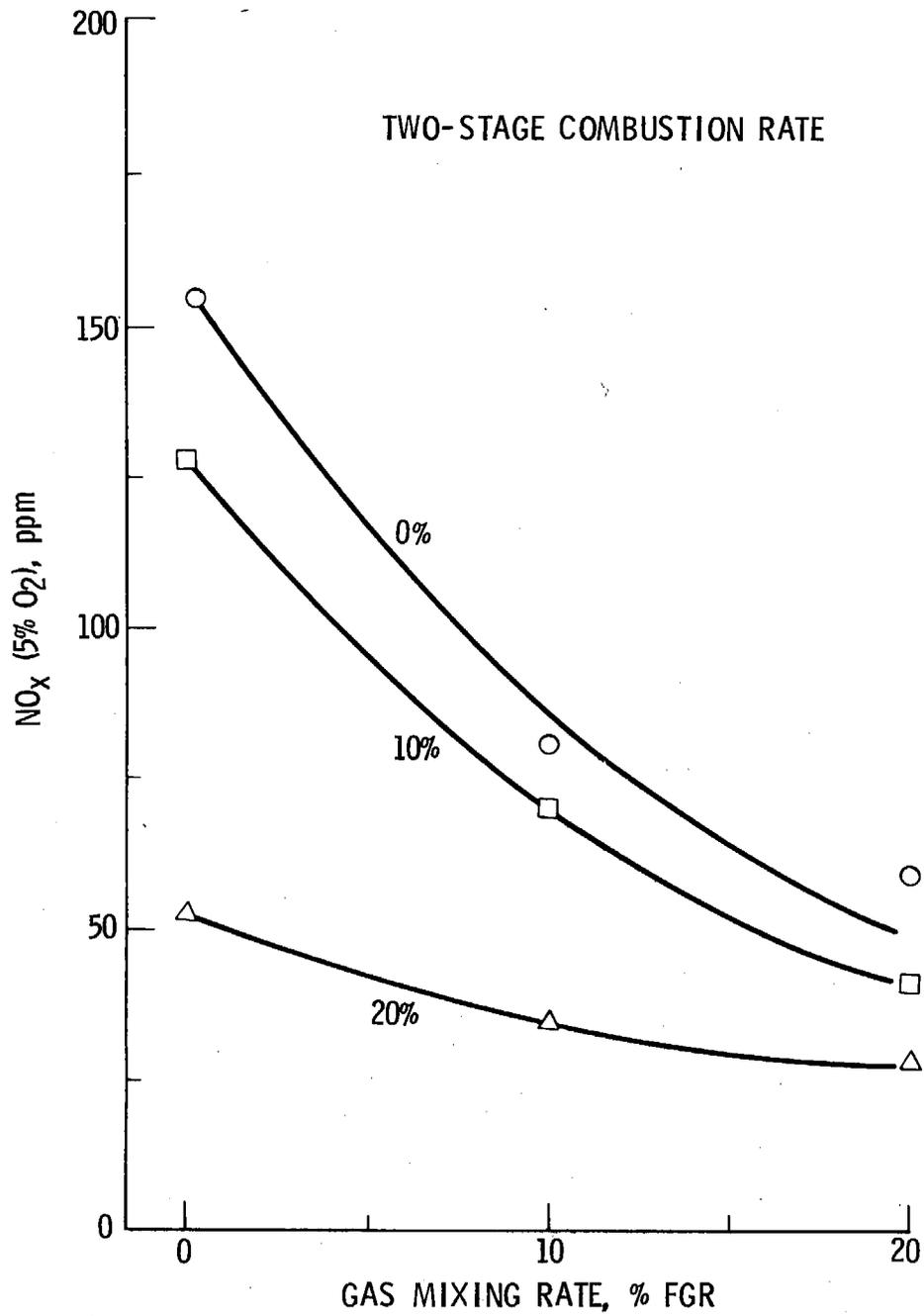


Figure 2-21. Effect of staged combustion and flue gas recirculation for low NO_x burner with gaseous fuel at full load (156 MW) (Ref. 2-14)

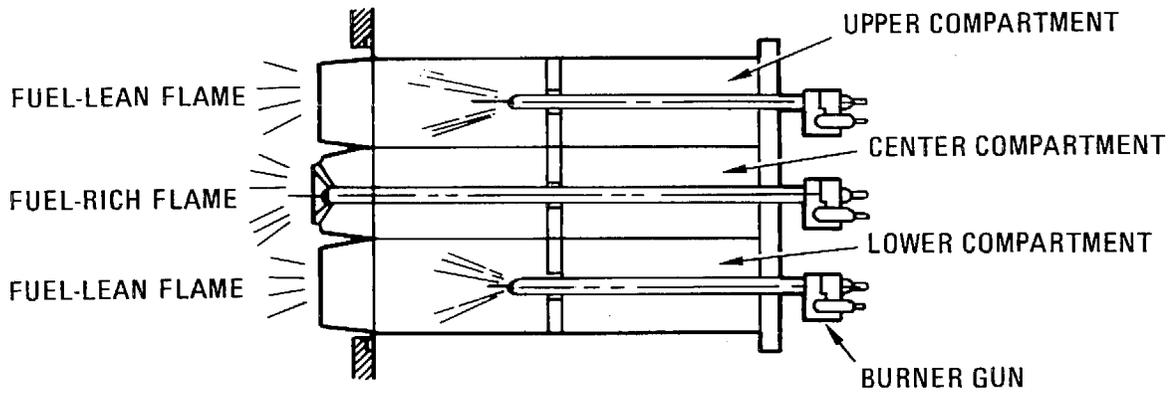


Figure 2-22. Structure of spray premix T-burner (off-stoichiometric combustion type burner) (Ref. 2-15)

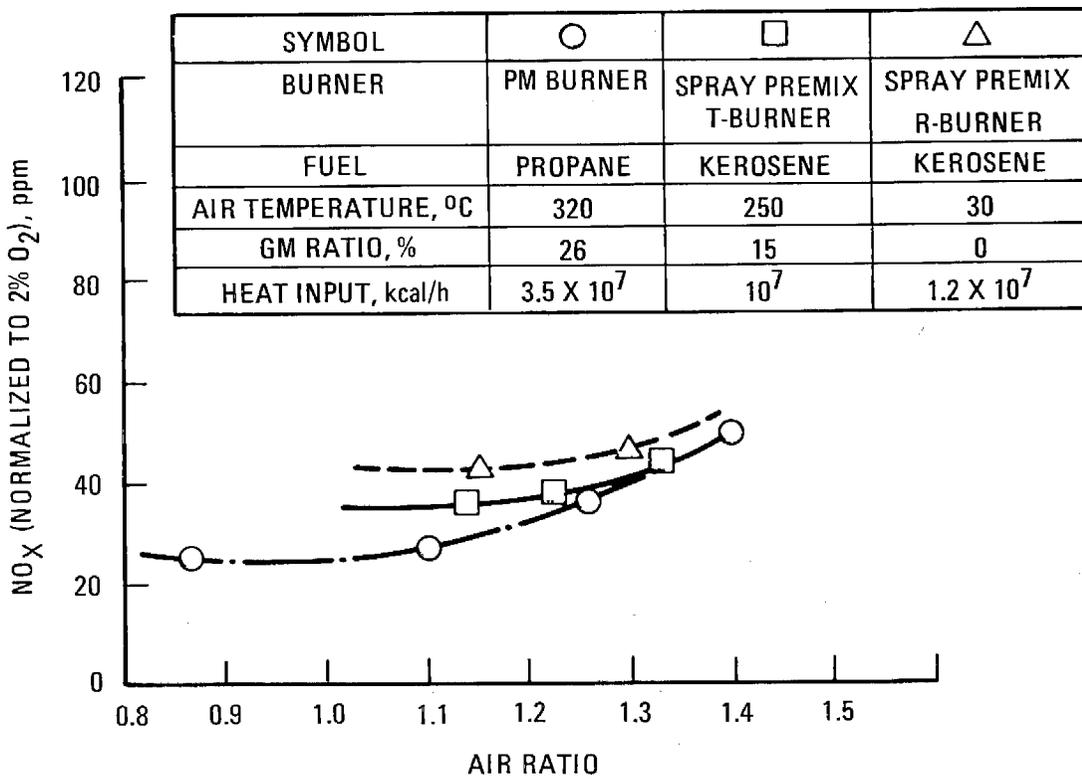


Figure 2-23. NO_x versus overall air ration (Ref. 2-15)

Other variations of the premix concept are available for utility boilers using gaseous fuels and for industrial boilers. These are designated as the premix (PM) and spray premix R-burner, respectively. The effect of FGR, burner load, operating air ratio, and combustion air temperatures are shown in Figure 2-24. In virtually all cases, NO_x levels of less than 60 ppm (2% of O_2) are reported (Ref. 2-15).

NO_x levels produced by another OSC type burner installed on a boiler using grade C oil are shown in Figure 2-25. The main feature of this burner developed by the Volcano Company (Ref. 2-4) is the dissimilarity of the fuel-injection orifice diameters in the atomizer nozzle tip. Air is uniformly distributed around the atomizer. Therefore, OSC is achieved, those regions around the larger fuel holes being fuel rich and fuel lean zones being produced around the smaller holes. The burner tends to increase soot emissions at low excess air because of the resultant oxygen deficiency in some of the flame zones.

The OSC type burners are being developed by Babcock Hitachi, IHI, and others for coal application. Because of the development status of these burners and since the principal focus of this study is to evaluate applicability of LNB to existing oil-fired utility boilers, detailed discussions of coal-fired applications are not included in this report.

An example of the amount of NO_x reduction that can be expected in coal-fired boilers is shown in Figure 2-26. Approximately 35% reduction is realized with LNB. When combined with TSC and FGR, approximately 55% reduction is achieved (Ref. 2-16).

2.4.2.5 Combination Types

Several LNBs combine the methods described. The SRG burner developed by Nippon Furnace Kogyo Kaisha, Limited, (NFK) is illustrated in Figure 2-27. It combines both TSC and self-recirculation principles (Ref. 2-17). It has been adopted mainly to oil heating furnaces and boilers. Characteristics are shown in Figure 2-28.

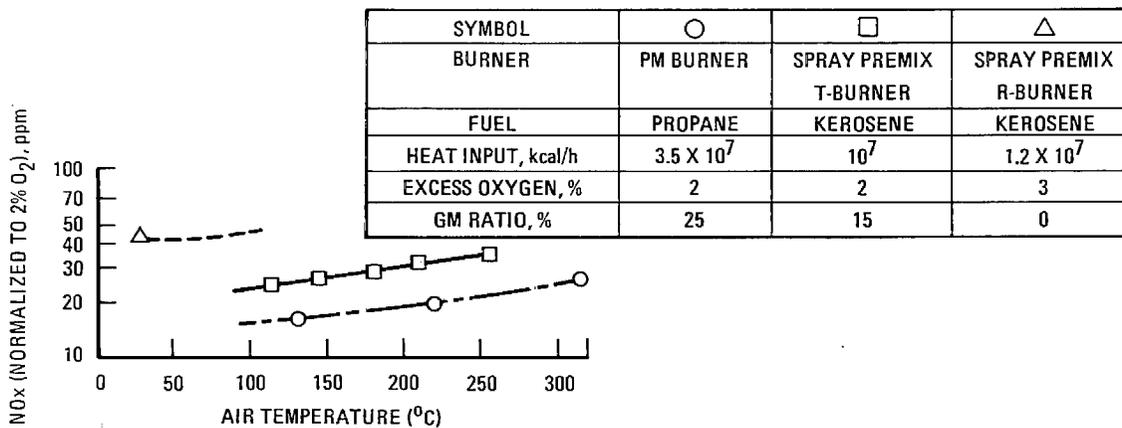
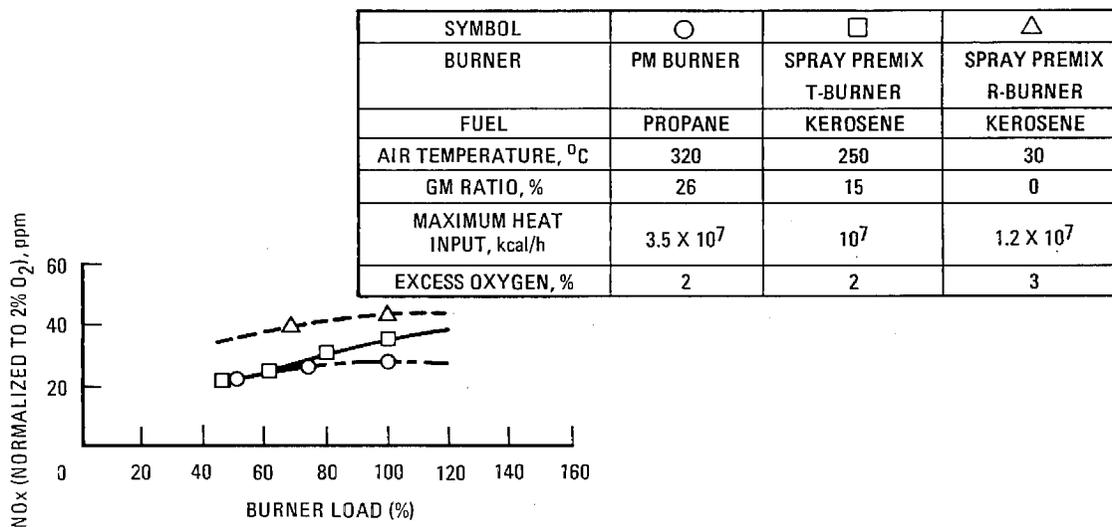
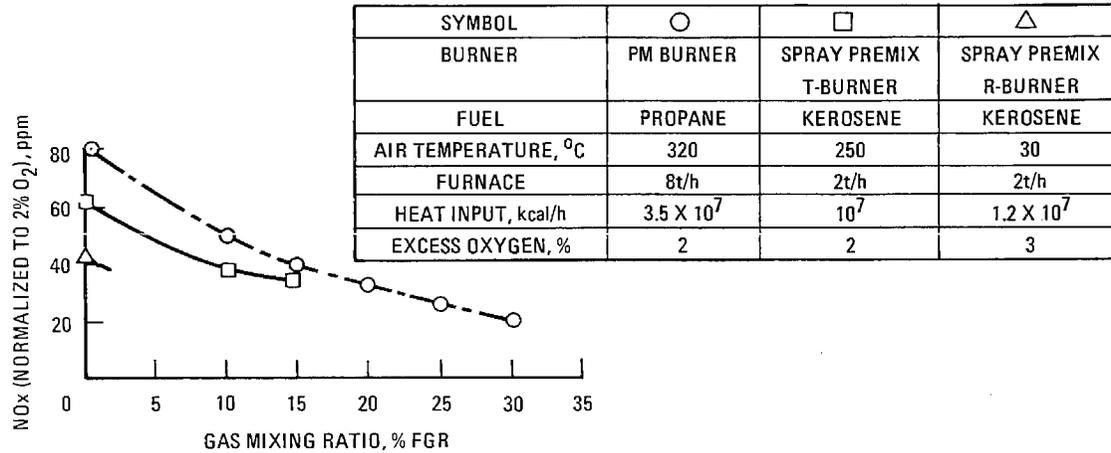


Figure 2-24. Effect of various parameters on a premix burner (Ref. 2-15)

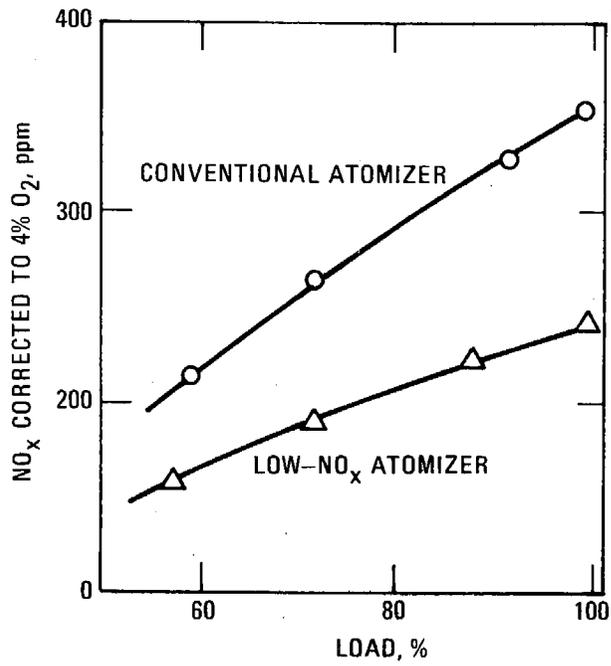


Figure 2-25. Effect of low NO_x atomizer on NO_x emissions (boiler capacity: 55 t/hr, ~235 MW_e; fuel, grade C heavy oil; air temperature, 280°C, 535°F) (Ref. 2-4)

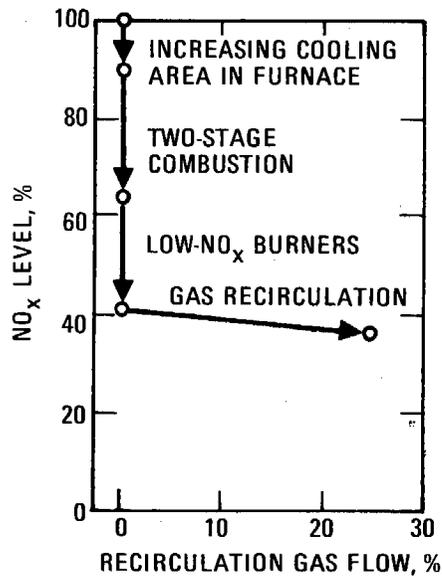


Figure 2-26. NO_x reduction in coal-fired boilers; low NO_x burners in combination with other combustion modifications (Ref. 2-16)

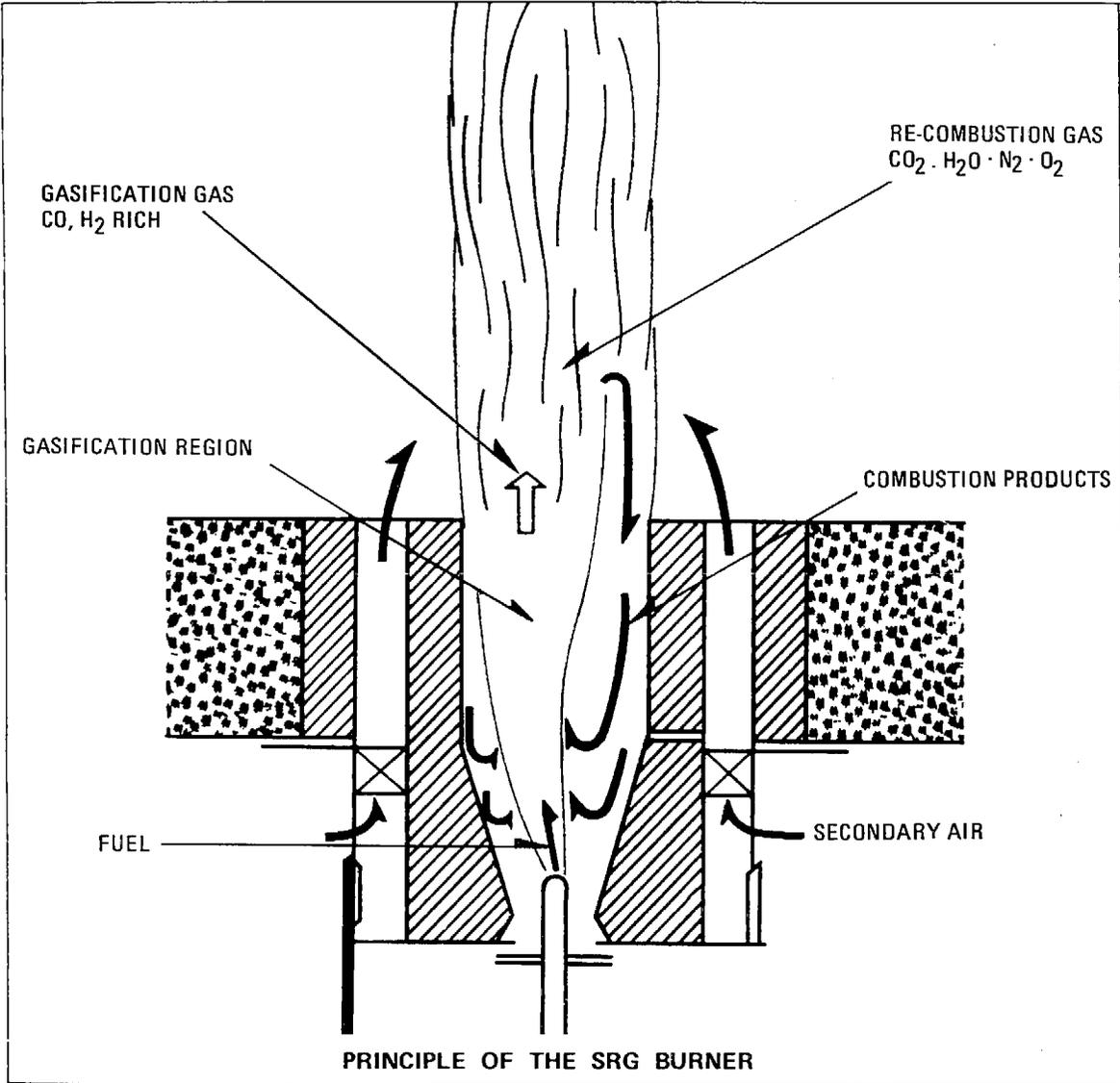


Figure 2-27. Principle of self-recirculation gasification burner (Ref. 2-17)

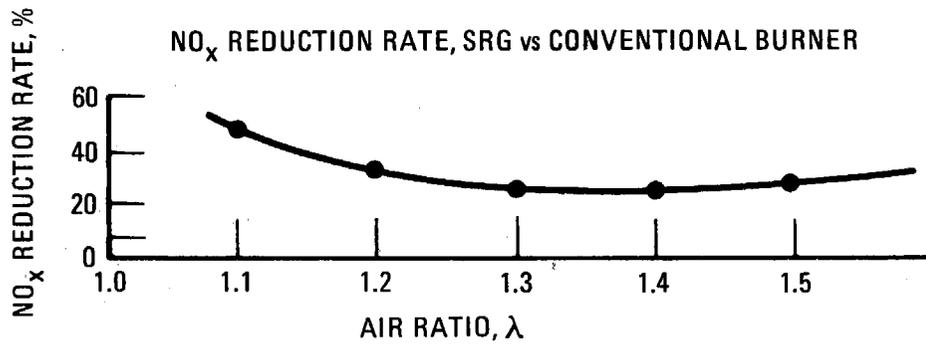
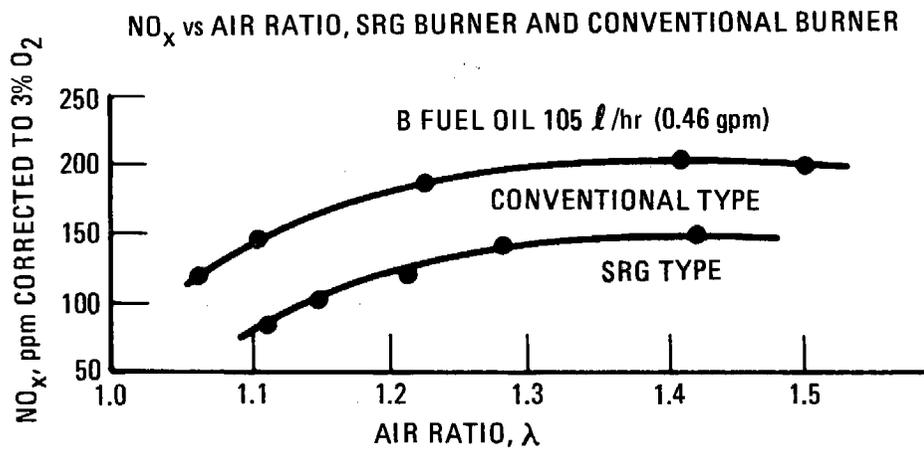


Figure 2-28. Characteristics of self-recirculation gasification burner (Ref. 2-17)

Hitachi Zosen has commercialized LNBS that combine staged (OSC) combustion and self-recirculation for liquid and gaseous fuel applications. All the air is fed to a central premix zone, with a portion of the fuel forming an oxygen-rich primary zone. Subsequently, the fuel burns rapidly in the combustion chamber, minimizing both thermal and fuel NO_x. Fuel for the second stage is fed into the combustion chamber through several second-stage nozzles located in a circular pattern around the primary combustion zone. The high-velocity fuel jets aspirate flue gas to complete the combustion in a fuel-rich zone, at a low heat release rate and temperature. No decrease in combustion efficiency is claimed (Ref. 2-18).

Relative to a nonstaged burner, NO_x reductions in the range of 70 to 80% are observed for liquid (with low fuel nitrogen content) and gaseous fuels (Table 2-10). The effect of the amount of secondary fuel, overall

TABLE 2-10. LOW NO_x BURNER PERFORMANCE (Ref. 2-18)

Fuel	% Fuel N	NO _x (3% O ₂), ppm		% NO _x Reduction
		No Secondary Fuel	With Secondary Fuel Injection	
Methane (CH ₄)	0	77	15	81
Propane (C ₃ H ₈)	0	82	18	78
Kerosene	Not Available	98	25	74
Heavy Oil A	~0.2	117	32	72

^aBurner capacity 400 x 10⁴ kcal/hr (16 x 10⁶ Btu/hr), 4 burners, flue gas temperature 850°C (1560°F).

stoichiometric ratio, and air preheat temperatures is shown in Figures 2-29 through 2-31. These burners are available in capacities ranging from 50×10^4 kcal/hr (2×10^6 Btu/hr) to 300×10^4 kcal/hr (120×10^6 Btu/hr).

2.4.3 Selective Noncatalytic Reduction

Application of SNR as a thermal DeNO_x process to reduce NO in combustion effluents using ammonia (thermal DeNO_x described in Section 2.3.2) has been patented by the Exxon Research and Engineering Company (ERE) (Ref. 2-19).

In commercial applications, NO_x reduction rates of 35 to 65% have been reported (Table 2-11) although higher efficiencies have been reported in laboratory tests conducted in the U.S. and Japan.

2.4.3.1 Laboratory Tests

Laboratory experiments conducted in the U.S. and Japan (Refs. 2-4, 2-7, and 2-20) have indicated the potential for NO_x reductions in excess of 90% for emissions emitted from the combustion of gaseous and liquid fuels (Figures 2-32 through 2-34).

In addition to influencing the extent of the NO_x conversion reaction, temperature, ammonia injection rate, and residence time are also key factors that affect the amount of unreacted ammonia that is emitted. Test data (Figure 2-35) indicate that the concentration of unreacted ammonia at the injection temperature of 965°C (1770°F) increases significantly at NH₃/NO ratios greater than 2.0 (molar ratio of NH₃ to initial NO concentration). At a lower reaction temperature, 870°C (1600°F), the amount of ammonia carryover increases substantially because of the slower chemical reaction. If the reaction is allowed to occur at higher temperatures than the optimum 955°C (1750°F), at temperatures above 1000°C (1830°F), there is virtually no NH₃ carryover (breakthrough). However, this is at the expense of NO conversion as can be seen in Figure 2-33.

Ammonia injection rates also depend on the initial concentration of nitric oxide. Experimental data (Figure 2-36) show that lower molar ratios of NH₃ to NO are needed to achieve a specific process efficiency when the initial NO concentration is greater than 400 ppm. These experimental data further indicate that the percent oxygen in the flue gas may also have some effect on required NH₃ injection rates.

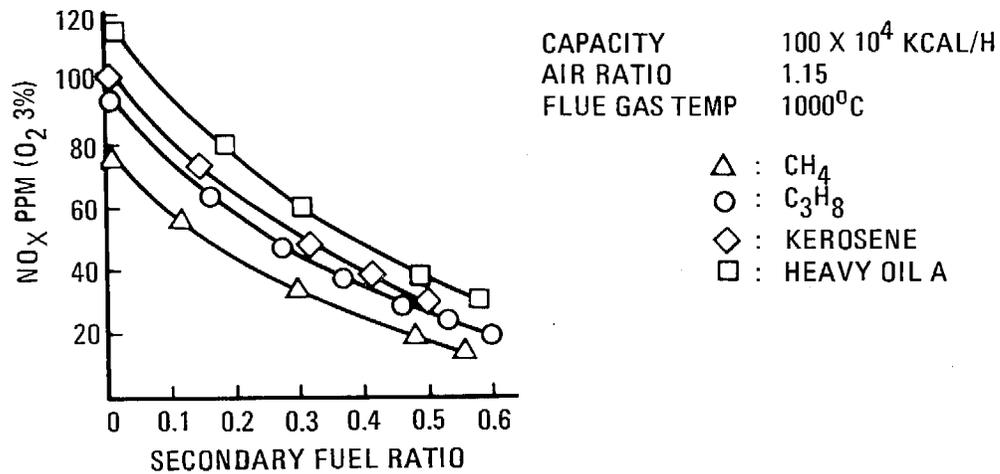


Figure 2-29. Effect of secondary fuel on low NO_x burner emissions (Ref. 2-18)

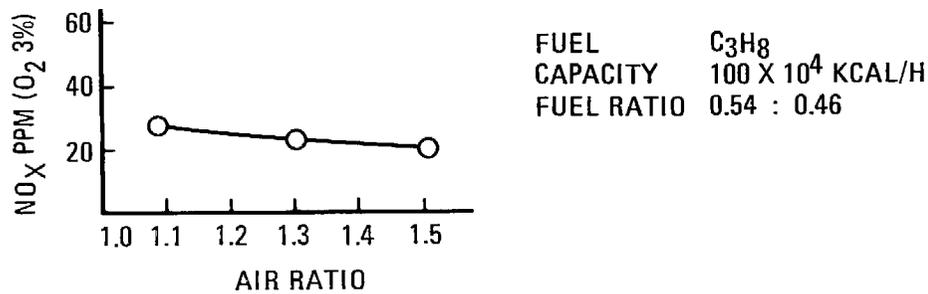


Figure 2-30. Effect of overall stoichiometric air ratio on NO_x emissions (Ref. 2-18)

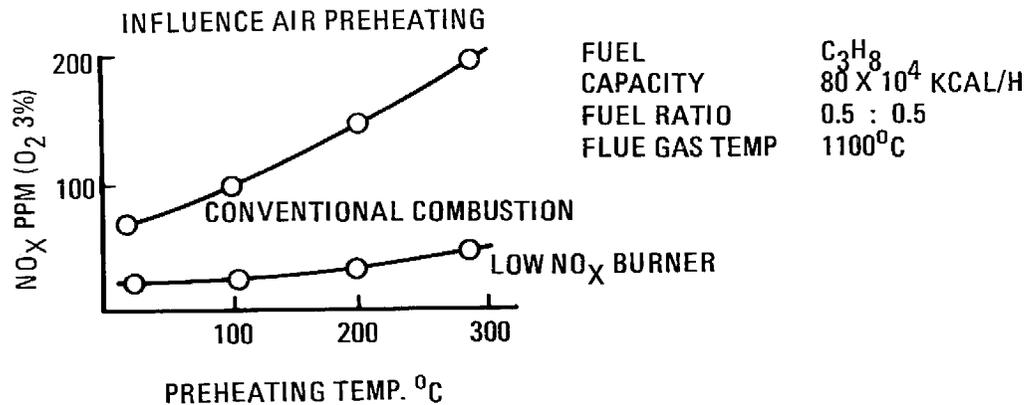


Figure 2-31. Effect on preheat temperature on NO_x formation (Ref. 2-18)

TABLE 2-11. LARGE THERMAL DeNO_x INSTALLATIONS

Process Developer	User	Plant Site	Gas Source	Fuel	Capacity, Nm ³ /hr (10 ⁶ Btu/hr)	Gas Temp, °C	Initial NO _x @3% O ₂ , ppm	NH ₃ /NO _x	H ₂ /NO _x	%NO _x Reduction	NH ₃ , ppm	Start Date	Ref.
MHI ^a	Chubu Electric	Chita	Utility boiler	Low-S oil	1,036,000 350 MW	850-1030	110-140	1.5	0	45	NA	2/77	2-4, 2-21
MHI	NA ^b	NA	Utility boiler	Low-S oil	1,000,000 350 MW	NA	NA	NA	NA	NA	NA	c	2-22
MHI	MCI ^d	Mizushima	Industrial boiler	Low-S oil	160,000	NA	NA	NA	NA	NA	NA	c	2-22
MHI	MCI	Mizushima	Industrial boiler	High-S oil	500,000 x 2	NA	NA	NA	NA	NA	NA	c	2-22
MHI	MCI	Yokkaichi	Industrial boiler	High-S oil	160,000	NA	NA	NA	NA	NA	NA	c	2-22
MCI	MCI	Mizushima	Industrial boiler	Low-S oil	540,000	NA	NA	NA	NA	NA	NA	75	2-4
TT ^e	Mitsui Petro-Chem	Chiba	Industrial boiler	Naphtha	120,000	670-780	130	2.0	NA	35-40	NA	12/75	2-4, 2-21
TT	Tonen Sekiyu Kagaku	Kawasaki	Cogen boiler	Low-S oil, gas	423,000 x 2 (1135x2)	705-800	140	1.5	0.4	60	40	76, 78	2-4, 2-21, 2-23
TT	Tonen Sekiyu Kagaku	Kawasaki	Industrial boiler	Low-S oil, gas	(215)	950	196	1.8	0	55	10	7/77	2-21, 2-23
TT	Kykyto Petro	Chiba	Vacuum pipestill	Low-S oil, gas	160,000 (190)	920	156	2.0	0	63 ^f	30	10/77	2-4, 2-21
TT	Toa Nenryo	Kawasaki	CO boiler	CO	314,000 (400)	705-800	170	1.5	0.5	50	80-100	3/78	2-4, 2-21, 2-23
TT	Toa Nenryo	Kawasaki	Atomospheric pipestill	Low-S oil, gas	254,000	920	156	2.0	0	63 ^f	30	3/78	2-4, 2-21

^aMHI = Mitsubishi Heavy Industries

^bNA = Not available

^cIn service

^dMCI = Mitsubishi Chemical Industries

^eTT = Tonen Industries

^f30 to 40% at NH₃/NO_x = 0.5

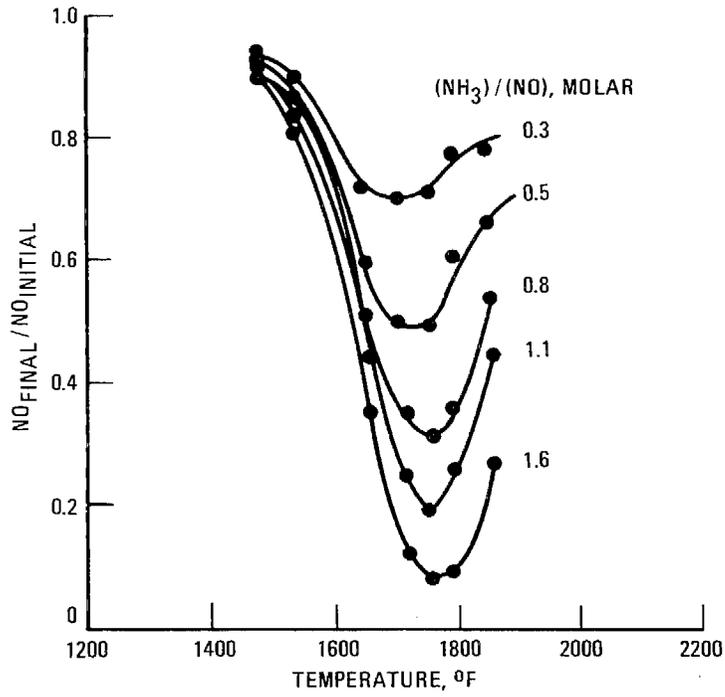


Figure 2-32. Effect of flue gas temperature on thermal DeNO_x performance (Ref. 2-20)

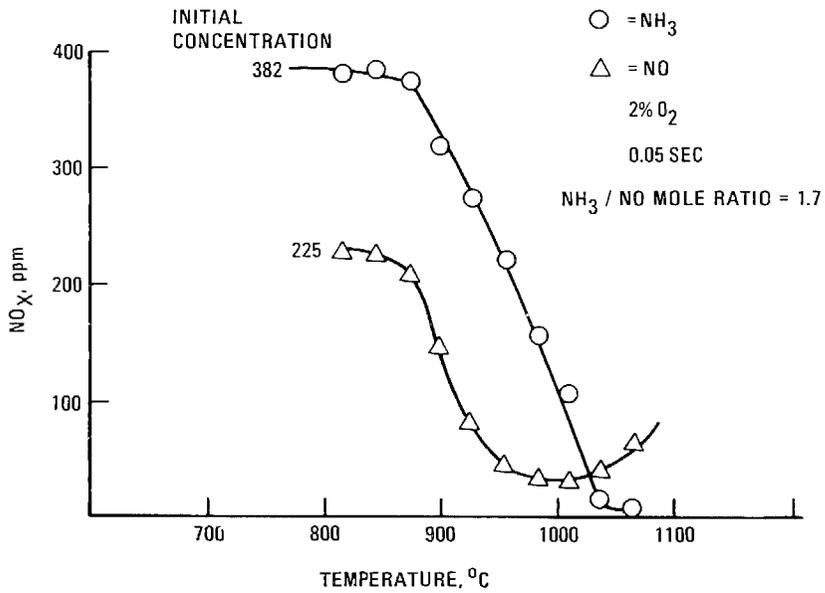
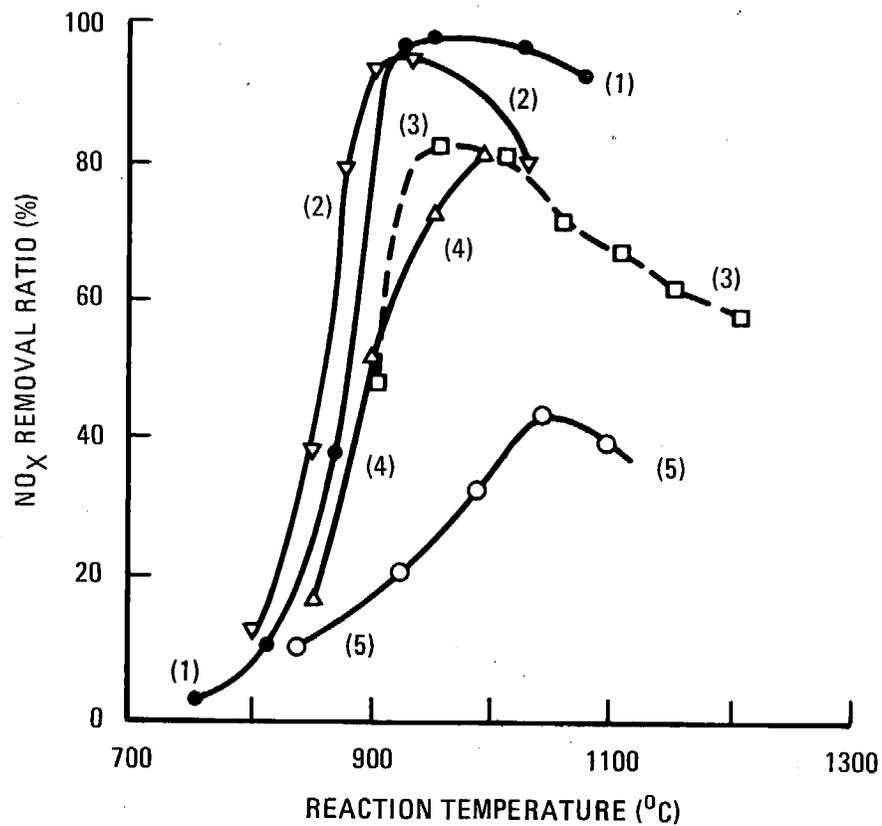


Figure 2-33. Thermal DeNO_x Performance as a Function of temperature (laboratory data) (Ref. 2-7)



RESEARCH ORGANIZATION	REACTOR	INITIAL CONCENTRATION			REACTION TIME (sec)
		NO (ppm)	NH ₃ (ppm)	O ₂ (%)	
(1) EXXON (U.S.)	SILICA TUBE	826	2540	4.6	0.13-0.17
(2) MCI (JAPAN)	SILICA TUBE	200	400	2.0	0.4
(3) CHUBU ELECTRIC (JAPAN)	SILICA TUBE	200	240	1.0	0.2
(4) OKAYAMA UNIVERSITY (JAPAN)	SILICA TUBE	500	667	1.0	0.1-0.13
(5) CRIEPI (JAPAN)	OIL FURNACE	225	225	1.0	0.11

Figure 2-34. Results of selective noncatalytic reduction laboratory tests conducted by five research organizations (Ref. 2-4)

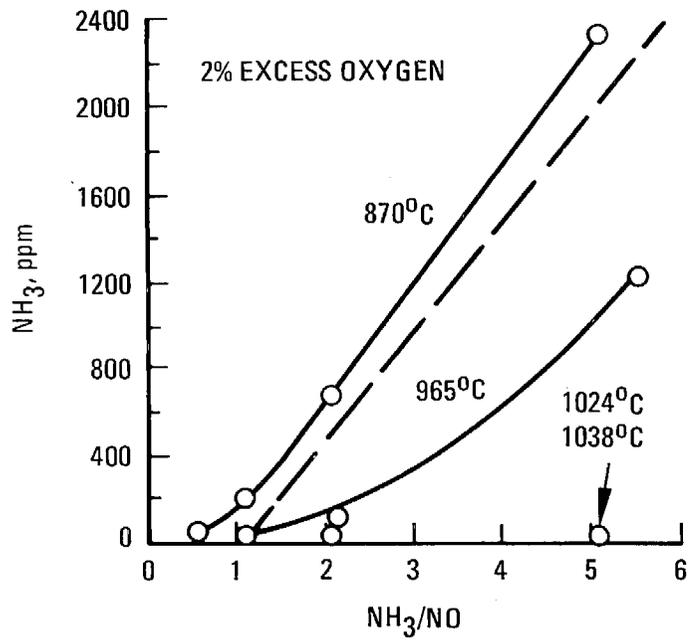


Figure 2-35. Effect of NH₃ injection rate on unreacted NH₃ carryover emissions (Ref. 2-20)

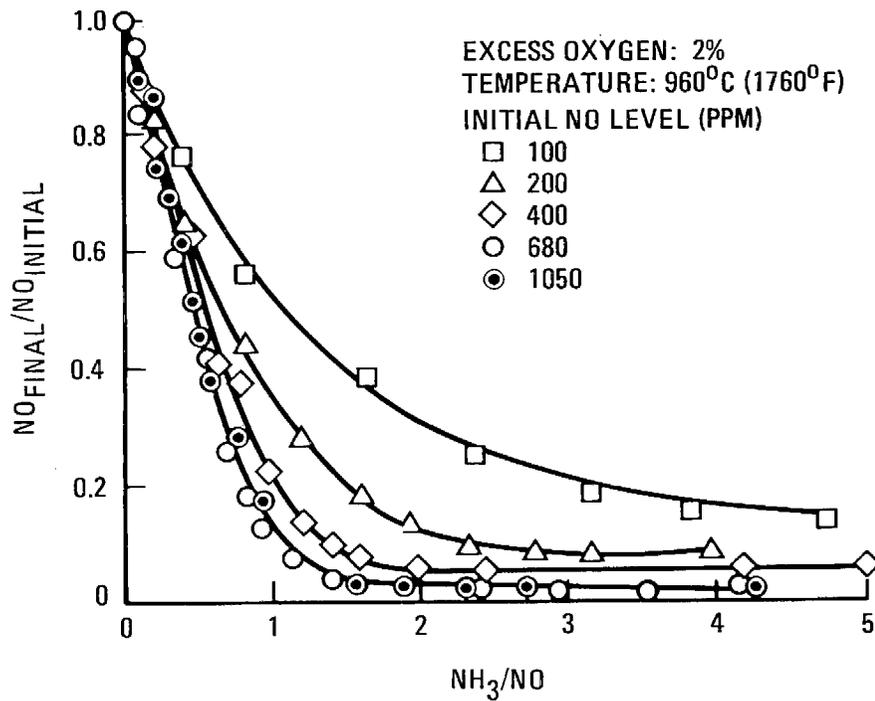


Figure 2-36. Effect of initial nitric oxide concentration and ammonia ratios on thermal DeNO_x (Ref. 2-20)

Experiments conducted by ERE show that for typical conditions, an ammonia injection ratio of 2.0 achieves the optimum maximum process efficiency. Figure 2-37 shows that minimal additional NO reduction is obtained by increasing the ammonia injection rate beyond the NH_3/NO molar ratio of 2.0.

The thermal DeNO_x process can be applied over a greatly widened range of temperatures if certain additives are injected with the ammonia. Of the many additives investigated, hydrogen is the most effective over the temperature range of from 700 to 1010°C (1290 to 1850°F) as shown in Figure 2-38. Figure 2-39 illustrates the effect of hydrogen in shifting the optimum reaction temperature measured in a commercial-size firetube boiler. The magnitude of this shift depends on the amount of H_2 injected relative to the NH_3 . For example, at H_2/NH_3 molar ratios on the order of 2:1, SNR of NO_x can be made to occur at 700°C (1290°F).

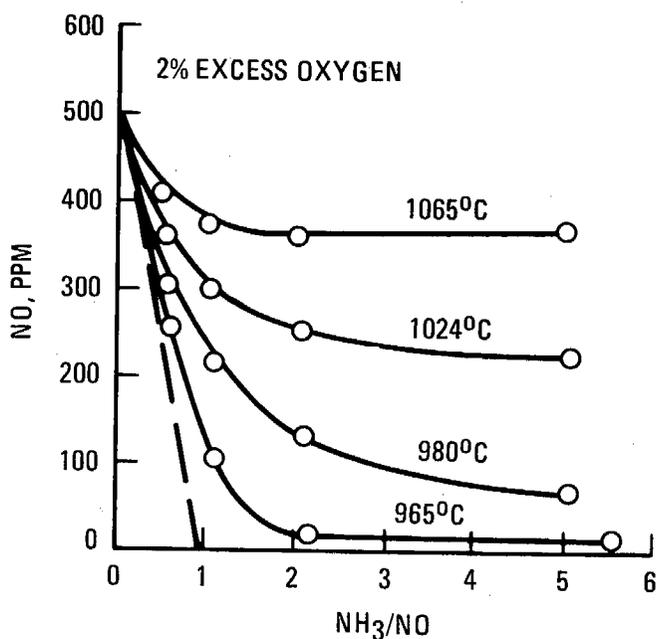
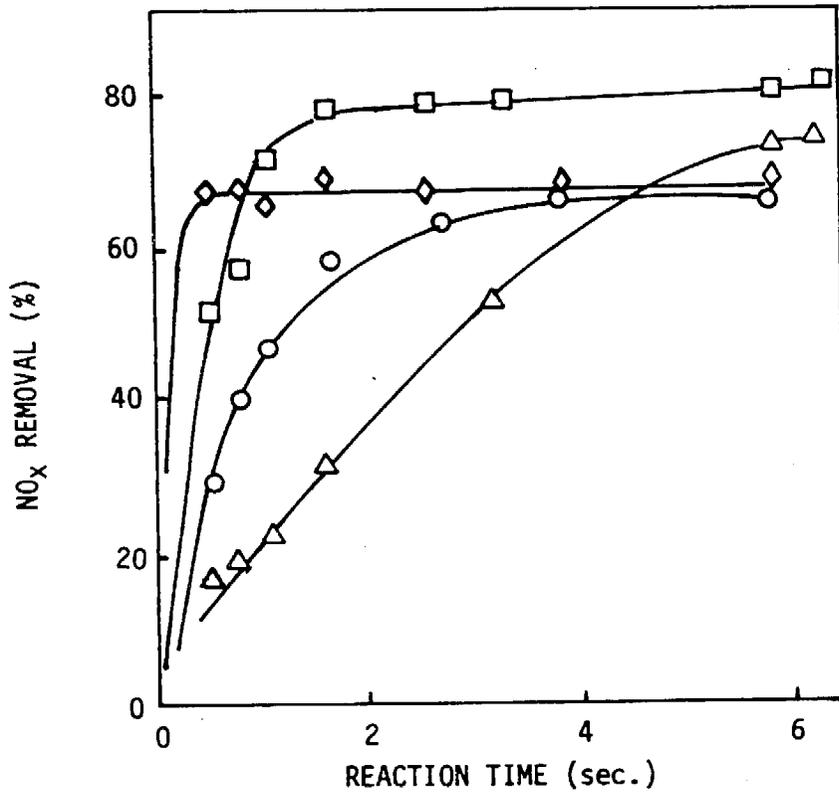


Figure 2-37. Effect of NH_3 injection rate on NO emissions (Ref. 2-20)



Marks	Composition of Inlet Gas						Reaction Temp. (°C)
	NO(ppm)	NH ₃ (ppm)	H ₂ (%)	O ₂ (%)	H ₂ O (%)	N ₂	
□	500	667	0	5	10	Balance	950
△	500	667	0	5	10	"	850
◇	500	667	3000	5	10	"	700
○	500	667	3000	5	10	"	650

Figure 2-40. Effect of reaction time, temperature, and gas composition on NO_x removal: Okayama University tests (Ref. 2-4)

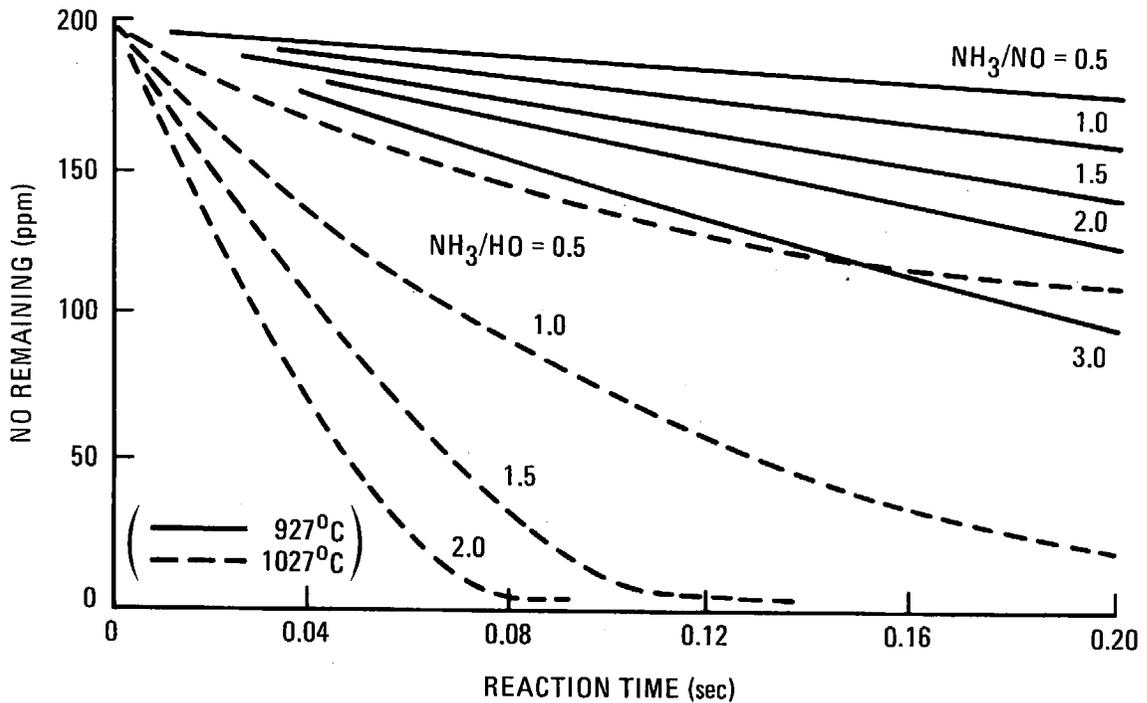


Figure 2-41. Effect of the NH_3/NO mole ratio and temperature on NO_x removal: CRIEPI studies (calculated for a gas similar to that from an oil-fired boiler containing 200 ppm NO, 1% O_2 , and 11% H_2O) (Ref. 2-4)

In Japan, Chubu Electric also has conducted extensive laboratory tests (Ref. 2-4). Maximum NO_x removal was obtained at 950 to 1000°C. When 240 ppm of NH_3 was used with 200 ppm NO, 80% of the NO was reduced at 1000°C, with a reaction time of 0.2 sec. The addition of H_2 at a mole ratio of 2.5 (H_2 - to - NH_3) shifted the optimum reaction temperature from 1000°C to about 800°C. The effects of temperature and NH_3/NO mole ratio on NO_x removal efficiency and NH_3 leakage were also studied. At 1100 and 1200°C, NO_x removal efficiency is low, 45 to 60% relative to 60 to 95% at 950 to 1000°C. It has been postulated that a portion of the NH_3 is converted to NO at the high temperatures. At the high temperatures ammonia emissions are also low (Figure 2-42). MHI has studied SNR jointly with Mitsubishi Chemical Industries (MCI) and has constructed a large-scale installation for Chubu Electric at Chita Station (Ref. 2-4). Their laboratory test results are generally consistent with others in terms of NO_x removal rates and residence time requirements. The latter are illustrated in Figure 2-43, which indicate that at 950°C a maximum residence time of 0.4 sec is required for maximum NO_x reduction. At 850°C, the duration required for the reaction to proceed exceeds 1.0 sec.

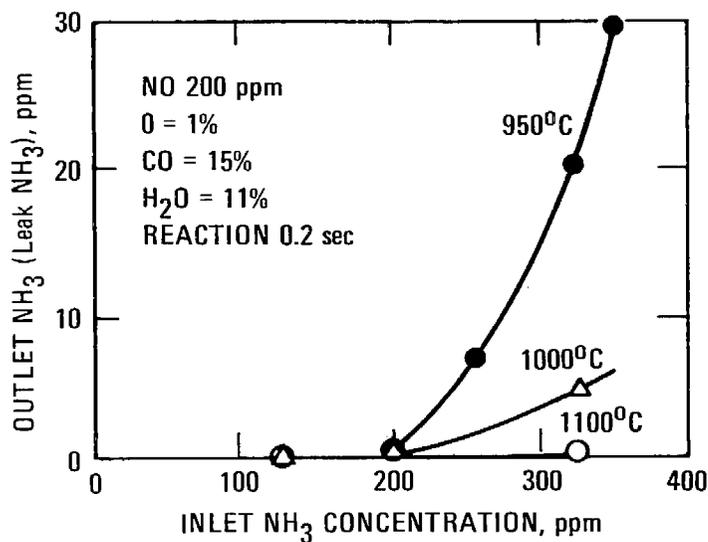


Figure 2-42. Inlet and outlet NH₃ at different temperature levels: Chubu Electric selective noncatalytic reduction tests (Ref. 2-4)

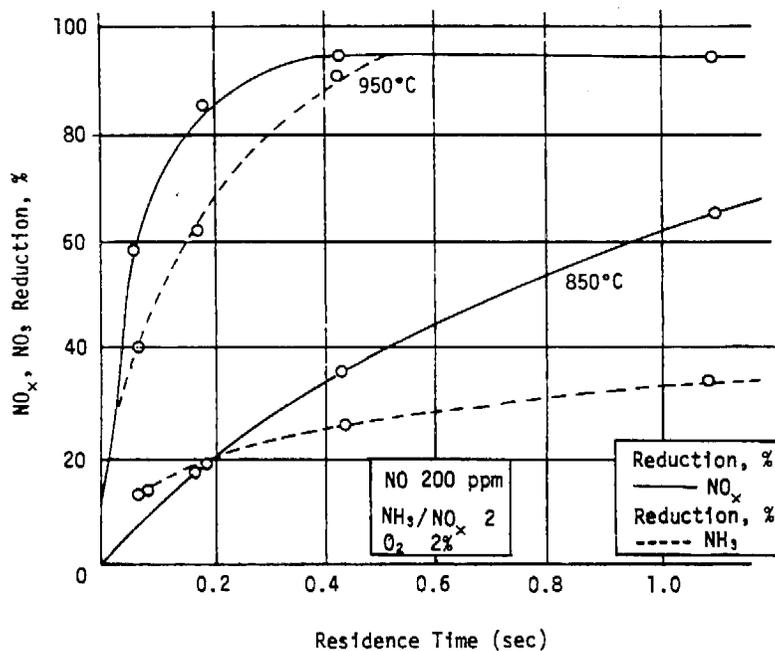


Figure 2-43. Effect of residence time laboratory test data for the MHI-MCI joint study at Chita Station (Ref. 2-4)

Poor mixing of ammonia with the flue gas may cause ammonia carryover to occur also at NH_3/NO molar ratios much lower than 2.0. In general, NH_3/NO molar ratios can be expected to range from 1.0 to 2.0 in large scale applications of the thermal DeNO_x process. The actual injection rate used for specific applications will depend on the desired NO_x reduction, flue gas conditions and source configurations, and ammonia emission considerations.

2.4.3.2 Large Scale Applications

Exxon has reported the effect of flue gas temperatures and ammonia injection rates for application of thermal DeNO_x applications on commercial boiler and furnace installations (Figures 2-44 and 2-45) (Ref. 2-21).

In Japan, MCI has conducted large scale tests at its own plants (Ref. 2-4). The characteristics and performance of major SNR plants are presented in Table 2-11. MHI and MCI have recently completed a large SNR installation which treats flue gas from a 375 MW utility oil-fired boiler at the Chita Power Station of Chubu Electric. Tonen Technology, a subsidiary of Toa Nenryo, has constructed medium-size commercial SNR plants (Table 2-11).

All of the units remove 40 to 60% of NO_x , using 1 to 2 moles NH_3 per mole NO_x . Because of the low gas temperatures, hydrogen was required in some cases to achieve the desired rate of NO_x reduction.

Mitsubishi Kakoki Kaisha has built many small SNR units (3000 to 6000 Nm^3/hr) to treat flue gas from heating furnaces. Although the removal ratio is not as high as by SCR, SNR is simple, less expensive, and useful for gas sources for which a high NO_x removal ratio is not needed (Ref. 2-4).

In the U.S., a demonstration test of a thermal DeNO_x system installed on an oil field steam generator has been reported (Ref. 2-25). A detailed discussion of the results are presented in Section 3.4.

Due to the nature of the process, with its relatively narrow operating temperature limits, requirements for good NH_3 mixing, and adequate reaction time, it appears to be more suitable to constant load sources with fixed emission characteristics. It has however, been applied on the No. 2 boiler at Chita Station of Chubu Electric Power Company, which has an operating load

that ranges from 100 to 30% (375 to 113 MW). The boiler generates 1225 tons/hr of steam at 375 MW of electric power, and the total gas volume exceeds 1,000,000 Nm³/hr. It burns a low-sulfur oil (0.2% S), and the flue gas

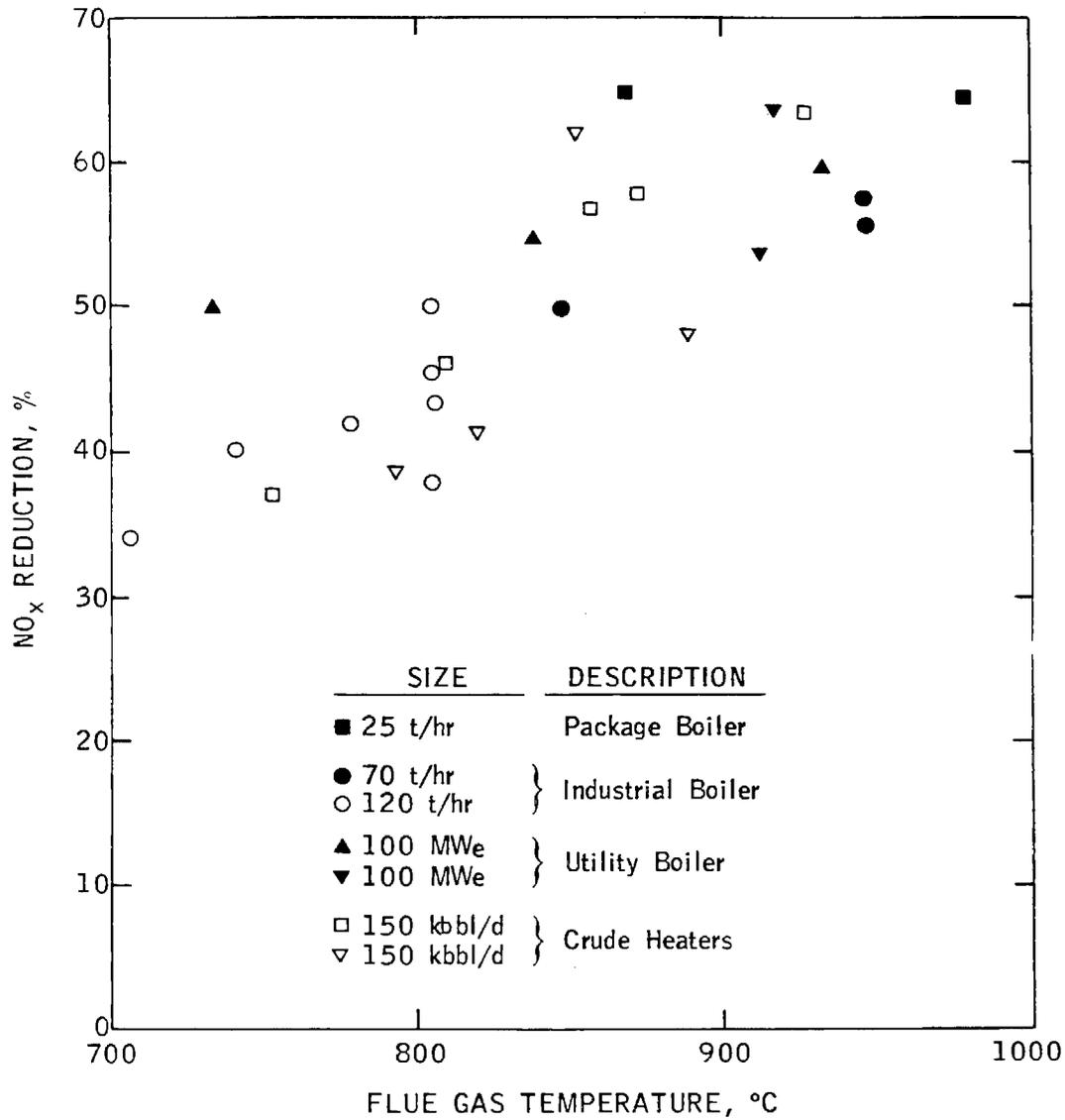


Figure 2-44. Performance of thermal DeNO_x systems in commercial applications (Ref. 2-24)

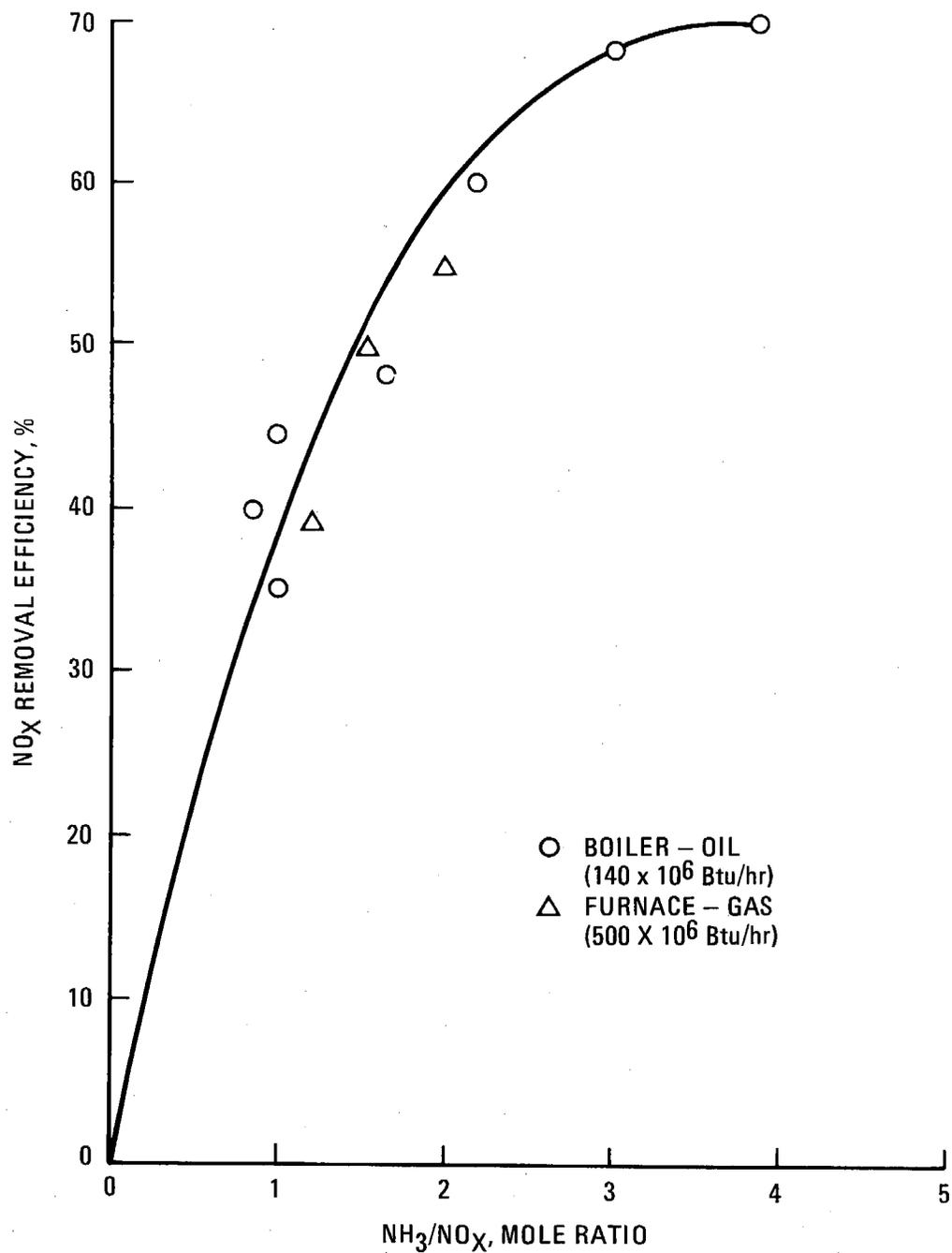


Figure 2-45. Effect of NH₃ mole ratio on NO_x removal efficiency during commercial tests of the thermal DeNO_x process (conducted at the Kawasaki Refinery of Exxon's Japanese affiliate, Tonen Petrochemical K. K.) (Refs. 2-6 and 2-8)

contains about 100 ppm SO_x , of which about 3 ppm is SO_3 , and 110 to 140 ppm NO_x , virtually all of which is NO. Because of temperature fluctuation due to the boiler load, 15 water-cooled ammonia injection nozzles were placed in two locations between the secondary superheater and reheater (Figure 2-46).

The gas temperature at 150 to 375 MW (40 to 100% load) ranges from 900 to 1150°C at the front nozzles and 800 to 1030°C at the rear ones. Ammonia is injected from the rear nozzles at 290 to 375 MW (78 to 100% load, 930 to 1030°C), from both nozzles at 225 to 290 MW (60 to 70% load), and only from the front nozzles below 60% load (below 1000°C). When the boiler load drops below 50%, NH_3 is seldom added because the NO_x emissions are generally within regulatory limits.

Operating conditions for 40% NO_x removal with less than 20 ppm NH_3 carryover are illustrated in Figure 2-47 (Ref. 2-26). A NH_3/NO_x mole ratio of 1.5 may be used at full load, with smaller ratios at lower loads.

A comparison of the calculated NO_x removal efficiencies and unreacted NH_3 carryover with those observed in actual plant operation can be made (Figure 2-48). The observed removal efficiency was slightly lower when the initial NO_x concentration was 110 ppm than when it was 140 ppm. In both cases, the predicted NO_x removal performance and the actual operating data were in good agreement. Actual levels of unreacted NH_3 were a little larger than the calculated amount. A NO_x removal efficiency of about 40% has been obtained with NH_3 emissions of 30 ppm by using 1.5 mole of NH_3 per mole of NO.

Operation of the SNR system at the Chita Station was initiated in February 1977, and NO_x removal has been 40 to 45%. It has been reported as virtually trouble-free except for deposits of ammonium salts with particulates in the air preheater (Ref. 2-4). Initially, deposits of ammonium salt formed, thereby increasing the pressure drop. After two months of operation, a water wash was required for their removal. The problem has been relieved by increasing the soot blowing capacity. It is estimated that a water wash will be required about twice a year. It usually gives no visible plume, but a plume has been reported in the winter when the outlet NH_3 concentration exceeded about 40 ppm.

BOILER TYPE: MITSUBISHI – CE CONTROL, RADIANT REHEAT DIVIDED
EVAPORATION: 1225 T/H, 375 MW
PRESSURE: 176 ATG
TEMPERATURE: 571/540.6°C

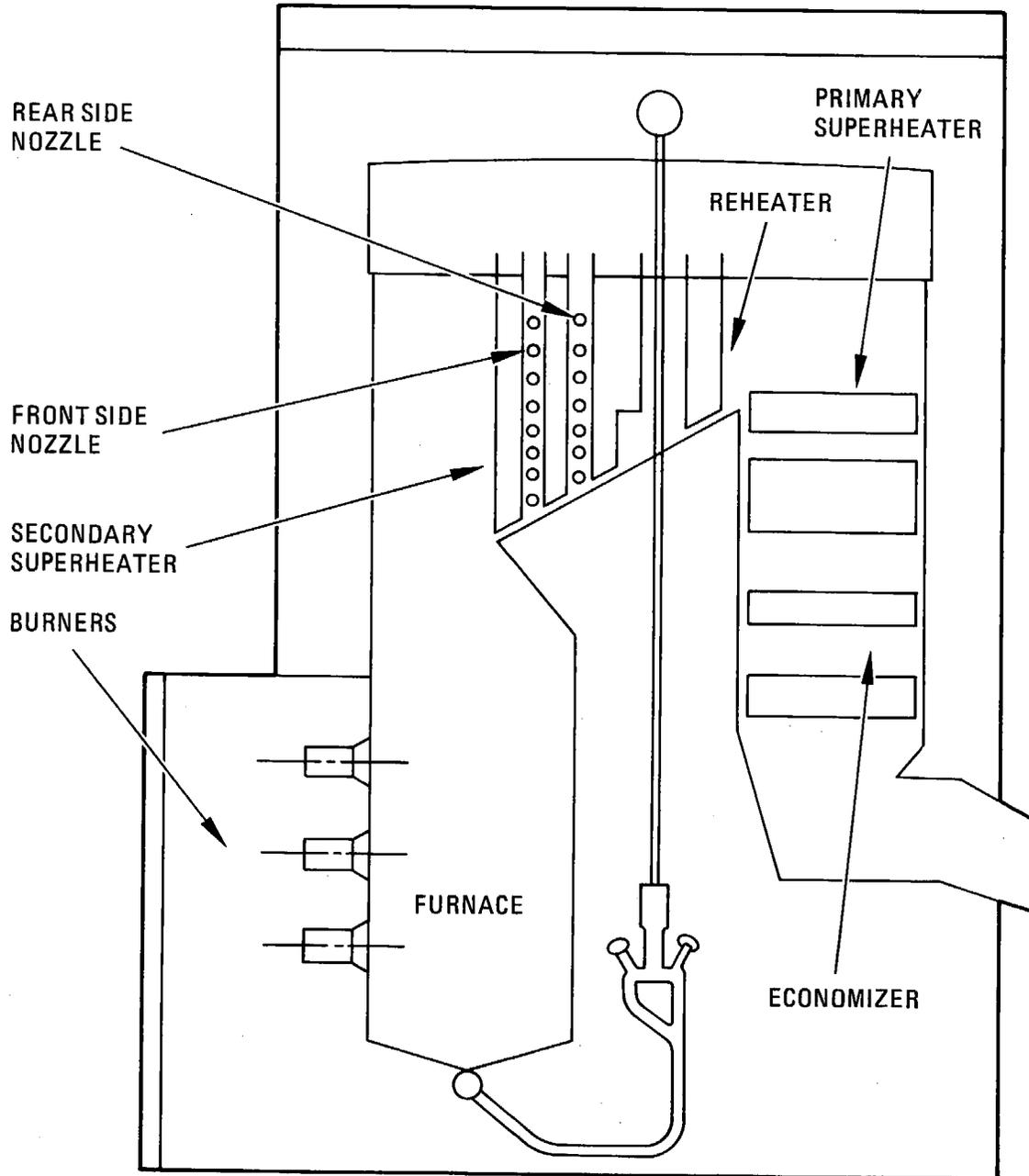


Figure 2-46. Location of NH_3 injection nozzles in the No. 2 boiler thermal DeNO_x installation at Chita Station (Ref. 2-4)

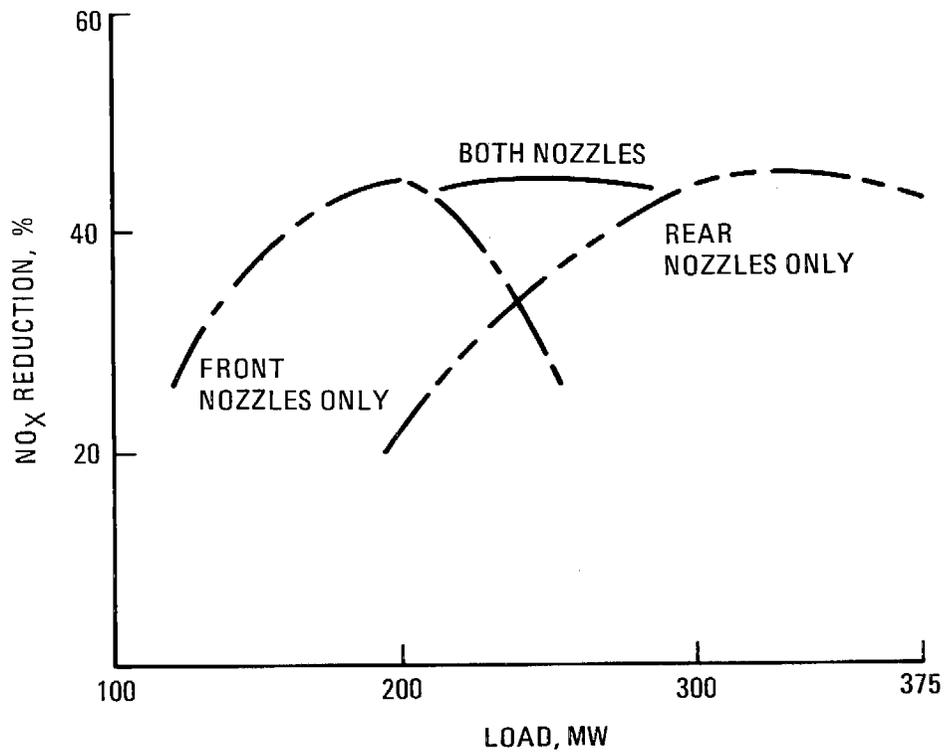
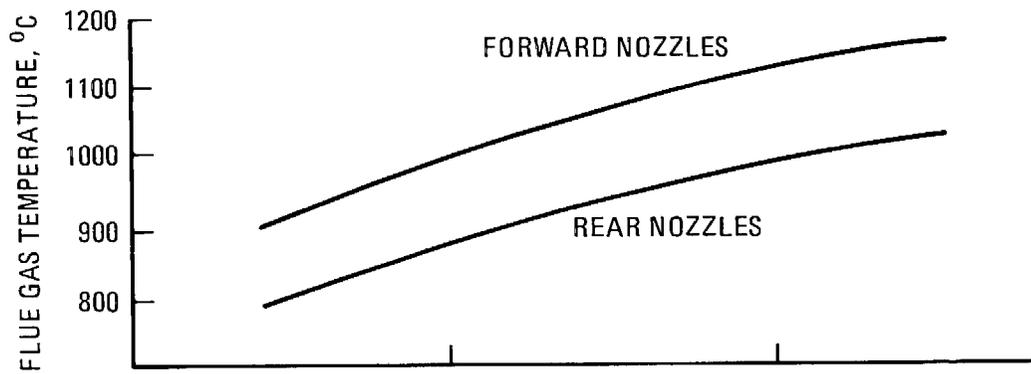


Figure 2-47. Effects of NH_3 injection position and load on NO_x reduction rates (Refs. 2-4 and 2-26)

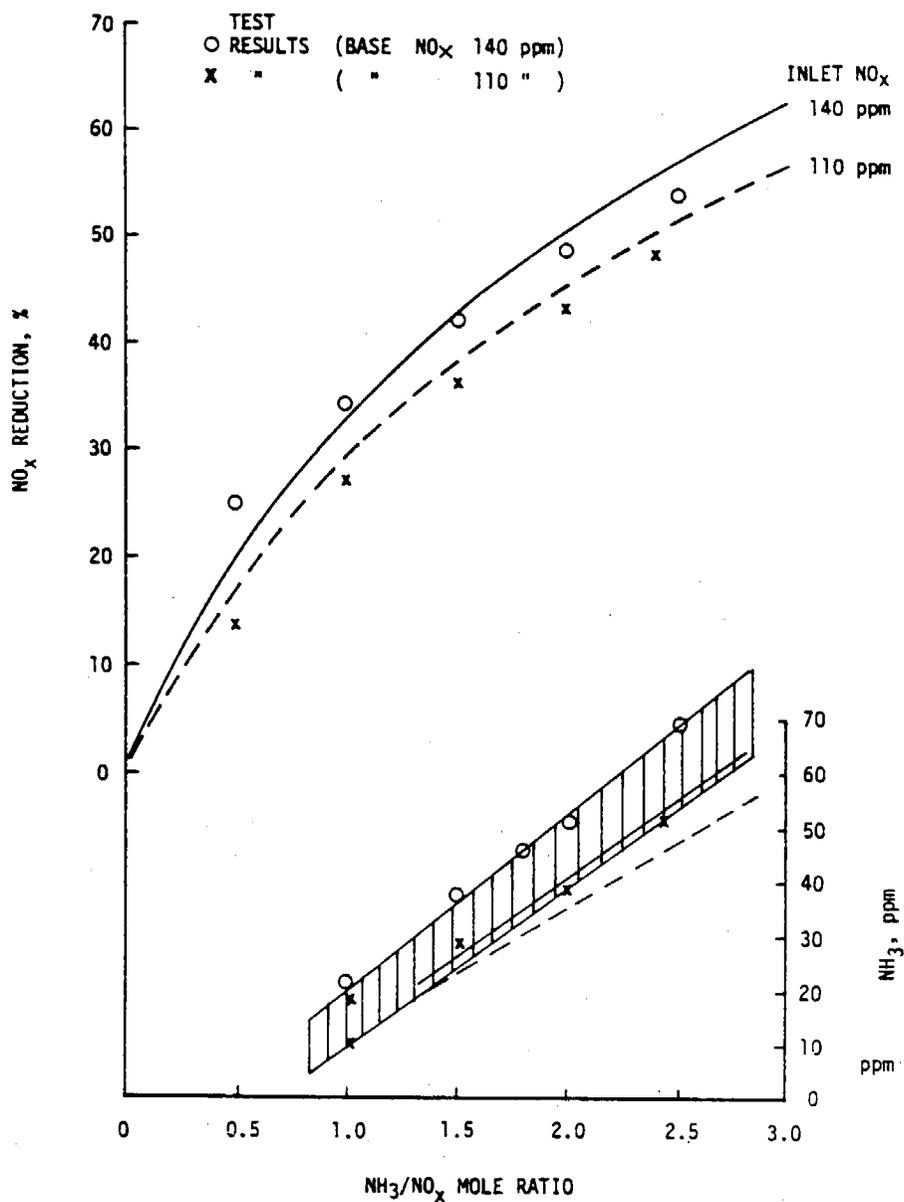


Figure 2-48. Comparison between test results and predicted performance of the No. 2 boiler at Chita Station (Refs. 2-4 and 2-26)

A thermal DeNO_x installation for an industrial boiler which can generate 120 tons/hr of steam (flue gas 120,000 Nm³/hr, 40 MW_e) has been operated intermittently by Mitsui Petrochemical since 1976 at its Chiba plant (Ref. 2-4). The plant has five boilers, and the specific boiler chosen for the SNR installation was selected because of a relatively large volume for its capacity and the availability of space to locate ammonia injection nozzles. The nozzle locations have a temperature range of about 700 to 800°C, which is slightly lower than the optimum reaction temperature of 850 to 1000°C for NO_x reduction by NH₃. Therefore, H₂ has been used to obtain optimum NO_x reduction at the 700 to 800°C range. Three nozzles were installed, and a total of 2 moles NH₃ and 8 moles H₂ injected for each mole of NO_x. Steam is used as the NH₃ carrier, air not being used because of the presence of H₂. Usually 35 to 40% of the NO_x is removed, and the NH₃ carryover emissions are 10 to 15 ppm.

Initially the boiler burned 0.8% sulfur oil, and the unreacted NH₃ ranged from 20 to 30 ppm. After a few weeks operation plugging of the air preheater with ammonium bisulfate deposits was reported (Ref. 2-4). Subsequently, sulfur-free fuel, gas or oil (about 0.02% S), has been used, and operation has been trouble-free.

Mitsui Petrochemical recently installed an SCR unit for a larger boiler (200,000 Nm³/hr) which burns low-sulfur oil (0.2 to 0.6% S) (Ref. 2-4). The air preheater has experienced no plugging problem with NH₄HSO₄ because the NH₃ carryover has been maintained below 5 ppm.

There are five relatively large SNR units in Japan constructed in 1976 or later for oil or petrochemical companies. They have been used when a pollution alert is issued or when the total NO_x emissions from the refinery or the petrochemical plant exceed regulatory limits. The DeNO_x units can be operated continuously if necessary and can remove 45 to 57% of the NO_x with the addition of 1 to 2 moles of NH₃ per mole of NO_x. In some cases, hydrogen (0.5 mole H₂ per mole of NH₃) is required.

2.4.4 Selective Catalytic Reduction

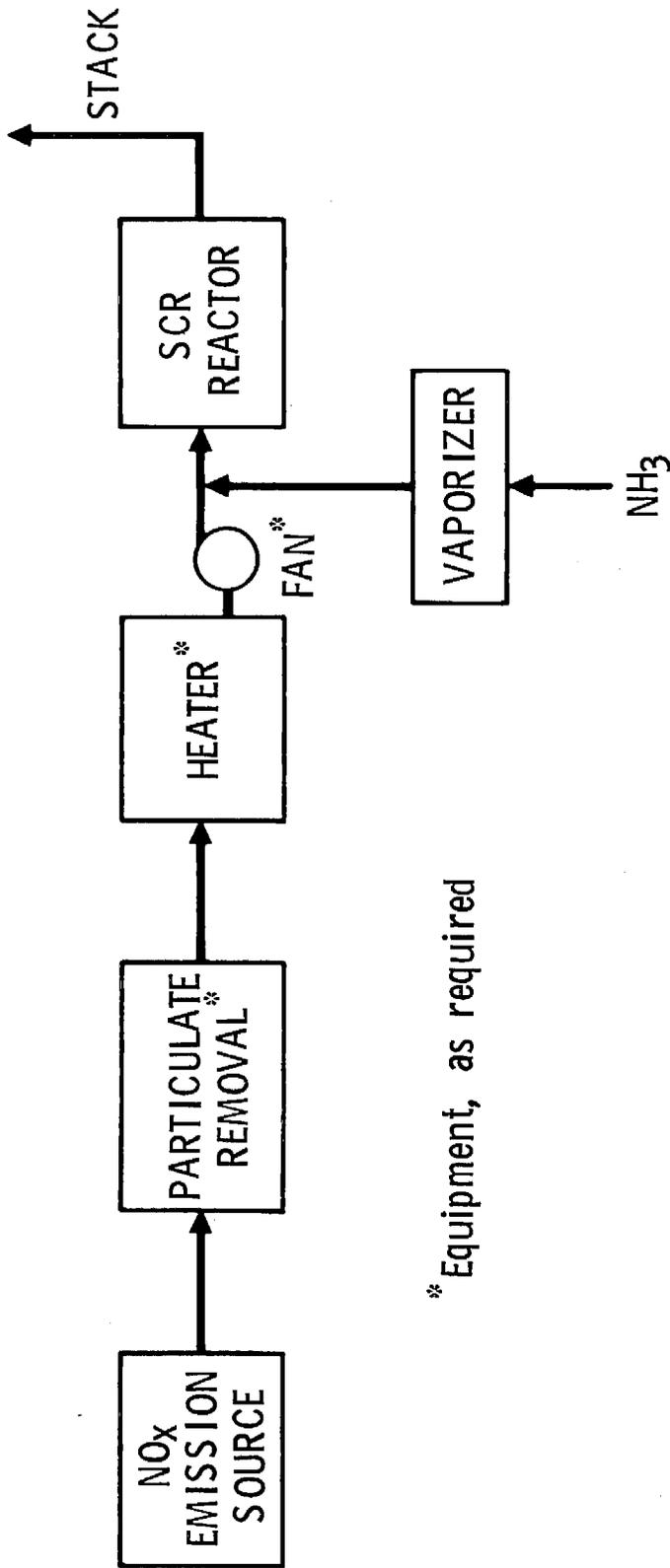
As discussed in Section 2.3.3, the SCR process (Figure 2-49) takes advantage of the selectivity of NH_3 to reduce NO_x to N_2 and H_2O in the presence of a catalyst. Limited experimental work on SCR has been done in the U.S. but most of the effort has been centered in Japan, primarily in the area of treating gases from the combustion of liquid and gaseous fuels.

Over 70 commercial SCR installations have been constructed (Table 2-12). Ninety percent NO_x removal, if specified, is reported as being achieved in commercial installations.

Many of the commercial installations use granular catalysts in fixed bed reactors to treat clean gas from the combustion of LNG, liquid petroleum gas (LPG), kerosene, or off-gas from the petrochemical industry. The remaining use various types of reactors with moving beds or parallel-flow catalysts to treat semidirty gas from the combustion of low-sulfur oil or dirty gases from the combustion of high sulfur or from coke ovens and iron ore sintering machines.

Base metal oxide catalysts that operate in the temperature range of 300 to 400°C (570 to 750°F) are most frequently used. They are less expensive, more resistant to SO_x poisoning, and do not produce N_2O as has been reported for some noble metal catalysts (Ref. 2-27).

Catalyst composition is usually a proprietary item; little is known about the actual compositions in use. Japanese development has been mainly with base metals such as iron, vanadium, chromium, manganese, cobalt, nickel, copper, and barium. Experimental results and NO_x conversion rates vary widely for these catalysts, depending on operating conditions and gas characteristics. The metals are normally deposited on a carrier, which was alumina in the earlier stages of development. It was found that in gases containing SO_x , the SO_3 reacted with the Al_2O_3 to form a sulfate, decreasing the available surface area and reducing catalytic activity over a period of time. Other problems affecting the use of catalysts include a decrease in its activity and an increase in the pressure drop resulting from particulate plugging. Methods to minimize these problems include parallel passage reactors, moving bed reactors, specially shaped catalysts, and catalyst regeneration.



* Equipment, as required

Figure 2-49. Simplified flow sheet of the selective catalytic reduction process

TABLE 2-12. SELECTIVE CATALYTIC REDUCTION PLANTS^a (LARGER THAN 10,000 Nm³/hr)

Processor Developer	User	Plant Site	Gas Source	Fuel ^b	Capacity Nm ³ /hr	Gas Pretreatment ^c	Type of Reactor ^d	Completion	MW _e	Installation ^e	% NO _x Removal ^f	Reference																																							
Hitachi, Ltd.	Kawatetsu Chemical Chiyoda Kenzai Kansai Paint Nishin Steel Nishin Steel Kansai Electric Chubu Electric Nippon Oils & Fats Company A Company B Company C Company C Company C Company C Company D Company E Company F Company G	Chiba Kaizuka Amagasaki Amagasaki Amagasaki Kainan Chita Amagasaki — — — — — — — — — — —	Coke Oven Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler	COG, BFG HO(HS) Kerosene HO(LS) HO(LS) Crude Oil LNG HO Kerosene HO(LS) HO HO HO HO HO Coal Kerosene Coal HO	500,000 15,000 16,000 20,000 19,000 300,000 2,000,000x2 20,000 30,000 490,000 466,000 466,000 441,000 735,000 280,000 980,000 400,000 53,000	ESP, H None H H H None None None SNR DS None None None DS — — — —	IMB IMB IMB FB IMB FB IMB IMB FBP ^g FBP ^g FBP ^g FBP ^g FBP ^g FBP ^g — FBP — — —	Oct 1976 Sep 1976 Oct 1977 Aug 1977 July 1977 Jun 1977 Apr 1978 Apr 1978 Sep 1978 Jul 1978 Jul 1978 Jan 1980 Feb 1980 May 1980 July 1980 Sep 1980 Mar 1981 Jul 1981 Oct 1979	165 5 5 7 7 115 700 7 10 175 156 156 156 250 110 90 125 18	R R R R R — N R R R R R R — — — — — — — —	95 70 90 90 — — 90 90 50 30 30 30 80 90 80 80 80	2-4, 2-26, 2-28																																							
													Mitsubishi H.I.	Sumitomo Chemical Osaka Gas Tokyo Electric Fuji Oil Kyushu Electric Company H Company I Chubu Electric	Sodegaura Takaishi Yokosuka Sodegaura Kokura — — Chita	Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler	HO(LS) LNG HO(LS) HO(LS) LNG 1,690,000x2 1,010,000 HO(LS) HO(LS) HO(LS)	300,000 15,000x2 40,000 200,000 1,690,000x2 1,010,000 490,000 1,920,000	ESP, HE None	IMB FB FBP FBP ^g FB FBP ^g FBP ^g FBP ^g FBP ^g — — — — — — — — — —	Sep 1976 Dec 1976 Mar 1977 Jan 1978 Oct 1978 Feb 1978 Feb 1978 Feb 1978 Feb 1978 Sep 1978 Mar 1981 Jul 1981 Oct 1979	100 5 14 67 600 350 156 700 600 156 500 375 375 375 375	— — R N N R R R R R — — — — — — — — — —	— — 80+ 86+ — 40 40 80+	2-4, 2-22 2-26																										
																										Ishikawajima H.I.	Chubu Electric Ajinomoto Company J Company K Chugoku Electric Chugoku Electric Tohoku Electric Company L Company M Company N Company D Company P	Taketoyo Kawasaki — — Kudamatsu Kudamatsu Miyata — — — — — — — — — — — — —	Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler Boiler	Crude Oil HO(LS) HO(LS) HO(LS) Crude Oil HO(LS) HO(LS) HO(LS) HO(LS) HO(LS) HO(LS) HO(LS) HO(LS) HO(LS)	20,000 180,000 960,000 480,000 1,000,000 1,900,000 1,660,000 470,000 1,320,000 1,000,000 1,000,000 1,000,000 1,000,000	None None SNR SNR None None None None None None None None None None None None None None None None None	FBH MB FBH ^{g,h} FBH ^{g,h} FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH FBH	Apr 1977 Jan 1978 Apr 1978 Jun 1978 Apr 1979 Apr 1979 July 1979 Aug 1981 Apr 1980 Jul 1980 Mar 1982 May 1982 July 1982	7 70 350 156 375 700 600 156 500 375 375 375	— R	— — 50-60 50-60 — 80 60 — — — — — — — — — — — — —	2-4, 2-29													
																																							Hitachi Zosen	Idemitsu Kosan Shindeikyowa P.C. Toshin Steel Kawasaki Steel Nippon Satetsu Kansai Oil	Chiba Yokkaichi Hyogo Chiba Chiba Sakai	Boiler Boiler Furnace SM Furnace Boiler	CO HO(HS) Kerosene Coke, Oil HO HO	350,000 440,000 71,000 762,000 10,000 150,000	H ESP, DS, HE, H None DS, ESP, HE, H None —	FB FB FB FB FB FB FB FB FB FB FB FB FB FB FB FB FB FB FB FB	Oct 1975 Nov 1975 May 1976 Nov 1976 Dec 1976 1979	145 120 — 254 3 50	— —	93 80 — 95 — —	2-1, 2-30

TABLE 2-12. SELECTIVE CATALYTIC REDUCTION PLANTS^a (LARGER THAN 10,000 Nm³/hr) (Continued)

Processor Developer	User	Plant Site	Gas Source	Fuel ^b	Capacity Nm ³ /hr	Gas Pretreatment ^c	Type of Reactor	Completion	MW _e	Installation ^e	% NO _x Removal ^f	Reference
Sumitomo Chemical	Sumitomo Chemical Higashinohon M. Nihon Ammonia Sumitomo Chemical Sumitomo Chemical Sumitomo Chemical Maruichi Kokan Sumitomo Chemical Sumitomo Chemical	Sodegaura	Boiler	HO(HS)	30,000	ESP	FB	July 1973	10	-	-	2-4
		Sodegaura	Furnace	LPG	200,000	None	FB	May 1974	70	-	>90	
		Sodegaura	Furnace	LPG	250,000	None	FB	Jan 1975	80	-	>90	
		Nihon Ammonia	Furnace	LPG	200,000	None	FB	Apr 1975	70	-	-	
		Sumitomo Chemical	Furnace	LPG	200,000	None	FB	Apr 1975	70	-	-	
		Sumitomo Chemical	Furnace	LPG	100,000	None	FB	-	3	-	-	
		Maruichi Kokan	Furnace	LPG	10,000	None	FB	Mar 1976	80	-	-	
		Sumitomo Chemical	Boiler	HO(HS)	240,000	Wet ESP, HE, H	FB	Oct 1976	100	-	-	
		Sumitomo Chemical	Boiler	HO(HS)	300,000	Wet ESP	IMB	-	-	-	-	
		Mitsui Toatsu	Mitsui Toatsu Osaka Pet. Chem. Mitsui Toatsu Nishinohon M. Idemitsu Pet. Chem.	Takaishi Takaishi Takaishi Takaishi Ichihara	Furnace Furnace Furnace Furnace Boiler	Off Gas Off Gas Off Gas Off Gas Off Gas	87,000 91,000 170,000 363,000 300,000	None None None None None	FB FB FB FB FB	Feb 1976 Sep 1976 Jan 1977 June 1977 Oct 1977	29 30 55 121 100	-
Mitsui Engineering	Mitsui Pet. Chem. Ukishima Pet. Chem.	Chiba Chiba	Boiler Boiler	CO HO(LS)	200,000 210,000	ESP, HE, H None	FB FBT	Oct 1975 July 1977	70 70	-	90 >90	2-4, 2-31
Sumitomo Chemical Engineering	Toho Gas Toho Gas Toho Gas Toho Gas	Sorami	Boiler	Naphtha	31,000x2	None	FB	Oct 1977	10	-	-	2-4
		Sorami	Boiler	Naphtha	23,000	None	FB	Dec 1977	8	-	-	
		Sorami	Boiler	Naphtha	23,000	None	FB	June 1978	8	-	-	
		Sorami	Boiler	Naphtha	19,000	None	FB	July 1978	6	-	-	
Mitsubishi Kakoki	Nippon Yakin Toho Gas Toho Gas Toho Gas Toho Gas	Kawasaki	Boiler	HO(HS)	14,000	H	FB	July 1978	5	-	-	2-4
		Sorami	Furnace	Naphtha	19,000	None	FB	Oct 1978	6	-	-	
		Kawasaki	Boiler	Naphtha	10,000	None	FB	Nov 1978	3	-	-	
		Chita	Boiler	Kerosene	30,000	None	FB	Oct 1977	10	-	-	
		Chita	Boiler	Kerosene	43,000	None	FB	Oct 1978	14	-	-	
JGC Corp.	Kashima Oil Fuji Oil Nippon Steel	Kashima	Furnace	HO(MS)	50,000	None	PP J	Nov 1975	17	-	95-98	2-4, 2-32
		Chiba	Boiler	CO	70,000	None	PP	July 1976	13	-	93-96	
		Kimitsu	Coke Oven	COG	150,000	None	PP I	Mar 1978	50	-	~95	
Asahi Glass	Asahi Glass	-	Furnace	-	70,000	None	IMB	-	13	PR	90 k	2-4
Kobe Steel	Kansai N.K.	Amegasaki	Coke Oven	COG	104,000	None ^m	IMB	Aug 1977	30	R	70-95 ⁿ	2-4, 2-33
Kurabo	Kurabo	Hirakata	Boiler	HO(HS)	30,000	None	CMB	Aug 1979	10	PR	93+	2-4

^a As of March 1979

^b COG = coke oven gas, BFG = blast furnace gas, HO = heavy oil, HS = high sulfur, LS = low sulfur, MS = medium sulfur, LNG = liquefied nitrogen gas, LPG = liquefied petroleum gas

^c ESP = electrostatic precipitator, H = heating, SNR = selective noncatalytic reduction, OS = desulfurization, HE = heat exchanger

^d IMB = intermittent moving bed, FB = fixed bed, FBP = fixed bed parallel plate, MB = moving bed, FBH = fixed bed honeycomb, FBT = fixed bed tubular catalyst, PP = parallel passage, CMB = continuous moving bed

^e PR = retrofit, N = new, PR = prototype test installation

^f Design or guarantee level; actual may be equal to or greater

^g Catalyst located in boiler ductwork

^h In combination with SNR

ⁱ Sintering machine

^j Low-temperature catalyst, ~200°C

^k Monthly water wash of catalyst required

^l 80 to 90% particulate removal; 20 to 50 mg/m³ inlet

^m Approximately \$500/hr between regeneration

ⁿ Data not available

In Japan catalysts used in clean gas applications are generally guaranteed for 2 years operation before replacement, and 1 year for dirty gas applications.

The formation of NH_4HSO_4 from unreacted NH_3 and SO_3 that may be present in the flue gas may be of some concern in certain applications. It is formed at temperatures in the range of 200 to 220°C as the gases are cooled in heat exchange equipment downstream of the reactor. The compound is corrosive and interferes with heat transfer, and at lower temperatures it can solidify necessitating steam blowing or water washing for its removal.

Factors affecting application of SCR will be discussed as well as general characteristics of the various processes and commercial installations.

2.4.4.1 Process Parameters

For 90% NO_x removal, space velocities (SV)* of 5,000 to 10,000 hr^{-1} have been used with granular catalysts treating dirty gases (Figure 2-50). Catalyst and reactor configurations for the various types of gases are shown in Figure 2-51. For clean gases, space velocities of 10,000 to 20,000 hr^{-1} have been used with highly reactive catalysts that would otherwise be poisoned by SO_x . The SV is usually less with parallel flow type reactors (Table 2-13).

Mole ratios, NH_3/NO_x , of approximately 1.0 are typical for 90% removal. The amount of unreacted ammonia (NH_3 in reactor effluent) is virtually zero when the NH_3/NO_x mole ratio is less than 0.8 and increases significantly when the ratio is larger than 1.0. The use of a large SV reduces the amount of catalyst, but lowers the NO_x removal efficiency and increases ammonia emissions.

The temperature range for catalytic reduction is usually 300 to 400°C (570 to 750°F). Low-temperature catalysts that are reactive at 150 to 250°C (300 to 480°F) have been developed for gases such as those from iron-ore

* Space velocity is defined as the ratio of the volumetric flow rate of gas passing through the reactor (at 0°C and atmospheric pressure) to the volume of the catalyst bed.

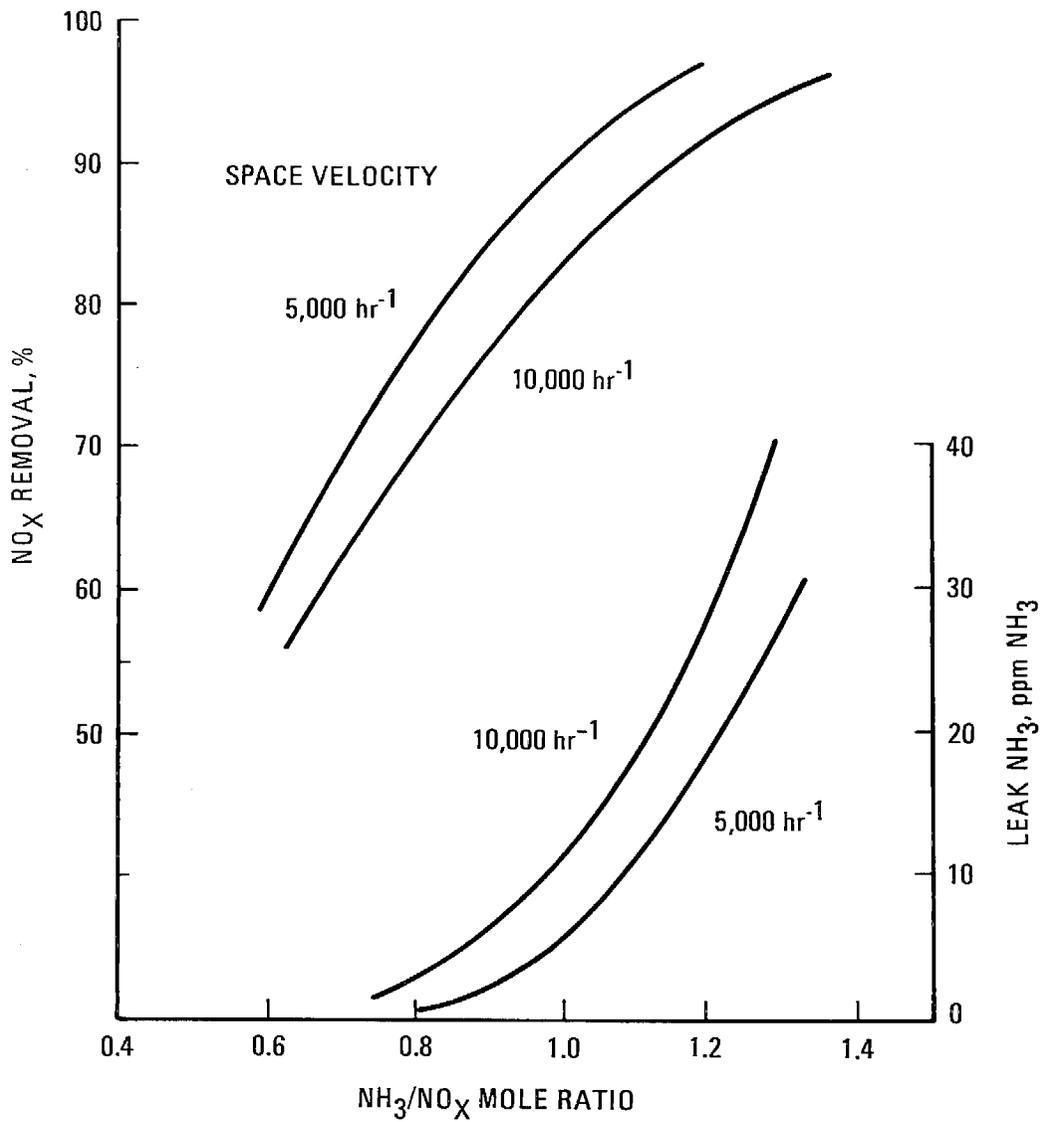


Figure 2-50. Typical operation data of selective catalytic reduction for an oil-fired boiler at 350 to 400°C, using granular catalyst (Ref. 2-4)

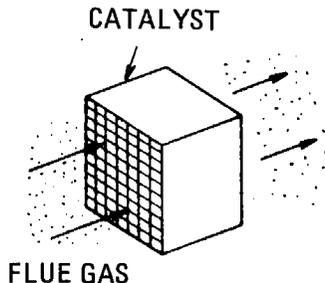
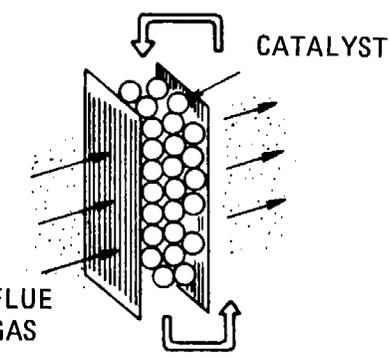
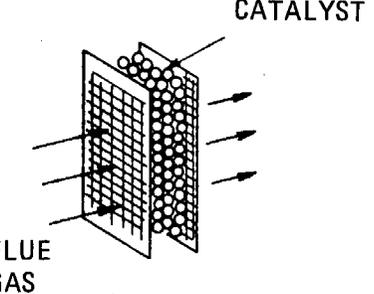
FLUE GAS	REACTOR TYPE	CATALYST SHAPE	PRINCIPAL STRUCTURE
DIRTY GAS (HIGH SULFUR OIL FUEL OR SEMI-DIRTY GAS (KEROSENE, LOW SULFUR FUELS))	(A) FIXED BED TYPE (PARALLEL) FLOW	PLATE' HONEYCOMB-TYPE CATALYST	
	(B) MOVING BED TYPE	PELLET TYPE CATALYST	
CLEAN GAS (LNG, LPG, AND NAPHTHA FUELS)	(C) FIXED BED TYPE	PELLET TYPE CATALYST	

Figure 2-51. Application of catalyst and reactor configurations (Ref. 2-4)

TABLE 2-13. COMPARISON OF CATALYSTS AND REACTORS (Ref. 2-4)

Catalyst Size (mm)	Moving Bed	Honeycomb,		Parallel Passage	Parallel Plate	
		Honeycomb (Metallic)	Tube (Ceramic)		(Ceramic)	(Metallic)
Diameter	4-8 ^b					
Thickness		0.5-1	1.5-3	7-10 ^e	8-10	1
Opening		4-8	6-20	7-10	8-14	5-10
Gas Velocity (m/sec) ^c	0.5-1.5	2-6	5-10	5-10	5-10	4-8
Bed Depth (m)	0.2-0.6	1-2	1.5-5	3-5	4-6	2-5
SV (1000 hr ⁻¹) ^d	5-10	5-8	4-8	3-5	1.5-3	2-5
Pressure Drop (mmH ₂ O) ^f	40-80	30-80	40-140	80-140	80-160	60-120

^a90% NO_x removal at an NH₃/NO_x ratio of 1.1 and a temperature of 350-400°C for dirty gas.

^bRing type catalysts with larger diameters are also used.

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

^dGas volume (Nm³/hr)/catalyst bed volume (m³).

^eThickness of envelope.

sintering machines and coke ovens. A catalyst being tested by Kureha Chemical in a 5000 Nm³/hr pilot plant installation is reactive at 150°C (300°F) but is poisoned by SO_x, and its use requires nearly complete desulfurization (Ref. 2-4). A catalyst developed by JGC is effective at 200°C (390°F) and is resistant to SO_x. Although ammonium bisulfate deposits on it below 250°C and reduces its activity, occasional heating of the contaminated catalyst to above 350°C (660°F) removes the bisulfate. MHI is developing a catalyst that will operate at temperatures up to 650°C (1200°F). Catalysts will be discussed in Section 2.4.1.2.

Currently, most SCR catalysts have a life of over 2 years when used on clean gas, 1 to 2 years on semidirty gas, and 1 year on dirty gas. The catalysts are being improved; however, some areas require additional work to improve catalyst performance and lifetimes.

Many dirty gases at a high temperature contain appreciable constituents in the vapor phase, such as vanadium in oil-fired boiler flue gas, and alkaline compounds in the gases from glass melting furnaces, cement kilns, and iron-ore sintering machines. These compounds may tend to deposit on the catalyst as liquids or solids even for the parallel flow type where solid particulates in the gas do not deposit. The deposits affect the catalyst in various ways. Vanadium rarely lowers the catalyst activity but can change the optimum reaction temperature. Alkaline compounds lower the activity appreciably. Although most of the alkaline compounds can be removed by a water wash, the catalyst is usually degraded to some extent (Ref. 2-4).

The particulates smaller than about 1 micron tend to enter the small pores of the catalyst carrier, slowly reducing the activity. This "blinding" can not be avoided even in the parallel flow type reactors.

Most of the SCR catalysts oxidize up to about 2% of SO₂ to SO₃. The oxidation ratio may be higher when the ammonia content in the gas is low.

Factors such as operating temperature, catalyst and reactor configurations, and other characteristics will be discussed briefly before describing application of SCR to commercial installations.

Catalyst Shape and Reactor Configuration

Plugging by particulates has been one catalyst problem area. For clean gases that contain particulate concentrations of less than about 30 mg/Nm^3 , a simple type of reactor with granular or ring tube catalyst in a fixed bed can be used without appreciable problems. Electrostatic precipitators (ESP) can be used to reduce the particulate content to 30 mg/Nm^3 for those gases with high particulate levels. Since SCR requires a temperature of 350 to 400°C , a hot ESP is needed. A hot ESP is applicable for low-sulfur coal where a cold ESP does not remove the ash efficiently. However, a hot ESP does not always work well with particulates from high-sulfur fuels, and therefore it is sometimes desirable to apply SCR to gases with high particulate contents.

For dust-laden gases, moving bed and parallel flow type reactors have been developed (Figure 2-51 and Table 2-14). The moving bed reactor uses a granular catalyst, which is charged from the top of the reactor and moves down intermittently or continuously while the gas flows across and through the catalyst layer. The granular catalyst discharged from the bottom of the reactor is screened to remove particulates and is returned to the reactor. If needed, the catalyst is heated to 700 to 800°C (1300 to 1500°F) to eliminate sulfur compounds and carbon before it is returned to the reactor.

The moving bed can treat gases containing particulate concentrations of up to about 300 mg/Nm^3 , e.g., flue gases from an oil-fired boiler. For gases with 30 to 100 mg/Nm^3 , an intermittent moving bed may be appropriate, moving the bed when the pressure drop reaches unacceptable levels. A continuous moving bed may be preferable for gases with 100 to 300 mg/Nm^3 . Flue gas from a coal-fired boiler containing about 20 g/Nm^3 should first be treated with an ESP or other means to reduce the particulate content to below 300 mg/Nm^3 (Ref 2-4).

The parallel flow type reactor uses a fixed bed where the gases pass through passages between the parallel catalyst layers. This type of reactor is expected to handle gas from a coal-fired boiler even without previous dust removal (Ref. 2-4).

TABLE 2-14. REACTORS FOR DUSTY GAS TREATMENT (Ref. 2-4)

Type	Process Developer	User	Plant Site	Gas Source	Fuel	Capacity (Nm ³ /hr)	Completion
Moving Bed	Hitachi Ltd.	Kawatetsu Chemical	Chiba	Coke Oven	COG/RPG ^a	500,000	Nov 1976
	Hitachi Ltd.	Chiyoda Kenzai	Kaizuka	Boiler	HO(RS) ^b	15,000	Oct 1977
	Hitachi Ltd.	Nippon Oils & Fats	Amagasaki	Boiler	HO	20,000	Apr 1978
	Mitsubishi H.I.	Sumitomo Chemical	Sodegaura	Boiler	HO(LS) ^c	382,000	Sept 1976
	Kobe Steel	Kansai N.K.	Amagasaki	Coke Oven	COG	104,000	Aug 1977
	Kurabo	Kurabo	Hirakata	Boiler	HO(RS)	30,000	Aug 1975
	Asahi Glass	Asahi Glass		Furnace		70,000	
Honeycomb	Mitsubishi H.I.	Fuji Oil	Sodegaura	Boiler	HO(LS)	200,000	Jan 1978
	Mitsubishi H.I.	Chubu Electric	Chita	Boiler	HO(LS)	1,920,000	Feb 1980
	Ishikawajima H.I.	Chubu Electric	Taketoyo	Boiler	Crude Oil	20,000	Apr 1977
	Ishikawajima H.I.	Ajinomoto	Kawasaki	Boiler	HO(LS)	180,000	Jan 1978
	Ishikawajima H.I.	Company E	—	Boiler	HO(LS)	960,000 ^d	Apr 1978
	Ishikawajima H.I.	Company F	—	Boiler	HO(LS)	480,000 ^d	June 1978
	Ishikawajima H.I.	Chugoku Electric	Kudamatsu	Boiler	Crude Oil	1,000,000	Apr 1979
	Ishikawajima H.I.	Chugoku Electric	Kudamatsu	Boiler	HO(LS)	1,900,000	July 1979
	Ishikawajima H.I.	Tohoku Electric	Niigata	Boiler	HO(LS)	1,660,000	Aug 1981
Parallel Passage	JCC	Kashima Oil	Kashima	Furnace		50,000	Nov 1975
	JCC	Fuji Oil	Chiba	Boiler	CO	70,000	July 1976
	JCC	Nippon Steel	Kimitsu	Coke Oven	COG	150,000	Mar 1977
Parallel Plate	Mitsubishi H.I.	Tokyo Electric	Yokosuka	Boiler	HO(LS)	40,000	Mar 1977
	Mitsubishi H.I.	Company C	—	Boiler	HO(LS)	1,010,000	Feb 1978
	Mitsubishi H.I.	Company D	—	Boiler	HO(LS)	490,000	July 1978
	Hitachi, Ltd.	Company A	—	Boiler	HO(LS)	490,000	June 1978
	Hitachi, Ltd.	Company B	—	Boiler	HO(LS)	550,000 ^d	June 1978
Tube	Mitsui Engineering	Ukishima Pet. Chem.	Chiba	Boiler	HO(LS)	220,000	Apr 1978

^a Coke oven gas/refinery off gas.

^b Heavy oil (high sulfur).

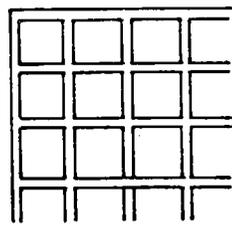
^c Heavy oil (low sulfur).

^d Combination with selective noncatalytic reduction.

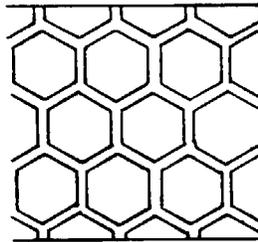
The parallel flow catalysts are produced in various shapes, including rings, tubes, plates, and honeycomb. There is also an arrangement in which a granular catalyst is carried in thin "envelopes" and held in place by metal mesh. The envelopes are suspended in the gas stream in such a way that the gas flows parallel to the surface. Five types of parallel flow catalysts are in use in Japan for SCR. These are classified as (1) metal honeycomb, (2) parallel plate, (3) ceramic honeycomb, (4) tubular, and (5) parallel passage (Figure 2-52). Reactors using catalyst types (2), (4), and (5) have a relatively wide passage for gases to flow and have little tendency for dust plugging. However, the wide clearances require a relatively high gas velocity of 16 to 32 ft/sec in order to create turbulent flow and produce a high NO_x removal efficiency. Consequently, a reactor with a long flow length is required to achieve the necessary SV; therefore the resultant pressure drop is relatively high. Also, it is possible that appreciable erosion of the catalyst may occur at the high-gas velocity when treating flue gas, as from a coal-fired boiler without prior particulate removal. Because of the larger surface area per unit volume, the honeycomb catalysts can avoid some of these problems by operating at lower velocities, of 3 to 16 ft/sec.

Metallic substrate honeycomb catalysts can generally provide more reactive surface in a given volume than a ceramic honeycomb. On the other hand, a ceramic honeycomb may be less susceptible to loss of activity in erosive (from fly ash) environments because the catalyst is present throughout the ceramic substrate rather than being deposited or etched on a metallic surface (Ref. 2-27).

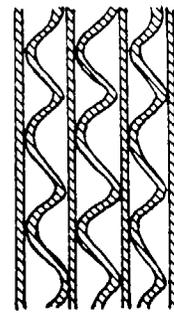
A parallel passage reactor originally developed by Shell was further developed by JGC for NO_x decomposition. The reactor uses small catalyst granules packed in thin envelopes made of metal mesh; these envelopes are placed in parallel as illustrated in Figure 2-53(a). The catalyst elements are 5 to 6 mm thick and are set about 7 mm apart. A unit assembly is made up of 35 elements, each 50 cm side and 1 m long to give a module 50 cm square and 1 m long in the direction of gas flow. The modules are stacked in the reactor. For a reactor four modules deep, the pressure drop is 6 to 8 in. H_2O . In order to preclude one of the potential problems of deposition of small amounts of dust on the mesh, JGC has developed a sand blast system to remove the deposit.



Honeycomb
(Ceramic)
(Grid Type)



Honeycomb
(Ceramic)
(Hexagonal)



Honeycomb
(Metal)
(Wave Type)

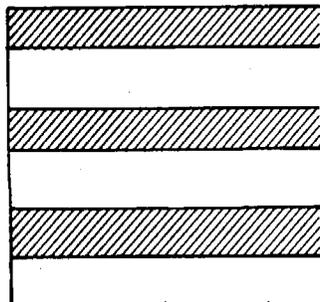


Plate (Ceramic)

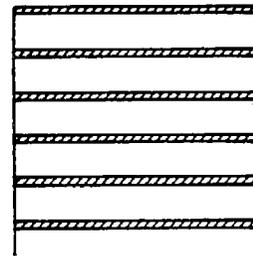
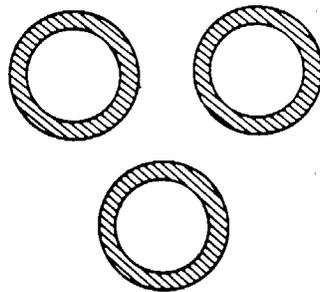
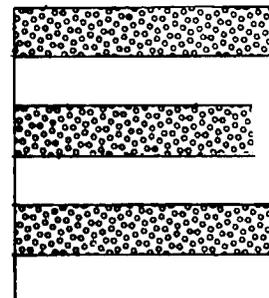


Plate (Metal)



Tube (Ceramic)



Parallel Passage

Figure 2-52. Cross sections of typical parallel flow catalysts (Ref. 2-4)

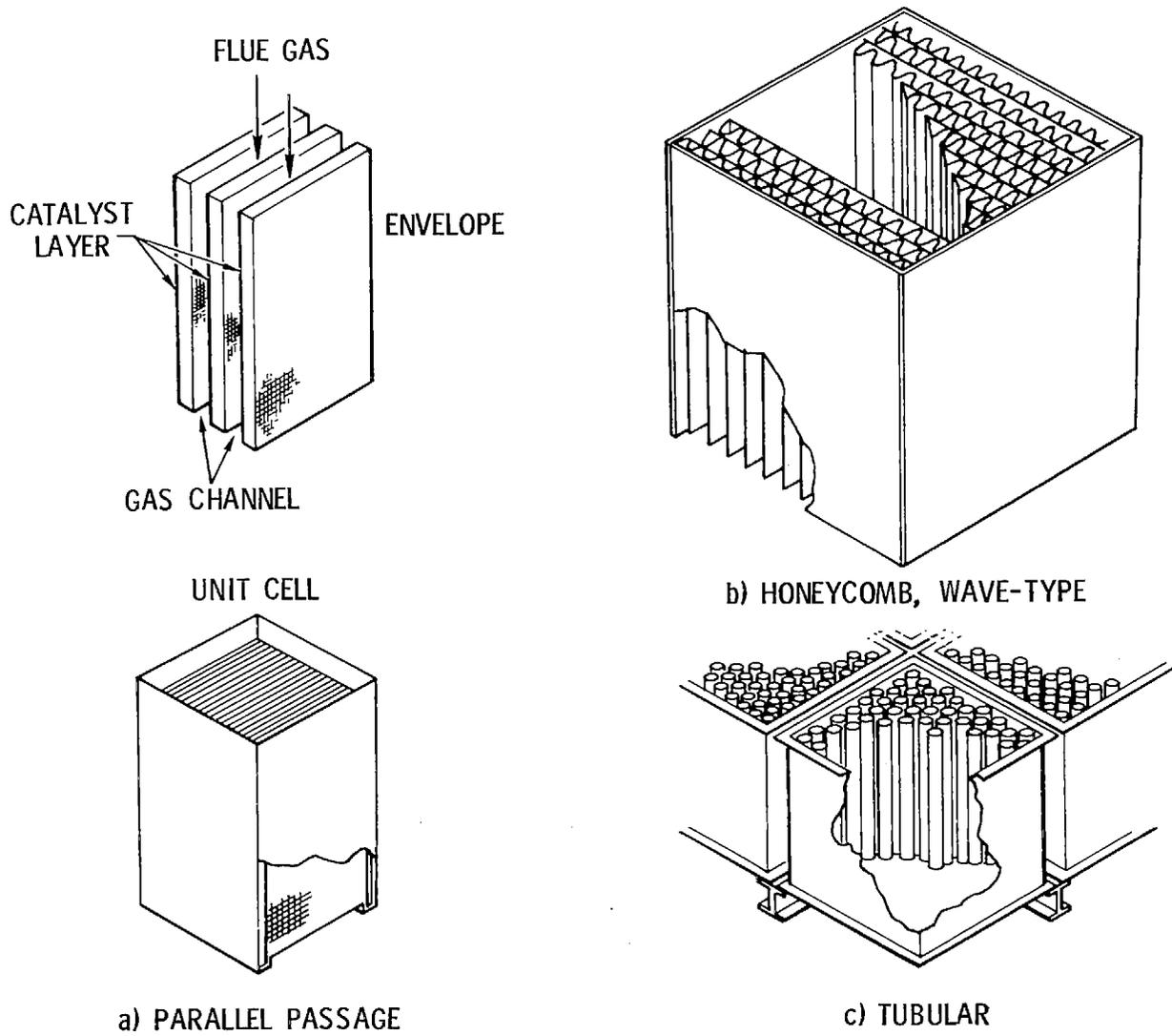


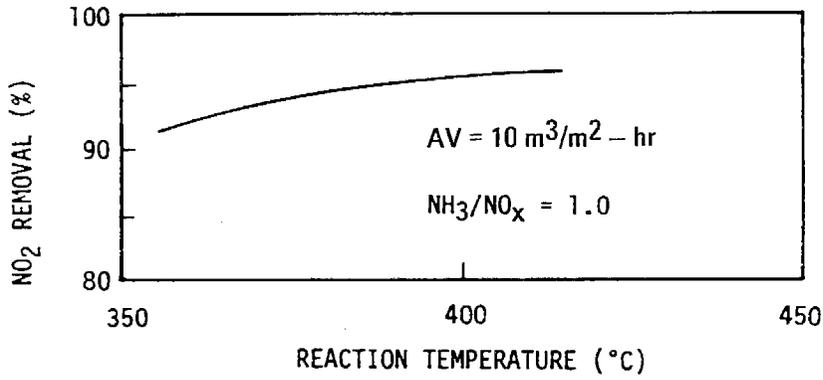
Figure 2-53. Parallel flow catalyst configurations (Refs. 2-4, 2-27, 2-30, and 2-31)

A large size honeycomb can be made with a metallic material by activating the surface chemically. A wave-type honeycomb configuration, designated as NOXNON has been developed by Hitachi Zosen for dirty gas applications in pilot plant tests [Figure 2-53(b)]. The spacing of the surfaces is 8 mm between the plates and 12 mm between the points at which the wavy element is attached to the plates. This gives a relatively large area per unit volume for the honeycomb (said to be 550 to 600 m²/m³) as compared to other parallel flow catalysts. Performance of this catalyst is shown in Figure 2-54.

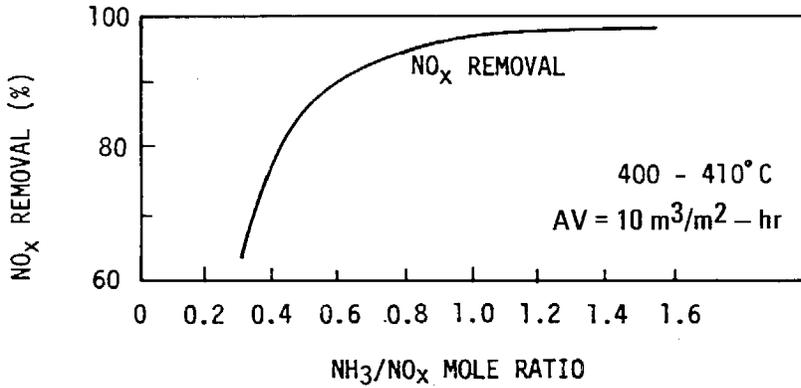
Hitachi, Ltd., has conducted tests with plate catalysts. The plates are made of a base with catalyst impregnated into the surface. The plate thickness and the spacing between them are roughly the same, each on the order of 10 mm. The plates are made up as modules about a meter square and used in the number required to give adequate NO_x removal. The length of the catalyst assembly, in the direction of the flow, depends on the degree of removal required, the gas velocity needed to get adequate mass transfer, and erosion caused by the dust in the gas. Figure 2-55 illustrates the catalyst plates, cells, and units installed in a reactor. Mitsubishi Heavy Industries (MHI) has also developed plate catalysts.

Tubular catalysts have been tested by several companies, including Kawasaki Heavy Industries, Ltd. (KHI) and Mitsui Engineering [Figure 2-53(c)]. The latter commercialized the catalyst for the Chiba plant of Ukishima Petrochemical. Tubes are spaced so that gas flows in parallel both inside and outside of the tubes. Mitsui Engineering has determined an optimum packing configuration wherein the tubes are not in contact with each other, resulting in a low-pressure drop (Figure 2-56). Maximum efficiency is obtained at low NH₃ emissions (Figure 2-57). At the Ukishima Petrochemical plant, tubes with 33 mm outer and 20 mm inner diameters and 1000 mm lengths are used.

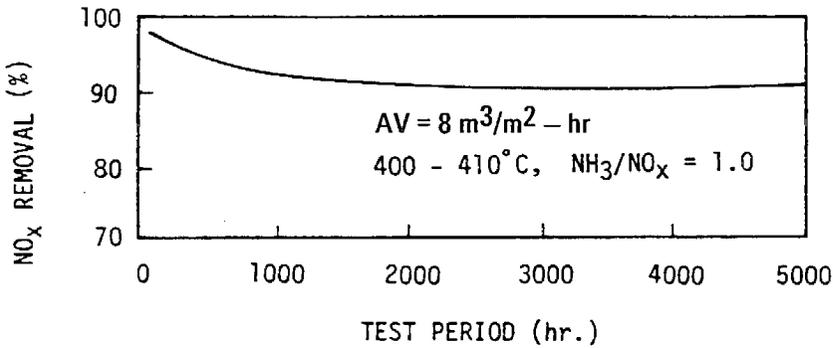
A thin-wall honeycomb catalyst with small openings can be highly efficient and has been used at a commercial SCR plant onstructed by MHI for Fuji Oil. Recently, IHI started operations with honeycomb catalysts at large plants for utility boilers. Full-scale experience is outlined in Section 2.4.4.2.



a) INITIAL EFFICIENCY AT VARIOUS TEMPERATURES

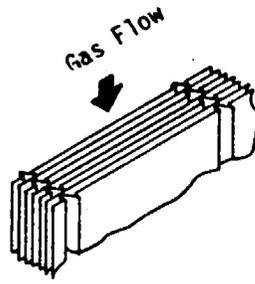


b) INITIAL EFFICIENCY AT VARIOUS NH₃/NO_x MOLE RATIOS



c) EFFICIENCY AS A FUNCTION OF TIME

Figure 2-54. Characteristics of NOXNON 500 catalyst (Refs. 2-4 and 2-30)



Shape of Catalyst Elements

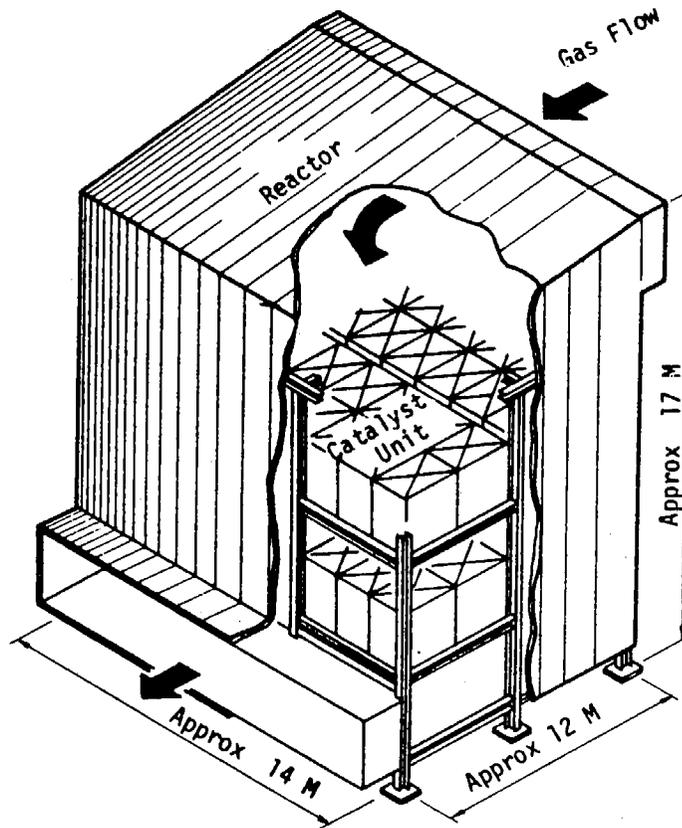


Figure 2-55. Outline of a reactor for a 600 MW boiler (Ref. 2-28)

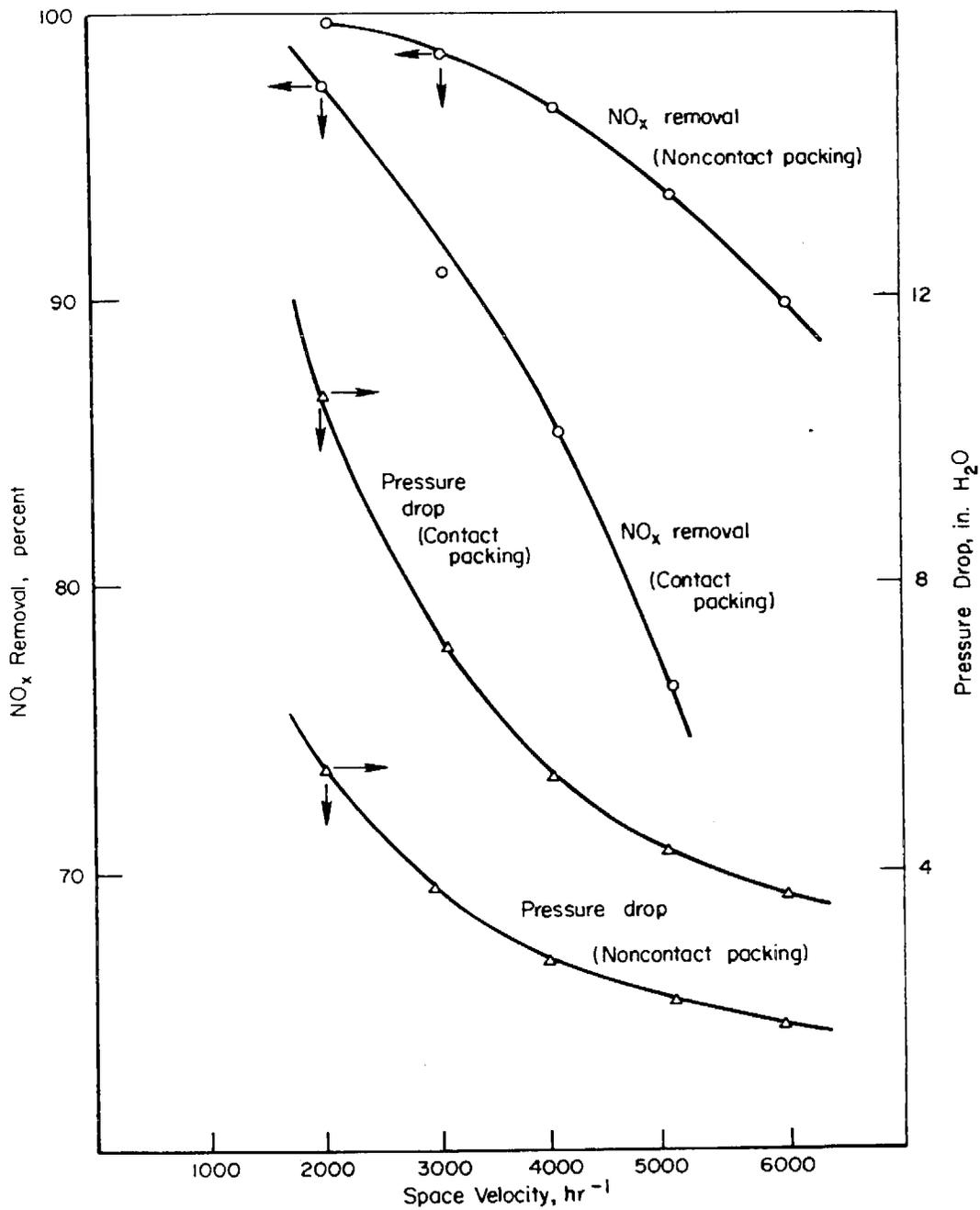


Figure 2-56. NO_x removal and pressure drop for tubular catalyst (Refs. 2-4 and 2-31)

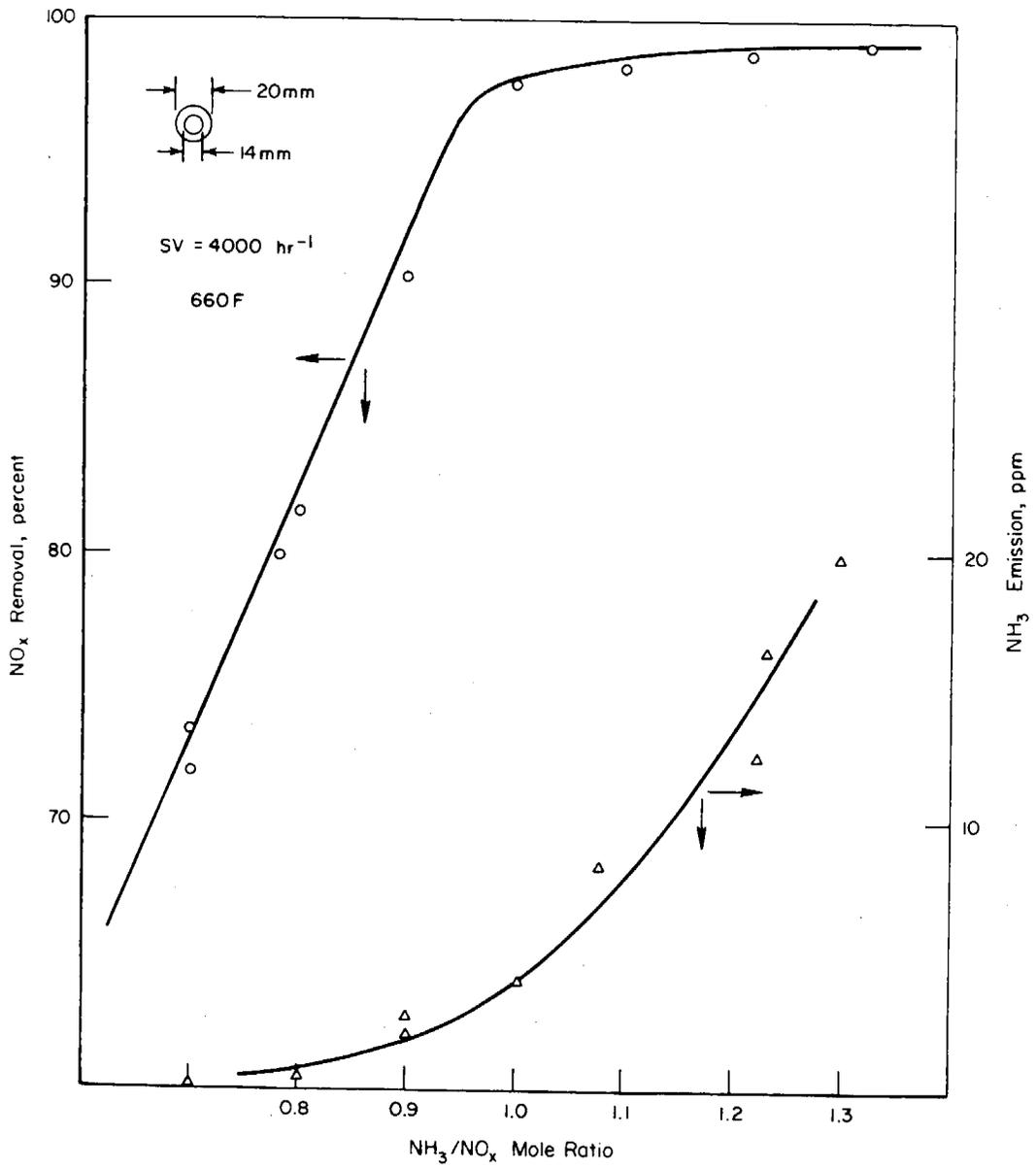


Figure 2-57. NO_x removal and NH_3 emissions for a tubular catalyst configuration (Refs. 2-4 and 2-31)

Operating Temperature

The temperature range required for catalytic reduction is typically 300 to 400°C (570 to 750°F). The process is relatively insensitive to temperature in this range because the side reactions that make temperature critical in noncatalytic reduction do not take place to any significant extent. The effect of temperature on performance is shown in Figure 2-58. NO_x removal flattens out above 570°F (300°C), but residual NH₃ continues to drop off. However, higher temperature levels are undesirable because of the larger gas volume, and with some catalysts NO_x removal performance starts to decrease.

Catalysts are available for low-temperature application by JGC Corporation (Ref. 2-32) (Figure 2-59) and others and were discussed in Section 2.4.4.1. High-temperature catalysts for operating up to 650°F (1200°F) for gas turbine combined cycle operation are being developed by MHI (Ref. 2-22). However, no specific information was available.

Space Velocity

The catalyst volume is a significant factor in NO_x decomposition, performance, pressure drop, and ultimately in cost. An example of the effect of SV is shown in Figures 2-60 and 2-61. Space velocities in the range of 5000 to 10,000 hr⁻¹ are usually considered for typical semidirty gas applications in Japan (Table 2-13). Higher velocities of up to 20,000 hr⁻¹ can be used for clean gases (Ref. 2-26), and dirty gases may require velocities in the range of 2000 to 3000 hr⁻¹. Superficial velocities of 2 to 10 m/sec (6 to 33 ft/sec) are typical for parallel flow catalyst configurations with corresponding pressure drops of 30 to 160 mm H₂O (1.2 to 6.3 in H₂O).

In Japan, honeycomb catalyst characteristics may also be specified in terms of "area velocity" (AV), or gas volume per hour per unit of apparent catalyst surface area (m³/hr-m²). An AV of 8 m³/m² × hr⁻¹ is equivalent to an SV of about 5000 hr⁻¹.

Ammonia Requirement and Equipment Turndown

For normal operation requiring 90% NO_x reduction, an NH₃/NO mole ratio of 1.0 is typical, generally producing NH₃ emissions of less than 10 ppm (Figure 2-62). Operation at reduced load generally does not pose any problem

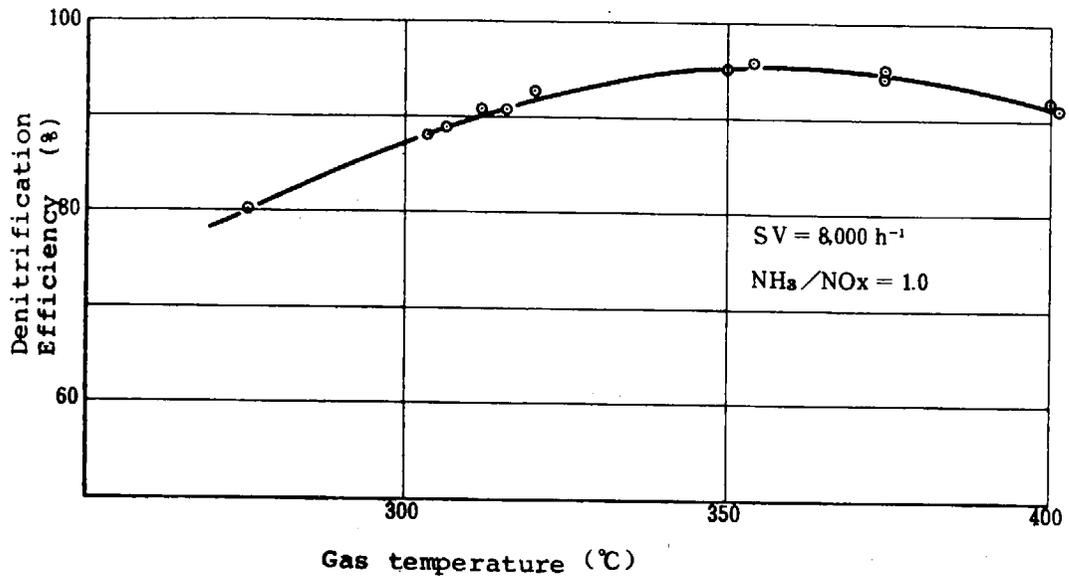


Figure 2-58. Gas temperature versus denitrification efficiency for the intermittent moving bed reactor at Shinnagoya Power Station (Ref. 2-29)

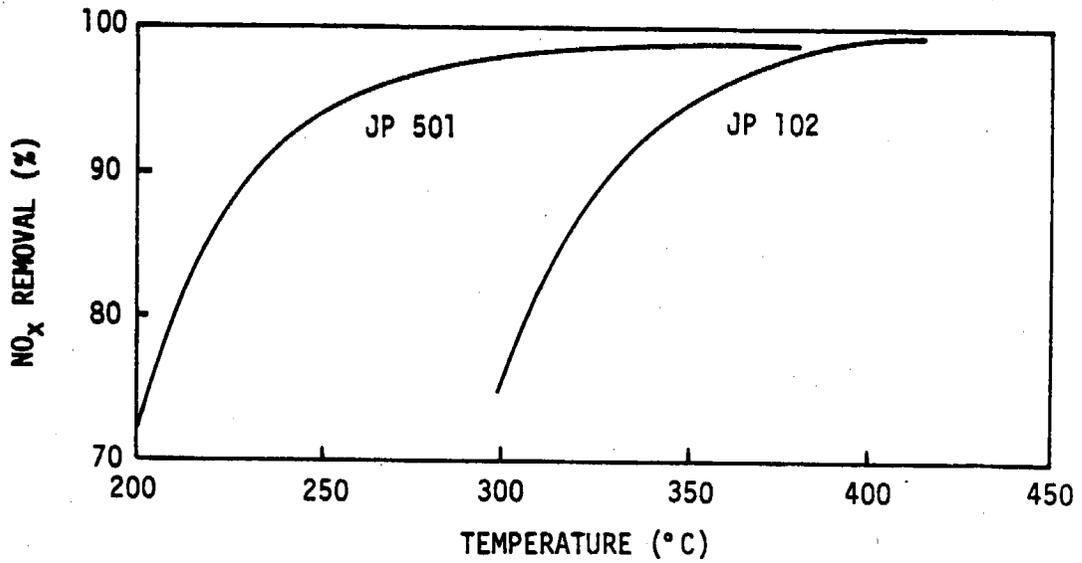


Figure 2-59. Effect of temperature on the activities of catalysts JP 501 and JP 102 (NO, 200 ppm; NH₃; 240 ppm; O₂, 3%; H₂O, 10%; space velocity, 20,000 hr⁻¹) (Ref. 2-4)

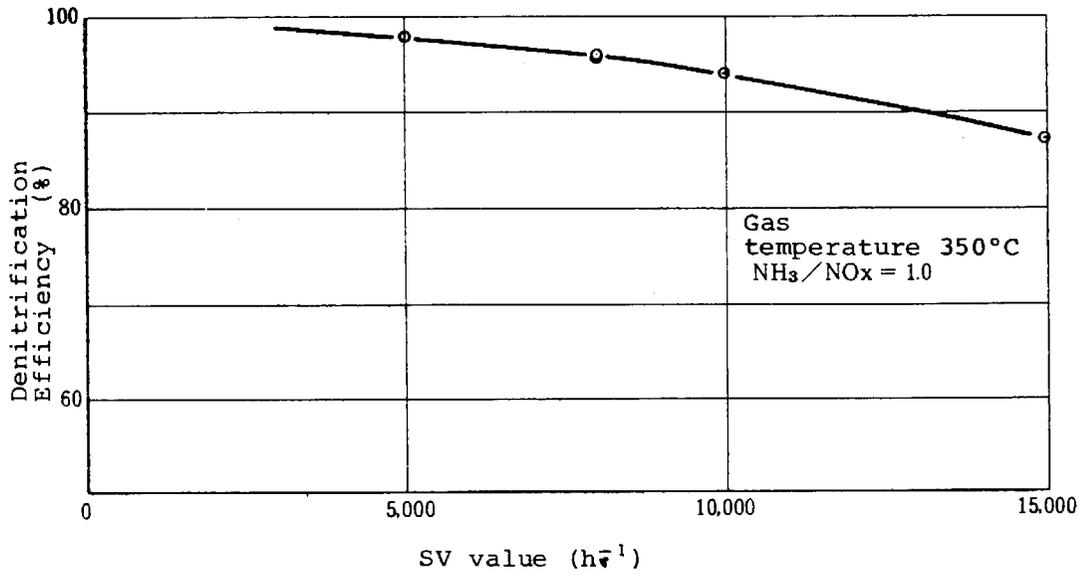


Figure 2-60. Space velocity versus denitrification efficiency for the moving bed reactor at Shinnagoya Power Station (Ref. 2-29)

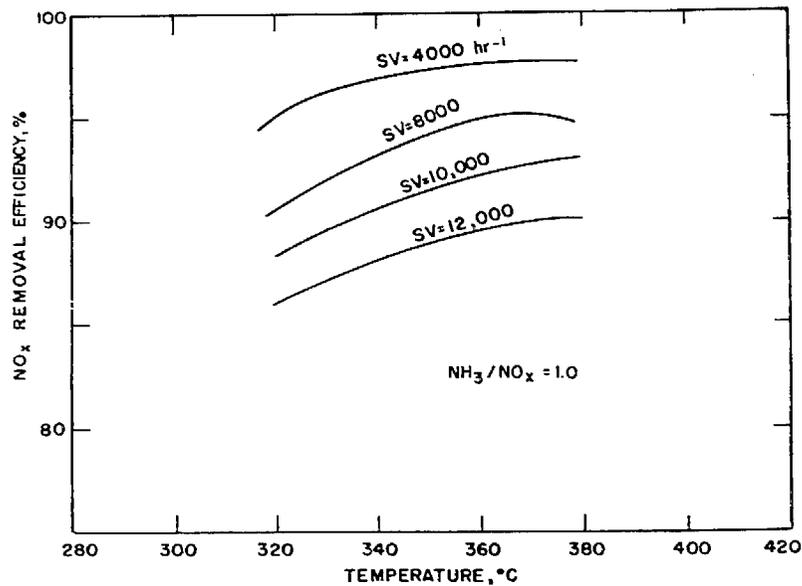


Figure 2-61. Effects of temperature and space velocity on NO_x removal efficiency for MHI process with a fixed bed reactor and dirty flue gases after use of an electrostatic precipitator (Ref. 2-8)

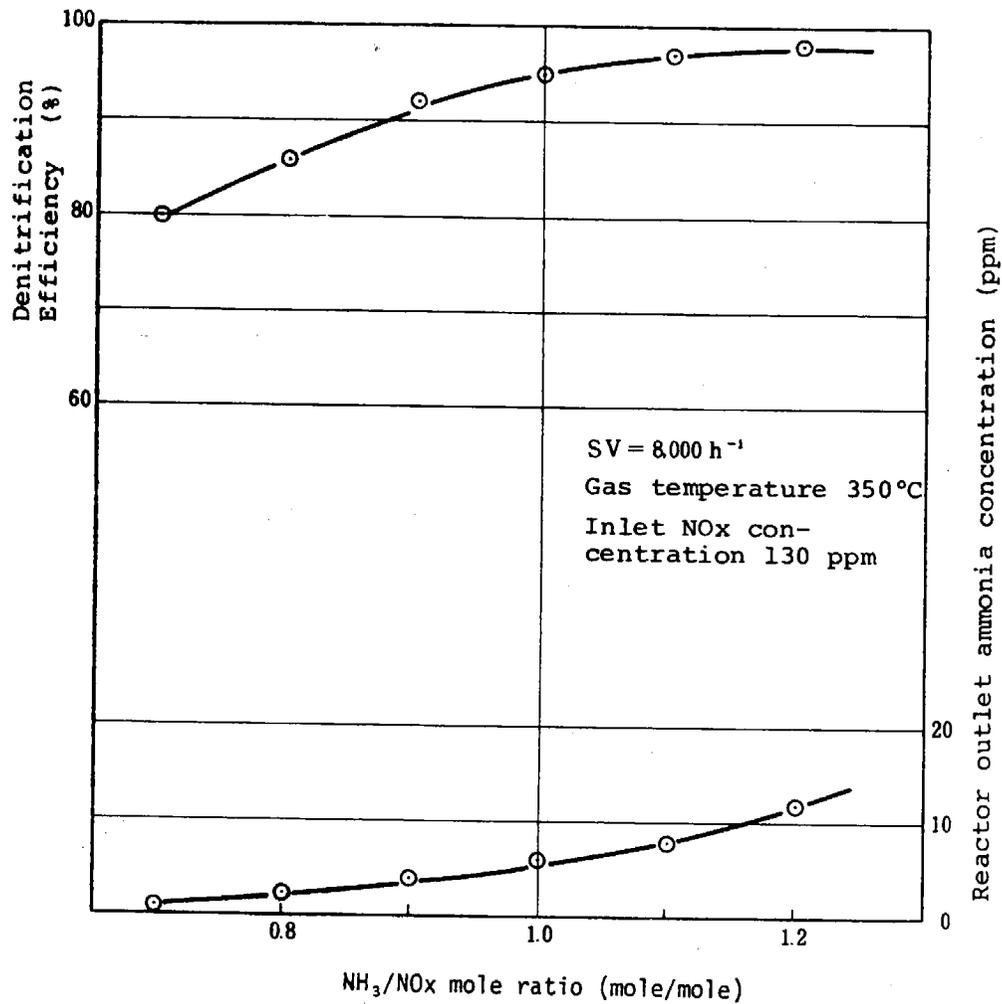


Figure 2-62. NH₃/NO_x mole ratio versus denitrification efficiency and reactor outlet ammonia concentration for the intermittent moving bed reactor at Shinnagoya Power Station (Ref. 2-29)

for SCR, as illustrated by the results shown in Figures 2-63 and 2-64. The decrease in efficiency caused by reducing the load to 25% is more than offset by the reduced SV, resulting in an overall increase in DeNO_x efficiency and a consistent NH₃ emission of less than 10 ppm.

2.4.4.2 Commercial Experience

Application of SCR in Japan was initiated commercially in 1973 and in the past several years has been in widespread use on primarily utility boilers as well as other industrial equipment such as furnaces, coke ovens, and sintering machines (Table 2-12).

Generally consistent performance of 90% NO_x removal has been achieved. Full-scale data are illustrated in Figure 2-58. In some instances, specification requirements of less than 90% were established (Table 2-12). In some units, the catalyst was installed in the ductwork to take advantage of existing fan overcapacity, with a resultant 30% NO_x removal being achieved. In three installations, the duct-SCR installation was combined with thermal DeNO_x to attain 50 to 60% NO_x reduction.

A reactor installation containing a hexagonal honeycomb catalyst for a 200,000 Nm³/hr (67 MW_e) boiler at the Fuji Oil Sodegaura refinery is shown in Figure 2-65. Heavy oil with a sulfur and nitrogen content of about 0.4 and 0.06 to 0.07%, respectively, is burned. Exhaust gas temperature is 330 to 400°C (625 to 750°F); particulate content is 20 mg/Nm³; inlet NO_x and SO_x concentrations are approximately 115 and 190 ppm, respectively. NO_x removal at a mole ratio of one and at an SV of 6500 hr⁻¹ is 86% (80% specified). For 90% removal and for fixed and moving bed reactors, reactor pressure drops in the range of 50 to 200 mm H₂O (2 to 8 in. H₂O) were reported (Table 2-15). Process power requirements are primarily due to fans needed to overcome the added resistance of the SCR reactor installation. While specific to each installation, approximately 0.12% of utility boiler output per 100 mm H₂O (4 in. H₂O) pressure were reported. In most cases, catalysts for dirty gas installations are expected to be replaced annually, medium dirty every 1 to 2 years, and clean gases every 2 years (Figures 2-66 and 2-67). Indications are that, especially in the latter two categories, longer lifetimes may be available (Refs. 2-26 and 2-36).

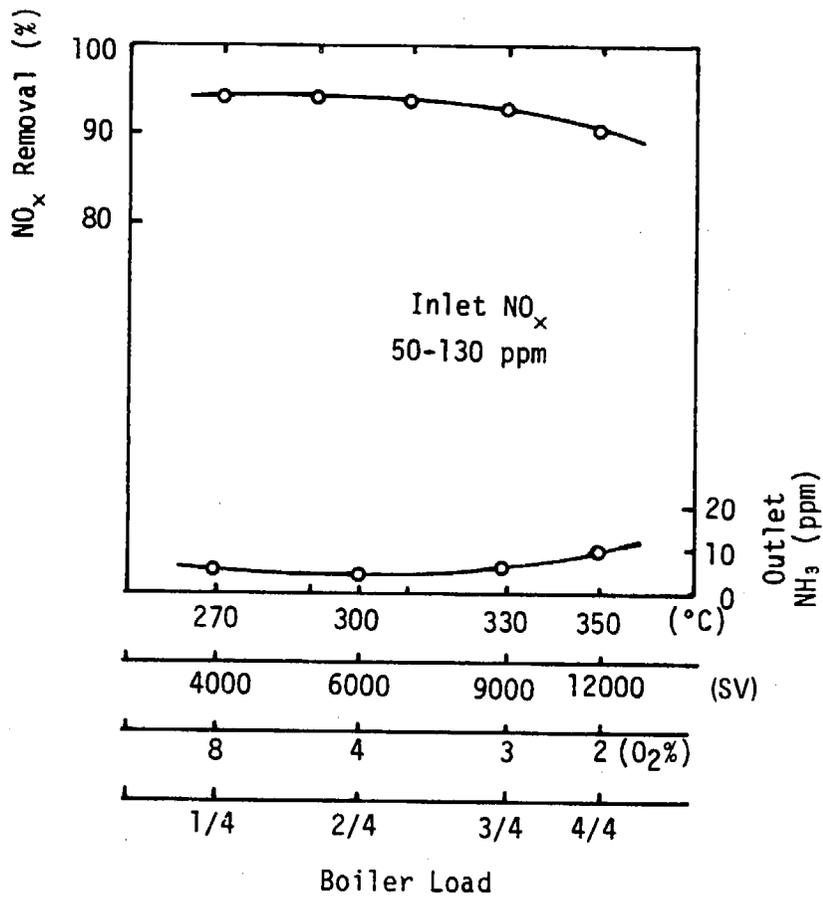


Figure 2-63. Results of clean gas treatment at different boiler loads ($\text{NH}_3/\text{NO}_x = 1.0$) (Ref. 2-27)

LS CRUDE OIL $SO_x = 50 \sim 70$ ppm
 $NO_x = 50 \sim 130$ ppm
 DUST = $20 \sim 60$ mg/N m^3
 [0.01 – 0.03 grains (SCF)]
 NH_3/NO_x MOLE RATIO = 1.0

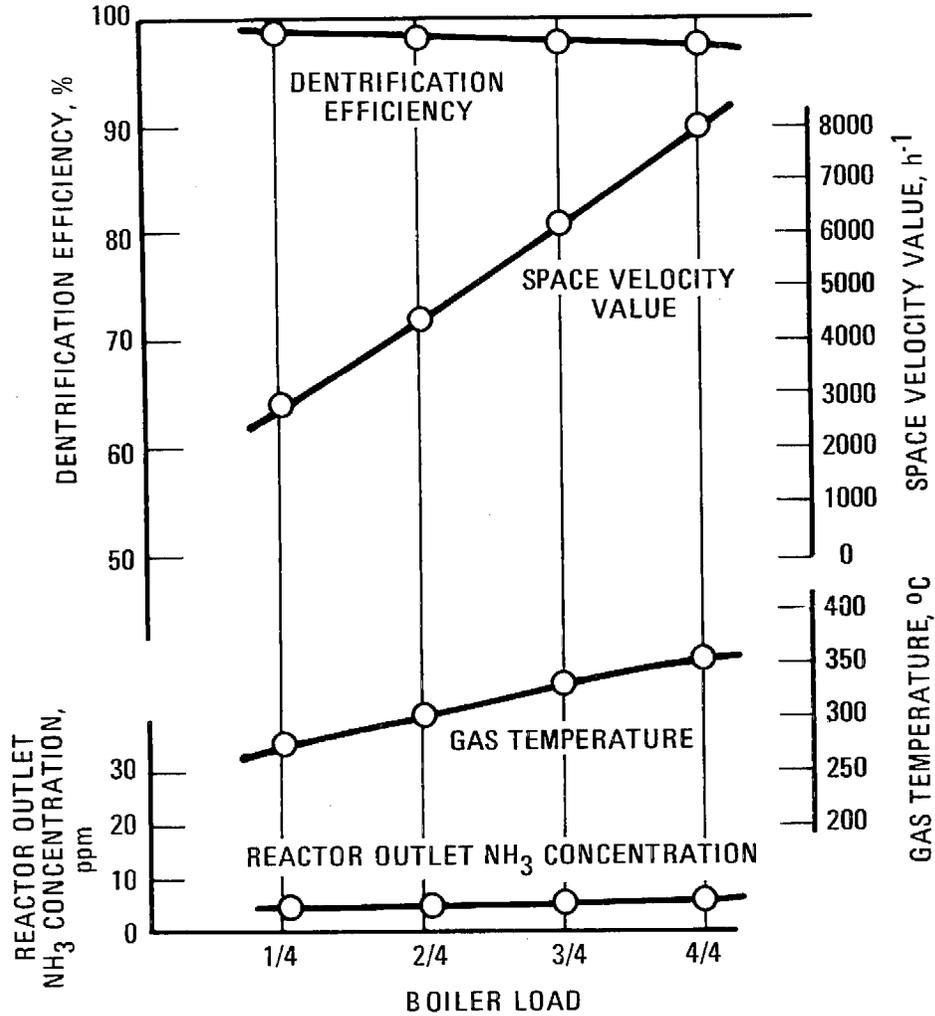


Figure 2-64. Relation between boiler load and denitrification efficiency for the intermittent moving bed reactor at Shinnagoya Power Station (Refs. 2-4 and 2-29)

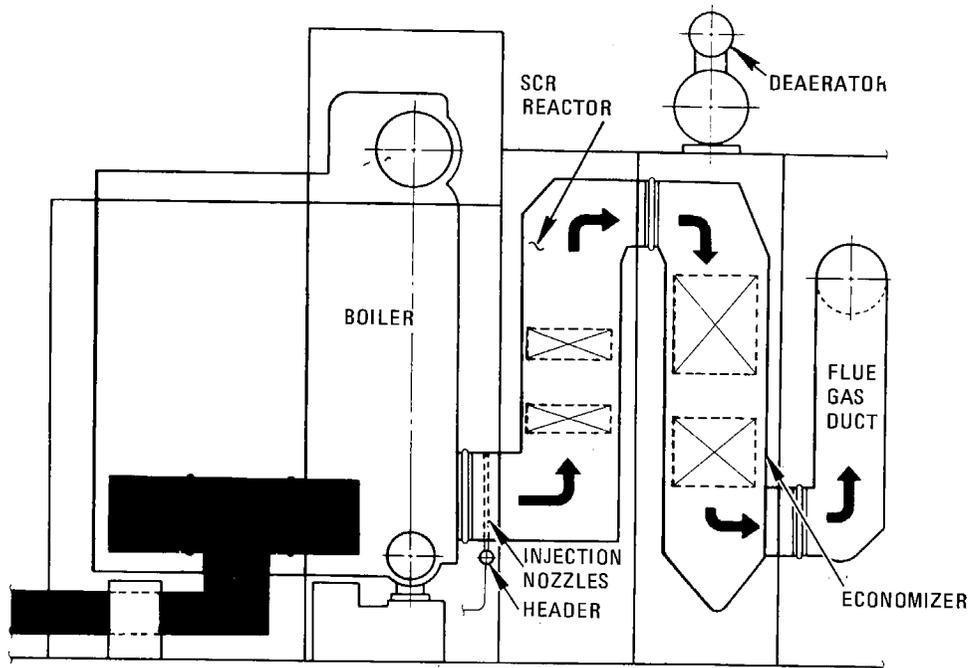


Figure 2-65. Selective catalytic reduction boiler installation (Refs. 2-22 and 2-36)

TABLE 2-15. SELECTIVE CATALYTIC REDUCTION REACTOR PRESSURE DROP

Process Developer	Catalyst Type	NO _x Removal, %	SV, -1 hr	Reactor Pressure Drop		Power Required % ^a	Reference
				mm H ₂ O	in H ₂ O		
Hitachi	Fixed Bed, Pellet	>80	20,000	136 ^b	5.4	0.15	2-26
Hitachi Zosen	Fixed Bed	93	5,000	170	6.7	-	2-4, 2-30
		80	10,000	160	6.3 ^c	-	
		95	4,000	50	2.0	-	
IHI	Honeycomb	90	6,000	40	1.6	-	2-4
JGC	Parallel Passage	95-98	4,000	110-180	5.5-7.1	-	2-4
		93-96	4,000	115-125	4.5-4.9	-	
Kobe Steel	Moving Bed	>90	10,000	40-60	1.6-2.4	-	2-4
Kurabo	Moving Bed, Spherical	93	8,000	65	2.6 ^e	-	2-4, 2-27
		>80	-	80 ^b	3.1	0.1	
Mitsubishi	Honeycomb	86	6,500	60-80	2.4-3.1	-	2-26 2-36
		90	4,000	100 ^d	5.1	0.3 ^g	
Mitsui Eng.	Tubular	90	6,000	100 ^f	3.9	-	2-4, 2-27
Sumitomo	Fixed Bed	90	7,000	50-60 ^f	2.0-2.4	-	2-4
		90	10,000	200 ^f	7.9	-	

^a% of output

^ctotal system Δp : 12.6 in H₂O

^etotal system Δp : 7.9 in H₂O

^btotal system Δp : 250, 100 and 500 mm H₂O, resp.

^dtotal system Δp : 130 m H₂O

^ftotal system Δp : 250, 100 and 500 mm H₂O, resp.

^gsteam for steam blowing as % of total generated.

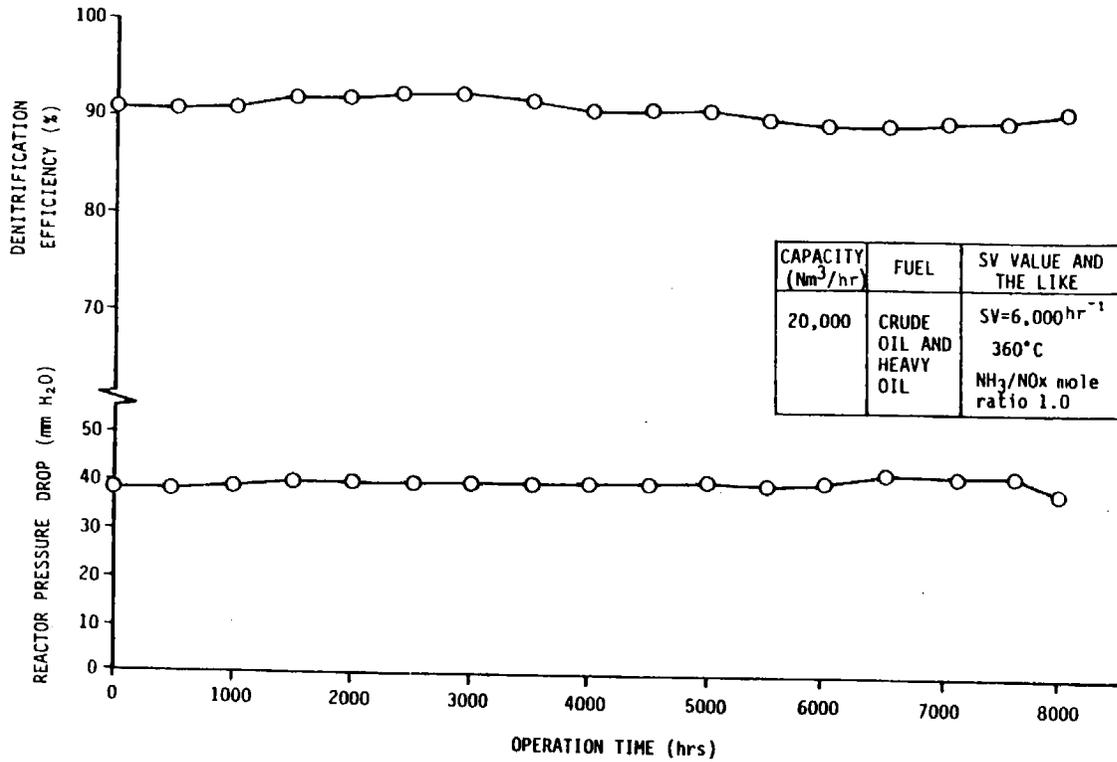
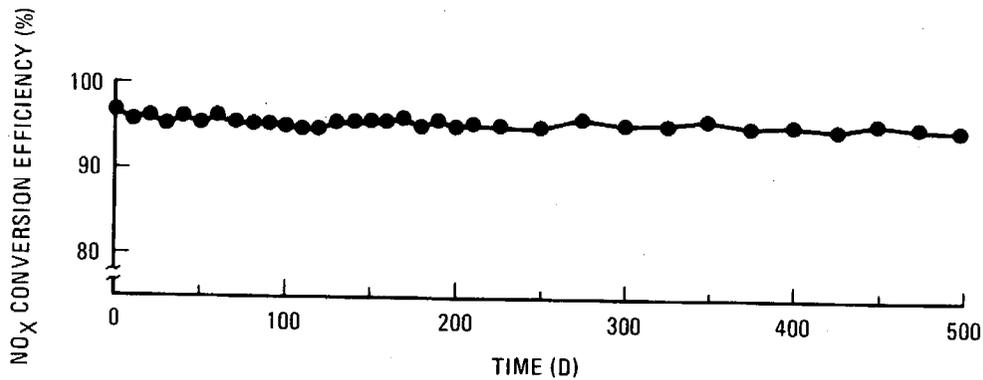


Figure 2-66. Catalyst life test results for the honeycomb catalyst at Taketoyo Station (Ref. 2-4)



FLUE GAS SOURCE: OIL FIRED BOILER OF THE OUTLET OF ESP.
 REACTION TEMPERATURE: 350°C (662°F)

Figure 2-67. An example of catalyst durability (Ref. 2-37)

U.S. experience has been limited to pilot plant scale operation utilizing the Hitachi-Zosen process. The installation is at a site provided by Georgia Power Company at Albany, Georgia, on a 0.5 MW_e slipstream, produced from the combustion of a typical medium sulfur coal (Ref. 2-34). According to Chemico Air Pollution Control, Envirotech Corporation, satisfactory catalyst performance has recently been observed with 2288 mg/Nm³ (1.0 grains/SCF) particulate loading in the flue gas (Ref. 2-35) passing through a metallic honeycomb catalyst, which is a feature of the Hitachi-Zosen process.

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3. APPLICABILITY OF NO_x CONTROLS TO SPECIFIED SOURCES

Eight stationary sources of NO_x emissions located in California, primarily in the Los Angeles area, were studied. These included utility boilers, simple and combined cycle turbines, an internal combustion engine, oil field steam generator, refinery heater, cement kiln, and glass melting furnace. The sources as well as the reduction criteria and control methods were defined for the study by the research staff of the California Air Resources Board; the control methods studied were the use of low NO_x burners (LNB), thermal denitrification (DeNO_x), and selective catalytic reduction (SCR) (Table 3-1).

The characteristics of each of the eight selected stationary sources, i.e., size, fuel, operation, and thermal input, are summarized in Table 3-2. The thermal input of the various equipment ranges from 12.6 million Btu/hr for the internal combustion (IC) engine to 1645 million Btu/hr for the utility boiler, corresponding to 1.3 and 175 MW_e, respectively.

No_x emissions range from 6.7 lb/hr NO_x as NO₂ (3.2 lb/10⁶ Btu input) for the IC engine to 627 lb/hr (0.38 lb/10⁶ Btu) for the utility boiler (Table 3-3). Other characteristics such as exhaust gas temperatures and conditions affecting the use of NO_x controls are shown in Table 3-4.

The individual sources and the potential for utilizing the various control methods are described in succeeding sections.

The results of this study have shown the feasibility of SCR achieving 90% NO_x removal in the various applications studied (Table 3-5). In general, thermal DeNO_x systems can be expected to reduce NO_x about 50% and are expected to meet the NO_x reduction criteria for the refinery heater and existing oil field steam generators.

The NO_x reduction potential of the LNB is influenced by the burner configuration, size, type of fuel burned (oil, gas, coal, and fuel nitrogen content), and type of combustion modifications (CM) implemented prior to the use of LNB. In no instance was its use capable of approaching 90% NO_x

TABLE 3-1. NO_x REDUCTION CRITERIA AND CONTROL METHODS STUDIED

Emission Source ^a	NO _x Reduction Criteria	Feasibility of NO _x Control Assessed ^{b, c}		
		Low NO _x Burner	Thermal DeNO _x	SCR
Utility Boiler	State-of-the-Art	X	- ^d	- ^d
Turbine (Simple)	90%	X	X	X
Turbine (Combined Cycle)	90%	X	X	X
I. C. Engine	90%	X	X	X
Oil Field Steam Generator	70% (New) 55% (Existing)	X	X	X
Refinery Heater	50%	X	X	X
Cement Kiln	90%	X	X	X
Glass Furnace	90%	X	X	X

^aSee Table 1-1 for identification of specific sources

^bApplication of only individual control methods assessed per study ground rules

^cSee Table 1-7 for applicability

^dNot part of study

TABLE 3-2. EMISSION CHARACTERISTICS OF SOURCES STUDIED

EMISSION SOURCE ^a	SIZE	FUEL	THERMAL INPUT		MW ^e	OTHER
			BTU/HR	(000,000)		
UTILITY BOILER	175 MW	NO. 6 OIL	1645		175	WITH EXISTING TWO-STAGE COMBUSTION OR OFF-STOICHIOMETRIC FIRING
TURBINE (SIMPLE)	121 MW	JP-5	1720		121	8 TURBINES
TURBINE (COMBINED CYCLE)	236 MW	NO. 2 OIL	1480		236	2 TURBINES, 2 WASTE HEAT BOILERS
I. C. ENGINE	2000 HP	NATURAL GAS	12.6		1.3 ^b	2 CYCLE, SUPERCHARGED
OIL FIELD STEAM GENERATOR	50 MMBTU/HR OUTPUT	RECOVERED CRUDE OIL	62.5		6.6 ^b	FORCED DRAFT
REFINERY HEATER	65 MMBTU/HR INPUT	REFINERY GAS	65		6.8 ^b	NATURAL DRAFT
CEMENT KILN	45 TPH	COAL	180		18.9 ^b	DRY PROCESS
GLASS MELTING FURNACE	-- ^c	NATURAL GAS	146		15.4 ^b	FLAT GLASS (FLOAT PROCESS)

^a See Table 1-1 for identification of specific sources

^b Electrical output equivalent based on 9400 Btu/kW

^c Capacity not disclosed

TABLE 3-3. NO_x EMISSIONS FROM STATIONARY SOURCES STUDIED

EMISSIONS SOURCE ^a	CURRENT NO _x EMISSIONS		
	ppm, Dry, 3% O ₂	lb/hr as NO ₂	lb/10 ⁶ BTU Input
UTILITY BOILER	288	627	0.38
TURBINE (SIMPLE)	415	588	0.34
TURBINE (COMBINE CYCLE)	76	140	0.09
I. C. ENGINE	3365	40.2	3.19
OIL FIELD STEAM GENERATOR	335	22.2	0.39
REFINERY HEATER	77	6.7	0.10
CEMENT KILN	274	146	0.81
GLASS FURNACE	834	220	1.51

^aSee Table 1-1 for identification of specific sources

TABLE 3-4. STATIONARY SOURCE EMISSIONS NO_x REMOVAL CRITERIA

Emission Source ^a	Current Emissions		Exhaust Gas Temp, °F (°C)	Other Emissions (Uncontrolled) Affecting NO _x Controls		
	NO _x , lb/hr ^b	% O ₂ at Stack Exit		SO ₂	Particulates	Offsetting Factors
Utility boiler	627 ^c	2-3	155(69)	NA ^d	NA	--
Turbine (Simple)	588	15	300(149) ^e	NA	NA	--
Turbine (Combined) Cycle	140	14	300(149)	NA	NA	--
I. C. Engine	40.2	18	650(343)	NA	NA	--
Oil Field Steam Generator	22.2	4	450(232)	885 ppm (80.3 lb/hr)	0.064 gr/SCF (147 mg/Nm ³)	Regulatory Requirements - 90% SO ₂ Removal ^f
Refinery Heater	6.7	4	770(410)	NA	NA	--
Cement Kiln	146	14	390(199)	NA	0.01 gr/SCF (23 mg/Nm ³)	Periodic Water Wash of Catalyst
Glass Furnace	220	5	450(230) ^g	NA	0.023 gr/SCF (54 mg/Nm ³)	Electrostatic Precipitator

^aSee Table 1-1 for identification of specific sources

^bAs NO₂

^cAt full load

^dNot affected

^eTemperature at turbine exit: 900°F (482°).

^fSO₂ removal by wet scrubbing reduces particulates

^gTemperature at second regenerator exit: 1000°F (540°C)

TABLE 3-5. FEASIBILITY OF NO_x CONTROL METHODS FOR SOURCES STUDIED

STATIONARY SOURCE ^a	STUDY CRITERIA, % REDUCTION	NO _x CONTROL METHODS		
		LNB	THERMAL DENO _x	SCR
UTILITY BOILER	STATE-OF-THE-ART	YES	N/S ^b	N/S
STATIONARY TURBINE	90	N/I ^c	NO	YES
COMBINED CYCLE TURBINE	90	N/I	NO	YES ^d
I. C. ENGINE	90	N/I	NO	YES
OIL FIELD STEAM GENERATOR	70 (NEW) 55 (EXISTING)	NO	YES	YES ^e
REFINERY HEATER	50	NO	YES	YES
CEMENT KILN	90	NO	NO	YES ^f
GLASS FURNACE	90	NO	NO ^g	YES

^aSee Table 1-1.

^bN/S = Not specified as part of study.

^cN/I = Not implementable

^dReheat of exhaust gas, 41.4 bbl/hr required. Equivalent 108% of fuel burned for waste heat boiler.

^eReheat of exhaust gas, 0.5 bbl/hr required. Equivalent 0.13% of fuel burned in steam generator.

^fReheat of exhaust gas, 4.6 bbl/hr required. Equivalent 14.4% of thermal input to kiln.

^gPotential for 50% reduction without major modification may be feasible.

reduction. In some limited cases with low-nitrogen fuel oils (approximately 0.1 to 0.2%), use of LNB in utility boilers resulted in a 55% NO_x reduction.

The potential for further reduction in NO_x emission rates resulting from the use of LNB in combination with CM currently in use on oil-fired utility boilers in the Los Angeles basin, i.e., two-stage firing (TSC) and off-stoichiometric combustion (OSC), appears somewhat limited. Further reductions of approximately 10% appear realistic with the addition of LNB, based on average conditions, bringing the total to 27 and 41% respectively, for the boilers with existing TSC and OSC.

The potential for meeting the NO_x reduction criteria defined in this study for the other emission sources with LNB was not evident and is reflected in the summary presented in Table 3-5.

3.1 UTILITY BOILERS

Oil-fired utility boilers operating in the South Coast Air Quality Management District (SCAQMD) were considered in this study. In response to the California Air Resources Board Research Staff interest, emphasis was placed exclusively on an evaluation of the NO_x reduction potential and applicability of using LNB on utility boilers of approximately 175 MW in size.

3.1.1 Source Characteristics

The boilers in the study size range all have single-wall, front-fired burners except for Huntington Beach units 3 and 4, which are horizontally firing burners (Table 3-6). The burners installed on the various boilers number 12, 16, and 24, with 16 being used exclusively for 175 to 180 MW units and 12 or 24 for 215 to 240 MW boilers.

Low sulfur (0.25%) residual fuel oil is burned and contains approximately 0.25% fuel-bound nitrogen.

3.1.2 NO_x Emissions

NO_x controls currently in use with the boilers being studied are either staged combustion (overfire air - OFA), OSC (burners out of service - BOOS), or both (Refs. 3-1 and 3-2). NO_x emissions are generally in the range

TABLE 3-6. BOILER CHARACTERISTICS^a

Utility	Plant & Unit	Unit Rating, MW, Net	Unit Type	Boiler Mfr	Total Number of Burners	% Excess Air	NO Control Method	Heat Rate BTU/KWH	Flue Gas Vol, SCFM, 3%, O ₂	NO _x Emissions	
										ppm, dry, O ₂	lb/hr
SCE	Alamitos 1	175	WFF ^b	B&W	16	13	OFA ^d	9,990	303,000	425	935
	Alamitos 2	175	WFF	B&W	16	13	OFA	9,990	303,000	416	920
SCE	El Segundo 1	175	WFF	B&W	16	10	BOOS, OFA	9,990	270,000	271	590
	El Segundo 2	175	WFF	B&W	16	10	BOOS, OFA	9,990	270,000	271	590
SCE	Redondo 5	175	WFF	B&W	16	13	OFA	9,990	303,000	306	675
	Redondo 6	175	WFF	B&W	16	13	OFA	9,990	303,000	306	675
DWP	Haynes 1	230	WFF	CE ^c	12	10-20	BOOS ^d	9,100	367,000	210	560
	Haynes 2	240	WFF	CE ^c	12	10-20	BOOS	9,100	367,000	210	560
	Haynes 3	228	WFF	B&W	12	10-20	BOOS	9,100	373,000	225	610
	Haynes 4	235	WFF	B&W	12	10-20	BOOS	9,100	373,000	225	610
DWP	Scattergood 1	180	WFF	CE ^c	16	10-20	BOOS	10,070	293,000	225	480
	Scattergood 2	180	WFF	CE ^c	16	10-20	BOOS	9,980	293,000	225	480
SCE	Huntington Beach 1	215	WFF	B&W	24	15	BOOS	9,200	348,000	245	610
	Huntington Beach 2	215	WFF	B&W	24	15	BOOS	9,200	348,000	295	738
	Huntington Beach 3	215	HO ^b	B&W	24	15	OFA	9,180	348,000	240	608
	Huntington Beach 4	225	HO	B&W	24	15	OFA	9,180	365,000	297	788

d. OFA = Overfire Air (2 stage)
BOOS = Burners out of Service (off-stoichiometric)

a. Refs. 3-1, 3-2, 3-3.

b. WFF = wall front firing

HO = horizontal opposed fired

c. Peabody Burner

of 240, 300, and 425 ppm (dry, 3% O₂) for staged combustion; 210, 225, and 295 for off-stoichiometric; and approximately 270 for the combined methods. These are summarized in Table 3-6.

With 0.25% fuel-bound nitrogen, the maximum possible fuel NO_x emissions for the Southern California Edison (SCE) units would be approximately 330 ppm and for the Los Angeles Department of Water and Power (DWP) boilers, 370 ppm (Table 3-7). Operating with 0.25% nitrogen oil, the conversion rate of fuel nitrogen to NO_x is approximately 58% (Ref. 3-4). Therefore, the maximum estimated uncontrolled fuel NO_x is about 200 ppm (Table 3-7).

Bench scale tests with residual oils containing 0.25% fuel nitrogen exhibit fuel NO_x emissions of 216 ppm (dry, 3% O₂). At that condition, approximately 45% of the total NO_x formed is thermal. On that basis, the total full-load uncontrolled emissions of the boilers are estimated as 360 ppm.

Data for oil-fired boilers are also available from several other sources. For single, wall-fired units with all burners active, emissions of 345 ppm at full load are reported in Ref. 3-5. Elsewhere (Refs. 3-6, 3-7, and 3-8), uncontrolled emissions are given as ranging from 300 to 367 ppm, (dry, 3% O₂) (Table 3-8). The major fraction of the units were oil-fired and operated in the Los Angeles basin; therefore, the fuel nitrogen content is expected to be the nominal 0.25%.

Using an average of 360 ppm (for the front wall-fired units) as the uncontrolled level, the effects of existing control measures are shown in Table 3-9, generally ranging from 15 to 40% NO_x reduction.

3.1.3 Combustion Modification NO_x Control Alternatives

The more common CM techniques used on oil-fired boilers to reduce NO_x emissions are OFC and flue gas recirculation (FGR). Other techniques which have been tested are water injection (WI) and reduced air preheat (RAP). However, the latter two have found little application because of resultant efficiency losses (Ref. 3-10). Use of LNB, either installed with or without other modifications is practiced extensively in Japan (Ref. 3-11).

TABLE 3-7. ESTIMATED NO_x LEVELS FROM FUEL-BOUND NITROGEN

Unit	Fuel Oil Consumption at Full Load, bbl/hr ^a	Maximum Possible Fuel NO _x ^b		Estimated Uncontrolled Fuel NO _x ^c	
		lb/hr	ppm ^d	lb/hr	ppm ^d
Alamitos 1&2	265	720	327	418	190
El Segundo 1&2	250	680	312	394	181
Huntington 1	305	830	333	481	193
Beach 2	305	830	331	481	192
3	305	830	328	481	190
4	320	870	327	505	190
Redondo Beach 5&6	280	760	345	441	200
Haynes 1	355	965	362	560	210
2	370	1006	378	583	219
3	352	955	352	554	204
4	362	985	362	571	210
Scattergood 1	305	830	388	481	225
2	285	775	362	450	210

^aRef. 3-3.

^b0.25% fuel nitrogen, NO_x as NO₂.

^c58% conversion of fuel nitrogen to NO for oil containing 0.25% N (Ref. 3-4).

^d3% O₂, dry.

TABLE 3-8. UNCONTROLLED NO_x EMISSIONS FROM OIL-FIRED BOILERS

Boiler Type	Emissions ppm, dry	MW	References
Front Wall Fired	345	180-240	3-5
Front Wall Fired	360-367	180-250	3-8
Opposed Firing	300	~ 200	3-6
Tangential Divided	350	320-335	3-7
Test Burner	360	---	3-9

TABLE 3-9. EMISSION REDUCTION RESULTING FROM EXISTING COMBUSTION MODIFICATION NO_x CONTROL METHODS

Utility	Unit Desig. & MW	Burners, No.	Firing ^c Config	NO _x Control Method	Emissions, ppm, dry, 3%O ₂		% Reduction		
					Controlled	Uncontrolled			
SCE	Alamitos	1, 175	16	WFF	2-stage	425	360	--	
		2, 175	16	WFF	2-stage	416	360	--	
	El Segundo	1, 175	16	WFF	OSC, 2-stage	271	360	25	
		2, 175	16	WFF	OSC, 2-stage	271	360	25	
	Redondo	5, 175	16	WFF	2-stage	306	360	15	
		6, 175	16	WFF	2-stage	306	360	15	
	Huntington Beach	1, 215	24	WFF	OSC	245	360	32	
		2, 240	24	WFF	OSC	295	360	18	
		3, 228	24	HO	2-stage	240	300	20	
		4, 235	24	HO	2-stage	297	300	--	
	DWP	Haynes	1, 230	12	WFF	OSC	210	360	42
			2, 240	12	WFF	OSC	210	360	42
3, 228			12	WFF	OSC	225	360	38	
4, 235			12	WFF	OSC	225	360	38	
Scattergood		1, 180	16	WFF	OSC	225	360	38	
		2, 180	16	WFF	OSC	225	360	38	
Ref. 3-8	180-250	--	WFF	OSC	253-270	360-367	25-31		

^aLow sulfur oil (0.25% fuel nitrogen)

^bFrom Ref. 3-2.

^cWFF: wall, front fired, HO: Horizontal opposed.

^dSee Table 3-3.