

Chapter 3

EMISSION CONTROL TECHNOLOGY

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3.1 AUTOMOBILE EMISSION CONTROL

3.1.1 How it became possible — socio-technological analysis —

If stated simply, Japan's goal for the automobile emission control requirement for passenger cars is an exact copy of the US goal, which was demanded in the Clean Air Act of 1970, called the Muskie Act. However, Japan achieved the goal in 1978, five years earlier than in California, while it has not yet been achieved at federal level in the United States. Japan was the first to succeed in the development and mass production of low emission motorcars necessary for the restoration of clean air in urban areas. Perhaps, Japan's success and its implementation of a very stringent emission control regulation may have had no small influence on the attitudes of other countries, especially of the U.S., towards the same problem.

What drove Japan to become the leader in this hard race and what was the cause of its success? It was not because Japan was more advanced in automobile technology but rather it was a result of the people's serious concern over air pollution, and a result of political strife between the central and local governments. It was also a result of severe competition among automobile makers seeking a larger share of the market. The stringent regulation was possible to plan and implement not because the technology meeting the requirement was already available but the technology was advanced and became available because the stringent regulation was planned and enforced.

Before reviewing the present status of automobile emission control technology, it would be worthwhile looking at the history of its development as an example of the interplay between social needs and technology.

In order to relate the history of automobile emission control systematically, one must start from the Clean Air Act of 1970 of the United States known as the Muskie Act. The Clean Air Act called for the reduction of each of three kinds of major emissions from automobiles to one tenth of the current level in 1970. Carbon monoxide, hydrocarbon and nitrogen oxide were three major pollutants, and their emissions were to be reduced to 3.4 g/mile,

0.41 g/mile and 0.4 g/mile, respectively.

The reduction requirement, to one tenth, was determined from a rough estimate of the measures necessary to restore and maintain good air quality with the foreseeable increase in the amount of traffic.

A remarkable, and even revolutionary, aspect of the Clean Air Act was that the requirement for reduction was solely determined from the demand for restoring good air quality and no special heed was paid to the availability of the technology to meet the requirement. It was only considered at the time of implementation.

In 1970, no developed technology was available which could reduce the emissions of carbon monoxide and hydrocarbon to the required levels and no technical possibility was foreseen which could reduce the emission of nitrogen oxide to one tenth of the current level. The reduction of nitrogen oxide was considered much more difficult than the treatment of carbon monoxide and hydrocarbon because carbon monoxide and hydrocarbon are byproducts of fuel combustion and, therefore, can be removed by introducing them into an afterburner or oxidizing catalytic bed. On the other hand, nitrogen oxide is formed by a reaction between nitrogen and oxygen in the air at a high temperature. Therefore, either the suppression of formation of nitrogen oxide within the engine or the reduction of nitrogen oxide by some reducing agent is necessary for lowering the nitrogen oxide emission, both of which were not technically feasible at that time.

However, in the Clean Air Act of the U.S., the date of the implementation of

Table 3.1

The progression of auto-emission control standards for carbon monoxide (CO), hydrocarbon (H.C.) and nitrogen oxide (NO_x) in Federal, California and Japanese regulations expressed in g/mile

	CO			H.C.			NO_x		
	Fed.	Cal.	Japan	Fed.	Cal.	Japan	Fed.	Cal.	Japan
1973			29.4			4.7			3.5
1975	15	9.0	3.4	1.5	0.9	0.4	3.1	2.0	1.9
1976	15	9.0		1.5	0.9		3.1	2.0	1.0
1978	15	9.0		1.5	0.41		2.0	1.5	0.4
1980	7.0	9.0		0.41	0.39		2.0	1.0	
1981	3.4	7.0		0.41	0.39		1.0	0.7	
1983	3.4	7.0		0.41	0.39		1.0	0.4	
Clean Air Act	3.4	effective 1975		0.41	effective 1975		0.4	effective 1976	

the regulation was set as 1975 for carbon monoxide and hydrocarbon and 1976 for nitrogen oxide. The waiving of the implementation was possible only when it was sufficiently proved that in spite of all the efforts of the automobile makers, the technology meeting the requirements was non-existent. Constant examination and assessment of the emission control technology became necessary. The task was assigned to the Academy of Science. It was also proposed that the regulation would be implemented when at least a single technical possibility was proved to be available.

Thus the US Clean Air Act of 1970 was revolutionary in that it aimed to promote the development of the necessary technology by legal enforcement and by competition among automobile makers.

Japanese automobile emission control regulation basically followed the outline of the US Clean Air Act of 1970. The kinds of pollutants to be controlled, the target level of the emission control requirement for each pollutant and the planned date of implementation were exactly same. The legal procedure for the waiver was similar. In place of the Academy of Science in the United States, a committee called the Investigation Committee for Motor Vehicle Pollution Control Technology was set up and assigned the task of investigating and assessing the availability of the demanded emission control technology.

Thus Japan had started automobile emission control regulation following in the footsteps of the United States. However, later developments caused a change in their positions and the United States was forced to follow in the footsteps of Japan. This is clearly shown in Table 3.1. It compares the progress of the emission control requirements in the United States and in Japan. In the United States, the federal and Californian requirements are also compared. The target for hydrocarbon was attained in Japan as scheduled in 1975 but it was only attained in 1978 in California and in 1980 at the federal level. The target for carbon monoxide was also reached in Japan in 1975 as scheduled, but in California it was delayed six years to 1981 and at the federal level it has not been reached yet. The situation for nitrogen oxide was similar. Although Japan could implement the planned regulation in 1978 with two years delay, California postponed the implementation seven years, and at the federal level it has not been implemented yet. Although the emission reduction requirements for CO and hydrocarbon were very severe, they were rather easy problems technically when compared with the requirement for nitrogen oxide. CO emission can be reduced drastically by bringing the air fuel ratio close to the stoichiometric ratio. The emission of hydrocarbon can be reduced by preventing evaporation from the fuel tank and the blow-by from the crank case. In either case, the remaining constituents in the exhaust gas can be removed by passing them through a thermal reactor or an oxidizing catalyst.

Though it seemed simple, the United States delayed five years more than Japan before its implementation. What caused such a difference? The key to the problem is Japan's early shift to lead-free gasoline. Japan started to decrease the lead content in regular gasoline gradually from 1971 and the shift to lead-free gasoline was completed in 1975. The shift to lead-free gasoline was not an easy task because the octane number must be kept at the same level regardless of the decrease in lead content by increasing the content of aromatic hydrocarbon in the gasoline. Another problem associated with the use of lead free gasoline for existing vehicles was the valve seat recession problem which causes engine stalling, hard-start and reduced output. Therefore, the complete transition to lead-free gasoline was a gradual process taking five years. However, just at the time of enforcement of emission control of CO and hydrocarbon, lead-free gasoline was available. The availability of lead-free gasoline made the stringent emission control requirement possible. On the contrary, the United States was rather slow in shifting to lead-free gasoline.

It is worthy to note that in Japan regulation for carbon monoxide and hydrocarbons was implemented as scheduled but the implementation of regulation for nitrogen oxide was two years behind schedule. This was caused partly by the difficulty of controlling the emission of nitrogen oxide. But the major reason was something else.

The oil crisis shocked the world in 1973. The pendulum of public concern once swung fully towards environment began to swing towards energy. In the United States, the implementation of the regulations on carbon monoxide and hydrocarbon was postponed without sufficient reason. In Japan, although the regulation of these two pollutants was implemented as initially scheduled because it was planned before the oil crisis, the implementation of the regulation of nitrogen oxide became quite uncertain.

Japanese automobile makers had agreed to the enforcement of the regulation demanded in the Clean Air Act of the U.S. and were preparing for its complete implementation by developing the necessary technology. However, it was evident that they agreed to the regulation because they thought the technology meeting the requirement was indispensable for their export of cars to the United States once the regulation was implemented there. Therefore it was natural that most of them lost any motivation for developing technology meeting the nitrogen oxide emission control regulation once they found the United States was postponing every emission control requirement. Probably, they exerted influence on the government so as to postpone the implementation of the regulation of nitrogen oxide emission control. The government was said to be inclined to postpone the scheduled implementation.

Such an attitude of the central government aroused serious concerns in

municipal governments. At that time, the municipal governments of major cities like Tokyo, Yokohama, Osaka and Kobe were all supported by the progressive parties, including the socialist and the communist parties, and were very eager to control pollution in urban areas. They were in constant conflict with the central government by trying to enforce more stringent pollution control regulation than that required by the central government.

They had already made plans for air pollution control presuming that the automobile emission control regulation would be implemented according to the schedule. Indefinite postponement would totally scrap the plans.

When the mayors of the major cities assembled to discuss the problem in 1974, Tokyo mayor Ryokichi Minobe proposed the setting up of a committee, completely independent from the government one, to investigate the state of technology of nitrogen emission control and to examine the feasibility of the implementation of the planned regulation. The proposal was soon accepted but the problem was to find experts who would work for the committee which would have to unveil the facts which all the automobile makers wanted to conceal.

The committee summoned six automobile makers, Toyota, Nissan, Honda, Mazda, Fuji and Isuzu, and interviewed them individually. Although they unanimously denied totally the technical feasibility of implementing the regulation according to the schedule, evaluation of the current state of the technology was different between large makers and small makers. Toyota and Nissan strongly denied any remarkable achievement in the emission control technology and insisted that any requirement below 1.9 g per mile was impossible to meet. Honda and Mazda, on the other hand, admitted that the emission control of 1 g nitrogen oxide per mile could be met readily. Honda, especially, boasted 0.4 g per mile had already been reached by their experimental vehicle fitted with the newly invented CVCC engine, although it was still plagued with the problem of drivability.

The committee drafted a report on the technical feasibility based on the results of the interviews and the analysis of published materials and acquired data. As there was no direct evidence showing the feasibility of the proposed regulation, the committee had to depend on a more elaborate method of technology assessment. They analyzed the available technical data and estimated the effects of various factors influencing the emission of nitrogen oxide, such as air fuel ratio and the amount of recycling gas, and then synthesized these effects to simulate the performance of an improved engine of which the performance data was not available. In spite of such efforts, the performance of the reduction catalyst was impossible to estimate because scientific data showing the results of experiment under the actual conditions of the exhaust gas or close to them were not available. Concerted intentional concealment of data was suspected.

The report was not a simple survey of the published data of the emission performance of the tested vehicle, but rather it was a report of a system design showing the feasibility of a new engine using various methods of emission control technology.

The report had no small impact on public opinion. It aroused strong reactions from both sides. It especially provoked the Environmental Agency. A director general publicly attacked the report as unscientific speculation. The attack again triggered reaction against the apparent attitude of the central government to loosen the control over emission and pollution. Therefore it was not so strange that the technical feasibility of nitrogen oxide emission control became one of the most important social concerns in 1974.

In the midst of such social concern, the Investigation Committee for Motor Vehicle Pollution Control Technology of the central government advised the postponement of the planned 1976 regulation on nitrogen oxide emission control on the ground that the technology meeting the requirement was not yet available.

The decision did not calm the situation. Doubt and protest against the decision were continuously expressed by people annoyed by automobile emission and finally a scandalous fact which ultimately reversed the decision was brought to the Diet by the secretary general of the Japanese Communist Party. The Investigation Committee for Motor Vehicle Pollution Control Technology was commissioned as a neutral committee consisting of scholars and experts and meetings were held behind closed doors. The public was completely excluded from the proceedings. However, it was learned that the secretary of the automobile makers' association was allowed to attend every meeting, to take note of the proceedings and report them to the automobile makers.

This meant that the committee was completely open to and constantly watched by the automobile makers. One wonders if the necessary neutrality could be possible in such a situation. The disclosed notes revealed that the discussion leading to the final decision was far from technical but was a kind of political deal. The disclosure again ignited the social concern over the problem. In the midst of the concern, a fact was revealed. A vehicle completely meeting the Muskie goal had already been developed by Mitsubishi. A technical feasibility existed. It was fitted with an engine invented by Professor Kumagai of Tokyo University. The committee, being well aware of the fact, had completely neglected it when they made the final decision.

Amidst public protest and anger, all the members of the committee were forced to resign and the decision they made was virtually scrapped.

The dissolution of the committee and the organization of a new one showed the automobile makers that the assessment from now on would be made on a genuinely technological basis and if at least one company had developed

feasible technology, the regulation would be implemented. Seeing this, every automobile maker rushed to develop nitrogen oxide control technology meeting the original 1976 requirement, or the Muskie requirement. The technological development in the year after this event was amazing. All the automobile makers, except Toyota, announced that they had succeeded in developing technology satisfying the Muskie requirement. Honda, Mitsubishi and Toyo Kogyo announced that they were ready to market cars meeting the Muskie requirement if some tax benefits were allowed.

It was evident that these companies had already succeeded in the development of cars meeting the requirement when the Investigation Committee concluded that it was not technically feasible. They had concealed or were compelled to conceal the facts. It should be mentioned that they were rather supportive to the activity of the technology assessment committee formed by the seven cities. Their attitudes contrasted remarkably with the reluctant and offensive attitudes of Toyota and Nissan. Probably, they wanted more stringent control to be implemented at that time so that they could enjoy the advantage in expanding their share in the market which had been monopolized by Toyota and Nissan.

Now it had become clear that the goal, once thought unattainable, could be reached in various ways such as engine modification, lean combustion, stratified combustion, rich-lean combustion, exhaust gas recycling, dual bed catalysts, three way catalysts, etc. The main concern of automobile makers had shifted and fierce competition was now focused on fuel economy. The result was marvelous. It turned out that the introduction of nitrogen oxide emission control did not decrease the average fuel economy at all but on the contrary the average fuel economy was improved about 30% in four years from 1976 to 1980.

A major reason for the opposition to exhaust emission control was the decrease in fuel economy. It was based on the ideas of automobile engineers. They believed there was a definite trade-off between the emission control and the fuel economy. There is some truth in this but they neglected the fact that the automobile engine is far from ideal and there remains abundant room for its improvement. The improvement required scientific research on the combustion process in the engine. This was also the research necessary for the reduction of nitrogen oxide emission. Therefore, the same research that enabled the satisfactory control of nitrogen oxide emission undoubtedly contributed to the improvement in fuel economy. An interesting question to pose would be whether the fuel economy would be improved further if the stringent emission control were removed now. Experts agree that there is no factor which would further improve the fuel economy even if the emission control is now abolished. The lesson we learn from history is that the emission control was not detrimental

to the fuel economy. Rather it facilitated the improvement of fuel economy by forcing the automobile makers to investigate the combustion process in the engine, which did not concern them until then.

The present example tells us that once the target is fixed, free competition is the best means of ensuring the development of technology. However, free competition is not enough to fix the target by itself, especially when the goal is a non-economical one. Social enforcement backed by people's will is necessary.

3.1.2 Present state of technology

(i) Lean combustion system. The generation of all three pollutants can be reduced by lean combustion or making the air-to-fuel ratio (A/F) higher than the stoichiometric ratio. The concentrations of these pollutants in the exhaust varies with the air-to-fuel ratio, as shown in Fig. 3.1. Carbon monoxide and hydrocarbons are high for rich mixtures. They diminish to very low levels when the air-fuel exceeds the stoichiometric ratio 14.6. The amount of nitrogen oxide is at the maximum for the stoichiometric ratio and diminishes for both rich and lean mixtures.

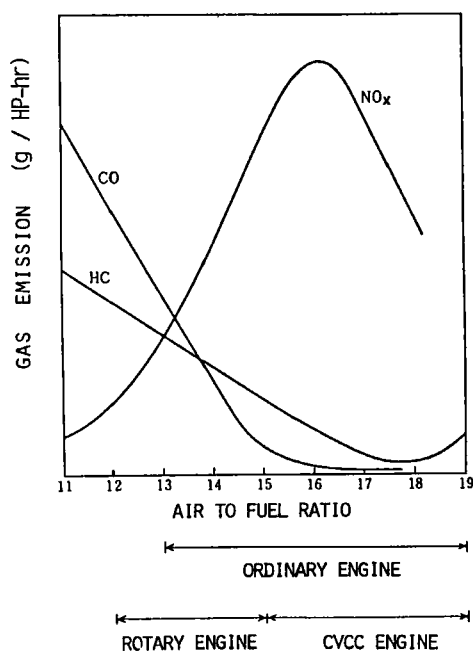


Fig. 3.1. The emissions of carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) from automobile engines vary with air-to-fuel ratio.

Therefore, if we employ a sufficiently lean mixture having an air-to-fuel ratio as high as 20, the levels of pollutants in the exhaust can be kept sufficiently low. This is the principle of lean combustion. Although the principle is simple, its embodiment as technology is not a simple task. It requires considerable modification of the engine. First, the distribution of the air-fuel mixture among cylinders must be improved so that the difference among air-to-fuel ratios in the cylinders is virtually eliminated. This is because, when the average A/F is high, a slight deviation from the average will produce too lean a mixture which is difficult to ignite.

In order to eliminate variation of the A/F among cylinders and to provide exactly the same mixture to all of them, the carburetor must be improved so as to produce a completely homogeneous mixture. Second, the lean mixture, though flammable, is difficult to ignite and tends to cause a misfire or a failure of ignition which causes an increase in hydrocarbon emission. The ignition can be facilitated by making a rich mixture around each ignition plug. This is called stratified combustion. It usually required separate fuel injection pumps. Honda solved the problem by merely providing an auxiliary carburetor. This provided an ignitable mixture around the ignition plug. This is the principle of the CVCC engine which made Honda famous world-wide.

The outstanding merit of the lean combustion engine is that it can be used in a leaded environment where lead-free gasoline is not available.

(ii) Catalytic removal system. The catalytic removal system removes the three pollutants in the exhaust by letting the gas pass through a catalytic converter. A catalyst has been used to remove carbon monoxide and hydrocarbon. This is an oxidizing catalyst. In order to remove nitrogen oxides from the exhaust, another type of catalyst which can reduce nitrogen oxides to nitrogen is necessary. This is called a reducing catalyst. For the reducing agent, carbon monoxide and hydrocarbons present in the exhaust gas are used, thereby enabling simultaneous removal of all three pollutants. However, as the complete simultaneous removal of all three pollutants is difficult, a combination of the reducing and oxidizing catalysts is usually used. The reducing catalyst, which is placed first, reduces nitrogen oxide using the carbon monoxide and hydrocarbons present and the oxidizing catalyst then oxidizes the remaining carbon monoxide and hydrocarbons when more air is introduced.

The reducing catalyst can now be called a three-way catalyst. It can reduce or remove all three pollutants simultaneously if the composition of the exhaust is in the right range, which depends on the air/fuel ratio. A three-way catalyst is used alone or in conjunction with an oxidizing catalyst. The critical factor ensuring good performance of the three-way catalyst is the maintenance of the air/fuel ratio at an appropriate value very close to the

stoichiometric ratio i.e. 14.6. For that purpose, automatic control of the air/fuel ratio is essential. The system for this essentially consists of an oxygen sensor, an electronic control device, which is usually a microprocessor, and a fuel injection system or an electromechanical carburetor. If the air/fuel ratio is kept strictly around 14.6, the three-way catalyst alone can lower the levels of the three pollutants to the levels satisfying the control requirements. It often happens that a lower A/F is preferred as strict adherence to the stoichiometric ratio cannot be ensured. In such a case an oxidizing catalyst is placed after the three-way catalyst and the remaining carbon monoxide and hydrocarbons are oxidized over the catalyst when more air is introduced.

(iii) Other methods of reducing emission. The generation of nitrogen oxide during combustion can be reduced considerably by lowering the temperature of combustion. An effective way of lowering the temperature is to dilute the inflammable mixture by introducing inert gas. The exhaust gas recycling system is a system which utilizes the exhaust gas from the engine as the inert gas for dilution. The exhaust gas recycling method is the surest way of reducing the emission of nitrogen oxide without modifying any other process or the structure. It can be applied to any system, whether it be the prototype or an improved system, and it can reduce the emission considerably. In a prototype engine, recycling of 10% of the exhaust gas can reduce the emission to one third of the original level. In the improved system, though the percentage of reduction becomes smaller, recycling of around 10 or 20% of the exhaust gas can effectively reduce the emission to a considerable extent.

Lowering the combustion temperature by increasing the heat loss by making the engine out of a good heat-conducting metal such as aluminium can also contribute to reduction of the emission, although it also reduces the fuel economy.

(iv) Emission control of the diesel engine. The emission control of the diesel engine poses another difficult problem. The three-way catalyst cannot be used because the diesel engine must be operated with an oxidizing air-to-fuel ratio in order to prevent smoke generation. Lean combustion can reduce the emission of nitrogen oxide but as the combustion in the diesel engine is not combustion of the premixed mixture, lean combustion is not so effective as in the gasoline engine.

The remaining effective measures are exhaust gas recycling, injection retard and engine modification. The injection retard is effective both for reduction of smoke and nitrogen oxide but fuel economy deteriorates. Although exhaust gas recycling is considerably effective in reducing nitrogen oxide emission, it increases smoke emission. Modification of the combustion chamber is sometimes effective.

By joint application of these techniques, the exhaust quality has been improved considerably. In 1981, the regulation specifying the emission control requirement for the diesel powered passenger car, which is to be obligatory from 1986, was announced. The new requirement is 3.4 g/mile for CO, 0.64 g/mile for hydrocarbon and 1.1 g/mile for nitrogen oxides.

Emission control from diesel engine powered trucks is still a difficult problem. According to the regulation in 1983, the NO_x concentration in the exhaust from a direct injection type diesel engine must be lower than 610 ppm and an average of 470 ppm. The requirement for 1974 was an average of 770 ppm, which means only 40% reduction in ten years.

3.2 NO_x EMISSION CONTROL FROM STATIONARY SOURCES

It is well known that nitrogen oxides (NO_x) are among the major species causing photochemical smog. In Japan, the ill effects of photochemical smog were first seen in early 1970 when many junior high school students in Tokyo were affected. Since 1973, progressively tighter NO_x emission standards have been established for all stationary pollution sources, consequently, the Japanese emission standard has become the most stringent standard in the world. In order to comply with emission standards, NO_x abatement technology for stationary sources has improved significantly. As a result, NO_x control technology for coal combustion boilers, for example, is now exported to European countries. However, atmospheric NO_x levels have not yet dropped enough in spite of innovative emission controls. Control technology, particularly for dirty fuel combustion facilities, is still inadequate. The development of economical NO_x control technology for developing countries also requires attention.

Anthropomorphic sources of NO_x are classified into mobile sources such as cars and stationary sources such as boilers. Although the contribution from each source category varies from area to area, the contribution of stationary sources is significant especially in areas with heavy industry. NO_x emitted by stationary sources comes almost entirely from combustion processes. Although NO_x is defined as the total of NO and NO_2 , more than 90% of NO_x at the end of combustion is in the form of NO. The NO from the combustion process has two different origins. One is from nitrogen gas in the air and the other is from nitrogen compounds in the fuel. The NO from nitrogen in the air is called thermal NO_x while NO_x from fuel nitrogen is called fuel NO_x .

There are two general approaches to NO_x reduction. The first involves combustion modification methods and the second is the NO_x removal methods. The former methods aim at controlling the NO_x concentration at the combustor exit or the furnace outlet by modifying the combustion process through changing

fuel type, improving the burner design or changing the furnace configuration. Since NO formation is strongly influenced by the combustion process, the details of the NO_x formation process during combustion provide many useful ideas for NO_x control by combustion modification. The latter NO_x removal methods reduce or remove NO_x after combustion is complete and the exhaust gas leaves the combustor or the furnace. NO_x removal processes usually require the construction of a large scale decontamination facility before the exhaust gas reaches the stack, so this method is expensive compared to combustion modification methods. Hence, combustion modification methods are the economically favored methods for NO_x emission reduction.

Next, we will discuss in greater detail combustion modification methods and NO_x removal methods respectively.

3.2.1 Combustion modification methods for NO_x reduction

An engineer's first task in applying any combustion modification method to a particular combustion process, is to clarify whether the NO formed in a process is thermal NO or fuel NO. If the NO from the process is predominantly thermal NO, an effective control method will achieve at least one of following:

- decrease of flame temperatures;
- decrease of furnace oxygen levels;
- decrease of residence time in the high temperature region.

On the other hand, if the process NO is predominantly fuel NO, a control method based on any of the following is effective:

- 1) decrease of fuel nitrogen content;
- 2) decrease of furnace oxygen level;
- 3) control of fuel and air mixing conditions at the burner.

The type of NO can be roughly predicted from the fuel nitrogen content and the

Table 3.2

Nitrogen content in fuels ¹⁵⁾

Fuel	Nitrogen content (wt%)
Crude oil (Middle East)	0.09-0.22
No.6 heavy oil	0.1-0.4
No.4 heavy oil	0.05-0.1
light oil	0.002-0.03
kerosene	0.0001-0.0005
coal	0.2-3.4
LPG, City gas	0

maximum temperature in the furnace. If the nitrogen content in the fuel is under 0.01% and the maximum temperature is over 1500°C, the observed NO is mainly thermal NO. On the other hand, if the fuel nitrogen content is over 0.5

Table 3.3

Summary of combustion modification method for control of NO_x

Name of Technology	Principle	Type of NO reduced	Type of fuel liquid	Average reduction rate
<u>Fuel Modification</u>				
1) Low nitrogen fuel	Decrease of Nitrogen	fuel NO	liquid fuel and coal	*
2) Emulsified oil fuel	Decrease of Temperature and Oxygen	thermal NO	liquid fuel	30-50%
<u>Operation Modification</u>				
3) Low excess air ratio combustion	Decrease of Oxygen	fuel NO and thermal NO	all fuel	10-20%
4) Low load combustion	Decrease of Temperature	thermal NO	all fuel	10-30%
5) Low temperature air preheating	Decrease of Temperature	thermal NO	all fuel	10-30%
<u>Low NO_x Burner</u>				
6) Self recirculation burner	Decrease of Oxygen and Temperature	thermal NO	liquid	20-40%
7) Rapid mixing burner	Decrease of Temperature	thermal NO	gas and liquid fuel	20-40%
8) Off-stoichiometric combustion burner	Decrease of Oxygen and Temperature	fuel NO and thermal NO	all fuel	30-40%
<u>Furnace Modification</u>				
9) Two staged combustion	Decrease of Temperature and Oxygen	fuel NO and thermal NO	all fuel	30-50%
10) Fuel gas recirculation	Decrease of Temperature	thermal NO	all fuel	30-50%
11) Water or steam injection	Decrease of Temperature	thermal NO	gas and liquid fuel	30-50%
12) Staged fuel injection	Removal by Reducing Species	fuel NO and thermal NO	all fuel	30-50%

* depends on fuel employed

wt.% and the maximum temperature is under 1400°C , the observed NO is mainly fuel NO. In general, the NO from the combustion of light oil, gasoline and gaseous fuel without ammonia is thermal NO while the NO from the combustion of the residual oil and coal is mainly fuel NO (Table 3.2).

The various combustion modification methods developed so far are listed in Table 3.3.

We will now discuss the most practical combustion modification methods listed in the table.

(i) Low NO_x burner. Use of a low NO_x burner (LNB) is an attractive control technique since it requires only replacement of burners without modification of the furnace. Hence, this method is relatively inexpensive. The principle of a LNB is either:

- (1) control of NO formation by forming a local reducing region in the flame through changing the burner structure; or
- (2) formation of a thin flame having a large surface area to increase radiative heat transfer to the boiler wall and consequently reduce the flame temperature.

Examples of systems based on the former principle are the self-recirculation burner and the off-stoichiometric burner. An example of the latter principle is the rapid mixing flame.

a) Self-recirculating burner

This burner was developed for the furnace of petroleum chemical plants. A diagram of the burner is shown in Fig. 3.2. In this burner, the initial part

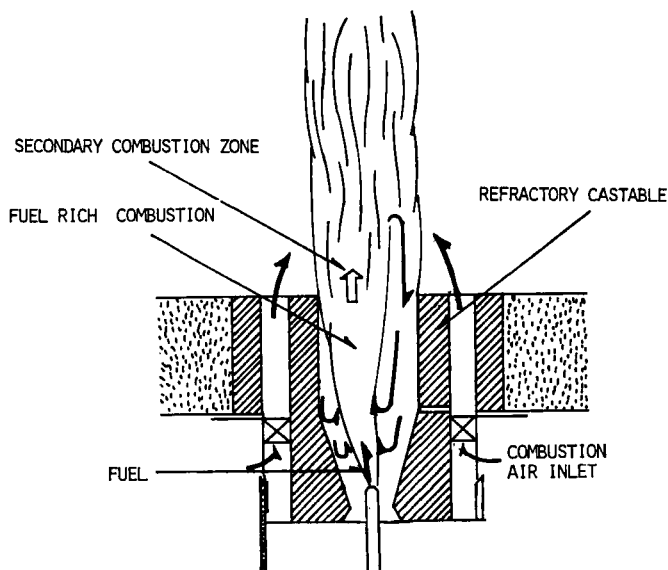


Fig. 3.2. Self-recirculating-type burner

of the flame is surrounded by the cylindrical burner wall in order to reduce the entrainment of ambient air to the fuel. Hence, only a limited amount of air is recirculated from the proximal section of the burner and entrained into the flame. Because of lack of oxygen, a very fuel-rich combustion takes place in this burner section and consequently NO formation is suppressed. The afterburning of unburnt species such as CO, H₂ and HC takes place at the burner opening where secondary air is supplied.

This type of burner can be used to control thermal NO and can be used to improve the fuel economy. This burner can reduce NO_x levels by 30 to 40%. The cost of this burner (capacity : 100 l oil/hr) is around 2000 to 5000 US dollars.

b) Off-stoichiometric combustion burner

This burner can be applied to the control of both thermal and fuel NO from boilers using gaseous, liquid or coal fuels.

In Fig. 3.3 we show the relationship between emissions of thermal NO and fuel NO from a premixed flame as a function of air ratio. The emission level of thermal NO peaks near the stoichiometric point. Hence, if combustion conditions can be reduced below the stoichiometric point, NO emissions can be reduced. In practice, off-stoichiometric combustion means that half of the burners are operated at an air ratio lower than 1.0 (point A in Fig. 3.3) and the other half of the burners are operated at an air ratio higher than 1.0

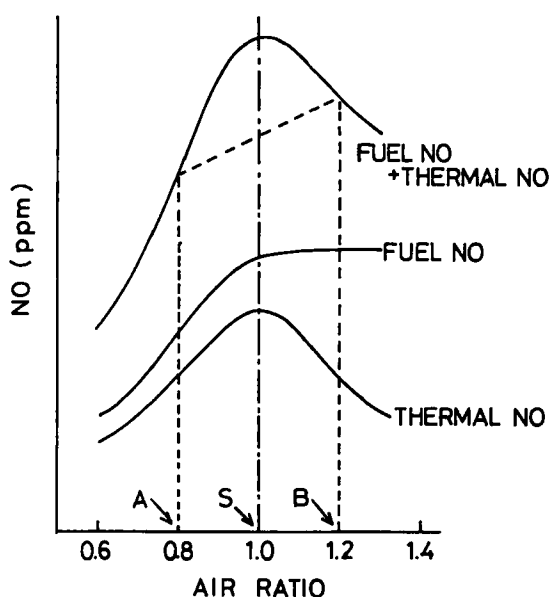


Fig. 3.3. Emissions of thermal NO and fuel NO from a premixed flame as a function of air-to-fuel ratio.

(point B in Fig. 3.3). An example of this type of burner is called the PM (Pollution Minimum) burner developed by Mitsubishi Heavy Industry. In this burner system, all the burners are operated under premixed fuel-air conditions. The upper and lower burners on both sides of the furnace are operated at an air ratio of 1.2 and the center burner is operated at an air ratio of 0.8. The system reduces NO emissions by 30 to 40%.

c) Rapid mixing type burner

This burner reduces thermal NO by forming a thin, flat flame. When the thin flat flame is formed, the flame temperature drops due to the increased radiant heat transfer to the furnace walls and consequently the emission of thermal NO is reduced. Because of this principle, this burner is suitable for water-cooled wall furnaces.

This burner has the advantage of improved combustion efficiency, and reduced CO and soot emissions, as well as reduced thermal NO emissions. An example of the rapid mixing type burner designed for liquid fuel combustion is shown in Fig. 3.4. In liquid fuel combustion, the fuel is atomized radially and rapidly mixed with air consequently forming a large surface thin flat flame (Fig. 3.4). Accordingly, the flame area is large compared to a conventional burner. This burner was developed by the Nippon furnace industry under the name of the NFK-TRW burner.

This type of burner is used in boilers burning gaseous or liquid fuel with little or no nitrogen. This burner reduces NO emissions by about 40%.

(ii) Emulsified oil combustion. This method has the advantage of not requiring the reconstruction of the furnace. In addition it increases combustion efficiency and suppresses soot emissions. The method is applicable to small scale boilers.

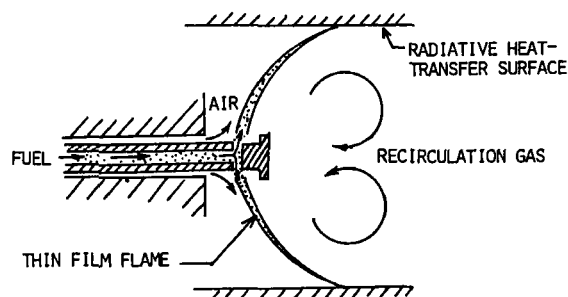


Fig. 3.4. Rapid mixing burner.

Emulsified fuel is made by dispersing water in oil with the aid of small amounts of emulsifier. Emulsions are classified into i) water droplets in oil which is called the W/O type and ii) oil droplets in water which is called the O/W type. Usually, the W/O type emulsion is used because of low viscosity and easy handling. When emulsified fuel is atomized in a high temperature atmosphere, the water in the oil is instantly evaporated and induces secondary atomization. This initiates very rapid and efficient combustion. As combustion heat is partly lost by the vaporization of water, the flame temperature is reduced and thermal NO emission is reduced. In the case of emulsified oil combustion, the efficient combustion allows the air ratio to be held near the stoichiometric point without the formation of CO or soot. The emission of fuel NO can thereby be reduced while keeping high combustion efficiency. This method can be mainly applied to combustion facilities which use liquid fuel of low nitrogen content.

The disadvantage of this method is the reduction of energy efficiency. However, this can be compensated for by the increased combustion efficiency and the decrease in the air ratio. The NO reduction of this method is between 30 and 40%. The cost of emulsification is only 5% of the fuel cost. The emulsification unit for a boiler of $40,000 \text{ m}^3/\text{h}$ requires an area of only 4 m^2 .

(iii) Two-stage combustion. The two-stage combustion method (TSC) is effective for both thermal NO and fuel NO not only for gas or liquid combustion but also coal combustion. Furthermore, the TSC method may be more effective in reducing NO compared to the low NO_x burners.

The principle of TSC is illustrated in Fig. 3.5. The primary combustion is

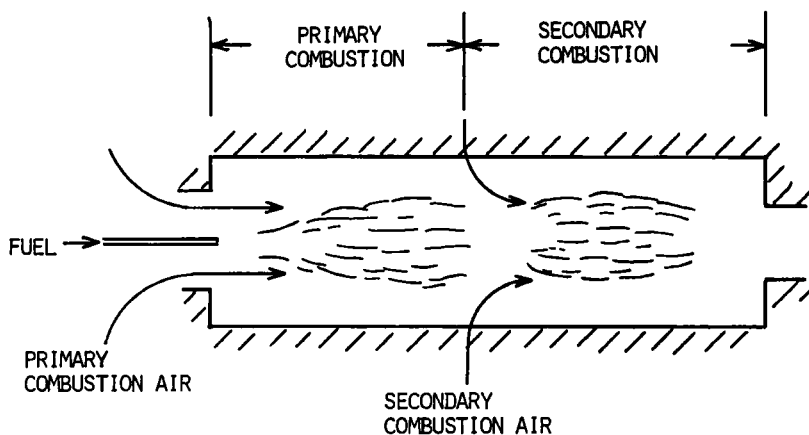


Fig. 3.5. The principle of two-stage combustion.

kept fuel-rich by controlling combustion air. Then, fuel lean combustion follows at the secondary stage where the combustion air is introduced. Thermal NO can be reduced by this method because the temperature distribution becomes flat and the peak temperature, which is the main cause for the formation of thermal NO, is reduced. The fuel NO can also be reduced because the fuel nitrogen is mostly converted to N_2 at the primary stage under the fuel-rich combustion. Sadakata examined the optimum TSC conditions for NO_x reduction experimentally and found that the location of the air injection point during the second stage was important.²⁴⁾ The effect on the final NO levels of the air injection point in the second stage is shown in Fig. 3.6. The final NO_x is sharply decreased as the injection point is moved downstream. This shows that the air injection point should be located at least 1200 mm downstream from the burner port. Wendt et al. found the same for coal combustion²⁵⁾. Sadakata also found that there is an optimum air ratio for the efficient reduction of NO_x .¹⁵⁾ Fig. 3.7 shows the effect of the primary air ratio on the final emission of NO from methane-air turbulent combustion. In this figure, the dotted line shows the NO emissions at the primary stage while the solid line shows the final NO emissions. Although the primary stage NO decreases with a decrease in the primary air ratio, the final NO level reaches a minimum when the air ratio equals 0.8 and then increases again as the primary air ratio is reduced. This

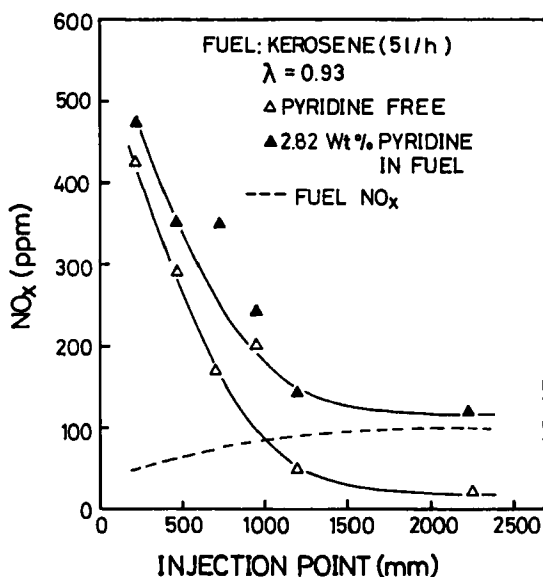


Fig. 3.6. Effect of the injection point of secondary stage air on the final NO_x emission.

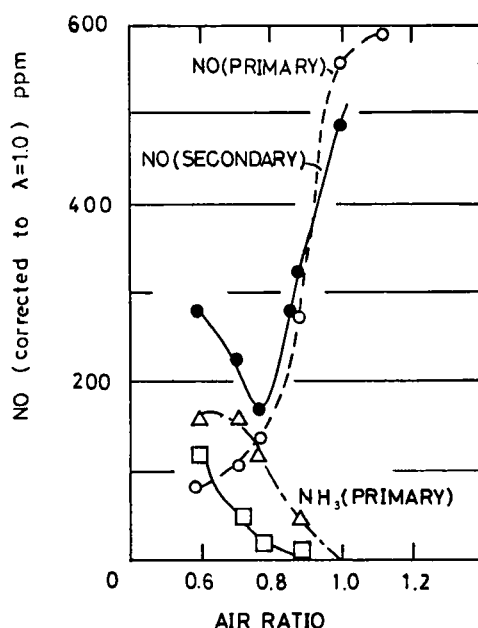
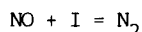


Fig. 3.7. Emissions of nitric oxide and ammonia from the combustion of a fuel doped with 0.23 vol.% ammonia as a function of primary air ratio.³⁾

is because a high concentration of intermediate reduced species such as NH_3 or HCN is formed instead of NO at very low air ratios and these intermediate species are converted to NO during the secondary stage combustion. On the other hand, the level of intermediate species formed at a primary air ratio of 0.8 is nearly the same level as that of NO. Under such conditions, NO and the intermediate species react and form N_2 by the following chemical reaction.



TSC can be applied to gas and oil combustion boilers and high temperature furnaces using residual oil such as glass fusion furnaces and rotary cement kilns. It can also be used in utility plant coal combustion boilers and small scale coal combustion furnaces. An example of applying the TSC method to a boiler is shown in Fig. 3.8. In this case, the burner port at the upper boiler section is used as the secondary air injection port. The NO_x reduction was around 30%. The TSC method can be applied also to fluidized coal combustion. In this case, secondary air is injected into the freeboard above the bed. The reduction in this case is around 20%.

The disadvantage of TSC is that the heat energy efficiency is lowered because of the reduced flame temperature. However, this disadvantage can be

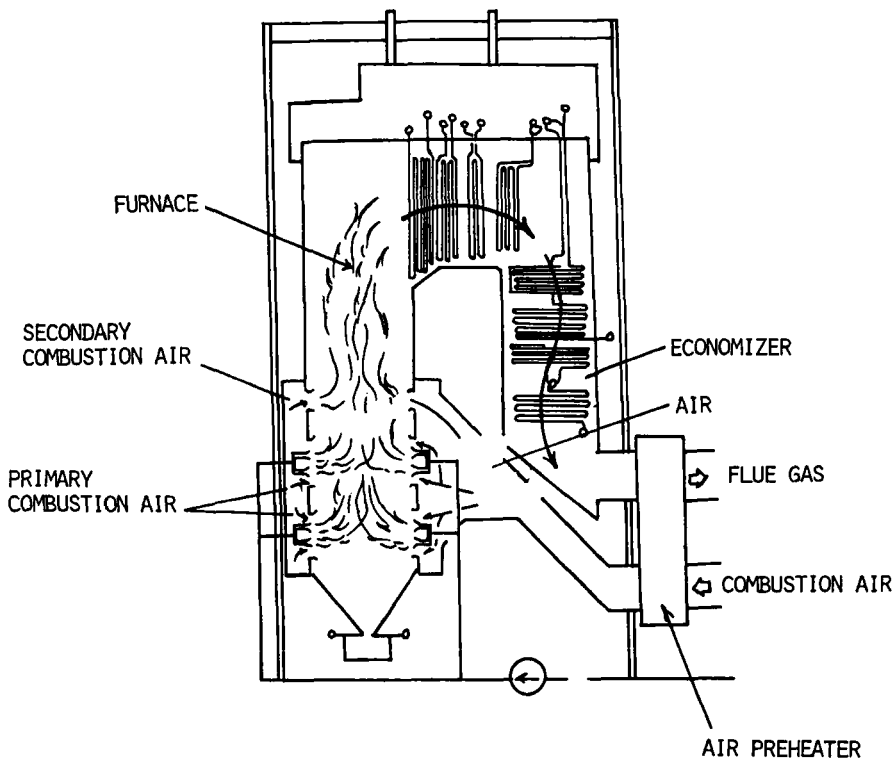


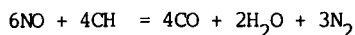
Fig. 3.8. Two-stage combustion applied to a power plant boiler.⁴⁾

offset by preheating the combustion air with high temperature flue gas since the flame temperature can thereby be raised. It was shown by Sadakata that air preheating has only a slight effect on the final emission level of fuel NO. Another disadvantage of TSC is that it produces elevated levels of unburnt species such as CO, HC and soot. However, this problem can probably be solved by improving the secondary stage mixing of unburnt species and injected air.

(iv) Staged-fuel injection method. The staged-fuel injection method (SFIM) has three advantages: i) it is useful for both thermal NO_x and fuel NO_x , ii) it can be applied to the combustion of gaseous, liquid and solid fuels and iii) it can be applied to many different types of furnaces such as boilers, rotary cement kilns or glass furnaces.

The idea of NO reduction by hydrocarbon injection was first proposed by Myerson.²⁷⁾ He tried injecting various kinds of hydrocarbons such as isobutane or gasoline into a simulated flue gas containing NO in an attempt to reduce NO levels by oxidizing hydrocarbon with NO. He obtained a rapid reduction of NO

in the presence of oxygen. He presented the following global reaction mechanism:



The SFIM is mainly based upon Myerson's study. The outline of this method is illustrated in Fig. 3.9. In this method, secondary fuel is injected at the position where the primary fuel lean combustion is complete. NO is rapidly reduced by hydrocarbon radicals through the above reaction leaving behind the unburnt hydrocarbon species, CO and HCN. These species are removed by tertiary air injected into the downstream region.

As previously mentioned, this method can be applied to a broad range of combustion facilities including boilers or rotary cement kilns and as well as to the combustion of various fuels including coal. A pulverized coal combustion facility is shown in Fig. 3.10 as an example. This NO_x control technology was developed by Mitsubishi Heavy Industry and named "MACT" (Mitsubishi Advanced Combustion Technology). The process is unique in that pulverized coal is used as the injected hydrocarbon. HC, CO and HCN are almost entirely removed by introducing tertiary low oxygen level air for afterburning. A final NO level of 50 ppm can be realized by this method if low NO_x burners are employed at the same time.

The disadvantage of this method is that it can only be used in large scale boilers since it requires additional furnace volume for both NO reduction by hydrocarbon and for the secondary combustion to remove unburnt species. As a result, the cost of this method is significantly higher than other low NO_x methods or the two-stage combustion method.

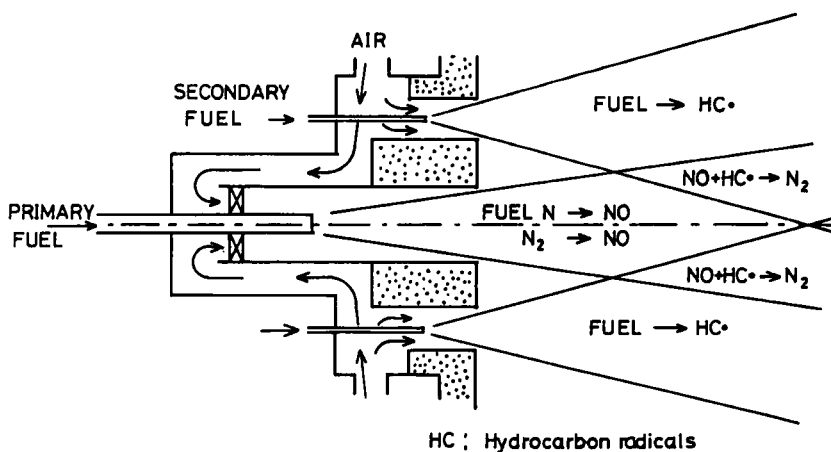


Fig. 3.9. Principle of staged fuel injection.⁶⁾

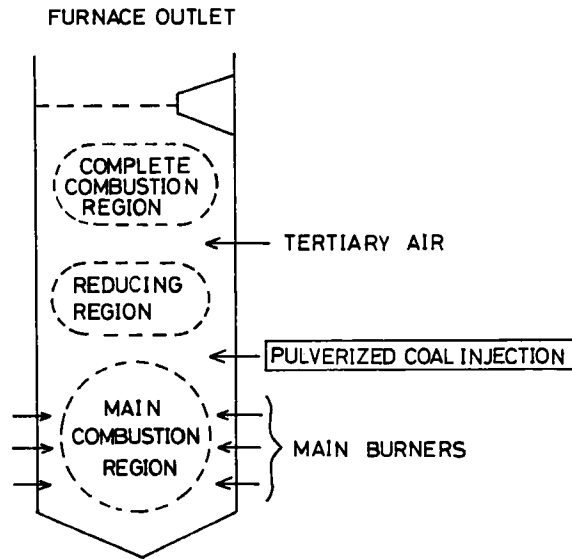


Fig. 3.10. Staged fuel injection applied to pulverized coal combustion.⁷⁾

(v) Other methods. We will briefly explain other forms of NO_x control technology.

Low nitrogen fuels can be substituted for high nitrogen fuels in certain cases. However, this method is only useful for fuel NO . The disadvantage of this method is, of course, an increase in fuel cost.

Low excess air ratio combustion is the method used for controlling the air ratio near 1.0 in order to reduce both thermal NO and fuel NO by lowering the combustion oxygen level. Although this method can easily be employed in various conventional facilities, the reduction of NO obtained by this method is relatively low compared to other methods. Furthermore, emissions of unburnt species such as CO and soot tend to increase unless some improvements in fuel-air mixing and fuel atomization are carried out. Hence, an improvement of the burners is sometimes required in order to utilize low excess air ratio combustion.

Low heat release rate combustion is a method of reducing the combustion heat release rate in order to reduce thermal NO by a decrease in flame temperature. Here, the combustion heat release rate is defined as the quantity of heat released by combustion per unit volume per unit time in the combustion chamber. The disadvantage of this method is that a high heat release rate is sacrificed in exchange for the reduction of NO_x .

Low temperature air preheating is a method of decreasing the preheat

temperature of combustion air in order to reduce thermal NO_x by a reduction of the flame temperature. A disadvantage of this method is a lowered thermal efficiency due to a lowering of the flame temperature.

In the flue gas recirculation method the flue gas is recycled from the furnace outlet, cooled and mixed with combustion air in order to reduce thermal NO by reducing the flame temperature. However, this method has the following disadvantages. It will not reduce fuel NO since fuel NO is insensitive to temperature change. Furthermore, the flame tends to be unstable when this method is used. The repair costs for a flue gas recirculation system are relatively high compared to that of low NO_x burners. This method is applicable only to large scale furnaces with flue gas volumes larger than $10^5 \text{ m}^3/\text{h}$ since the repair cost for this method in medium or small scale furnaces is too high.

In the water or steam injection method, water or steam is injected into a furnace in order to decrease thermal NO by reducing the flame temperature. The disadvantage of this method is the lowered energy efficiency since the combustion heat is partly consumed by water vaporization.

3.2.2 NO_x removal methods

NO_x removal processes can be classified into dry processes and wet processes, referring to the reagent used for NO_x removal.

Dry processes reduce NO levels without using a liquid absorbent. One type of these processes is where a reducing gas such as NH_3 and CO is sometimes introduced into the flue gas to reduce NO with the help of a catalyst. In another type of dry process the NO_x is removed by a solid absorbent such as activated carbon or molecular sieve.

Wet processes use liquid absorbents. This requires the following two steps:

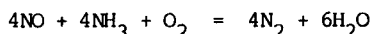
- i) Oxidation of NO to NO_2 or N_2O_5 by O_3 .
- ii) Absorption of N_2O_5 by water to HNO_3 or absorption of NO_2 or SO_2 by NaOH with final reduction to N_2 . The wet process was initially more highly developed than the dry process. However, the wet process has the following disadvantages. First, it requires large amounts of electrical energy to form O_3 which is necessary to oxidize NO during the primary oxidation process. Second, an absorption tower is usually needed for the secondary absorption process where large volumes of flue gas must contact the liquid phase reagent and, third, the wet process usually needs water treatment to remove alkali or acid.

On the other hand, the catalytic dry process requires only a small surface contact area with a catalyst since the reduction reaction on the catalyst is very rapid. This allows the dry process to be used on a small scale. Furthermore, the dry process does not, of course, require water treatment. Hence, this process is potentially more economical. Unlike SO_x , NO_x can be

converted in the gas phase to a non-pollutant, stable species, N_2 , so the dry process holds greater promise for future development than the wet process.

Next, we will review several workable dry processes.

(i) Non-catalytic reducing method. As the combustion flue gas usually contains over 1% O_2 , an injected reducing species such as CO or H_2 is oxidized by O_2 before reducing NO. Many researchers have sought a reducing species which can reduce NO selectively in the presence of O_2 . Of them, Lyon at Exxon research found that NH_3 can selectively reduce NO in the presence of O_2 at temperatures between 800 and 900°C.³⁰⁾ Although the exact reaction mechanism is not yet known, the overall reaction is as follows:



The above equation indicates that some O_2 is necessary for the reaction to proceed.

The non-catalytic NO_x removal method is an application of this reaction. NH_3 is introduced into the furnace or the flue in the 800 to 1000°C temperature zone in the presence of oxygen. The above reaction proceeds and NO is reduced within 0.5 sec. More than 90% of the NO is reduced when the temperature is between 900 and 1000°C. However, only a 40% NO reduction has been obtained when this method is applied to a real furnace. This may be because of the increasingly poor mixing between NH_3 and NO with the increase in furnace size since the turbulent mixing time is directly proportional to the furnace size. Hence, the reduction rate must be improved by improving the NH_3 injection method. This may be a chemical engineering task.

The advantage of this method is its low cost because it does not require a catalytic reactor in the flue system. Furthermore, this method can be applied to both clean flue gas and to dirty flue gas such as residual oil or coal flue gas. On the other hand, it has the disadvantage of leaving some unreacted NH_3 in the flue gas after the injection since excess NH_3 is sometimes required to attain a high reduction rate. The unreacted NH_3 may corrode the heat exchanger. Furthermore, NH_3 reacts with SO_3 to form NH_4HSO_4 (acid ammonium sulfate) which can corrode the air preheater of the boiler. In order to correct these problems, the excess of NH_3 compared to NO must be reduced.

This method is very cheap compared to the selective catalytic method which will be discussed next.

(ii) Selective catalytic method. As previously mentioned, a residence time of 0.5 sec in the high temperature zone of the furnace is required for the non-catalytic method to work well. Hence, the application of the non-catalytic method has been limited. In the selective catalytic method, NO_x is selectively reduced by NH_3 at low temperatures with the help of a solid catalyst. This method has been widely accepted compared to the non-catalytic reducing method. The method is illustrated in Fig. 3.11. NH_3 is introduced into the flue

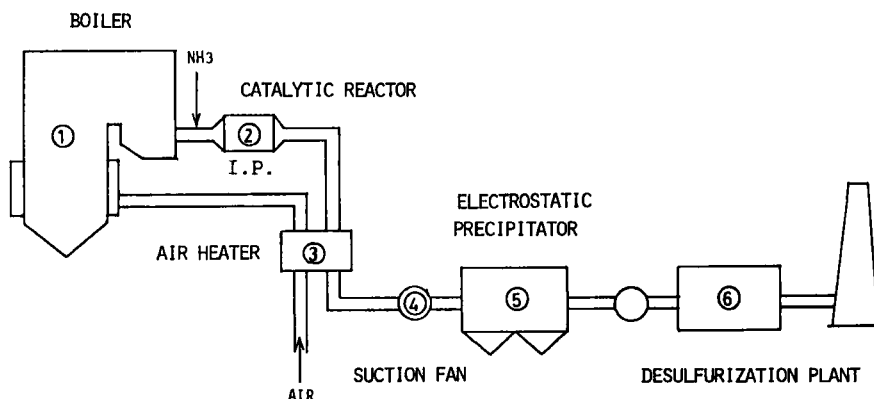


Fig. 3.11. Process flow sheet of selective catalytic method.

upstream of the reactor which is labeled I.P. in the figure. The flue gas mixed with NH_3 flows into the catalytic reactor where the selective reduction of NO by NH_3 occurs on the catalyst surface. The reactor temperature ranges from 200°C to 400°C . The catalysts employed here include, V_2O_5 on TiO and CuO on TiO_2 . Usually, TiO_2 is selected as a carrier because of its sulfur resistance. The NO reduction by this method sometimes exceeds 90% when the SV value is 10 hr^{-1} . The SV value is defined as the special velocity with units of flue gas volume treated per cubic metre catalytic volume per hour. Special provisions are necessary for using this method in particle-laden gas streams. One must use a catalyst which will not become blocked by particles. A dustproof catalyst which can be used in coal combustion flue gas with particle burdens of 20 to 30 g/m^3 has been developed recently. More than 200 combustion facilities currently use this denitrification process in Japan.

This method is most commonly used in boilers. However, it is also used in metal heating furnaces, oil heating furnaces, cokes ovens and sludge and garbage incinerators. Just as with the non-catalytic method, this method has the disadvantage of causing corrosion from acid ammonium sulfate formed after the NO reduction from excess NH_3 reagent. So, excess NH_3 injection should be minimized. Another serious disadvantage of this method is the cost.

(iii) The cost of the selective catalytic method. The construction and operational costs for the selective catalytic process in Japanese 700 MW boilers constructed from 1978 to 1981 are shown in Table 3.4 with the contribution of the catalyst to the total cost. The catalyst contributes around 20% of the total construction cost for the gaseous fuel boilers while it is over 60% for the coal boilers. Note that the total cost per KW for coal

Table 3.4

Cost of the selective catalytic method for various fuels¹⁰⁾

Boiler Name	A	B	C	D	E	F
Fuel	Natural gas	Natural gas	Low sulfur oil	High sulfur oil	Low sulfur coal	High sulfur coal
<u>Design specifications</u>						
Inlet NO _x (ppm)	50	100	200	200	400	400
Outlet NO _x (ppm)	10	20	40	40	80	80
Reduction rate (%)	80	80	80	80	80	80
SV (h ⁻¹)	20,000	16,000	4,000	3,000	2,400	2,000
NH ₃ /NO _x mole ratio	0.92	0.86	0.83	0.83	0.82	0.82
<u>Construction cost</u>						
Total (10 ⁶ \$)	8.5	9.0	16.8	21.0	27.8	31.7
\$/kw	12.1	13.1	24.0	30.0	39.7	45.2
Contribution of catalyst (%)	17.6	21.1	49.2	52.3	60.4	63.7
<u>Operating cost</u>						
Total (10 ⁶ \$)	3.53	3.78	7.40	9.07	15.7	18.0
mill/kwh	0.80	0.90	1.70	2.10	3.65	4.2
Contribution of catalyst (%)	10	12.5	37	40	53	56

combustion boilers is three times higher than gaseous fuel boilers and twice as high as liquid fueled boilers. This is because a very expensive catalyst such as titanium must be used for a coal combustion boiler because cheaper catalysts such as alumina are easily attacked by the sodium or halogen in the coal flue gas. Furthermore, one cannot increase the SV value (flue gas flow volume/catalyst volume) for a coal boiler since the increased flue gas velocity causes abrasion of the catalyst by fly ash. This means a large volume of catalyst is required for coal systems. The catalyst contribution to the operational cost of a coal boiler is also 2 to 3 times higher than that of oil or gaseous combustion boilers since the catalyst life in coal combustion boilers is less than two years while for natural gas or oil combustion boilers lifetimes are over four years. The operational cost of the selective catalytic method depends significantly on the catalyst life. Hence, the development of long lived catalysts is very important.

3.2.3 Choosing the NO_x control technology and the cost for individual facilities

The appropriate NO_x control technology and its cost is dependent on the type and the scale of the pollution generating facility. Hence, it is necessary to analyze the potential control technology and the repair and operational costs for each facility. The repair costs include the total cost for repairing and exchanging burners, storage, transport facilities and a duct. It is expressed in units such as dollars per 10³ m³ flue gas treated per hour. The operational cost is expressed as the ratio of the cost with NO_x control technology to the cost without NO_x control technology. The cost calculations were carried out primarily by Mitsubishi Research Institute³³⁾ under the supervision of the author. Basic data for the calculations were obtained from several burner and boiler makers and from the literature. The cost, of course, depends on local conditions such as site price, labor and material costs, price of electricity or price of water. Hence, the reader must note that the costs calculated here cannot be strictly compared to costs in other countries.

(i) Large-scale industrial boilers. The average NO_x emission levels corrected to 3% oxygen in the flue for the large scale industrial boilers (flue gas volume over 40,000 m³/hr) without NO_x control are 290 ppm for No.6 heavy oil (0.2%N) and 600 ppm for coal (1%N).

Applicable types of NO_x control technology for the large scale industrial boiler are "Flue gas recirculation (FGR)", "Two stage combustion (TSC)" and "Low NO_x burners (LNB)". The NO_x level can be reduced to 50 ppm for gaseous fuel, 60-100 ppm for light fuel and 290 ppm for coal by using a combination of the above methods.

The cost for controlling the above techniques for large scale industrial boilers using No.6 oil is shown in Table 3.5. A multiplicative correction factor must be applied to the above costs when one uses fuels other than No.6 oil. The cost of employing LNB is relatively low. The repair cost for coal combustion boilers is 15 times higher than for No.6 oil fueled boilers. This is because of high maintenance and repair costs for the delivery system. On the other hand, the operating cost is 30% less than for No.6 oil, because the cost of coal is lower than heavy oil.

(ii) Medium scale industrial boiler. The average NO_x emission level corrected to 4% oxygen in the flue for a medium scale industrial boiler (flue gas volume from 5,000 to 40,000 m³/h) without NO_x control is 220 ppm for No.6 oil (0.2%N) and 350 ppm for coal (1%N).

The appropriate types of NO_x control technology for medium scale industrial boilers are nearly the same as for large scale boilers. However, water or steam injection and emulsified oil fuel methods are also applicable. The NO_x level can be reduced to 35 ppm for gaseous fuel, 100 ppm for liquid fuel and

Table 3.5

Reconstruction and operating cost for several NO_x control technologies applied to large scale industrial boilers

Applicable Technology	Reconstruction cost ($\$/10^3 \text{ m}^3/\text{h}$)	Increase rate in operating cost (%)
FGR	325	50
TSC	125	30
LNB	100	0
FGR+TSC	450	80
TSC+LNB	200	30
FGR+LNB	425	50
FGR+TSC+LNB	525	80

FGR: Flue Gas Recirculation

TSC: Two Stage Combustion

LNB: Low NO_x Burner

230 ppm for coal.

The control costs are shown in Table 3.6. The cost of water or steam injection (WSI) is the lowest of the available methods. The cost per 10^3 m^3 per hour of flue gas for medium scale boilers is 3 to 10 times higher than that for large scale boilers.

(iii) Small-scale industrial boilers. The average NO_x emission level corrected to 4% oxygen in the flue for small scale industrial boilers (flue gas volume under $5,000 \text{ m}^3/\text{h}$) is 240 ppm for No.6 heavy oil (0.2%N) and 350 ppm for coal (1%N).

Table 3.6

Reconstruction and operating cost for applying each NO_x control technology to medium scale industrial boiler

Applicable Technology	Reconstruction cost ($\$/10^3 \text{ m}^3/\text{h}$)	Increase rate of operational cost (%)
FGR	850	50
TSC	350	30
LNB	1000	0
WSI	250	10
FGR+TSC	1250	80
TSC+LNB	1350	30
LNB+WSI	1250	10

WSI: Water or Steam Injection

Suitable types of NO_x control technology for small scale industrial boilers are "Two-stage combustion (TSC)", "Low NO_x burners (LNB)" and "Water or steam injection (WSI)". The flue gas recirculation method is not applicable to this scale of boiler. The NO_x level can be reduced to 25-40 ppm for gaseous fuel, 30 to 100 ppm for liquid fuel and 230 ppm for coal.

The costs are shown in Table 3.7.

Table 3.7

Reconstruction and operating cost for applying each NO_x control technologies applied to small scale industrial boiler

Applicable Technology	Reconstruction cost ($\$/10^3 \text{ m}^3/\text{h}$)	Increase in operating cost (%)
TSC	850	30
LNB	1350	0
WSI	850	10
TSC+LNB	2150	30
LNB+WSI	2150	10
TSC+WSI	1650	40
TSC+LNB+WSI	3000	40

(iv) Rotary cement kiln. The temperatures in the rotary cement kiln are about 1450°C for the kiln body and 1800°C for the flame temperature. The NO_x emission level is as high as 800 to 1200 ppm without NO_x control technology. The conversion from No.6 oil to coal has progressed quickly in Japan and now more than 90% of all Japanese cement kilns use coal. However, the flame temperature cannot be changed easily since the product quality is closely related to the calcination temperature. Thermal NO_x cannot be controlled by decreasing flame temperature. Selective NO_x removal using a catalyst is also difficult since alkaline metals such as Na, K and Ca from the cement materials poison the catalyst. NO_x reduction in a conventional rotary cement kiln is difficult. The possibility exists for NO_x control in the new suspension preheater (NSP) rotary cement kiln. The NSP method is an improvement over the conventional suspension preheater (SP) method. In the NSP process, the calcination furnace is moved to a position between the suspension preheater and the rotary cement kiln as is shown in Fig. 3.12. About 40 to 60% of the total process fuel is consumed in the NSP calcination furnace for the decarbonization process which had previously been carried out in the rotary kiln for the conventional S.P. method. The advantages of the NSP process are that the kiln length can be shortened by 50% because the calcination section is separated from the kiln and thermal NO formation is reduced since the gas temperature

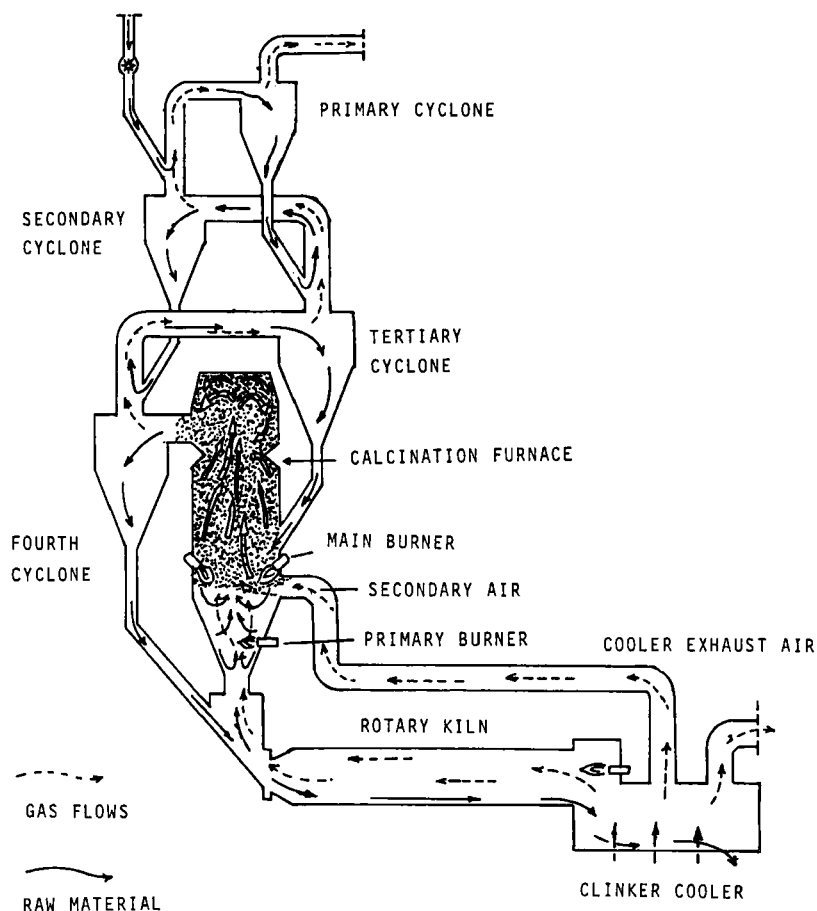


Fig. 3.12. New suspension preheater type cement kiln with denitration calciner.

during calcination is in the range 750–900°C. The appropriate method for reducing NO in the NSP kiln is by using the two-stage combustion method in the calcination furnace. Fuel-rich combustion or low excess air ratio combustion is used in the upstream part of the calcination furnace. Pulverized coal is injected through the primary burner and then secondary air from the clinker cooler is injected for downstream afterburning of unburnt species such as CO, hydrocarbon and soot. It has been reported that calcium particles act as a NO_x removal catalyst in the calcination furnace.³⁵⁾ Reduction rates of 20–30% can be achieved by this method. The reduction rate is likely to be further improved since this technology is still being developed.

The annual repair and maintenance costs for the TSW method are \$15,000 to \$95,000 $10^3 \text{ m}^3/\text{h}$. Accordingly, the total maintenance cost for a NSP plant of $110 \times 10^3 \text{ m}^3/\text{h}$ flue gas capacity is from \$1.6 million to \$10 million which is 3 to 13.0% of the total construction cost of the NSP plant.

(v) Glass fusion furnaces. Glass fusion furnaces are classified into continuous tank furnaces and batch-type crucible furnaces. In a continuous tank furnace, the combustion air is usually preheated to 1000-1300°C. As a result, the flame temperature is increased to 1700-1800°C and the furnace temperature is 1400-1550°C. The emission level of NO_x may reach 800-2000 ppm without NO_x control technology. NO_x emission levels from a batch-type crucible furnace are 100-150 ppm because the flame temperature ranges from 1300 to 1400°C. Therefore, NO from the continuous tank furnace is mainly thermal NO based on the Zeldovich mechanism. However, a fuel NO contribution of 100-150 ppm is also expected since No.6 oil containing 0.1-0.2 wt.% N is the usual fuel.

The stringent combustion conditions of the glass furnace greatly restrict the application of ordinary NO_x control technology. For example, NO_x control based on a lower flame temperature is ruled out because of the high flame temperature required for glass fusion. Methods based on the formation of a local reducing region in the furnace cannot be used because of the soot contamination produced in the reducing region which lowers the glass quality. Catalytic NO_x removal is not suitable since the flue gas has high dust and SO_x levels. The NH_3 removal method is unsuitable since excess NH_3 from the process corrodes the furnace lining. The low excess air ratio method is the only suitable method for thermal NO suppression under the high temperature, oxidizing conditions of a glass furnace. In order to reduce the air ratio to near 1.0 without soot formation a burner capable of thorough atomization is required. For this purpose, the ultrasonic burner was developed by the Nippon-Gaishi Kogyo company. This burner achieves good atomization using ultrasonic waves generated by a resonator located at the exit of the atomizing air. The pressurized oil burner has also been developed for the same purpose. The pressurized oil burner can form the thin fan type flame required for high heat efficiency. The NO reduction rate of this burner is 20 to 30%.

The maintenance costs of the pressurized oil burner are \$15,000-\$20,000 $10^3 \text{ m}^3/\text{h}$ flue gas. This relatively high cost is due to the high pressure pipe system needed, although the fuel cost is decreased by 20-30% due to the high heat efficiency.

(vi) Waste incinerators. The NO emission level from incinerators of city garbage is 150 to 200 ppm without NO_x control technology. City incinerators produce mainly fuel NO since city garbage includes high nitrogen content compounds such as proteins and the combustion chamber temperature is controlled

between 700 and 900°C. There are two types of waste incinerator. The multi-stage type and the fluidized bed type. The two stage combustion method is the most suitable NO_x control technology for waste incinerators. NO emissions can be reduced by 40% when this method is incorporated in the original design of the incinerator and by 20-30% when the method is applied to an existing incinerator.

The non-catalytic reducing method using NH_3 is also suitable for incinerators. This method reduces NO by around 50%.

The maintenance costs for the non-catalytic method are around $\$20,000/10^3 \text{ m}^3/\text{h}$ flue gas while the operational cost is 25-100 mill per 1t waste.

(vii) Heating furnaces for metal rolling. The NO_x emission level from a metal rolling heating furnace is 70-120 ppm for gaseous fuel, 70-140 ppm for liquid fuel and 400 ppm for coal without NO_x control technology.

Types of NO_x control technology for a medium scale industrial heating furnace include "Two-stage combustion" and the "Low NO_x burner". The NO_x level can be reduced to 30-50 ppm for gaseous fuel, 30-80 ppm for liquid fuel, and 230 ppm for coal by using TSC and LNB in combination.

(viii) Lime kilns. The average NO_x emission level from a lime baking furnace without NO_x control technology is 100 ppm for No.6 oil (0.2%N) combustion and 300 ppm for coal (1%N) combustion.

Types of Technology suitable for NO_x reduction from a lime burning furnace are "Flue gas recirculation", "Two stage combustion" and the "Low NO_x burner". The NO_x level can be reduced to 40-60 ppm for liquid fuel and 250 ppm for coal by using them in combination.

(ix) Metal fusion furnace for aluminum degumming. The average NO_x emission level from a metal fusion furnace for aluminum degumming is 300 ppm at 10% oxygen in the flue for No.6 oil combustion (0.2%N) without NO_x control technology.

The types of technology suitable for NO_x reduction from a metal fusion furnace are "Two-stage combustion" and the "The low NO_x burner". The NO_x level can be reduced to 180 ppm for No.4 oil and 230 ppm for No.6 heavy oil by using the above methods in combination.

3.3 SO_x EMISSION CONTROL FROM STATIONARY SOURCES

In Japan, the problem of oxides of sulfur (SO_x) from industry was first publicly recognized in the early 1960s when citizens in Yokkaichi suffered from an asthma caused by sulfur oxides emitted from a chemical complex located near the city. This asthma was called "Yokkaich Zensoku". SO_x emission standards for stationary sources were established in 1962 and have been revised downward more than 15 times so far. In order to comply with the emission regulations, facilities have progressively converted from high sulfur oil to low sulfur oil.

Flue gas desulfurization processes have been developed and installed in more than 1100 stationary SO_x sources. As a result, SO_x levels in the atmosphere have decreased to one third of the original peak level in the ensuing twenty years. For SO_x , both emission regulation and the development of sulfur control technology have worked effectively. However, the global SO_x problem has not yet been solved, as is evidenced by acid rain. Conventional desulfurization technology which was developed mainly for power plants in Japan cannot be straightforwardly applied to stationary sources in other parts of the world such as Europe and China since the scale of facilities is different, SO_x emission levels are different and the costs are different. Conventional technology is usually too expensive to use for a small stationary source. From this point of view, desulfurization technology is not yet fully mature and must be further developed to fill these various needs. The need for economical technology is especially pressing.

In this section, representative established technology will first be introduced and then developing technology will be discussed.

3.3.1 Sources of SO_x

SO_x sources may be classified into natural sources such as volcanoes and artificial sources such as power plant boilers. Artificial sources contribute about 50% to the total atmospheric sulfur burden. The influence of artificial sources on human health is more severe than the above figure indicates since artificial sources are usually located near human residential areas. The contribution of artificial sources varies from one country to another. However, the contribution of combustion facilities is significant compared to other sources in the U.S.A. and Japan.

Table 3.8 shows the typical sulfur content of gaseous, liquid and solid fuels. Note that the sulfur content in residual oil and coal is considerably

Table 3.8

Sulfur content in fuels

Fuel	Sulfur content (wt%)
Crude oil (Middle East)	1.3-4.2
No.6 heavy oil	0.16-3.4
No.4 heavy oil	0.10-1.79
light oil	0.06-0.90
kerosene	0.0-0.32
coal	0.5-2.0
LPG, City gas	0.02

higher than other fuels. Unlike NO_x , all of the SO_x from a combustion facility comes from the sulfur originally contained in the fuel. According to our study³⁶⁾, the conversion rate of fuel sulfur to SO_x ranges from 70 to 90% for pulverized coal combustion. Another 10 to 30% of fuel sulfur is retained by the fly ash. Hence, the emission level of SO_x can be predicted from the sulfur content in the fuel.

The form of sulfur compound in the fuel varies from fuel to fuel. The sulfur in heavy oil is in the form of polycyclic sulfide, as shown in Fig. 3.13. Sulfur compounds in coal are classified into inorganic and organic sulfur compounds. The inorganic sulfur consists of sulfate (CaSO_4 , FeSO_4 , BaSO_4 , etc.), sulfide (PbS , ZnS , FeS , CaS etc.) and free sulfur⁸⁾ of the inorganic sulfur compounds, iron pyrites (FeS_2) predominates. The organic sulfur is bonded chemically to the carbonaceous coal substrate.

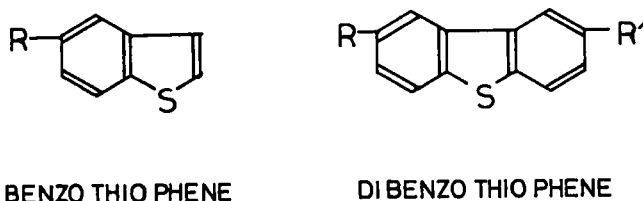


Fig. 3.13. Typical polycyclic sulfide in heavy oil.

3.3.2 Formation and behavior of SO_x in the combustion furnace

The conversion from fuel sulfur to SO_x is largely carried out during combustion in the furnace. The fuel sulfur is initially converted to SO_2 during combustion. However, for fuel-rich combustion, the fuel sulfur is partly converted to H_2S (hydrogen sulfide) which is easily oxidized to SO_2 in the excess oxygen conditions found downstream. The fuel sulfur is, however, partly converted to SO_3 . The SO_3 is, then, converted to sulfuric acid in the downstream low temperature region and causes the corrosion of the metal surfaces of the heat exchanger. The SO_3 also tends to form fine particles of sulfuric acid under humid, low temperature conditions. These particles easily bypass the desulfurization process and cause respiratory troubles after they are released into the atmosphere.³²⁾ The emission of SO_3 may influence the behavior and level of other pollutants, for example, submicron fly ash or mercury in coal combustion. An increase of the SO_3 level also improves the collection efficiency of fly ash by an electrostatic precipitator.³⁷⁾ This is because the condensation of sulfuric acid decreases the electrical resistivity of fly ash to the optimum level for high collection efficiency. It has also

been shown that both sulfur and mercury are condensed on the soot carbon rather than the mineral fly ash.³⁸⁾ The mechanism of mercury condensation may be as follows. Sulfur is condensed on the soot carbon particle in the form of hydrogen sulfide or sulfuric acid and, then, mercury vapor is absorbed by hydrogen sulfide or sulfuric acid. The selective condensation of sulfur on the soot particles was shown by Okazaki.³⁹⁾

The emission level of SO_3 from the combustion of natural fuel containing 5.5 wt.% of sulfur is around 40 ppm.⁴⁰⁾ On the other hand, the emission of SO_3 from pulverized coal combustion is lower than that of heavy oil. This is because the SO_3 condenses to form sulfuric acid on the surface of soot carbon and submicron fly ash particles.

The SO_3 is formed mainly in the flame zone by the oxidation of SO_2 by super-equilibrium oxygen radicals. Hence, the most important variable influencing SO_3 emission is the air ratio since the oxygen level in the flame zone is determined by the air ratio. Fig. 3.14 shows the effect of air ratio on SO_3 emission for gas combustion. It clearly shows that low air ratio combustion is effective for the control of SO_3 as well as NO . Hence, the air ratio can be used to control SO_3 emission levels.

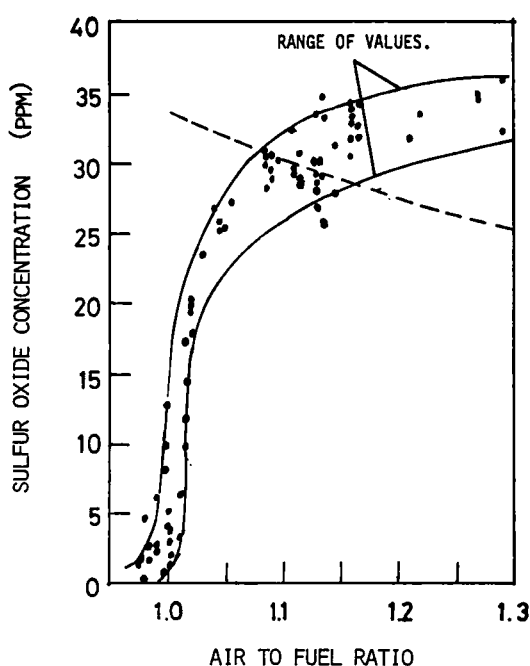


Fig. 3.14. Effect of excess air on sulfur oxide emission from gas combustion.¹⁹⁾

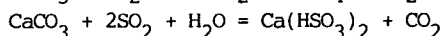
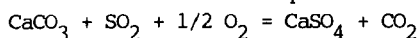
3.3.3 SO_x control technology

Desulfurization technology is classified into wet and dry processes similar to NO_x removal processes. However, the desulfurization process most commonly used in power plant boilers is the wet process. The advantage of the wet process is that it can be used on dirty flue gas with high particle burdens while still realizing a high reduction rate. On the other hand, the wet process requires a large scale absorbing tower to provide the large surface contact area between flue gas and absorbing liquid. Because of this, the construction cost for the wet process approaches half the cost of the main combustion furnace. Furthermore, the wet process requires extensive water treatment to remove or recover the final product and consequently it needs large amounts of fresh water. Utility costs are therefore high. Another disadvantage of the wet process is that the collection efficiency of the sulfuric acid mist which is formed from SO_3 is low. The SO_3 is sometimes more toxic than SO_2 .

The development of a dry process to replace the wet process continues. Unlike NO , it is impossible to convert SO_x to a nontoxic, stable, gaseous species. The final product must be a solid such as CaSO_4 , Na_2SO_4 , MgSO_4 . Therefore, the dry process needs the solid-gas reaction. This type of reaction is generally very slow in the low temperature region of flue compared to a catalytic reaction such as $\text{NO}-\text{NH}_3$ in the NO_x removal process. A large scale reactor is needed compared to the catalytic reactor of the NO_x removal process. Furthermore, the handling of solid particles or powder is necessary in this process since the reaction product has to be continuously purged from the reactor and recycled solid particles have to be fed into the reactor. For all of these reasons, development of the dry process has not been completed yet.

Next, we will introduce examples of established desulfurization processes and then we will discuss the newly developing dry process.

(i) The lime and gypsum method. This is the representative wet process. The operating principle is the removal of SO_x by contacting the flue gas with a lime slurry. Initially, SO_2 in the flue gas is absorbed by reaction with the lime slurry and converted to CaSO_4 .



The acid calcium sulfite ($\text{Ca}(\text{HSO}_3)_2$) is finally oxidized by air in the oxidizing tower to form gypsum (CaSO_4) which can sometimes be utilized commercially in cement or gypsum board. This method has the advantage of not requiring expensive chemicals such as caustic soda. This process is especially attractive in Japan where the cost of lime is relatively low. Another advantage is that soot and fly ash which are not collected by the electrostatic precipitator can be caught at the absorbant tower. The disadvantage of this

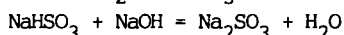
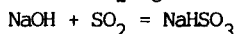
process is that special care has to be taken to avoid problems with the scale caused by the lime slurry.

This process has been frequently used in large scale boiler desulfurization processes such as power plant boilers.

The SO_x removal rates approach 70% for this process.

(ii) The soda method. The principle of this method is to remove SO_2 by contacting flue gas with an aqueous NaOH solution using a conventional gas-liquid contact unit such as a packed column, a spray tower, or a venturi type scrubber.

Initially, the SO_x is absorbed by reaction with the aqueous NaOH solution and converted to Na_2SO_3 as follows.



Na_2SO_3 is oxidized by air to Glauber's salt (Na_2SO_4) in the oxidizing tower. The Glauber's salt is sometimes recovered and sold. The advantage of this process is the lack of scale problems found in the lime-gypsum method. The disadvantage of this process is that it requires expensive chemicals such as NaOH .

This method is suitable for small scale facilities. There are many units in operation since the system is relatively simple.

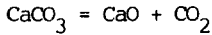
(iii) Active carbon absorption method. Active carbon absorption is currently the typical dry process. In this process SO_x is absorbed in the flue using the activated carbon. SO_2 in the flue gas is initially absorbed onto the active carbon. The oxidation of SO_2 to SO_3 takes place in the active carbon and finally the SO_3 is reacted with H_2O in the flue gas and changed to H_2SO_4 . The absorbed sulfur is purged from the carbon by heating it up to 400°C or by contacting with water and recovering the sulfuric acid.

This method is still very costly. The cost is primarily determined by the cost of the active carbon. The success of this process depends on the development of a cheap and efficient active carbon source.

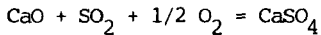
(iv) Direct desulfurization method. The ideal method of controlling SO_x is to directly remove SO_x in the furnace without a flue gas desulfurization process. To this end, numerous studies of desulfurization in fluidized bed coal combustion (FBC) have been undertaken. This method is very different from other desulfurization technology and the early development of direct desulfurization in FBC has been carried out mainly in Europe rather than in Japan. Direct desulfurization in FBC is expected to solve the difficulties of dry process SO_x removal.

In this method CaCO_3 is put directly into the bed so that simultaneous combustion and desulfurization occurs. The reaction scheme is as follows. CaCO_3 is thermally cracked to CaO and CO_2 at temperatures between 750°C and

1000°C.



Then, CaO absorbs SO_2 to form CaSO_4 in the presence of oxygen



In some experiments, the optimum temperature region for the above reaction was found to be 800°C to 900°C. If the above desulfurization reaction can be completed in the bed, then flue gas desulfurization is unnecessary. However, a serious problem was found in the research and development process. Fig. 3.15 shows the effect of the mole ratio of calcium to sulfur on the desulfurization rate. The reduction rate at a Ca/S ratio of 1 is only 30 to 50% which is insufficient for practical use. A Ca/S ratio of at least 4 to 5 is necessary in order to attain a reduction rate of 95% which is equivalent to that of a wet process. A Ca/S ratio of 5 means that 50 kg of CaCO_3 is required to burn 100 kg coal. The cost of supplying CaCO_3 and recovering or treating the solid effluent stream is prohibitive. Unless this ratio can be reduced to near the stoichiometric ratio (Ca/S=1), this method will not be implemented. There have been efforts to overcome this problem - for example; using finely pulverized CaCO_3 particles of about 10 micron diameter to create a large surface area for reaction, or by using an artificial desulfurizing agent such as portland cement particles⁴²⁾ instead of CaCO_3 , or by pretreatment of the desulfurization agent by NaCl.⁴³⁾ These trials have not yet been successful. The reader may

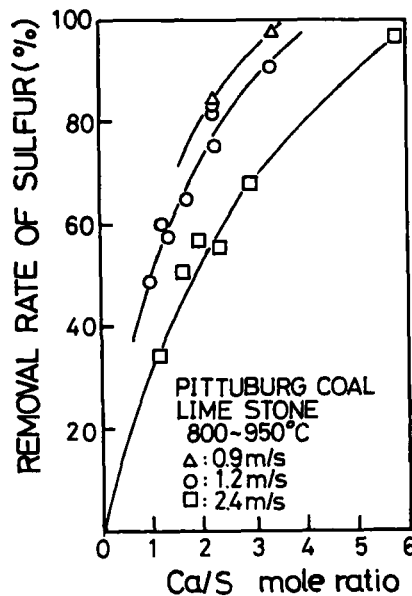


Fig. 3.15. Effect of Ca/S ratio on desulfurization rate.²⁰⁾

understand that numerous problems have to be solved to develop direct desulfurization of fluidized bed coal combustion in the future.

3.3.4 The cost of desulfurization processes

The construction cost of the wet desulfurization process is plotted against the plant size expressed by the flue gas volume to be treated in Fig. 3.16. The construction cost is proportional to the flue gas volume to be treated to the order of 0.8. The construction cost of the desulfurization unit for a 1000 MW power plant is from 65 million dollars to 110 million dollars. In general, the construction cost of the wet desulfurization process is three times higher than that of the dry NO_x removal process using NH_3 and catalyst.

The actual construction costs of wet type desulfurization units constructed after 1982 are shown in Table 3.9. All of the processes listed in Table 3.9 are lime and gypsum processes. The average cost is around \$100/kw which is twice or three times that of the NO_x removal process for a coal combustion facility. This is because the desulfurization process requires large scale facilities such as the absorbing tower compared to the NO_x removal process. The construction cost does not vary with the type of flue gas for the

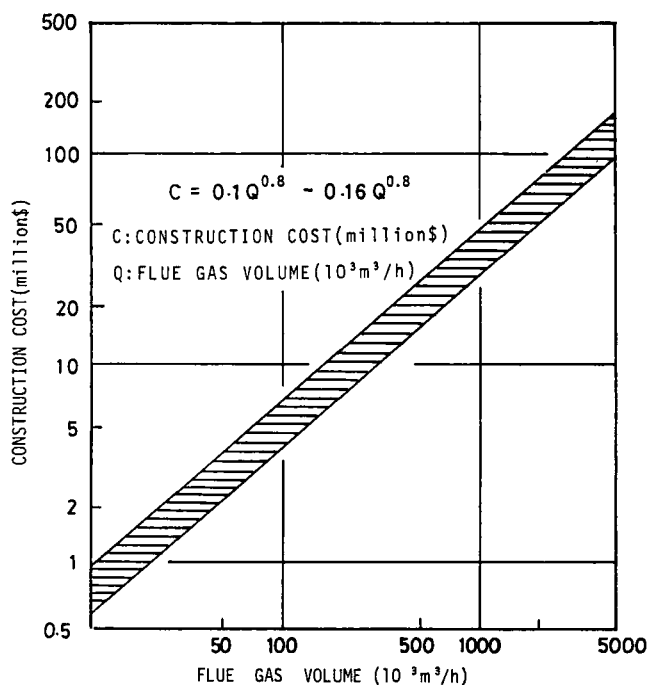


Fig. 3.16. Construction cost of wet desulfurization plant.²³⁾

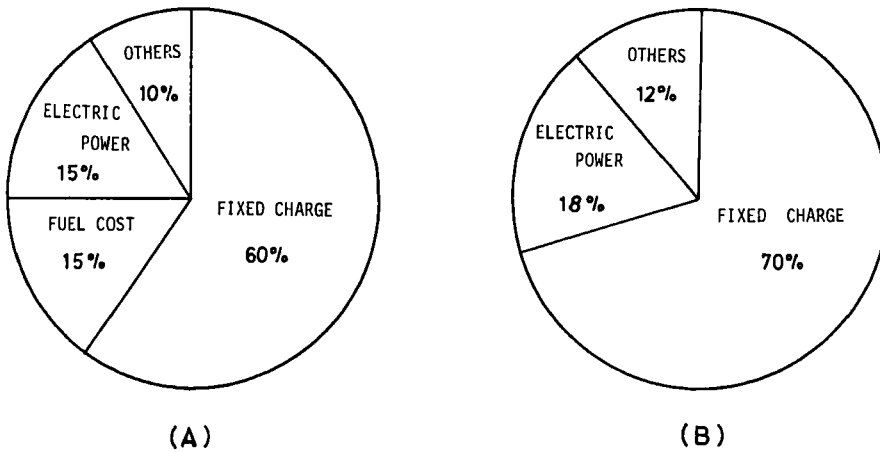


Fig. 3.17. Breakdown of the total annual cost of flue gas desulfurization¹⁰⁾
(A) after burner, (B) air-air heater

Table 3.9

Cost of desulfurization process¹⁰⁾

Name of boiler	A	B	C	D
Fuel	Heavy oil	Heavy oil	Mixture of Coal and oil	Coal
Boiler power (MW)	85	13	600	700
Inlet SO ₂ (ppm)	1500	1500	1000	600-700
Outlet SO ₂ (ppm)	35	5	40	30-35
Reduction rate (%)	98	99.7	96	95
Inlet dust (mg/Nm ³)	180	150	150	30-150
Outlet dust (mg/Nm ³)	40	70-80	45	10-20
Reduction rate (%)	78	50	70	70-80
Construction cost (\$/kw)	90	95	105	100

desulfurization process. That is, the costs for the coal combustion facilities C and D were the same as those of the heavy oil combustion facilities A and B.

The breakdown of the total annual cost is shown in Fig. 3.17A for the case of afterburners and in Fig. 3.17B for the case of using an air-air heater system to reheat flue gas. In both cases, fixed charges account for more than half the total cost. The cost for the electric power accounts for 15 to 18% of the total cost. The electricity is used primarily for fan power.

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