

Notes

- * SO_x Control
- * NO_x Control
- * Emission Standards

ultraviolet or strong visible-light absorption and suitable sampling techniques have successfully been used for measuring SO₂ concentrations in stack gases.

10.3 METHODS OF SULPHUR DIOXIDE CONTROL

A number of methods²⁵⁻³⁵ have been used to reduce the concentration of SO₂ in effluent gases so as to meet the stipulated requirements. They fall broadly into four groups.

1. Minimizing the SO₂ concentration by making improvements in process technology
2. Using fuels of low sulphur content
3. Efficient dilution of gases by employing tall stacks
4. Reducing the concentration of SO₂ in stack gases by subsequent treatment.

10.4 PROCESS CHANGES

Until the sixties, most sulphuric acid plants were designed for about 98.5 per cent conversion in four stages. On economic grounds, this was considered the optimum level of oxidation, but led to concentrations of SO₂ in stack gases in the region of 2000 ppm and more, which was considered very high, especially in densely-populated areas. An emission concentration of 500 ppm or less can be achieved by making use of the double-conversion double-absorption (DCDA) technique in existing and new plants. The adoption of this technology not only reduces the SO₂ concentration in the gases, but helps increase the plant output. In a 450 tonnes/day plant manufacturing H₂SO₄, the SO₂ emissions were reduced from 10.6 to 1.2 tonnes/day, thereby increasing the conversion efficiency of SO₂ from 96.4 to 99.6 per cent.

Oxidation of SO₂ is favoured by high pressures. It is reported that using a pressure of 22 atm, and 9 per cent SO₂ in the mixture, a conversion efficiency of 99.7 per cent is achieved. The unconverted SO₂, when absorbed in H₂SO₄ at 22 atm. pressure, can be reduced to concentrations as low as 30-40 ppm before entering the stack. The use of oxygen instead of air decreases the plant size and the volume of gases. Thus the use of DCDA process, high pressure and pure oxygen can bring down the emission concentration substantially.

In the DCDA process the sulphur trioxide formed due to partial conversion in the earlier stages is removed in a primary absorber. Unconverted gases, heated by the gases entering the absorber, are returned for further conversion in the next stages. As a result of this, the overall conversion efficiency increases. It is also possible to use a higher inlet concentration of SO₂ (10-12 per cent) as against the 8 per cent usually employed. This increases

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the capacity of the unit as well as its thermal efficiency when suitable heat-recovery methods are incorporated.³⁶ DCDA is attractive because it requires just one more absorption tower than the conventional process. In the Indian context, it is estimated that any existing plant of capacity 50 tonnes/day and above can be made into a DCDA system. It should be noted that an emission in the 500 ppm level will not be very polluting if plant capacities are small (50 tonnes/day or less), but bigger and newer sulphuric acid plants with capacities of 100-750 tonnes/day can lead to critical pollution levels, especially if they are located in densely-populated areas. In such cases it becomes necessary to reduce the emission concentration to 100 ppm or even less. In one of the reconditioned plant manufacturing 200 tonnes/day of H₂SO₄, the cost of switching over to DCDA technology was Rs 1.4 lakhs, in 1977. The capacity, as a result of this, shot up to 300 tonnes/day of H₂SO₄ and the emissions were reduced to 400-500 ppm of SO₂ and 30 mg/m³ (100 ppm) of acid mist. A typical process flow sheet for the process (DCDA) is shown in Fig. 10.1.

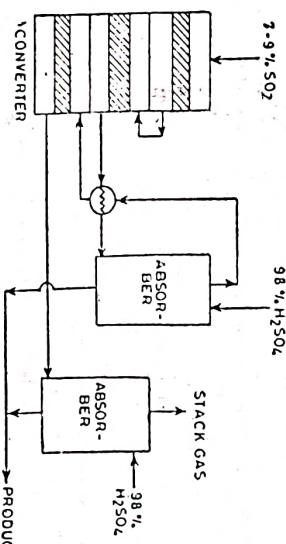


Fig. 10.1 Double-conversion double-absorption (DCDA) system in the manufacture of sulphuric acid

10.5 DESULPHURIZATION OF FUELS

Sour natural gas can be freed of hydrogen sulphide by scrubbing with monoethanolamine or other amines. The sulphur can be recovered by dry catalytic conversion (Claus process) when molten sulphur is obtained.

Heavy or residual fuel oils contain between 0.5 and 5 per cent sulphur, depending upon their source and treatment during refining. The conventional HDS process for desulphurization of fuel oil is very commonly employed. The oil is treated with hydrogen, over a catalyst, at temperatures ranging from 400 to 550 °C and pressures from 35 to 70 atm. Sulphur can be recovered the same way as from natural gas.

Coal when mined, contains organic and inorganic sulphur varying from 0.2 to 7 per cent of the dry weight. Coal washing is a common practice, parti-

cularly for coals with high ash contents. As much as one third of the sulphur can get reduced, though in actual practice the reduction is much less. Almost all coals dissolve in solvent oils at high temperatures (450°C) and pressures (70 atm.), in the presence of hydrogen which prevents polymerization and helps interaction with the organic sulphur present. The hot-coal residue can be cast into moulds and used. Coal gasification appears to be a promising method for the vast coal reserves in India. Coal gas can be scrubbed free of sulphur and converted to methane for use in gasburning devices.

10.6 DILUTION USING TALL STACKS

Dilution by tall stacks (as high as 400-450 m) will have to be widely practised until direct control methods are employed for the removal of SO₂. It is quite common practice to curtail operations during adverse meteorological conditions so as to keep the ground-level concentration of SO₂ within acceptable limits.

10.7 REDUCTION OF SULPHUR DIOXIDE CONCENTRATION

There are more than 60 processes under different stages of development and an innumerable number of patents on methods and process equipment for the removal of SO₂ from stack gases. They are broadly classified under two heads:

- ✓ 1. Wet processes
- ✓ 2. Dry processes

General schemes for the two are shown in Figs. 10.2 and 10.3.



Fig. 10.2 Generalized dry scheme for SO₂ removal from effluent gases.

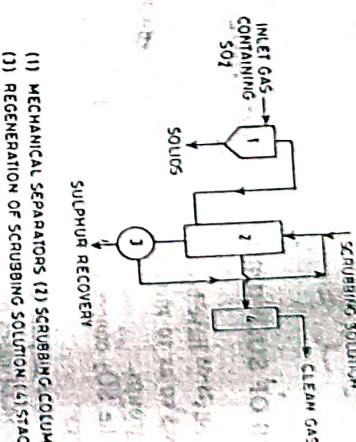


Fig. 10.3 Generalized wet scheme for SO₂ removal from effluent gases.

10.8 WET PROCESSES

Wet scrubbing²²⁻²⁴ can be a physical absorption of SO₂ or a chemical reaction. The absorbent should have a large capacity for absorbing SO₂ at a fast rate so as to reduce the size of the equipment. Besides, it should be possible to regenerate the absorbent to make the process viable in practice. SO₂ is only slightly soluble in water so, its use as an absorbent is ruled out. Even so, a process has been patented in Japan, where the concentration of SO₂ in the exit gases can be reduced to about 100 ppm by scrubbing with water (1.9 l of water/m³ of gases). Low pressure steam, normally available in the plant, can be employed for stripping SO₂. In actual practice, a chemical reaction is incorporated since mass transfer with chemical reaction enhances the rate of absorption.

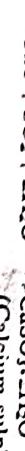
Sulphur dioxide being acidic in nature, is readily absorbed by alkaline solutions. There are a number of such scrubbing solutions.

1. Lime/limestone solution/slurries
2. MgO slurries/Mg(OH)₂ solution
3. NaOH solution
4. Na₂SO₃-NaHSO₃ solution
5. Na₂CO₃ solution
6. NH₃-liquor solution
7. Dimethylaniline solvent
8. Xylidine-water system
9. Ammonium sulphite solution

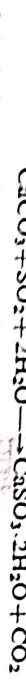
10.8.1 Lime/Limestone Solution/Slurry

In the Battersea process a small amount of chalk slurry added to slightly alkaline river water is used for scrubbing the gases. The liquid effluent, however, needs to be disposed of, setting restrictions on the location of the plant.

Of all the chemicals listed above, lime/limestone are the cheapest and readily available. In the Calsox process scrubbing is done by lime/limestone solution/slurry in contactors such as venturi, turbulent bed, floating bed or even gravity scrubbers. The overall reactions for lime and limestone are,



(Calcium sulphite dihydrate)



Calculations for the equilibrium constant indicate that the reaction of lime and SO_2 is more favourable than limestone and SO_2 . In the first case the formation of calcium ion, the critical step in both reactions, is dependent only on the presence of CaO . In the second, calcium-ion formation depends on the presence of limestone as well as H^+ concentration. The limestone system will therefore, operate at a lower pH than the lime system. It has been determined that the optimum pH range for the limestone system is between 5.8 and 6.2 and for the lime system about 8.0. The lime/limestone process carried out at high pH results in a soft pluggage of calcium sulphite and at low pH in a hard scale of calcium sulphate. A cyclic lime process is shown in Fig. 10.4. Calcium sulphite formed is readily oxidized to calcium sulphate which is deposited in the scrubber and lines. This difficulty can be overcome by the incorporation of a delay tank where the deposition of calcium sulphate is increased by the addition of chalk. The calcium sulphate can be settled and filtered out. The main disadvantage of the method is the disposal of calcium sulphate.

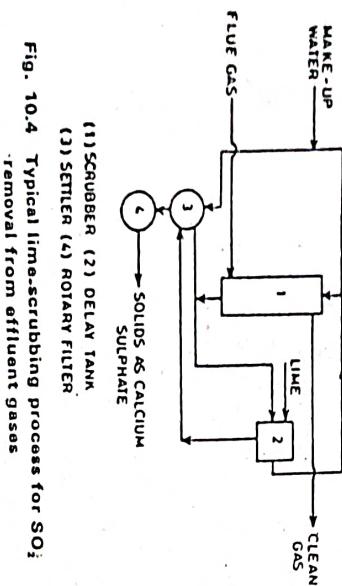


Fig. 10.4 Typical lime-scrubbing process for SO_2 removal from effluent gases

10.8.2 Ammonia Scrubbing

In this process, aqueous ammonia solution is used for scrubbing the stack gases, when the SO_2 content is reduced to below 100 ppm. This method is ideally suited for SO_2 removal in fertilizer plants where NH_3 or aqueous NH_3 is available as liquid waste. Ammonium sulphate, the product of reaction, can be concentrated for use as a fertilizer. The absorber operates at a

high pH for maximum SO_2 removal. The mist eliminator immediately follows effectively removes ammonium sulphite mist. The latter operates at low pH to minimize ammonia loss into the atmosphere.

The reactions occurring are:

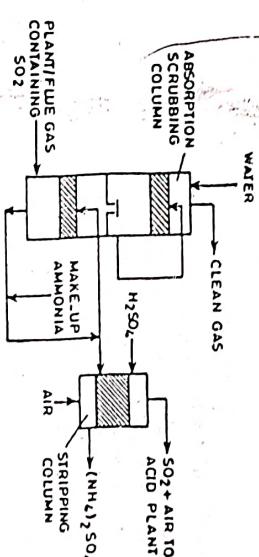
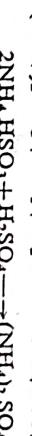


Fig. 10.5 Absorption of SO_2 in ammonia

another process, ammonium sulphite-bisulphite solution is used for scrubbing SO_2 out. The solution, after scrubbing, is reacted with HNO_3 to obtain ammonium nitrate, and to regenerate SO_2 . The reactions occurring are,

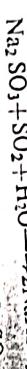


It is essential to avoid the formation of ammonium sulphate by using oxidation inhibitors. A SO_2 concentration as low as 100 ppm, in the exit gases, can be obtained by this method.

Alternatively SO_2 can be absorbed in aqueous ammonium sulphite solution by scrubbing the gases in a column filled with wooden packing. To minimize NH_3 loss and maintain a favourable equilibrium in the absorption operation, the temperature should be kept below 35 °C. SO_2 can be liberated by the addition of H_2SO_4 , which also converts NH_3 to ammonium sulphate.

10.8.3 Double-Alkali Process

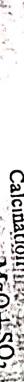
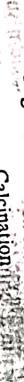
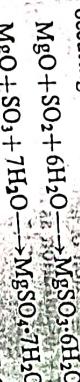
Here two alkalis, viz. sodium hydroxide and calcium oxide are used. The advantage of using NaOH as alkali is that no solids are formed during the reaction. This reduces erosion and wear of the nozzles, pipes, pumps, etc. Besides, the removal efficiency of SO_2 is very high. It is desirable to regenerate NaOH from the scrubber effluent. This can be done by reacting it with lime/limestone outside the scrubber system, thus avoiding scaling due to lime products without interrupting the scrubber operation. The process concept is quite feasible as the consumable chemical is only lime/limestone which is quite readily available indigenously. The only precaution required is a minimal loss of NaOH. Coagulants can be used for the removal of calcium sulphate particles. The reactions occurring are:



10.8.4 Absorption of Sulphur Dioxide in Magnesium Oxide with Sulphur Dioxide Recovery

More than 95 per cent of SO_2 present in stack gases can be removed by the use of MgC-water slurry as a scrubbing medium. Sulphur trioxide and acid mist can also be removed by this method. The resulting stream is then centrifuged and the hydrated salt obtained dried. The anhydrous sulphite is calcined to MgO and SO_2 . The SO_2 obtained is scrubbed free of MgO , cooled, and sent to the drying tower of the sulphuric acid plant. During calcination, coke can be added to reduce sulphate to sulphite. This process has been commercialized in Japan for the scrubbing of boilerhouse gaseous effluents.

The reactions occurring during the different steps are:



A flow sheet based on the dolomite injection process is shown in Fig. 10.6

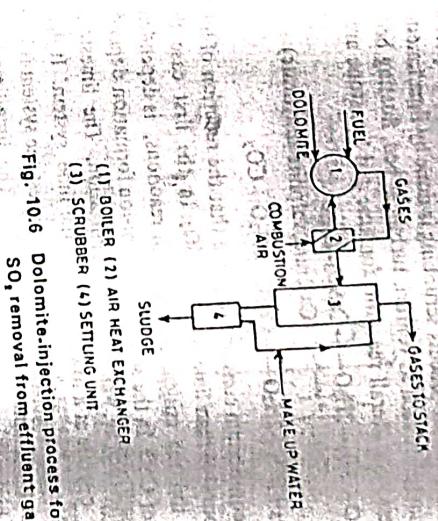


FIG. 10.6 Dolomite injection process for SO_2 removal from effluent gases

10.8.5 Absorption by Sodium Carbonate/Bicarbonate Solutions

Sulphur dioxide can be absorbed in a highly alkaline solution of soda ash. Sodium sulphite formed can be used in the paper and pulp industry. By this process it is possible to remove SO_3 and acid mist along with SO_2 . An oxidation inhibitor may be necessary to avoid/minimize the formation of sulphate from sulphite. The main reactions occurring are:



The concentrated liquor can be processed to obtain sulphite crystals, or spray dried. One unit based on this process is already operating in western India.

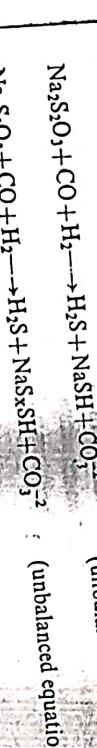
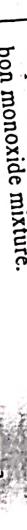
Alternatively, SO_2 can be absorbed in a solution of sodium carbonate bicarbonate in the presence of a reducing agent, forming thiosulphate which inhibits the formation of sodium sulphite.



The thiosulphate solution is partially reduced by H_2S to form elemental sulphur by the reaction:



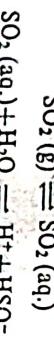
The remaining thiosulphate can be completely reduced to produce H_2S and carbon monoxide mixture.



The mixture of the polysulphide solution can then be stripped of H_2S and used in the partial reduction step. The remaining solution can be recycled for the absorption step.

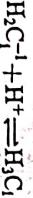
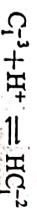
10.8.6 Citrate Process

The absorption of SO_2 is highly dependent on the pH of the scrubbing solution, but SO_2 in aqueous solution is acidic due to the formation of H^+ ions:



The pH of the system tends to decrease, which lowers the rate of absorption of SO_2 . The continuous decrease in pH can be arrested by the use of a buffer. In this process, the buffering action is provided by citric acid or its sodium salt.

In the actual process the flue gases, after removal of particulate matter enter an absorption tower where a buffered citrate solution (working pH = 4.5) is used as an absorbing medium. The reactions occurring can be represented as:

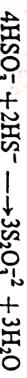


In the above equations C_1 represents citrate. Excellent buffering action takes place by the three dissociation-equilibrium steps and the range of pH varies from 3 to 5. Additional pH adjustment can be done by the addition of Na_2CO_3 or $NaOH$ to form sodium citrate which acts as an absorbing medium.

The bleed liquor from the absorption unit can be processed for sulphur recovery by treatment with a reducing agent such as H_2S at 60–70 °C and atmospheric pressure, when elemental sulphur is obtained by the overall reaction,



As mentioned earlier, SO_2 forms a complex thionate with the thiosulphate formed by the reaction of H_2S and SO_2 . H_2S reacts with the thiosulphate and polythionates to form sulphur as per the reactions:



10.8.7 Other Scrubbing Solutions

Very high removal efficiencies have been reported with the use of potassium sulphite-bisulphite as scrubbing solution. Bisulphite and pyrosulphite are formed during the reaction with SO_2 . The pyrosulphite is converted to bisulphite, by steam stripping, from which SO_2 can be liberated.

Some processes make use of organic solutions for the scrubbing operation. Dimethyl amine, xylylidine and dimethyl aniline have been used but are generally confined to applications where the SO_2 content in the gases is on the higher side (more than two per cent). Methyl ammonium sulphite-sulphite system also finds application where the SO_2 content has to be reduced to 100 ppm. The limitation of the large quantities of scrubbing liquid required, and aspects such as volatility and flammability of these organic materials have to be kept in mind.

10.9 DRY PROCESSES

There are, broadly, two types of dry methods employed for the removal of SO_2 from the exit gases.²²⁻²⁴

1. Oxidation/reduction
2. Use of metal oxides (limestone, MgO or others)

(a) Oxidation/Reduction

In the catalytic oxidation (CAT-OX) or Monsanto process, principally used in sulphuric acid plants, a fixed/fluidized bed reactor with V_2O_5 catalyst at 400–500 °C is used for good conversion efficiency. If the exit gases are at a lower temperature, they may be heated. The flow diagram for the process is shown in Fig. 10.7. In a modified oxidation process, SO_2 and oxygen present in the stack gas are adsorbed on the surface of an active carbon catalyst which catalyzes the oxidation of SO_2 to SO_3 . SO_3 subsequently reacts with the moisture present to form H_2SO_4 in the pores of the active carbon. The combined effect of absorption and catalysis by the active carbon can lead to an almost complete conversion of SO_2 . Regeneration of the catalyst can be done by either heating the carbon so that H_2SO_4 is reduced to SO_2 which

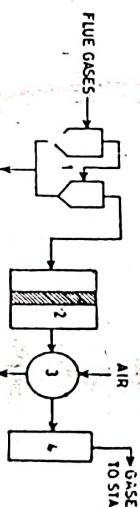


Fig. 10.7 Catalytic oxidation of SO_2

can subsequently be used in the manufacture of H_2SO_4 , or by washing the catalyst with water which takes away the H_2SO_4 formed. Figure 10.8 shows the Lurgi Sulphacid process based on the above principle.

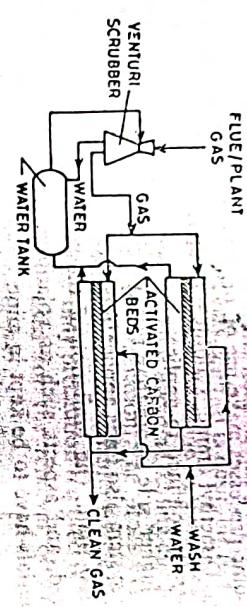


Fig. 10.8 An outline of the Lurgi sulphacid process based on the combined effect of adsorption and catalysis. Purports only essential features, with details left out

In the Westvaco process the activated-carbon catalyst with the adsorbed/absorbed H_2SO_4 is regenerated by bringing it into contact with H_2S in a fluidized bed at $150^{\circ}C$ when the H_2SO_4 is converted to elemental sulphur. A fraction of elemental sulphur is recovered from the carbon by direct vaporization in a stripper. The remaining sulphur is reacted with hydrogen to provide the H_2S required in the earlier step. A rough flow sheet for the process is given in Fig. 10.9.

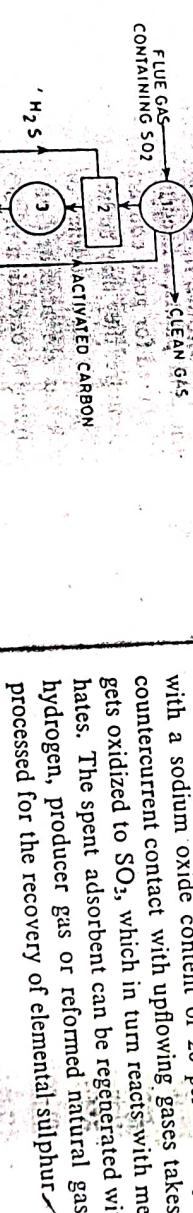


Fig. 10.9 An outline of the Westvaco process for the treatment of effluent gases containing SO_2 . Purports only essential features, with details left out

In the Scot process (Shell Clauss off-gas treatment process), where almost complete removal of sulphur or its compounds is possible, the gases are reduced, when sulphur and its compounds are converted to H_2S . H_2S is then selectively absorbed by an amine solution after removal of water by condensation. Sulphur can be regenerated from the spent liquor by the low-

Cobalt/Molybdenum catalyst supported on alumina at a temperature of $300^{\circ}C$. Any light hydrocarbon can also be used in case hydrogen is not readily available. The gases from the reactor are cooled, water condensed out, and led to an absorption unit where ethanol amine solution is used as an absorbing liquid. Stripping of the amine solution regenerates the solution for re-use in the absorption unit.

(b) Use of Metal Oxides

In a process using lime the solution or slurry is pumped through an atomizer in a spray drier, where it comes in contact with hot flue gases. A fabric filter following the drier acts as a secondary absorber as well as helping to remove particulate matter. The collected particles can be recycled into the slurry tank to increase reagent use. The problems of plugging and solid disposal are reduced but the equipment cost is high.

Magnesium oxide reacts with SO_2 , forming sulphate. With a working temperature in the range of $100-180^{\circ}C$ in the entrainment-type absorber, the bulk of the solids are collected in a suitable separation device and reused. The remaining solids are mixed with ammonia-water-air to produce ammonium sulphate, and the adsorbent reused.

In another process, sodium aluminate is used to remove SO_2 in a fluidized bed. The adsorbent is regenerated by treating with synthesis gas at $600-700^{\circ}C$. H_2S formed can be converted to elemental sulphur. The alkalinized alumina process employs a co-precipitate of sodium and aluminium oxides with a sodium oxide content of 20 per cent by weight. In the adsorbent counter-current contact with upflowing gases takes place, during which SO_2 gets oxidized to SO_3 , which in turn reacts with metal oxides to form sulphates. The spent adsorbent can be regenerated with a reducing gas such as hydrogen, producer gas or reformed natural gas. The H_2S formed can be processed for the recovery of elemental sulphur.

10.10 ECONOMIC CONSIDERATIONS

The economics²¹ of the process chosen depends on the availability of raw materials and markets for the by-products such as sulphur, ammonium sulphate, calcium sulphate, etc. formed. The capital cost is least for lime scrubbing and most for MgO (where the final by-product is in the case elemental sulphur) scrubbing. The operating cost is least in the case of ammonia scrubbing, as the by-product in this case (ammonium sulphate) has good marketability. For smaller plants, lime scrubbing is recommended.

It is necessary to take all possible precautions to minimize the release of SO_2 into the atmosphere. It is of particular significance in India where population densities are rather high in urban areas. DCDA technology should be adopted for all sulphuric acid contact plants where the tail gases can

174 Pollution Control for Specific Pollutants

still contain as much as 500 ppm of SO₂. Further reduction of SO₂ can be done by any of the processes outlined above, depending on the local availability of the adsorbent and markets for the by-products, if any.

REFERENCES AND BIBLIOGRAPHY

1. Strauss, W., *Industrial Gas Cleaning*, Pergamon Press, Lond. (1966).
2. Theodore, L. and A.J. Buonicore, *Industrial Air Pollution Control and Design*, Marcel Dekker, New York (1977).
3. Cherenkisoff, N. and R.A. Young, (Eds.), *Air Pollution Control*, CRC Press, Ohio (1976).
4. Ledbetter, J.O., *Air Pollution Handbook*, McGraw-Hill, U.K. (1978).
5. Parkar, A., *Industrial Air Pollution Handbook and Gas Cleaning*, Mir Publishers, Moscow (1972).
6. Gordon, G., *Momentum Transfer Operations*, Tata McGraw-Hill, New Delhi (1972).
7. Gupta, S.K., *Momentum Transfer Operations*, McGraw-Hill, New York (1979).
8. Steinfeld, J.H., *Air Pollution*, Physical and Chemical Fundamentals, Marcel Dekker, New York (1975).
9. Perry, H., *Chemical Engineers Handbook*, McGraw-Hill, New York (1973).
10. Danielson, J.A., *Air Pollution Engineers Manual*, E.P.A., Research Triangle Park, NC (1973).
11. Ross, R.D., *Air Pollution and Industry*, Van Nostrand Reinhold, New York (1972).
12. Faith, W.L., *Air Pollution Control*, Wiley Interscience, New York (1968).
13. Ross, R.D., *Air Pollution*, Wiley Interscience, New York (1960).
14. Stern, A.C. (Ed.), *Control of Air Pollution Sources*, Marcel Dekker, New York (1971).
15. Marchello, J.M. (Ed.), *Gas Purification*, McGraw-Hill, New Delhi (1976).
16. Koal, A.L. and F.C. Reinsfeld, *Gas Purification*, Tata McGraw-Hill, New York (1966).
17. Crawford, M., *Air Pollution Control*, McGraw-Hill, New York (1974).
18. Perkins, H.C., *Air Pollution Control*, Marcel Dekker, New York (1979).
19. Parikh, P.P. and B.N. Jaito, "Sulphur dioxide and removal of SO₂ in a rain system", *Atmospheric Environment*, 16 (4): 775-783 (1982).
20. Fischer, B.E.A., "The treatment and removal of SO₂ in a rain system", *Atmospheric Environment*, 16 (4): 775-783 (1982).
21. Basell, W.D., "SO₂ emissions", *Chem. Engng. V. Panchaiyappan, Chemical Age of India*, 26 (4): 279-284 (1975).
22. Shanmugasundaram, S., S. Ahmad, and S. Ahamed, "Sulphur in Petroleum Refineries, Control and Recovery of Sulphur in Petroleum and Hydrocarbon Water", *Control and Recovery of Flue Gases*, "Petroleum and Hydrocarbon Water" Control, 26: 253 (1976).
23. Narayan, V., "Desulphurization of Waste of India", *Chem. Engng. V. Panchaiyappan, Chemical Age of India*, 26 (4): 279-284 (1975).
24. Shanmugasundaram, S., "Pollution from Fertilizer Plants: Treatment of Waste of India", *Chem. Engng. V. Panchaiyappan, Chemical Age of India*, 26 (4): 279-284 (1975).
25. "New look on sulphur plants", *Chemical Age of India*, 18 (6): 397 (1967).
26. Ganguly, N.D., "Sulphur—Its storage and recovery", *Chemical Age of India*, 18 (6): 397 (1967).
27. Ludwig, J.H. and P.W. Spacie, "Control of SO₂ Pollution", *Chem. Engng.* 63: 82 (1967).
28. Jimeson, R.M., "Utilizing Solvent Refined Coal in Power Plants", *Chem. Engng. Prog.* 62 (10): 53 (1966).
29. Brown, G.N. and S.L. Tossenece, et al., "SO_x recovery via activated carbon", *Sulphur Dioxide Processing*, "Reduction of SO_x and NO_x", SO_x Developments, AIChE p: 136 (1971).
30. Meyer, B. and C. Carlson, "Emission monitoring of SO_x and NO_x", *AIChE p: 35 (1975).*
31. Besset, D.F. and J.R. Small, "Emission monitoring of SO_x and NO_x", *AIChE p: 35 (1975).*
32. "Recovery of sulphur dioxide from fuel gases", *News Letter, British Chem. Engng.*, 13, (17): 923 (1960).
33. Rees, R.L., "The removal of oxides of sulphur from fuel gases", *J. Inst. Fuel*, 25: 350 (1953).
34. Kivovsky, J.R., P.B. Koradja and D.S. Hook, "Molecular sieve method", *Chem. Engng. Prog.*, 72 (8): 103 (1976).
35. Slack, A.V., "Air pollution: control of SO_x from power stacks", *Chem. Engng.*, 74 (25): 725 (1972).

11

Removal of oxides of Nitrogen

tyres and other insulating materials. Ambient quality standards specify a concentration of 100 microgram/m³, or 0.05 ppm on an annual arithmetic mean basis. The exit gases from thermal power stations, or nitric acid plants usually contain between 1000 and 2000 ppm of NO_x. The exhausts of diesel engines contain between 4000 and 8000 ppm of NO_x depending upon the state of the engine. The Indian Standards specify less than 24 kg NO_x/tonne of HNO₃ in the exit gases produced in new plants. The threshold limit value for NO₂ is 9 mg/m³. Damage to vegetation occurs at a concentration of 1 mg/m³ for 1 h exposure. Concentration of NO_x as low as 0.2 mg/m³ can lead to the formation of photochemical smog, a very unpleasant form of pollution that is frequently experienced in USA.

Table 11.1 NO_x Emission in United States and India (Bombay)

Source	USA 1973		India 1973 (Bombay only)	
	1000 Tonnes/year	%	Tonnes/day	%
All mobile sources	16250	45.1	27.7	28.0
Steam/electric boilers	16053	44.3	30.0	30.6
Industrial boilers	2069	5.7		
Chemical industry	115	0.3	35.7	36.4
Uncontrolled sources	1593	21.4	4.3	4.7

11.2 ANALYSIS OF NO_x

In the Saltzman method, as discussed in Ch. 2, NO is converted to NO_x using an oxidizing agent such as acidified K₂MnO₄. NO_x produced and already present is absorbed and is reacted with sulphamic acid to form the corresponding diazo compound. The diazo compound couples with α -naphthylamine to form α -naphthylamine-p-azobenzene-p-sulphonic acid, which is a red azo dye. The colour intensity of the dye produced is measured with a colourimeter. The accuracy of the method depends on the efficiency of the absorption step. For absorption 0.1 N NaOH is recommended.

In another laboratory method, a sample of the gas is collected in air-evacuated flasks containing dilute H₂SO₄ and H₂O₂. Oxides of nitrogen get converted to HNO₃, which is measured colourimetrically using nitrophenol disulphonic acid after removing H₂O₂ by heating. Photometric analyzers and chemiluminescent methods²² form the basis for continuous monitoring.

YEC⁵: NO_x causes widespread and extensive health and other hazards next to SO₂. It corrodes metal surfaces, damages building surfaces, reduces visibility due to smog formation, retards growth of biomass and causes bronchitis and other chronic pulmonary ailments. It takes part in photochemical reactions in the atmosphere, the products of which cause irritation to the eyes, reduce visibility, eat fabrics, damage leaf structure of plants and reduce the life of

CONTROL MEASURES

Include absorption in solutions, adsorption, and catalytic oxidation. Improved design of combustion engines/furnaces, as well as their proper maintenance and operation also help reduce pollution due to NO_x .

3.1 Absorption Methods

Water is the cheapest liquid that can be used as an absorbent but the solubility of NO_x is quite low and it is not completely absorbed. For automotive exhausts, a molten-salt absorbent consisting mainly of sodium, lithium, potassium carbonates enters the venturi-scrubber-type unit where it is brought into intimate contact with the exhaust gases at a high temperature. Venturi demister, after the open-ended venturi diffuser, recovers the molten which trickles back into the salt trough below.

or absorption of gases^{21,22,23} containing NO_x from boilers and pro-

cess industries, aqueous solutions of magnesium hydroxide, magnesium

nitrate, calcium hydroxide and ammonia, or their combinations, are

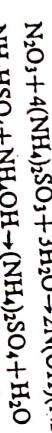
used. calcium hydroxide and ammonia, or their combinations, are

3.1.1 Absorption in Magnesium Hydroxide-Magnesium Carbonate Slurry

Gases containing NO_x are led to a gravity scrubbing unit where they brought into intimate contact with the liquid droplets at 30-40 °C. The loss in the gas through the spray column is low, which is necessary. For large flow rates of gases, are to be handled, as is usually the case. For packed-bed and venturi scrubbers can also be employed. Magnesium hydroxide can be recovered from the used-up slurry by heating to 200 °C with ammonium hydroxide. Nitrogen oxide produced during the reaction can be recycled back into the nitric acid plant. This increases the throughput of the nitric acid plant as well as reducing the NO_x pollution.

3.1.2 Absorption in Ammonium Sulphite and Bisulphite Solutions

Absorption of NO_x from effluent gases is carried out in packed columns. The area for transfer is high and the pressure loss low. The flow of the scrubbing liquid and gases is counter-current, so transfer rates are higher. The concentration level of NO_x in the exit gases is reduced to 1 ppm from an initial concentration of more than 1000 ppm. The ratio bisulphite to sulphite is kept between 0.1 and 0.4 from the viewpoint of operation and cost. The reactions occurring are

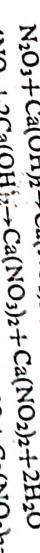


The absorbent is finally converted to ammonium sulphate and processed for fertilizer use. This method is ideal when the gases containing NO_x are the exhaust from a fertilizer plant.

Absorption in Calcium Hydroxide Solution

The gases containing nitrogen oxides are absorbed in calcium hydroxide solution obtained from the slaking of lime. The cost of the slaking unit adds to the cost of the process. The calcium nitrite produced in the mass transfer-chemical reaction step is converted to calcium sulphate (by adding H_2SO_4) in lead-lined tanks which in turn is processed for use as a fertilizer.

The reactions occurring are:



Absorption in Ferrous Sulphate Solution

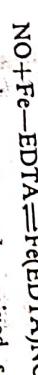
Aqueous FeSO_4 solution in a concentration range of 0.0625 to 0.5 g mole/l is used for the removal of NO due to its high absorption rate, easy regeneration and low cost. NO reacts with Fe^{+2} according to the reaction.



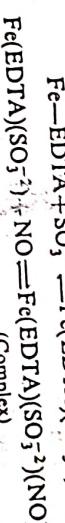
(Complex)

The forward reaction is second order (first order with respect to both NO and Fe^{+2}) and the reverse reaction is first order with respect to FeNO^{+2} .

The absorption capacity for NO can be increased by the addition of chemicals to the FeSO_4 solution. The reaction with Fe-EDTA forms a complex with NO as before,



The absorption can also be carried out in a mixed solution of Fe-EDTA and Na_2SO_3 . The reversible reactions occurring are:



$\text{Fe(EDTA)}(\text{SO}_3^{2-}) + \text{NO} \rightleftharpoons \text{Fe(EDTA)}(\text{SO}_3^{2-})(\text{NO})$

(Complex)

Absorption of NO_x can also be done in Na_2SO_3 and NaHSO_3 solutions. The kinetics of absorption and reaction are well reported and can help in the design of proper absorption equipment.

Absorption in Other Media

SO_2 and NO_2 can simultaneously be absorbed in alkalinized alumina ($\text{Na}_2\text{O Al}_2\text{O}_3$). The absorbed SO_2 leads to the formation of sodium sulphate, whereas NO_2 gives NaNO_3 . NO can also be absorbed by the reacting system

$\text{NaClO}_2 + \text{NaOH}$ which contains 2 moles/l of the former and 0.7 moles/l of the latter. H_2O_2 is also used as an absorbing medium in some applications.

A process suited to fertilizer units has been developed where NO_x in the tail gases is scrubbed with an aqueous urea solution, where the final products are CO_2 , H_2O and N_2 which can be safely let out into the atmosphere. The flow-sheet for this process is given in Fig. 11.1.

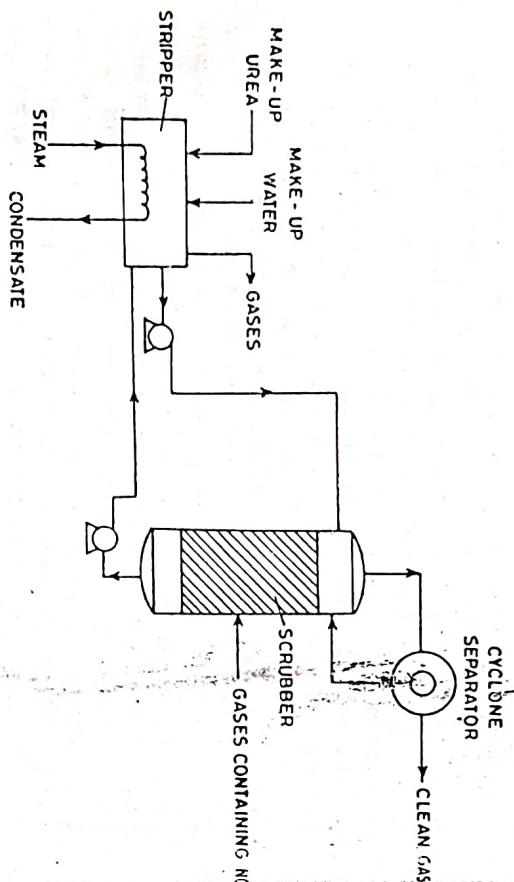


Fig. 11.1 Removal of NO_x by urea scrubbing

11.3.2 Adsorption of NO_x

For adsorption of NO_x , NO is first oxidized to NO_2 which can be adsorbed by silica gel, activated carbon, etc. The adsorbent is regenerated by heating and NO_2 evolved is reused for HNO_3 manufacture. Silica gel has practically no adsorption capacity for NO . Dry silica gel is reported to catalyze the oxidation of NO to NO_2 but moist or saturated silica gel has no effect on oxidation. As silica gel has a high capacity for adsorbing moisture, it should be used selectively when the gases contain appreciable amounts of moisture.

Natural zeolites can be employed to remove NO_x levels up to 200 ppm. Their capacity for removal is, however, limited to about 2.2 kg/100 kg of zeolite. The zeolite bed is regenerated by hot air or steam when NO_x or HNO_3 are respectively desorbed. These, in turn can be used in the process. Activated carbon adsorbs NO_x quite efficiently when the carbon bed is fresh. Repeated regeneration of the activated carbon reduces its adsorption capacity to as little as 50-60 per cent due to the presence of oxygen which is invariably present in the exhaust gases.

By far the best adsorbents for commercial applications are under different trade names, such as Purasiv-N developed by Union Carbide. Besides NO_x , these adsorbents can adsorb other pollutants such as SO_2 and mercury

vapour. The basic requirement for the use of these commercial adsorbents is that NO should first be oxidized to NO_2 . NO_x in the exit gases can be reduced to less than 10 ppm. The process is ideally suited to applications where NO_x recovered by regeneration can be reused in the nitric acid plant. The temperature of gases is around 320°C , which eliminates the use of high-temperature alloys. The operating cost is about 25 per cent lesser than the catalytic-reduction process. The capital cost, however, is as much higher. The adsorbent is not affected by the presence of oxygen and its life is fairly long. As mentioned earlier, the use of adsorbents is practical only for nitric acid exhaust gases as, in the case of exhausts from other stationary sources, NO_x disposal becomes a problem.

11.3.3 Catalytic Reduction of NO_x

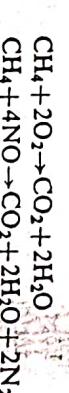
In the manufacture of HNO_3 , the absorption system leaves as much as 0.3 per cent of NO_x . Oxygen is also normally present to the extent of 3 per cent. For inefficient absorption columns, the percentage of NO_x can be even higher. NO_x can be reduced to nitrogen^{24,25} when the tail gases from the nitric acid plant are mixed with H_2 , NH_3 or other hydrocarbons, and catalytically reduced. Platinum, palladium, copper oxide or rhodium supported on alumina, kieselguhr, silica or diatomaceous earth in the form of a honeycomb are used for the catalytic reduction. The concentration of the active component in the catalytic pellet is between 0.1 and 1 per cent by weight. The catalytic reduction of NO_x has some distinct advantages over other methods. The reduction of NO_x to acceptable values is possible by making use of one or more stages in series. The products of reduction present no disposal problems. The heat of reaction evolved is sufficient to drive a turbine or an air compressor for pumping the gases through the process equipment and the chimneys.

Catalytic Reduction Using Methane

The hydrocarbon serves two purposes. In the first stage, all higher oxides of nitrogen are reduced to NO . In the second stage, the latter is reduced to nitrogen. Besides, oxygen in the tail gases reacts simultaneously with the hydrocarbon to produce CO_2 and water vapour and thus supplies the heat necessary to maintain the reaction temperature at 400°C . With methane, the reactions occurring are:



(First stage)



(Second stage)

Figure 11.2 shows the process flowsheet for the process. The tail gases are first preheated to 400°C in the preheater and mixed intimately with methane. The mixture is then led to the reactor which is in the form of a cylindrical vessel made of heat-resistant alloys. The sulphur compounds must be removed first as they poison the catalyst. The activity falls off with time, but

with higher temperatures of the inlet gases the effect of decreasing catalytic activity can be prolonged.

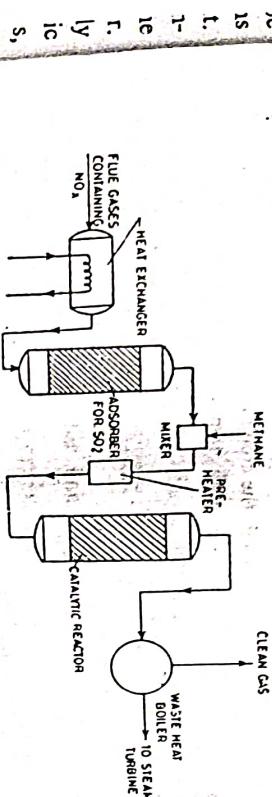


Fig. 11.2 Catalytic reduction of NO_x using methane

Catalytic Reduction Using Ammonia

The use of hydrocarbons requires a supply of endothermic heat for the catalytic reactions. This entails expensive operations and the use of expensive control devices. Ammonia reacts selectively with NO and NO_2 , with platinum as catalyst, as per the equations.



Twice the stoichiometric proportion of ammonia is added to the tail gases containing NO_x under a pressure of 10 atm and 300-400 °C temperature. NO_2 retards the activity of the catalyst and, therefore, it is best to reduce NO_2 to NO in the presence of Ruthenium as catalyst, using a stream of hydrogen. A single reactor with two separate catalyst beds can be used for the purpose. The top bed normally contains the Ruthenium catalyst which effectively conducts the reaction between hydrogen and NO_2 to give NO . The bottom or lower bed contains the platinum catalyst which effects the reduction of NO by ammonia. As much as 1 to 5 times the stoichiometric proportion of hydrogen may be required for the reduction of NO_2 to NO . The quantity of NH_3 required varies between 1 and 4 times the stoichiometric proportion for the reaction where NO is reduced to N_2 .

11.3.4 NO_x Emission Control for Automobile Exhausts

Most of the NO_x formation occurs in the combustion zone^{21,22} during the burning of fuel in the internal combustion engine. The concentration of NO_x is governed mainly by the flame temperature and the availability of oxygen at that temperature. The mode of operation also decides the quantity of NO_x formed. The NO_x emission is highest during acceleration due to the high volume of exhaust gases and also during steady running of the

vehicle at high speeds. This occurs when the air-fuel ratio is also high. At air-fuel ratios of 16 and above the flame temperature decreases, which in turn decreases the NO_x concentration. Some other factors such as the compression ratio, deposit build-up in the combustion chamber and rise of cooling-water temperature also increase NO_x emissions.

Diesel engines, both mobile and stationary, exhaust combustion gases at a much higher rate than petrol engines. Though the NO_x concentration in their exhaust gases is lower than that for petrol, their overall contribution to NO_x levels in ambient air is comparatively much higher due to higher gas-exhaust rates. Maximum NO_x is emitted when the temperature of the charge, due to combustion in the engine, is augmented by compression by the rising piston. The lowest NO_x emission occurs when the fuel is injected at a very slow rate. Lower peak temperatures are attained in this situation. Temperature alone cannot totally characterize the NO_x pollution but it is reported that one has to take into account the total temperature-concentration-time profile.

The types of fuel-injection systems, the air-fuel ratio, commencement of combustion and manifold pressure are the variables which should be considered for effective NO_x concentration reduction in the exhaust gas. One must remember that present-day combustion systems are designed for a high degree of performance, efficiency and reduced CO levels. Any changes in the design variables to reduce NO_x would have repercussions on the efficiency of combustion and increase CO levels. A possible solution would be to incorporate indirect injection of fuel at as slow a rate as possible. Recycling of a part of the exhaust gases back into the engine is reportedly the best way to control NO_x emission for both gasoline and diesel engines. The temperature of the recycled gases must be low (cooling necessary) but well above the ambient temperature to prevent condensation of volatiles and help vaporization of the fuel. The recycle ratio can be 20-25 per cent of the volume of air-fuel mixture. The reported advantages of recycling of exhausts include a reduction of more than 80 per cent in NO_x concentration in the exhaust gases, 50 per cent in CO levels and 50-80 per cent in piston-ring wear. There is a nominal increase of about 2 per cent in fuel consumption. A slight modification in the engine would be necessary for incorporating the recycling of gases. The long-term measures include the use of a gas-turbine engine and the replacement of internal-combustion engines by electric motors. But there are a number of technical and economic problems which have to be surmounted for this to become a practical solution.

In USA the emission standards for automobiles have become quite stringent since 1971. Most of the effort has been concentrated on the reduction of NO_x levels in automobile exhausts based on the catalytic removal discussed earlier. The catalysts found useful are platinum-coated aluminate, rare-earth oxides, manganese oxide, cobalt oxide, copper chromates, calcium aluminate, ferric oxide, etc. and their combinations, supported on inert

gases such as alumina, aluminate and silica. The variation of the quantity of catalyst in the pellet is rather wide-between 1 and 10 per cent. The reducing gases and hydrocarbons provide the necessary reducing conditions. The compounds of sulphur make the catalyst ineffective. Other pollutants present in the exhaust gases, therefore, require the use of dual removal system. A control on air-fuel ratio is also necessary for a simultaneous control on NO_x , CO and unburnt hydrocarbons.

1.3.5 NO_x Pollution Control for Combustion Operations

As in the case of automobiles, combustion of oil, coal or gas in industrial furnaces, kilns, driers and boilers leads to the formation of NO_x .^{21,22} The basic reaction occurring is,



Excess air is used for complete combustion. For 10 per cent excess air used or combustion, about 2 per cent appears in the flue gases whereas at 1500 K, would lead to about 1.5 ppm of NO_x in the flue gases. When the concentration of NO_x level would increase to 1600 ppm. When the concentration also increases, the NO_x concentration also increases. Oxygen in the flue gases increases the NO_x levels in the flue gases. NO_x oxygen in the flue gases increases the NO_x levels in the flue gases. Temperature, oxygen concentration and length of time of combustion are important parameters for deciding the NO_x levels in the flue gases. Temperature, oxygen concentration and length of time of combustion are important parameters for deciding the NO_x levels in the flue gases. Temperature, oxygen concentration and length of time of combustion are important parameters for deciding the NO_x levels in the flue gases.

a) Recirculation of Flue Gases

In this method a part of the flue gas is recirculated and used for combustion. This makes the combustion deficient in oxygen with the result that the peak combustion temperature is reduced. As much as 90–95 per cent of the peak combustion temperature is reduced.

b) Low Excess-Air Utilization

Less excess air is used here. This increases the N/O ratio and reduces the formation of NO_x . Better control of combustion. Burners using gas left unburnt and there is a possibility of CO formation. Or oil use less excess air for combustion.

c) Two-Stage Supply of Air

Here, about 90 per cent of the air required for combustion due to the burner. The rest of the air required for combustion due to the burner flame. This reduces the NO_x formation where it occurs above the burner flame. This reduces the levels of oxygen have reduced flame temperature and slightly reduced levels of NO_x concentration by 40 per cent matters most. Reductions in the NO_x concentration by this modification.

(d) Tangential Firing
The burners here are located tangentially around the combustion chamber radiating heat to a concentric cooling area. The peak temperatures, as a result, are reduced, thus reducing NO_x emissions.

(e) Using Clean-Up Devices
Use is made here of catalytic reduction, absorption and adsorption as discussed earlier.

REFERENCES AND BIBLIOGRAPHY

- Strauss, W., *Industrial Gas Cleaning*, Pergamon Press, Lond. (1966).
- Theodore, L. and A.J. Buonicore, *Industrial Air-Pollution Control and Design Particulates*, Marcel Dekker, New York (1976).
- Chernemisoff, N. and R.A. Young, (Eds.), *Air Pollution Control and Design Handbook*, Marcel Dekker, New York (1977).
- Ledbetter, J.O., *Air Pollution Handbook*, McGraw-Hill, U.K. (1978).
- Parkar, A., *Industrial Air-Pollution Handbook*, Mir Publishers, Moscow (1972).
- Gordon, G. and I. Peisakhov, *Dust Collection and Gas Cleaning*, Mir Publishers, Moscow (1972).
- Gupta, S.K., *Momentum Transfer Operations*, Tata McGraw-Hill, New Delhi (1979).
- Steinfeld, J.H., *Air Pollution, Physical and Chemical Fundamentals*, McGraw-Hill, New York (1975).
- Perry, R.H. and Chilton, C.H., *Chemical Engineers Handbook*, McGraw-Hill, New York (1973).
- Danielson, J.A., *Air Pollution Engineers Manual*, E.P.A., Research Triangle Park, NC (1973).
- Ross, R.D., *Air Pollution and Industry*, Van Nostrand Reinhold, New York (1972).
- Faith, W.L. and A.A., *Air Pollution*, Wiley Interscience, New York (1972).
- Faith, W.L. and A.A., *Air Pollution Control*, Parts I and II, Wiley Interscience, New York (1972).
- Strauss, W. (Ed.), *Air Pollution Control*, Tata McGraw-Hill, New York (1968).
- York (1971).
- Stern, A.C. (Ed.), *Air Pollution, Vol. III, Academic Press*, New York (1974).
- Marchello, J.M. (Ed.), *Control of Air Pollution Sources*, Marcel Dekker, New York (1966).
- Koal, A.L. and F.C. Reinsfeld, *Gas Purification*, McGraw-Hill, New York (1960).
- Crawford, M., *Air Pollution Control*, Tata McGraw-Hill, New Delhi (1976).
- Perkins, H.C., *Air Pollution*, McGraw-Hill, New York (1974).
- Matajan, S.P., "Pollution control in chemical and allied Industries", *Short Term Course, Q.I.P. Indian Institute of Technology, Silver Jubilee Seminar*, Indian Institute of Technology, Bombay (1983).
- "Environmental pollution control and techniques", *Proceedings, Central Labour Institute, Bombay* (1978).
- "Air pollution control and techniques", *Proceedings, Central Labour Institute, Bombay* (1978).

The first national ambient air quality standards for six pollutants were established. These are given below.

(i) Suspended particulate matter (SPM)

(ii) Sulphur dioxide

(iii) Carbon monoxide

(iv) Photo-chemical oxidants (ozone)

(v) Lead and

(vi) Nitrogen dioxide

These standards were entered in FEDERAL REGISTER, 36, No. 86 of part II of U.S.A. on April 30th, 1971.

As per the "National Ambient Air Quality Standards" of Clean Air Act (1970) of U.S.A., the pollutant exposures covered by air quality criteria are given in Table 9.1.

Table 9.1. National Ambient Air Quality Standards of U.S.A.
(Reference: Air Pollution, WHO)

Contaminants	Primary Standards		Secondary Standards	
	$\mu\text{g}/\text{m}^3$	ppm	$\mu\text{g}/\text{m}^3$	ppm
SPM	75	0.03	2.8 mg 24-h	60
	260	0.10	24-h	150
	80	0.03	a.a.m	60
	365	0.14	24-h	260
				1300
SO_2				0.500
CO	10,000	9.00	8-h	60
	40,000	35.00	1-h	do
Oxidants (ozone)	160	0.08	1-h	do
Lead			3-4 months	do
Nitrogen dioxide	1.5		- do -	
	100	0.05	a.a.m	- do -

Note: a.a.m = annual average mean
a.g.m = annual geometric mean

Emission Standards or Standards of Performance

Air quality standards define a desired limit on specific pollutant level in the air. This goal includes a long term value for exposure, (e.g.: Annual average concentrations as well as high 24-h concentrations in a year), and also one or more short-term values, (e.g.: 1-h average concentrations in a year). The monitoring of the samples should be uniformly followed over the 12 months of a year with a frequency of not less than once in a week. The sampling period of 8-h for each sample and analysed as per the prescribed procedure.

Emission standards are different from ambient air quality standards. They prescribe the maximum permissible emission levels for given pollutants at their source. These are classified into two types.

(a) National standards applied to new and modified sources.

(b) State standards apply to existing sources.

The emission standards framed by the Central Board for Prevention and Control are given in Table 9.2.

The emission limits prescribed are expressed as concentration of pollutants per unit volume of air under standard of normal conditions, written as Nm^3 . The standard conditions means that temperature of air is taken as 25 °C and pressure at 760 mm Hg and zero % moisture.

Table 9.2. Emission Standards

(Ref. Central Board for pollution Control, 1985)

PART - I

1. Cement
Standard for particulate matter emission

Capacity	Protected Area	Protected	Area
200 tpd and less	250 mg/Nm ³	400 mg/Nm ³	
Greater than 200 tpd	150 mg/Nm ³	250 mg/Nm ³	

2. Thermal Power
(a) Standard for particulate matter emission

Boiler size	Protected area	Old (before 1979)	Other area
Less than 200 MW	150 mg/Nm ³	600 mg/Nm ³	350 mg/Nm ³
200 MW and above	150 mg/Nm ³	150 mg/Nm ³	150 mg/Nm ³

(b) Standard for sulphur dioxide control (through stack height)

Boiler size	Stack height
Less than 200 MW	H = 14 (Q) ^{0.2}
200 MW to less than 500 MW	220 m
500 MW and more	275 m

$$Q = \text{Sulphur dioxide emission in kg/h}$$

$$H = \text{Stack height in metres}$$

3. Iron and steel
Standard for particulate matter

Process	Emission limits
Sintering plant	150 mg/Nm ³
Coke oven	150 mg/Nm ³
Blast furnace	150 mg/Nm ³

Steel making—during normal operation
During oxygen lancing

4. Fertilizer (Urea) Standard for particulate matter emission	Emission limits
Process Drilling Tower	50 mg/Nm ³
5. Nitric acid Standard for oxides of nitrogen	
3 kg of NO _x per tonne of weak acid (before concentration) produced	

6. Sulphuric acid Standard for sulphur dioxide and acid mist emission	Acid mist emission
Process Sulphur dioxide emission	
Single conversion	10 kg/tonne of concentrated
Single absorption (100 %) acid produced	50 mg/Nm ³
Double conversion 4 kg/tonne of concentrated	
Double absorption (100 %) acid produced	

Guidelines for Minimum Stack Height

Stack height

For all plants except thermal power plant

30 m

2. For plants where the sulphur dioxide emission is estimated as Q (Kg/hrs.) the stack height, H in meters is given by

$$H = 14(Q)^{0.2}$$

3. For plants where the particulate matter emission is estimated as Q (Kg/hrs.) the stack height, H in metres is given by

$$H = 74(Q)^{0.27}$$

4. If by using the formula given in 2 or 3 above, the stack height arrived at, is more than 30 m, then the higher stack should be used.

In no case should the height of the stack be less than 30 m.

PART - II

1. Calcium carbide
Standard for particulate matter emission

Source	Emission limit
Kiln	250 mg/Nm ³
Arc furnace	150 mg/Nm ³

(Contd.)

116. Fundamentals of Air Pollution

2. Copper, lead and Zinc smelting

Standard for particulate matter and oxides of sulphur

Concentrator smelter and converter	150 mg/Nm ³ for particulate matter off-gases must go for H ₂ SO ₄ manufacture. No release of SO ₂ /SO ₃ shall be permitted from the smelter or converter.
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3. Cannon Black

Standard for particulate matter emission

Year of Commissioning	Emission limit
New plants (Built and commissioned after January 1, 1985)	150 mg/Nm ³
Existing plants (Built and commissioned before December 31, 1984)	250 mg/Nm ³ (till December 31, 1986) 150 mg/Nm ³ (from January 1, 1987)

4. Fertilizer (Phosphatic)

Standard for fluoride and particulate matter

Process	Emission limit
Acidification of rock phosphate	25 mg/Nm ³ as total fluoride (F ⁻)
Granulation, mixing, rock grinding	150 mg/Nm ³ of particulate matter from each process

5. Oil Refineries

Standard for sulphur dioxide

Process	Emission limit
Distillation (atmospheric plus vacuum)	0.25 kg/Tc of feed*
Catalytic cracker	2.5 kg/Tc of feed
Sulphur recovery unit	120 kg/Tc of sulphur in the feed

* Feed indicates the feed for that part of the process under consideration only.

6. Aluminium

Standard for fluoride and particulate matter

Process	Standard
Calcination	250 mg/Nm ³ of particulate
Aluminium smelting	1 kg (F ⁻)/Tc of aluminium produced and 150 mg/Nm ³ of particulate matter

9.2 AIR QUALITY LEGISLATION

Some of the air pollution acts of U.S.A. are given below

The first air pollution control act was passed in 1955.

In 1963, CLEAN AIR ACT was passed

In 1965, Amended clean air act was passed

In 1967, Air Quality Act was passed

In 1970, Amended Air Quality Act was passed.

Indian Acts

India was the first country in the world to give the control and prevention of environmental pollution as a constitutional obligation by inserting Article 48-A in the constitution. Article 48-A states "The state endeavour to protect and improve the environment and to safeguard the forests and wild life of the country". Article 58-A also states. It shall be the duty of every citizen of India to protect and

improve the natural environment including forests, lakes, rivers, and wild life and to have compassion with living creatures.

In 1986, a new Ministry of Environment and Forests was formed by the Government of India, combining Department of Environment and Department of forests to give an integrated approach about the environmental protection and conservation.

The Air (Prevention and control of Pollution) Act was passed in May 16th, 1981 and amended in 1987. In 1986, the Government of India enacted an Umbrella Act called "Environmental Protection Act, 1986. This covers all aspects of environment including noise, air, water and hazardous chemicals etc.

Air pollution Act, 1981 is applicable throughout the country. AIR being a Central Government subject, so the Air Act provides more powers and freedom of action to the Central Board of Prevention and Control of Pollution.

The Amended Air Act 1987 provides important provisions, some of them are as follows.

- (i) Air Pollution Act is applicable for all air pollution generating sources.
- (ii) 'Noise Pollution' was also cover under this act.
- (iii) Establishment of new industries is also brought as statute requirement 'for prior approval' under this Act.
- (iv) Powers to closure, prohibition or regulation of industries,