

भारतीय मानक मसौदा
पेट्रोलियम रिफाइनरियों में वायु प्रदूषण का नियंत्रण — रीति संहिता
(पहला पुनरीक्षण)

Draft Indian Standard
CONTROL OF AIR POLLUTION IN PETROLEUM REFINERIES — CODE OF PRACTICE
(*First Revision*)

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ICS 13.040.99

Environment Protection Sectional Committee, CHD 32

Last date of comments: 19.01.2024

FOREWORD

(Formal clause to be added later)

All types of industrial units including petroleum refineries are sources of air pollution in varying degrees depending upon the technology and the operating practices adopted by them. In order to ensure uniform application of technology and operating practices, a code of practice, containing the latest available information on sources of air pollution, determination of emissions, control techniques, and measurement and monitoring of emissions and ambient air quality would provide a useful guide in the design and operation of a refinery, with a view to minimizing its effects on the environment. Codes of practice are standards which should be adopted by the respective industries for abatement of pollution by good housekeeping. Although limits at which corrective action is to be taken have not been specified, it is intended to incorporate these when more information is available on the subject.

IS 10179 was originally published in 1982. In this revision Reference clause has been incorporated and suitable modifications in relevant clauses have also been done based on the technological advancements over the last 40 years and emission norms in refineries notified by Ministry of Environment Forest and Climate Change and Environment Protection Rules. This revision has been taken up in order to bring out the standard in the latest style and format of the Indian Standards.

1 SCOPE

1.1 This standard covers the following:

- a) Major and minor air pollutants and their sources from refining operations,
- b) Emissions from refineries,
- c) Pollution control techniques and options,
- d) Operating practices to minimize and control emissions,
- e) Measurement of emissions, and
- f) Monitoring of emissions.

2 REFERENCES

<i>IS No.</i>	<i>Title</i>
IS 1448 (Part 18) : 2020	Methods of Test for Petroleum and its Products Part 18 Distillation of Petroleum Products (<i>third revision</i>)

3 TERMINOLOGY

Cenospheres — or chars are unburnt carbonaceous residues formed during combustion, when the volatile portion of a residual fuel vaporizes, leaving a residue of carbon and ash.

4 AIR POLLUTANTS FROM REFINING OPERATIONS

4.1 Major air pollutants that may be emitted from refining operations are sulphur compounds, hydrocarbons, nitrogen oxides, particulates including smoke, and carbon monoxide. Other emissions are aldehydes, ammonia and odours.

4.2 Major Pollutants

4.2.1 *Sulphur Compounds* — Sulphur dioxide constitutes the maximum proportion of sulphur compounds emitted from refineries. The main sources of sulphur dioxide emissions are combustion operations, such as process heaters, boilers and catalytic cracking regenerators, and sulphur dioxide extraction plants. Refinery flares, incinerators and decoking operations are other minor sources. The amount of sulphur dioxide emission depends upon the type and amount of fuel burnt and its sulphur content.

Other sulphur compounds emitted from refineries include hydrogen sulphide, sulphur trioxide and mercaptans from treatment processes. However, these emissions are in very small quantities since they result mainly from evaporation of leaks and vent losses from storage facilities.

4.2.2 *Hydrocarbons* — Emission of hydrocarbons results mainly from evaporation of light oils during storage and handling of crude and petroleum products and from leaks. Sources of hydrocarbon emissions include loading facilities, sampling, storage tanks, waste-water separators, blow-down systems, pumps, pump seals, compressors seals, pressure relief devices, heat exchangers, valves, vacuum jets, barometric condensers, air-blowing operations and compressor engines. The extent of these emissions depends upon design, maintenance and operating practices.

4.2.3 *Oxides of Nitrogen* — Combustion of fuel in process heaters and boilers, and in internal combustion engines used to drive compressors and electric generators, are the main sources of nitrogen oxides emissions in the refining industry. Nitrogen oxides are also released from catalytic cracking regenerators and from carbon monoxide (CO) boilers.

4.2.3.1 Combustion of fossil fuels produces nitrogen oxides partly from the combination of atmospheric nitrogen with excess oxygen in the furnace atmosphere, and partly from combination of the nitrogen present in the fuel. Formation of nitrogen oxides is mainly dependent on the flame temperature, the residence time at this temperature, and the excess air present in the flame.

4.2.4 *Particulates* — The major sources of emission of particulates in petroleum refineries are catalytic cracking unit regenerators. Minor sources include asphalt oxidizers sludge burners, emergency flares, boilers and furnaces during soot blowing and emergency operations, and incomplete combustion.

4.2.5 *Carbon Monoxide* — The only significant source of carbon monoxide in refineries is the catalytic cracking regenerator. This, however, is eliminated in units having a CO boiler. Minor sources include internal combustion engines used for compressors and electrical generator drives and incinerators where these are employed. Incomplete combustion in furnaces and boilers also generates carbon monoxide emissions.

4.3 Other Pollutants

4.3.1 *Aldehydes and Ammonia* — These are released in small amounts from catalytic cracking regenerators and combustion reactions.

4.3.2 *Odours* — Odours result from emissions of hydrocarbons and other compounds in very minute amounts. Human nose is capable of detecting odour much before its presence is indicated by any instrument. Odours are released during operations like treating, air-blowing, steam-blowing, and from drains, tanks, vents, barometric sumps, and waste-water separators.

5 EMISSIONS FROM REFINERIES

5.1 Petroleum refineries differ in the type of processing schemes employed, type of units used in a given processing scheme, the type of crude or crudes processed, varieties of end products, location, source of power, utilities requirements and operating and house-keeping practices. All these factors have a bearing in varying degrees on the quantities of emissions from each refinery. Consequently, it is desirable to undertake individual refinery measurements or calculations to estimate emissions rather than employ generalized emission factors for this purpose. Actual periodical monitoring of stack gases may be made to check the calculated values.

5.2 Sulphur Oxides — The main source of sulphur oxides is fuel combustion. Any *organic* sulphur contained in a fuel is oxidized to sulphur dioxide or sulphur trioxide during combustion. Normally about 98 percent of the fuel sulphur is converted to sulphur dioxide and the balance to sulphur trioxide during combustion. Eventually, however, considerably more of the sulphur dioxide is oxidized to sulphur trioxide in the ambient air, ultimately forming sulphate particulates. At present no known methods exist to determine the extent of this conversion, hence emissions are only evaluated to the extent of 98 percent conversion to sulphur dioxide and 2 percent to sulphur trioxide.

5.2.1 Emissions of oxides of sulphur are expressed in terms of sulphur dioxide. Knowing the quantity of fuel used, based either on flow meter readings or actual tank gauges, and the sulphur content of the fuel from actual laboratory analyses, the emissions of sulphur dioxide may be easily calculated. Actual monitoring of stack gases in such cases may not be necessary.

5.2.2 Where hydrogen sulphide removed during amine extraction is directly burnt at the flare or in process furnaces, the quantity of hydrogen sulphide may be obtained from direct measurement by flow meters and a laboratory analysis of the gas for hydrogen sulphide content. Where this is not possible, the quantity of hydrogen sulphide may be obtained indirectly from analyses of the treating unit feed and product for hydrogen sulphide and RSH. A material balance between the input and output streams will then give the quantity of hydrogen sulphide released.

5.2.3 In refineries employing Edleanu plants or sulphur dioxide extraction units, sulphur dioxide may be released directly into the atmosphere by way of leaks, vents, drains and in drying tower operations. An overall material balance on the unit including

sulphur dioxide storage, and sulphur content in feed, extract and raffinate streams, will indicate the net escape of sulphur dioxide to the atmosphere. Daily losses of sulphur dioxide from storage inventory if used will give a higher loss to atmosphere, since this loss also includes the sulphur dioxide loss due to entrainment or chemical combination in the raffinate and extract streams. These losses do not result in emissions.

5.3 Hydrocarbons — These emissions cannot be directly measured except in the case of unburnt hydrocarbons released during combustion operations. These may be measured by direct stack monitoring. The major sources of hydrocarbon emissions, however, are evaporation losses from storage tanks and from oil separators. These losses can only be estimated by empirical formulae based on extensive testing and experience.

5.3.1 Evaporation from Storage Tanks — The following five types of losses occur from storage tanks:

a) Breathing Losses — Losses resulting from the alternate increase and decrease of temperatures of the tank vapours and liquid surface, due to the absorption of heat through the tank shell and roof from the sun, and from daily variations in atmospheric temperature. During the day the air-vapour mixture is expelled from the tank, while fresh air is drawn into the tank at night. This causes the breathing cycle. These losses occur in cone or fixed roof tanks;

b) Filling Losses — Losses occurring during filling and emptying of storage tanks. When stock is pumped out air is drawn into the tank and the air is saturated by evaporation from the liquid surface. These vapours are then lost when fresh stock is pumped into the tank. These losses are primarily associated with fixed roof and variable space tanks;

c) Windage Losses — Losses mainly associated with floating roof tanks as a result of improper fit of the seal and shoe to the tank shell. Consequently, this allows fresh air to circulate through the vapour space, thus promoting evaporation. The greater the area of the openings through which air can enter, the greater the windage losses;

d) Wetting Losses — Losses taking place in floating roof tanks when a wetted tank wall is exposed to the atmosphere. The losses, however, are negligible; and

e) Boiling Loss — Losses caused by storage of highly volatile stocks at their bubble point. At this temperature boiling of the liquid starts and losses will be excessive. Refineries rarely allow this to happen.

5.3.1.1 Factors affecting the magnitude of evaporation losses are as follows:

<i>Factor</i>	<i>Affect on Loss</i>
a) Vapour pressure of the stock	Loss increases with vapour pressure
b) Temperature of the stock	Increase in temperature increases the vapour pressure and hence losses
c) Area of liquid surface exposed for evaporation	Proportional to the square of diameter of the tank
d) Volume of vapour space	Volume of vapour expelled during breathing is proportional to the total volume. It is, therefore, a function

- of tank outage. Breathing loss is greatest when inventory is lowest
- e) Diurnal temperature change in tank vapour space
Losses increase with increased diurnal temperature change
- f) Mechanical condition of tank
Windage loss is directly proportional to the area of openings through which air circulates
- g) Volume of liquid pumped
Filling losses are directly proportional to tank throughput
- h) Type of paint applied to outer surface
Paint colour and condition determines heat absorption and therefore loss.

5.3.2 Calculation — Losses may be calculated as given below. The equations given for breathing and filling losses from fixed roof tanks do not take into account the breather valve relief setting which may be as high as 5 kPa gauge and thus substantially reduce the hydrocarbon loss.

5.3.2.1 Breathing losses (fixed roof tanks)

$$B = \frac{0.45}{V_c} WK \left[\frac{P}{P_1 - P} \right]^{0.68} D^{1.73} H^{0.51} \Delta T^{0.5} F_p C$$

where

- B = Breathing loss in kg/day m^3 capacity,
 P = True vapour pressure at bulk liquid temperature in Pa,
 P_1 = Atmospheric pressure in Pa,
 D = Tank diameter in m,
 H = Average vapour space height, including correction for roof volume in m,
 ΔT = Average daily ambient temperature change in $^{\circ}C$,
 F_p = Paint factor (*see* Table 1),
 C = Adjustment factor for tanks smaller than 9 m in diameter (*see* Fig. 1),
 V_c = Capacity of tank in m^3 ,
 K = Liquid factor (*see* Table 2), and
 W = Density of liquid at storage conditions in kg/m^3 .

TABLE 1 PAINT FACTORS FOR FIXED ROOF TANKS
(Clause 5.3.2.1)

SL No.	COLOUR OF TANK		PAINT FACTOR (F_p) PAINT CONDITIONS	
	Roof	Shell	Good	Poor
(1)	(2)	(3)	(4)	(5)

i)	White	White	1.00	1.15
ii)	Aluminium (specular)	White	1.04	1.18
iii)	White	Aluminium (specular)	1.16	1.24
iv)	Aluminium (specular)	Aluminium (specular)	1.20	1.29
v)	White	Aluminium (specular)	1.30	1.38
vi)	Aluminium (specular)	Aluminium (specular)	1.39	1.46
vii)	White	Grey	1.30	1.38
viii)	Light Grey	Light Grey	1.33	1.44
ix)	Light Grey	Light Grey	1.46	1.58

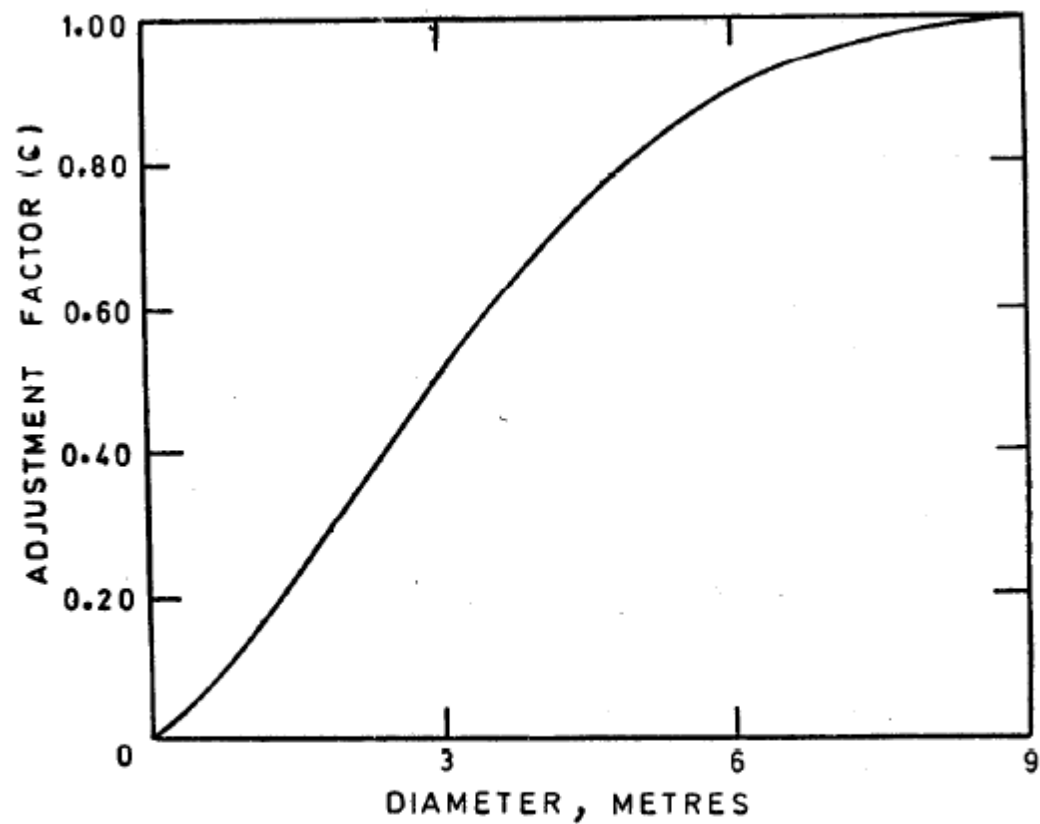


FIG. 1 ADJUSTMENT FACTOR FOR SMALL-DIAMETER
FIXED ROOF TANKS

TABLE 2 LIQUID FACTOR K (FIXED ROOF TANKS BREATHING LOSS)
(Clause 3.3.2.1)

SL No	LIQUID STORED	K
(1)	(2)	(3)
i)	Crude oil	0.014
ii)	Gasoline	0.024
iii)	Naphtha jet fuel (JP - 4)	0.023
iv)	Kerosene	0.020
v)	Distillate oil	0.019

5.3.2.2 Filling losses (fixed roof tanks)

$$F_t = 0.01 \frac{(180 + N) W m P}{6 N}$$

where

F_t = Filling loss (emptying plus filling) in kg/m³ throughput,

N = Number of tank turnovers per year

(annual throughput),
tank capacity

W = Density of liquid at storage conditions in kg/m³,

m = Liquid factor (see Table 3), and

P = True vapour pressure at bulk liquid temperature in Pa.

5.3.2.3 Filling losses (variable space tanks)

$$F_v = \frac{0.01 W m P}{V_t} (V_t - 0.25 V_e N)$$

where

F_v = Filling loss in kg/m³ throughput,

V_t = Volume of liquid throughput in m³/year,

V_e = Volume of expansion capacity in m³,

N = Number of turnovers per year,

W = Density of liquid at storage conditions in kg/m³,

m = Liquid factor (see Table 3), and

P = True vapour pressure at bulk liquid temperature in Pa.

TABLE 3 LIQUID FACTOR m (FIXED ROOF/VARIABLE SPACE TANKS - FILLING LOSS)
(Clauses 5.3.2.2 and 5.3.2.3)

SI No.	LIQUID STORED	m
(1)	(2)	(3)
i)	Gasoline	0.0003
ii)	Crude oil	0.000 225
iii)	Naphtha jest fuel (JP - 4)	0.000 324
iv)	Kerosene	0.000 295
v)	Distillate oil	0.000 276

5.3.2.4 Windage losses (floating roof tanks)

$$S = \frac{0.43 W K_t}{V_c} D^{1.5} \left[\frac{P}{P_1 - P} \right]^{0.7} V_w K_s K_c K_p$$

where

- S = Windage loss in kg/m³ capacity,
 W = Density of liquid at storage conditions in kg/m³,
 K_t = Tank construction factor (see Table 4),
 P = True vapour pressure at bulk liquid temperature in Pa,
 P_1 = Atmospheric pressure in Pa,
 V_w = Average wind velocity m/s,
 D = Tank Diameter in m (for $D > 45$ m use $DA/45$ instead of $D45$),
 K_s = Seal factor (1.00 for tight fitting modern seals and 1.33 for loose fitting older seals),
 K_c = Liquid factor (see Table 5),
 K_p = Paint factor (1.00 for light grey or aluminium and 0.90 for white), and
 V_c = Capacity of tank in m³.

TABLE 4 TANK CONSTRUCTION FACTOR K
(Clause 5.3.2.4)

SL No.	CONSTRUCTION OF TANK	K_t
(1)	(2)	(3)
i)	Welded tank — pan/pontoon roof, single/ double seal	0.045
ii)	Rivetted tank - pontoon roof, double seal	0.11
iii)	Rivetted tank - pontoon roof, single seal	0.13
iv)	Rivetted tank ‘ - pan roof, double seal	0.13

v) Rivetted tank - pan roof. sinele seal 0.14

TABLE 5 LIQUID FACTOR K_c (FLOATING ROOF TANKS — WINDAGE LOSS)
(Clause 5.3.2.4)

Sl No.	LIQUID STORED	K_c
(1)	(2)	(3)
i)	Gasoline	1.00
ii)	Crude	0.75
iii)	Naphtha jet fuel (JP.-4)	0.96
iv)	Kerosene	0.83
v)	Distillate oil	0.79

5.3.3 Evaporation from Oil Separators — Oil separators and skim ponds usually contain settled oil floating- on the water in the separator bays. This oil is skimmed by floating skimmers into the oil collection pipe. Since this is a slow process a large surface of the oil is exposed to evaporation, unless the separator is covered. For covered separators this loss is negligible. For uncovered separators the evaporation loss may be calculated as follows:

$$EL = \frac{(LE - 25) S}{0.159 (100 - LE)}$$

where

EL = Separator evaporation loss in m³/day,
 S = Separator slop oil pickup in m³/day, and
 LE = Light ends in influent oil, percent

For determining LE , distillation is required on the influent oil and the collected slop oil. Determine the temperature at 25 percent distillation on the collected slop oil as per IS : 1448. Using this temperature on the influent oil distillation curve find the percent distilled. Use this percentage as LE .

5.4 Oxides of Nitrogen — Emissions of oxides of nitrogen from refinery furnaces and boilers depend upon the fuel nitrogen content, and firing conditions, which depend upon the design of the furnace, type of firing and excess air. Consequently, emissions differ from furnace to furnace, and hence these emissions should be determined by individual stack sampling for any degree of accuracy. However, since refinery furnaces in general are relatively small, and have low flame temperatures and residence time, nitrogen oxides emissions from refineries are generally low. Consequently individual monitoring does not appreciably enhance the quality of data obtained, as compared to emissions estimated by using generalized emission factors.

5.5 Particulates — The major sources of particulates in refineries are catalytic cracking unit regenerators. Emissions from these may be estimated from the daily catalyst loss data based on daily inventory numbers. Losses from regenerators depend upon operating conditions and type of catalyst recovery equipment used. Consequently use of emission factors does not give a true picture of these losses.

5.5.1 Lesser sources include asphalt air blowing operations, fired heaters and boilers, sludge burners and emergency flare. Asphalt air blowing operations give rise to blowing losses which are dependent upon blowing temperatures. However, the off-gas is generally water scrubbed to recover the entrained oil droplets. The net loss therefore is of the order of 0.1 to 0.2

percent of the blowing charge. Reliable emission factors for blowing operations are not available, and the figures given above may be used for an approximate determination.

5.5.2 Particulates from combustion operations include smoke, cenospheres and ash. Smoke results from formation of sub-micron particles in local fuel-rich zones in the flame by cracking and polymerization of vapourized fuel. Most of the smoke particles burn out in the flame provided sufficient excess air is available for combustion. Very small amount of smoke in the flue gas is also visible. A dense black cloud of smoke leaving a furnace stack contains as little as 0.1 to 0.2 percent by mass of smoke particles. Atomization, air to fuel ratio and mixing are of primary importance in smoke formation. In refineries, since no solid fuel is used, smoke formation occurs only during start-ups, shutdowns, emergencies or during soot blowing operations.

5.5.3 Emission of cenospheres is related to the asphaltene content of the fuel. These burn slowly and hence longer residence time and high excess air reduce their formation. Larger combustion units, therefore, produce less cenospheres, as also lighter fuels.

5.5.4 Ash is the non-combustible residue remaining after combustion of the carbonaceous matter from cenospheres. Ash consists essentially of metallic constituents like vanadium, with small amounts of sodium, potassium, nickel and other trace metals. Ash concentrates only in heavier residual fuels, and even in these the amount is very low, usually of the order of 0.04 to 0.1 percent by mass. Lighter fuels like distillates, naphtha and gas have practically no ash.

5.5.5 Emissions of ash may be estimated by analysis of the fuel burnt. Cenospheres and smoke on the other hand may be determined by actual stack sampling of furnaces and boilers, except in the case of open sludge burners and flares. However, the total particulate emission from these sources is small when proper combustion control is exercised. Generally use of emission factors should suffice for estimating these emissions.

5.6 Carbon Monoxide —The only significant source is the catalytic cracking unit regenerator when CO boilers are not employed. No emissions of carbon monoxide are released when CO boilers are used. Where CO boilers do not exist the emissions can be accurately calculated based on stack gas analysis of carbon monoxide content and the quantity of air used for regeneration, which is measured and controlled. Emission factors do not give a reliable estimate, since carbon monoxide formation is largely controlled by operating conditions.

5.7 Aldehydes and Ammonia — Small amounts of aldehydes and ammonia are released from combustion in furnaces and boilers and catalytic cracking regenerators. These may be determined by actual stack sampling or by use of emission factors. Since the quantities are small, and not controllable, stack monitoring normally does not serve any purpose.

6 POLLUTION CONTROL TECHNIQUES AND OPTIONS

6.1 Control of air pollution is an expensive and complex problem because the character and quantity of refinery atmospheric emissions vary greatly from refinery to refinery. Controlling factors include crude oil capacity, type of crude oil, complexity of processing employed, operating practices followed, and the degree of maintenance and good housekeeping procedures in force. However, refinery air pollution control techniques exist which should permit refineries to operate in any community without constituting a serious air pollution problem.

6.1.1 Many techniques have been developed and used over many years and considerable experience has been gained in their application. Many others, on the other hand, are still in the development stage and may not as yet be available for general use. A specific technology selected to control a particular pollutant will often be effective in controlling other pollutants as well. However, this need not necessarily hold true in all cases. Additionally, particular technologies may also be effective or practical only for large installations or for new ones. Retrofitting in existing plants that have not left sufficient space for these processes is another problem that might preclude such installations. A realistic control strategy therefore requires the evaluation of the various factors involved.

6.1.2 These factors include the type and number of pollutants, the technical feasibility, size of the installation, cost benefits, commercial confidence and reliability, space availability and the possibility of creating other disposal problems.

6.1.3 The majority of refinery emissions occur during combustion for providing power and heat for processing operations. These include combustion of fuel in boilers for steam generation, combustion of fuel in process heaters, and combustion of carbon during regeneration of cracking catalysts. The combustion processes pose general problems such as the presence in the combustion gases of sulphur oxides and particulates which relate to the quantity of fuel burnt, and the production of nitrogen oxides and other minor pollutants. The control techniques and options available are discussed below from a general standpoint.

6.2 Control of Emissions from Refinery Process Gases — Nearly all refinery processes generate gases which generally contain hydrogen sulphide or other low molecular weight sulphur compounds. These gases are normally used as fuel in process heaters and boilers. Sulphur dioxide emissions therefore result if the sulphur compounds are not removed. The most common procedure for removal of hydrogen sulphide and light mercaptans involves scrubbing the gases with an absorption agent such as aqueous amine solution. The amine solution extracts the hydrogen sulphide, and is then regenerated by stripping hydrogen sulphide with heat and/or steam. The regenerated solution is reused for further absorption. The hydrogen sulphide recovered from this process can be converted to either sulphuric acid or elemental sulphur.

6.2.1 The use of this process however depends upon the quantity of gas and the sulphur content of the gas. Conversion of hydrogen sulphide to elemental sulphur also requires a certain minimum availability for the process to be viable.

6.3 Control of Emissions from Fuel Combustion — Combustion of fuel and residual fuel oils in particular can be a significant source of sulphur dioxide emissions from refineries. The major options available in this case are changing of fuel type or improving fuel oil quality.

6.3.1 Changing fuel type usually means switching to a cleaner type of fuel such as from residual oil to distillate, distillate to naphtha, and naphtha to gas. Cleaner fuel can also be obtained by switching from a high sulphur to a natural low sulphur fuel oil or crude. While the investment required for fuel switching may be comparatively lower relevant to other options, this often means competing for scarce supplies of the cleaner fuel with substantial cost debits. However, on a short term basis this may be the only viable alternative. Availability, applicability and cost are critical factors in employing this method.

6.3.2 Fuel quality can be improved by treatment of fuel to remove potentially polluting substances, prior to combustion. Hydrogen processing is a prime example of such an option. Technology for hydro desulphurization of both distillate and heavy residual fractions of crude is available. Hydro-treating reduces both sulphur and nitrogen but ratio of sulphur removal is higher. These processes, however, are extremely expensive, and are normally justifiable from product quality considerations rather than emission reduction.

6.3.3 Other major emissions from fuel combustion are oxides of nitrogen and particulates or smoke. Improved combustion techniques can substantially reduce both the formation of nitrogen oxides as well as emissions of smoke, carbon monoxide, hydrocarbons and acid smut. Proper burner maintenance, good atomization of liquid fuels, optimum excess air levels, and correct stack temperatures are all important factors in reducing emissions. Recently developed techniques include staged combustion, fuel gas recirculation, water and steam injection, and fluidized bed combustion. Considerable work has been done on all these, and it appears that staged combustion may be applicable to refinery furnaces and boilers in the near future. The rest, however, have been investigated mostly for large utility boilers. Hence, further research is needed before these can be commercially adopted. Moreover, the emissions of nitrogen oxides particularly are relatively small, and hence use of these new techniques may not be justifiable at this stage. Currently, for the control of NOX emissions, Low / Ultra NOX burners are being used in the industry to control air and fuel mixing at each burner, and thus reduce NOX emissions.

6.3.4 The possible sources of smoke in refinery operations may be classified into three categories, process furnaces and boilers, vent gas flares, and incinerators. Furnaces and heaters normally do not release any undesirable levels of smoke. Where gas is used

as a fuel, no smoke results. Whenever liquid fuels, such as residual fuel oils are burnt, adequate and relatively inexpensive equipment is available to prevent smoke with good operating practices and maintenance. Proper burner design for the specific fuel type, good atomization and air-fuel mixing are important factors to prevent smoke formation with all fuels.

6.3.5 Vent gas flares, on the other hand, may be a major source of smoke. Flares are necessary as a safety measure to handle unexpected losses of vapour. These are released from process units in emergencies caused by compressor failures, excessive pressure in the units, line breaks or leaks, power failures and fires. Since large surges of gas cannot be vented to furnaces or other enclosed burning equipment, flares are usually designed to safely dispose off these gases. Smoke from these flares results from an inadequate supply of air in the combustion zone. Several techniques have been developed that virtually eliminate smoke. The most widely used is injection of large quantities of steam into the combustion zone with uniquely designed flare tips. Another method uses a venturi scrubbing section at the bottom of the stack followed by reheating of the stack gas. However, occasions when large quantities of gases are released to the flare are very rare, since they result only from emergencies. Under normal operating conditions, most refinery flares are practically non-existent except for the burning of the pilot, and these do not produce any smoke.

6.3.6 Where fuel desulphurization or change of fuel is not possible, waste gas treatment is another way of emission reduction for both gaseous and particulate emissions. Electrostatic precipitators have been successfully used for dust removal. However, for sulphur dioxide and nitrogen oxides emission control, progress in developing suitable processes for fuel gas treatment has been rather slow because of the magnitude and complexity of the problem. For example, removal of sulphur dioxide from flue gases by scrubbing has been successfully operated, abroad, in large power plants for a number of years. The flue gases are washed with very large volumes of water to which a little lime or chalk is added. However, these processes are not very popular on account of the cold wet fumes of washed gases that descend on the neighbourhood, where they may cause worse pollution than if the fuel gas had not been washed and had dispersed naturally.

6.3.7 The technical and economic feasibility of most processes is closely related to plant size. Consequently, their major usage has been in large power plants. Such treatments have not been tried on the smaller refinery furnaces and boilers. The most promising processes under investigation include lime-dolomite injection, catalytic oxidation and alkali-alumina absorption. Potassium sulphite scrubbing system is also receiving some attention. However, problems still exist in establishing commercial viability and confidence. Byproduct disposal also creates serious problems for some locations. Consequently, the use of flue gas treatment as an option for abatement of refinery emissions has not found much favour and may not be practicable.

6.4 Control of Emissions from Catalyst Regeneration — Catalytic cracking unit regenerators are a major potential source of particulate matter emissions and also small amounts of sulphur oxides and oxides of nitrogen, as well as some aldehydes and ammonia. Of these, the last three do not lend themselves to any control as of today. Particulate matter, however, has always lent itself to control more from the standpoint of the economic recovery of the catalyst. The Particulate matter emissions from Catalyst regenerators are being controlled by use of Electro Static Precipitators / by Wet Scrubbing technology.

6.4.1 Normally two-stage conventional cyclones are located within the regenerator vessel for catalyst recovery. Additionally, a third external cyclone stage or an electrostatic precipitator, may be used before discharge of the flue gas to the atmosphere. As regard hydrocarbon emissions from catalytic cracking regenerators, the amount is generally small. Moreover, these hydrocarbons are completely consumed where cracking units are equipped with CO boilers.

6.5 Control of Carbon Monoxide Emissions — The only significant source of carbon monoxide emissions in petroleum refineries is the catalytic cracking regenerator. Concentration of carbon monoxide in the regenerator flue gases may be in the range of six to ten percent. These flue gases are generally released high in the air and at high temperatures, and result in very low ground level concentrations.

6.5.1 Carbon monoxide emissions from catalytic cracking units may be eliminated by incinerating the gases in waste heat CO boilers at temperatures from 1 100 K to 1 400 K. The heat of combustion of carbon monoxide and other combustibles, and

the sensible heat of the regenerator gases, are recovered by generating steam or heating the oil charged to the cracking unit. Carbon monoxide is completely oxidized to carbon dioxide. In addition, traces of aldehydes, hydrocarbons and cyanides are also destroyed. While these can be installed easily on new plants, retro fitting in existing units may present problems of location and availability of space.

6.5.2 A more recent development in this respect is high temperature regeneration using molecular sieve zeolite catalysts. This eliminates carbon monoxide and may be adapted to existing plants.

6.6 Control of Emissions in Storage — Hydrocarbons are the products of a refinery and hence there is an obvious economic incentive to prevent their loss to the atmosphere. Many air pollution control measures are therefore necessarily employed as accepted good practice. Hydrocarbon emissions in quantities normally released in refinery operations are invisible and non-toxic. Hydrocarbon vapour losses are the principal contaminants. In addition, objectionable odours may be caused by emissions of sulphur or nitrogen compounds. All these are associated with the movement and storage of oil and gas. However, the control methods developed, and in general use, are capable of sufficiently reducing or eliminating their emissions into the atmosphere. Refer GSR 186 (E), C. Fugitive Emissions for Control of Emissions in Storage which are the guidelines for control of Fugitive emissions from Tanks, Wastewater collection and Treatment.

6.6.1 Emissions from storage vessels are generally caused by evaporation of liquids or liquefied gases. The control of emissions from oil and gas storage facilities serves three purposes, namely reduction or elimination of air contaminant emissions, reduction or elimination of fire hazards, and the recovery of valuable products. This reduction is normally achieved by the use of floating roof or pressure storage for light hydrocarbons.

6.7 Control of Emissions by Dispersion — Another means of abatement of pollution is by dispersion of excess pollutants by use of taller stacks. This technique is of practical utility and has been successfully used in controlling ground level concentrations. It is the simplest and often the most economic. Tall stacks, however, may be a hazard to aircraft or entirely inadequate for certain local topographical and meteorological conditions. Further, since tall stacks do not eliminate but only disperse the pollutants, if the natural scavenging processes are not completely effective, they may contribute to regional pollution problems. They may also transfer the problem from one locality to another. Standard dispersion models may be used for calculating stack heights required (*see IS 8829**).

6.7.1 Additionally, the major methods used to further reduce emission of vapours and odours are as follows:

a) *Variable vapour space system* — As the storage tanks are filled or emptied out, or when the temperature changes, vapours from one or more storage tanks are displaced into or out of a special tank provided to hold these vapours. Excess vapours are piped into the fuel system or to a smokeless flare for incineration. Space availability and location of light hydrocarbon storage facilities are major factors affecting the feasibility of this control system.

b) *Vapour recovery systems* — These systems operate like variable vapour space systems, except that certain substances in the emissions are recovered. The excess vapours are compressed into an absorption unit for recovery of the condensable hydrocarbons. The non condensibles are either piped into a fuel system or a smokeless flare for incineration. The feasibility of this type of control is dependent on the proximity of a process unit.

c) *Materials and equipment* — Utilization of selective materials and equipment also assists in controlling emissions. For example, plastic balls have been proposed as a means of reducing evaporation losses in fixed roof tanks. These are spread as a layer floating on the top of the liquid surface. Use of proper paint for the tank shell and roof also influences the vapour and liquid temperatures. Breathing emissions may be reduced by as much as 25 percent by the use of aluminium paint rather than black paint and 25 percent by the use of white paint rather than aluminium paint. Emissions may also be reduced by using remote gauges and sampling device so as to eliminate the need to open tank gauge hatches for level reading and sampling. In the case of oil separators, installation of covers is also employed to reduce evaporation losses.

6.8 Sulphur Recovery — In many refineries sulphur removal from some refinery streams is a part of refining, from considerations of product quality rather than pollution abatement. These process units generate a potentially rich source for sulphur recovery units. Two important areas in this respect are hydrofining and amine extraction. Both these yield sour gases rich in hydrogen sulphide. Based on availability of hydrogen sulphide a sulphur plant may be an attractive way to reduce emissions as well as recover a useful product.

6.8.1 The classical method of sulphur recovery is the Claus process. The process is based on producing elemental sulphur, by first converting one-third of the hydrogen sulphide to sulphur dioxide and then using this to combine with the remaining hydrogen sulphide in the presence of a catalyst to form sulphur. Several types of catalysts have been used, but activated bauxite appears to be the most desirable from low cost, durability and activity considerations.

6.8.2 Plants with a single catalytic converter stage generally give efficiencies up to 85 percent. With two stages, efficiencies as high as 95 percent have been reported. A further 2 to 3 percent efficiency increase is possible by the addition of a third stage. Although this stage is not generally economically justifiable on recovery considerations, it would be desirable from its usefulness as a protective stage to maintain overall recovery.

6.8.3 An incinerator is normally provided to burn the residual gases prior to discharge to the atmosphere. Plant size is an important consideration in determining the viability of a sulphur recovery unit.

6.9 Increased Efficiency — By far the most important area of pollution reduction is in increased efficiency of energy utilization. Increased heat recovery and heat integration, particularly in older plants, helps reduce fuel consumption, thereby not only reducing pollution, but also manufacturing cost. Ideas such as addition of convection sections, air-preheating, flue gas steam generation, and improved burner designs, have been successfully utilized in process furnaces. Condensate recovery and low pressure flash steam saves both fuel and water in boilers. Conservation, therefore, helps to reduce pollution at source and avoids costly end cleanup processes. This should normally be the first area of attack in any pollution control programme, since it also helps conserve national resources.

7 OPERATING PRACTICES

7.1 Good operating practices and housekeeping are important not only from the standpoint of safe operations, but help improve the control of environmental pollution without any investment.

7.1.1 A regular and efficient preventive maintenance programme comes high on the list of good operating practices. On-stream inspection prevents emergencies and leaks. Similarly, proper sampling and loading procedures also aid in avoiding loss. Use of proper pump seals and glands minimize leakage from these sources.

7.1.2 A routine periodic check-up of safety valves prevents gas leakage to flare, as well as liquid blowdown, which ultimately increase flare losses. Similarly, floating roof tank seals should be regularly inspected for damage and leaks. Regular loss surveys can pinpoint sources of loss and leaks.

7.1.3 Proper furnace operation, burner cleaning, and adjustment of atomizing steam and excess air, are important in ensuring high efficiency of combustion, which will result in less fuel usage with consequent reduction in emissions. Optimum excess air utilization is important in minimizing nitrogen oxides emissions. High excess air levels are quite common, although this can be easily controlled by regular check of flue gas for oxygen content. Simple portable analyzers are easily available for this purpose. Complete combustion and minimization of particulate matter can be effectively controlled by proper atomization of oil fired. Correct usage of atomizing steam and proper fuel temperature are essential for good atomization.

8 MEASUREMENT OF EMISSIONS

8.1 An accurate knowledge of emissions from various sources is essential to assess the effect of emissions on air quality. This knowledge may be obtained either by calculations or by actual measurement. Of the refinery emissions, sulphur dioxide is perhaps the only one that lends itself to determination by calculation. Since oxides of sulphur are generated primarily from combustion of fuels, and since fuels are accurately measured both for quality and quantity by the refineries, the emissions of sulphur dioxide can therefore be easily calculated. Refinery emissions such as particulates and oxides of nitrogen cannot be calculated since their formation depends upon several parameters. For a correct estimate of these emissions, actual measurement has to be resorted to. In the case of hydrocarbon emissions from evaporation sources, these emissions are not measurable. The emissions of hydrocarbons may be calculated by indirect means from an estimation of losses from storage tanks by empirical formulae discussed earlier. In the case of losses from leaks, loading operations and other similar sources, the emissions can only be estimated by conducting regular loss surveys, and then calculating the evaporation losses from these sources.

8.1.1 Sampling to determine particulate emissions, on the other hand, is considerably more complicated than sampling for gaseous pollutants, particularly if any of the particulates are larger than one micron. In the first place, even if the particulates are evenly distributed in the gas at one point, they may become maldistributed, due to settling or centrifugal force, when the gas goes around a bend. It is, therefore, almost, always necessary to sample at a number of points over the cross-section of the duct to get an accurate sample. Secondly, each sample should also be taken isokinetically to have the proper loading of particulates per unit volume of gas. This means that the gas velocity in the sample probe should be exactly the same as the gas velocity in the duct at the sample point.

8.1.2 The samples may be analysed, to determine the concentration of pollutants, by a variety of methods. To ensure that standardized procedures are followed, relevant Indian Standards Methods of test should be used for analysis.

8.1.3 Properly designed and conditioned sample probes should also be employed to ensure that the correct sample is obtained without condensation of certain pollutants in the sampling line. These probes should also be standardized, and the appropriate Indian Standards should be followed.

9 MONITORING OF EMISSIONS

9.1 Monitoring of emissions, as well as ambient air quality, are necessary to ensure that quality criteria and emission limits are met as per the norms notified in GSR 186 (E) dated 18.03.2008 by Ministry of Environment Forest and Climate Change for both source and fugitive emissions and National Ambient Air Quality Standards notified under E(P) Rules for ambient air quality. Monitoring of ambient air quality is necessary in all cases, since this directly affects the health of the people in the vicinity of the plant, as well as in the surrounding neighbourhood. Before deciding on air quality monitoring it is necessary to have an idea of all the parameters that need to be measured, and the frequency of measurement. In terms of effects of pollutant on human beings, the major factor of importance is the concentration of a particular pollutant over a given period of time. Three periods are important in ambient air quality measurement; the 1 to 3 hourly maximum concentration, the 24 hour average concentration, and the annual mean, are necessary to decide upon the dose-response relationships. Where operations fluctuate considerably from time to time, continuous recorders may be required. However, most refinery operations are stable and steady operations, and the variations in emissions are relatively small. Consequently, it is adequate to measure the emissions over two hour periods and obtain the necessary hourly, daily and annual averages.

9.2 Several factors need to be taken into account in deciding upon continuous versus manual monitoring. Continuous instruments have to be imported, as against local availability of instruments required for manual purpose. The manual instruments are relatively cheap as compared to the more sophisticated continuous instruments. The accuracy of both, however, is adequate for the type of information required. The maintenance requirements, the type of manpower required, and the availability of such manpower, is much more difficult in the case of continuous instruments. In the case of emissions from various sources of refining operations, individual stack monitoring may be required in

certain cases only. Individual stack monitors are not of much use in oil or gas fired boilers and furnaces, since fuel is the main contributor, particularly towards sulphur dioxide emissions, and no control is possible once fuel sulphur is fixed. The emissions of particulates and oxides of nitrogen from stationary combustion sources are generally relatively very small. Hence, spot sampling for measurement for these pollutants should be adequate. Furthermore, individual stack monitors are of use only where control steps can be taken to reduce emissions. Furthermore, most emergencies in refineries cannot be tolerated except for short periods of time, and ultimately lead to a shutdown of the plant.

10 EMISSION FACTORS

10.1 The list of emission factors given in Table 6 has been provided to enable estimation of emissions from refinery processes, where more detailed calculation or measurement is not possible. These factors should be used with caution and reference should be made to the text prior to usage. Where possible, actual determination by direct measurement or from fuel analysis should be resorted to.

TABLE 6 EMISSION FACTORS FOR PETROLEUM REFINERIES

(Clause 10)

SL No.	PROOESSING UNIT	PARTI-UNIT	SULPHUR OXIDES (SO ₂)	CARBON MONO-OXIDE	HYDRO-CARBON S	NITROGEN OXIDES (NO _x)	ALDE-HYDES	AMMONIA
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
i)	Small furnaces and boilers (less than 1 x 10 ¹⁰ J/h)							
	Residual fuel —g/l oil burned	2.75	19.98SD	N	0.35	4.8	0.071	N
	Distillate fuel —g/l oil burned	1.0	19.98 SD	N	0.35	4.8	0.071	N
	Gas fuel — g/m ³ gas burned	0.90	1 998 _s	N	0.128	1.9		N
ii)	Medium furnaces and boiler (1 x 10 ¹⁰ - 1 x 10 ¹¹ J/h)							
	Residual fuel - g/l oil burned	2.4	19.98SD	N	0.35	6.6	0 071	N
	Distillate fuel - g/l oil burned	1.8	19.98 SD	N	0.35	6.6	0.071	N
	Gas fuel - g/ma gas burned	0.29	1 998 _s	N	0.048	2.8	0.048	N
iii)	Large furnaces and boilers (more than 1 x 10 ¹¹ J/h)							

	Residual fuel - g/l oil burned	1.2	19.98SD	N	0.25	8.3	0.017	N
	Distillate fuel - g/l oil burned	1.8	19.98SD	N	0.25	8.3	0.071	N
	Gas fuel - g/ma gas burned	0.29	1 998s	N	0.016	3.7	0.048	N
iv)	Fluid catalytic cracking units							
	Uncontrolled - g/l fresh feed	0.695	1.413	39.2	0.63	0.012	0.054	0.155
	ESP and CO boiler - g/l fresh feed	0.120	1.413	N	0.63	0.012	0.054	0.155
v)	Moving-bed catalytic cracking units g/l fresh feed	0.049	0.171	10.8	0.25	0.014	0.04	0.017
vi)	Fluid coking units							
	Uncontrolled - g/l fresh feed	1.50	—	N	N	N	N	N
	ESP - g/l fresh feed	0.019 6	—	N	N	N	N	N
vii)	Compressor internal combustion en-gines							
	g/ma ³ gas burned	N	1 998 ₃	N	19.3	14.4	1.61	3.2
viii)	Blowdown systems — g/l refinery							
	capacity (without control)	N	N	N	0 860	N	N	N
	— g/l refinery capacity (with control	N	N	N	0.014	N	N	N
ix)	Flare system — g/l refinery capacity	N	N	N	0.014	N	N	N
x)	Vacuum jets — g/l Vacuum distillate	N	N	N	0.37	N	N	N
xi)	Cooling towers — g/m ³ cooling water	N	N	N	0.72	N	N	N
xii)	Pipeline valves and flanges — g/l refining capacity	N	N	N	0.080	N	N	N

xiii)	Pump seals — g/l refining capacity	N	N	N	0.049	N	N	N
xiv)	Miscellaneous — (air blowing, sampling, etc) — g/l refining capacity	N	N	N	0.043	N	N	N
xv)	Process drains, g/l waste water (with control)	—	—	—	0.023	—	—	—
	g/l waste water (with control)	—	—	—	0.600	—	—	—
xvi)	Vessel relief valves, g/l refinery capacity	—	—	—	0.031	—	—	—
xvii)	Compressor seals, g/l refinery capacity	—	—	—	0.014	—	—	—

NOTES —

S = sulphur content percent by mass,

D = density in kg/litre,

s = sulphur content in kg/m³,

N = negligible, and

ESP = electrostatic precipitator.