

CHAPTER 4

CONTROL OF GASEOUS POLLUTANTS

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$$1 \text{ metric ton} = 10^3 \text{ Kg} = 10^6 \text{ g}$$

$$1 \text{ MT} = 10^{12} \text{ g} = 1 \text{ Tg}$$

$$(\text{MT} \equiv \text{Tg})$$

$$\text{M mega} \quad 10^6$$

$$\text{G giga} \quad 10^9$$

$$\text{T tera} \quad 10^{12}$$

CHAPTER 4

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CHAPTER 4

CONTROL OF GASEOUS POLLUTANTS

4.1 INTRODUCTION

Air pollutants include gaseous and particulate matter presented in the air. The general classification of air pollutants is as follows:

- Particulate
- Sulphur containing compounds
- Nitrogen containing compounds
- Organic compounds
- Carbon monoxide
- Halogen compounds.

Table 1 shows the typical gaseous pollutants and their sources. Air pollutants can also be grouped into two classes; primary and secondary pollutants. Primary pollutants are those emitted directly from sources. Secondary pollutants are often formed in the atmosphere by chemical reactions among primary pollutants and chemical species found in the atmosphere.

Normally the clean dry atmospheric air has certain chemical composition. Table 2 lists the important atmospheric gaseous and their concentration. Any other gases or an increase in the concentration of the listed gases is considered pollution specially

Table 2. Chemical Composition of Dry Atmospheric Air.

Substance	Volume (percent)	Concentration (PPM)
Nitrogen	78.084±0.004	780,900
Oxygen	20.946±0.002	209,400
Argon	0.934±0.001	9,300
Carbon dioxide	0.033±0.001	315
Neon		18
Helium		5.2
Methane		1.2
Krypton		0.5
Hydrogen		0.5
Henon		0.08
Nitrogen dioxide		0.02
Ozone		0.01-0.04

Table 1. Typical gaseous pollutants and their sources.

Key element	Pollutant	Source
S	SO ₂	Boiler flue gas
	SO ₃	Sulfuric acid manufacturing
	H ₂ SO ₄ vapors	Sulfuric acid manufacturing, pickling operations
	H ₂ S	Natural gas processing, pulp and paper mills, sewage treatment
	R-SH (mercaptans)	Petroleum refining, pulp and paper mills
N	NO, NO ₂	Nitric acid manufacturing, boiler flue gas
	HNO ₃ vapors	Nitric acid manufacturing, pickling operations
	NH ₃	Ammonia manufacturing
	Other N compounds (i.e. amines, pyridines)	Sewage, rendering, solvent processes
C	Inorganic CO	Incomplete combustion
	Organics: Volatile Organic Compounds Hydrocarbons Paraffins Olefins Aromatics Oxygenated hydrocarbons Aldehydes Ketones Alcohols Phenols Chlorinated solvents	Solvent uses, gasoline marketing, petrochemical plants Surface coating operations, petroleum processing, plastics manufacturing Dry cleaning, degreasing
Halogen F	HF	Phosphate fertilizer plant, aluminum plant
	SiF ₄	Ceramics, fertilizer plant
Cl	HCl	HCl manufacturing, PVC combustion
	Cl ₂	Chlorine manufacturing

if their presence results in damage to human beings, plants, animals or materials. Environmental agencies mostly concerned about the limit of increase of these pollutants in the atmosphere. Table 3 shows the US Federal ambient air quality standards. These ambient standards are different from source emission limits, where certain rate of pollutants are allowed to be emitted from certain industry. The ambient air quality standards are often obtained by studying the expected harmful of each pollutant taking care with its rate of production, accumulation and disappearance.

Table 3. Ambient Air Quality Standards.

Pollutant	Averaging Time	Primary Standard
Carbon monoxide	8 hr	10 mg/m ³ (9 ppm)
	1 hr	40 mg/m ³ (35 ppm)
Nitrogen dioxide	Annual average	100 µg/m ³ (0.05 ppm)
Sulfur dioxide	Annual average	80 µg/m ³ (0.03 ppm)
	24 hr	365 µg/m ³ (0.14 ppm)
	3 hr	
Suspended particulate matter	Annual geometric mean	75 µg/m ³
	24 hr	260 µg/m ³
Hydrocarbons (corrected for methane)	3 hr (6-9 a.m.)	160 µg/m ³ (0.24 ppm)
Ozone	1 hr	240 µg/m ³ (0.12 ppm)
Lead	3 months	1.5 µg/m ³

The control of gaseous pollutants is not necessarily accomplished by adding a control-equipment to the industry, it may be achieved by changing fuel sources, modifying or changing raw material or using alternative production procedures. Figure 1 illustrates the air pollution control system. Three points in the system are amenable to control action. These are control of emission source, atmospheric control and receptor-based control.

The control techniques often used to reduce the emission of gaseous pollutants are absorption, adsorption and condensation. Conversion methods, thermal or catalytic, are also one of the control processes. In the following presentation, the conversion processes, absorption, adsorption and condensation will be discussed. Control of sulphur dioxide and nitrogen oxides will be given more attention. These gases are considered the most important industrial pollutants. We will begin our discussion by presenting the principles of gases and the fundamental laws governed the atmospheric constituents.

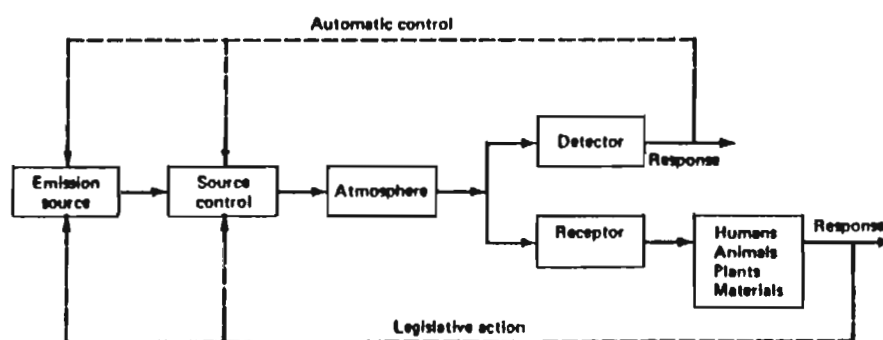


Fig. 4.1. Air Pollution Control System.

4.2 FUNDAMENTAL LAWS OF GASES

Atmospheric concentration:

Two concentration units are often used. These are:

- $\mu\text{g}/\text{m}^3$ (micro-gram/cubic meters)
- ppm (parts-per-millions)

At an atmospheric pressure and 25°C , the relation between ppm and $\mu\text{g}/\text{m}^3$ is found from

$$\frac{m_i}{V_a} = \frac{\rho_i V_i}{V_a} \frac{P M_i}{\rho_i R T} = \frac{V_i}{V_a} \frac{P M_i}{R T}$$

$$\frac{m_i}{V_a} = \frac{V_i}{V_a} \frac{M_i}{24.5}$$

where

m_i, M_i are mass and molar mass of gaseous pollutant,

V_a is the volume of air at temperature, T and pressure, P .

ρ_i, V_i are the density and volume of the pollutant

R is the gas constant = 0.08208 at 1 atm and 298K.

Then multiplying the right side by 10^9 to convert the mass to microgram and dividing by 10^6 so V_i/V_a can be expressed in ppm, then the following relation is obtained

$$\mu\text{g}/\text{m}^3 = \frac{\text{ppm} \times M_i}{0.0245}$$

Gas Temperature:

The temperature of the gas is either given in Fahrenheit and Celsius scales or in an absolute value. The following relations related these scales:

$$\begin{aligned} ^\circ\text{F} &= 1.8^\circ\text{C} + 32 \\ ^\circ\text{C} &= (^\circ\text{F} - 32)/1.8 \\ ^\circ\text{R} &= ^\circ\text{F} + 459.67 \\ \text{K} &= ^\circ\text{C} + 273.16 \end{aligned}$$

where

$$\begin{aligned} ^\circ\text{F} &= \text{degrees Fahrenheit (scale of } 32 - 212) \\ ^\circ\text{C} &= \text{degrees Celsius or centigrade (scale of } 0 - 100) \end{aligned}$$

°R = degrees Rankine
K = degrees kelvin

The absolute temperature is raised from the experimental finding of perfect gases under constant pressure. It has been found that below 32°F (0°C) the volume of gas changes 1/491.67 (1/273.16). So the volume of gas would be theoretically become zero at 491.67°F below 32°F (273.16 °C below 0°C). If $\Delta^\circ\text{F}$ and $\Delta^\circ\text{R}$ represent the temperature difference in Fahrenheit and Rankine scale and $\Delta^\circ\text{C}$ and ΔK be in the analogous scales, then

$$\begin{aligned}\Delta^\circ\text{F} &= \Delta^\circ\text{R} \\ \Delta^\circ\text{C} &= \Delta\text{K} \\ \Delta^\circ\text{C} &= 1.8 \Delta^\circ\text{F} \\ \Delta\text{K} &= 1.8 \Delta^\circ\text{R}\end{aligned}$$

Gas Pressure:

Pressure is defined as the force per unit area. It often given in the following units

- Pascal, Pa = Newton/m² (1 atm = 101.3 kPa)
- bar = 10⁶ dyn/cm² = 100 kN/m² (1 atm = 1.013 bar)
- pounds/in², psi (1 atm = 14.70 psi)
- millimeters of mercury, mmHg (1 atm = 760 mmHg)
- Feet of water, ft H₂O (1 atm = 33.91 ft H₂O)
- Kilograms (force)/cm², Kg/cm² (1 atm = 1.033 Kg/cm²)

Barometric pressure and atmospheric pressure are equivalent. They represent the atmospheric pressure at sea level, 45° north latitude at 35°F (1.7°C). Pressure measured in any closed system is often referred to as gauge pressure. Absolute pressure is then equal to the sum of the barometric (atmospheric) pressure and the gauge pressure.

Gas Density:

Density is defined as a mass per unit volume.

$$\rho = \frac{m}{V}$$

where, ρ = density, Kg/m³
m = mass, Kg
V = volume, m³

Gas density is function of temperature and pressure. Density of air at 101.3 kPa (760 mmHg) and 25°C is 1.184 mg/cm³ (0.0739 lb/ft³).

Gas density can be given by $\rho = \frac{PM}{RT}$

Where P is pressure
M is molecular weight
R is gas constant
T is gas temperature.

Gas Viscosity:

Viscosity represents the fluid resistance to flow. It has its lowest values for gases. It is related to the shear stress, τ , and the velocity gradient, dv/dy , by the following relation

$$\tau = \mu \frac{dv}{dy}$$

The variation of the gas viscosity with pressure is often negligible. Temperature dependency of the viscosity is found from

$$\frac{\mu}{\mu_0} = \left(\frac{T}{273.16}\right)^n$$

where μ is the viscosity at temperature T
 μ_0 is the viscosity at 273.16 K.
n is an empirical constant (n = 0.768 for air)

Viscosity is expressed in centipoise, Cp, which equals to 0.01 g/cm³ (6.72 × 10⁻⁴ lb/fts). Also 1 Cp equals 1 mPas. The ratio of absolute viscosity to the density is called kinematic viscosity, ν . It has a unit of cm²/s. in Cgs system.

The viscosity of air at atmospheric pressure and at 0°C and 20°C are 0.01716 Cp (0.1327 cm²/s) and 0.01813 Cp (0.1505 cm²/s) respectively. The corresponding values of water are 1.787 Cp (0.01787 cm²/sec) and 1.0019 Cp (0.010037).

The Gas Laws:

Boyle's law $P \propto \frac{1}{V}$ or $PV = \text{constant}$

Charle's law $V \propto T$ or $\frac{V}{T} = \text{constant}$

Combined law $\frac{PV}{T} = \text{constant}$

Avogadro's theory, at the same temperature and pressure:
(equal volumes of gases contain equal number of molecules, 6.03×10^{23})

Ideal Gas Law $PV = nRT$

$$n = \frac{m}{M} = \frac{V}{V_m}$$

where

- m, V mass and volume of a gas
- M molecular weight
- V_m is the molar volume

Molar volume is the volume of one mole of a gas. One mole of a gas contain Avogadro numbers of molecules. The molar volume of any gas is constant. It is given in the following table according to the used system.

System	T	P	V_m
SI	273.16K	101.3 kPa	22.41 m ³ /Kg mol
Universal Scientific	0°C	760 mmHg	22.41 L/g mol
Natural Gas Industry	60°F	14.7 psi	379.4 ft ³ /lb mol
	(15°C)	(101.3 kPa)	
American Engineering	32°F	1 atm	359 ft ³ /lb mol

Common values of the gas constant, R, are shown below:

Values of gas constant, R:

- 8.314 m³.Pa/mol K
- 0.08314 L.bar/mol K
- 0.08206 L.atm/mol K
- 62.36 L.mmHg/mol K
- 0.7302 ft³.atm/lb mol °R
- 10.73 ft³.psia/lb mol °R
- 8.314 J/mol K
- 1.987 Cal/mol K
- 1.987 Btu/lb mol °R

Dalton's Law of Partial Pressure:

$$P = \sum p_i$$

$$p_i = y_i P$$

- P is the total pressure
- p_i is the partial pressure
- y_i is the mole fraction

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Raoult's Law (Gas-Liquid Eqm):

$$p_i = x_i P_i$$

p_i = partial pressure
 x_i = mole fraction in solution
 P_i = vapour pressure

Henry's law (dilute solution):

$$p_i = H_i x_i$$

H = Henry's law constant

Graham's Law of Effusion:

$$\text{rate} \propto \frac{1}{\sqrt{\rho}} \quad \text{but} \quad \text{rate} \propto \frac{1}{t}$$

$$\frac{t_1}{t_2} = \sqrt{\frac{\rho_1}{\rho_2}} = \sqrt{\frac{M_1}{M_2}}$$

where

t is time required for a fixed volume to escape through a hole.
 ρ, M are density and molecular weight of the gas

4.3 CONVERSION METHODS

4.3.1 Thermal Processes

In these processes pollutants are oxidized to another unpollutant form by direct flame incineration. Almost all highly odorous pollutants, such as mercaptans, cyanide gases and hydrogen sulphite are combustible. Their concentrations in the flue gas are significantly reduced by incineration. Stringent air pollution regulations require an elimination of at least 90% of carbonaceous material according to the following formula

$$\frac{HC_{in} - [HC_{out} + (CO_{out} - CO_{in})]}{HC_{in}} > 0.90$$

Table 4 shows the major sources of hydrocarbons in the United State in 1980. Solvent industry and automobiles are the major source of hydrocarbons. Evidently, these sources are controlled by direct burning of exhaust gas to meet the ambient air quality standard.

Table 4. Major sources of hydro carbons.

Source	% Contribution
Solvent evaporation	45
Refuse disposal	2
Agriculture burning	7
Refineries	9
Gasoline marketing	5
Carbon black manuf.	2.5
Other stationary sources	5.5
Mobile sources	24
Total	100%

The advantages of thermal conversion processes are:

- 1- Complete destruction of all combustible pollutants.
- 2- Flexibility of adapting the incinerator to moderate changes in flow rate and concentration.
- 3- Its effectiveness is relatively insensitive to specific gaseous pollutants.
- 4- Absence of performance deterioration.
- 5- Possibility of economical waste heat recovery.

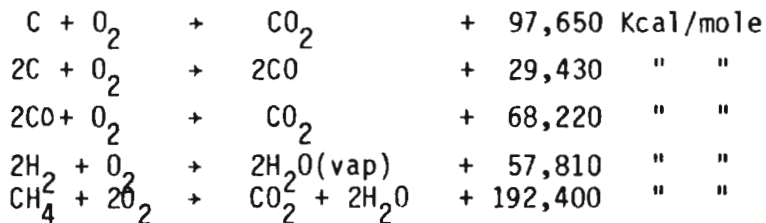
Thermal processes or incineration are basically a combustion process where air is used to oxidize the combustible pollutants. Combustion system is relatively simple devices. It consist of:

- Burners: to ignite the fuel and organic vapor
- Combustion chamber: to provide appropriate residence time for the oxidation process.
- Heat Recovery Section: to efficiently utilize the surplus amount of heat.

It is rather important to discuss in some detail the combustion basics before describing the thermal conversion processes. The following is some highlights on the combustion process.

Combustion Process:

Combustion is basically a fast chemical reaction involving the combination of oxygen with elements or compounds with a release of considerable amount of heat. It is often referred to as oxidation. Consider the following reactions:



In these reactions:

- 1- Mass must be conserved.
- 2- Number of moles or volumes may not be conserved.
- 3- A balanced chemical reaction is known as a stoichiometric reaction. In the stoichiometric reaction, molar proportions of the reactants are exactly as given by the stoichiometric coefficients, i.e. no excess of any is present.
- 4- These reactions can be represented in the following general form:



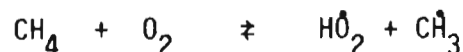
where

A and B are reactants

C and D are products

a, b, c and d are known as stoichiometric coefficients.

Combustion process looks simple but in reality it is not. The exact manner in which a reactant is oxidized does not occur exactly as given by the combustion reaction. Series of complex free radical chain reactions are involved. The following reactions represented a possible mechanism for methane oxidation, a more complex mechanism will result as the number of carbon atoms increases,





The detail combustion mechanism is not within our interest here. The most important issue is to achieve complete combustion of pollutants, the combustible materials. Complete combustion is effected by the following factors:

1- Temperature

Combustion is started at the ignition temperature. Heat must be added to the combustible material to raise its temperature to this limit. The ignition temperature depends on

- concentration of combustible materials
- inlet temperature
- rate of heat loss

Usually combustors are operated at higher temperature than the ignition temperature. The higher the temperature, the faster the combustion will proceed. Combustion of organic compounds occurs at 590 - 650°C (1100 - 1200°F). CO thermal conversion takes place at 700 - 820°C (1300 - 1500°F).

2- Time

Temperature of combustible materials must be raised within a period of time to allow ignition to start. The higher the temperature, the lower the time of contact. High residence time allows the use of lower temperature. This results in using a larger combustion chamber i.e. higher capital cost. Raising the operating temperature increases fuel usage i.e. additional operating cost. So the choice between higher temperature or longer residence time is basic on economic considerations.

3- Mixing

Proper mixing of combustible materials with air is required to achieve complete combustion. Unusually refractory baffles, swirl fired burners and baffle plate are used to increase the flow turbulence and improve the air-pollutants mixing. Carbon monoxide and unburned hydrocarbons are emitted by incomplete combustion. To achieve complete combustion, a sufficient supply of air (oxygen) must be present to convert all the carbon to carbon dioxide, CO_2 . This quantity is called stoichiometric or theoretical amount. The theoretical (stoichiometric) amount of air required is determined from the balanced chemical reaction describing the combustion (oxidation) reaction. Consider the reaction:



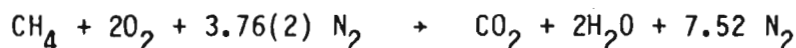
Knowing that, the molecular weight of carbon, hydrogen and oxygen are 12, 2, 16 respectively, the following information are obtained from the previous chemical reaction:

- 1- Every 16 Kg of methane reacts with 64 Kg of oxygen to form 44 Kg of carbon dioxide and 36 Kg of water.
- 2- Every 1 mole of methane reacts with 2 moles of oxygen to form 1 mole of carbon dioxide and 2 moles of water.
- 3- Every 1 volume of methane reacts with 2 volumes of oxygen to form 1 volume of carbon dioxide and 2 volumes of water.
- 4- Mass conservation must be fulfilled, i.e. 80 kg of reactants converted to 80 Kg of products.
- 5- Moles and volume may not be conserved. In the methane oxidation, 3 moles (volumes) of reactants produce 3 moles (volumes) of products. But this has not to correct all time. For example, in the reaction



3 moles (volumes) of reactants produce only 2 moles (volumes) of products. But 88 kg of reactants have been converted to exactly 88 kg of products.

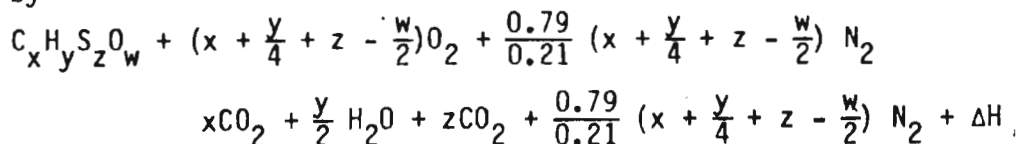
In industrial combustors, air is often used as the oxidizer. For simplicity, air can be considered as a mixture of 21% oxygen and 79% nitrogen on volume basis, i.e. one mole of oxygen is accompanied by $79/21 = 3.76$ moles of nitrogen. The oxidation of methane with air can be written as



Also the minimum amount of air required for complete combustion is known as theoretical air. In practice, it is difficult to achieve complete combustion with theoretical air. So excess air must be supplied to ensure complete combustion.

Calculations of Theoretical/Excess Air

Considered the generalized fuel with a chemical formula $\text{C}_x\text{H}_y\text{S}_z\text{O}_w$ where x,y,z and w represent the relative number of atoms of carbon, hydrogen, sulphur and oxygen respectively. The balanced chemical reaction of air oxidation of this fuel is given by



So for methane oxidation (with $x=1, y=4, z = w = 0$),
 the total air required = $2 + 7.53 = 9.53$ moles
 the total flue gases produced = $1 + 2 + 7.53 = 10.53$ moles i.e.

for every one mole (or standard ft³) of methane burned, 9.53 moles (or standard ft³) of air is required for complete combustion. Table 5 shows the stoichiometric amounts of O₂, N₂ and air required for complete combustion of some common chemicals. Also flue products are given in the table.

Normally, 50% excess air is used. The US EPA proposed the following expression for percentage excess air, %EA,

$$\%EA = \frac{\% O_2 - 0.5\% CO}{0.264\% N_2 - (\% O_2 - 0.5\% CO)} \times 100$$

It must be mentioned that not all mixtures of fuel and air are combustible. A mixture of combustible materials and air with certain concentration limits (flammability limits) is burning. These known as the upper explosive limit, UEL, and the lower explosive limits, LEL. UEL is defined as the concentration of fuel which produces a non-burning mixture due to a lack of oxygen. LEL is defined as the concentration of fuel below which combustion will not be self-sustaining. Table 5 also lists the flammability limits of some common chemicals.

As an example, methane has a flammability limits of 5% and 15% by volume. Any concentration of methane in air within these limits will support combustion, i.e. help in continued burning. Concentrations of methane below or above these limits will not burn and can quench the flame.

Flammability limits are not absolute. They are affected by temperature, pressure, combustor geometry and presence of other contaminants. The higher the temperature, the greater the activation energy of combustion and the easier flame to propagate. At high temperatures, 25% of LEL can propagate a flame.

Types of Flame:

Two different flame types are often recognized, namely yellow (luminous) flame and blue flame. The yellow flame results from thermal cracking of the fuel. Cracking occurs when hydrocarbons are intensely heated before they have a chance to combine with oxygen. The cracking release both hydrogen and carbon which diffuse to the flame to form CO₂ and H₂O. The carbon particles gives the flame the yellow appearance. Soot and black smoke formed due to incomplete combustion or flame temperature cooling.

Blue flame occurs when the fuel and air are well premixed before burning, so air-fuel mixture is gradually heated. Hydrocarbons are then slowly oxidized, going from aldehydes and ketones to CO₂ and H₂O. No cracking occurs and no carbon particles are formed. Incomplete combustion results in the formation of intermediates and partially oxidized compounds.

Table 5 Combustion constants and approximate limits of flammability of gases and vapors in air.

Substance	Lb/ft ³	Ft ³ /lb	Heat of combustion				For 100% total air (mol/mol of combustible) (ft ³ /ft ³ of combustible)						For 100% total air (lb/lb of combustible)						Flammability limits (% by volume)		
			(Btu/ft ³)		(Btu/lb)		Required for combustion			Flue products			Required for combustion			Flue products					
			Gross (high)	Net (low)	Gross (high)	Net (low)	O ₂	N ₂	Air	CO ₂	H ₂ O	N ₂	O ₂	N ₂	Air	CO ₂	H ₂ O	N ₂	Lower	Upper	
Carbon, C*	—	—	—	—	14,093	14,093	1.0	3.76	4.76	1.0	—	3.76	2.66	8.86	11.53	3.66	—	—	8.86	—	—
Hydrogen, H ₂	0.0053	187.723	325	275	61,100	51,623	0.5	1.88	2.38	—	1.0	1.88	7.94	26.41	34.34	—	8.94	—	26.41	4.00	74.20
Oxygen, O ₂	0.0846	11.819	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nitrogen (atm), N ₂	0.0744	13.443	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Carbon monoxide, CO	0.0740	13.506	322	322	4,347	4,347	0.5	1.88	2.38	1.0	—	1.88	0.57	1.90	2.47	1.57	—	—	1.90	12.50	74.20
Carbon dioxide, CO ₂	0.1170	8.548	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Paraffin series																					
Methane, CH ₄	0.0424	23.565	1013	913	23,879	21,520	2.0	7.53	9.53	1.0	2.0	7.53	3.99	13.28	17.27	2.74	2.25	2.25	13.28	5.00	15.00
Ethane, C ₂ H ₆	0.0803	12.455	1792	1641	22,320	20,432	3.5	13.18	16.68	2.0	3.0	13.18	5.73	12.39	16.12	2.93	1.80	1.80	12.39	3.00	12.50
Propane, C ₃ H ₈	0.1196	8.365	2590	2385	21,661	19,944	5.0	18.82	23.82	3.0	4.0	18.82	3.63	12.07	15.70	2.99	1.68	1.68	12.07	2.12	9.35
n-Butane, C ₄ H ₁₀	0.1582	6.321	3370	3113	21,308	19,680	6.5	24.47	30.97	4.0	5.0	24.47	3.58	11.91	15.49	3.05	1.55	1.55	11.91	1.86	8.41
Isobutane, C ₄ H ₁₀	0.1582	6.321	3363	3105	21,257	19,629	6.5	24.47	30.97	4.0	5.0	24.47	3.58	11.91	15.49	3.05	1.55	1.55	11.91	1.80	8.44
n-Pentane, C ₅ H ₁₂	0.1904	5.252	4016	3709	21,091	19,517	8.0	30.11	38.11	5.0	6.0	30.11	3.55	11.81	15.35	3.05	1.50	1.50	11.81	—	—
Isopentane, C ₅ H ₁₂	0.1904	5.252	4008	3716	21,052	19,478	8.0	30.11	38.11	5.0	6.0	30.11	3.55	11.81	15.35	3.05	1.50	1.50	11.81	—	—
Neopentane, C ₅ H ₁₂	0.1904	5.252	3993	3693	20,970	19,396	8.0	30.11	38.11	5.0	6.0	30.11	3.55	11.81	15.35	3.05	1.50	1.50	11.81	—	—
n-Hexane, C ₆ H ₁₄	0.2274	4.398	4762	4412	20,940	19,403	9.5	35.76	45.26	6.0	7.0	35.76	3.53	11.74	15.27	3.06	1.46	1.46	11.74	1.18	7.40
Olefin series																					
Ethylene, C ₂ H ₄	0.0746	13.412	1614	1513	21,644	20,295	3.0	11.29	14.29	2.0	2.0	11.29	3.42	11.39	14.81	3.14	1.29	1.29	11.39	2.75	28.60
Propylene, C ₃ H ₆	0.1110	9.007	2336	2186	21,041	19,691	4.5	16.94	21.44	3.0	3.0	16.94	3.42	11.39	14.81	3.14	1.29	1.29	11.39	2.00	11.10
n-Butene, C ₄ H ₈	0.1480	6.756	3084	2885	20,840	19,496	6.0	22.59	28.59	4.0	4.0	22.59	3.42	11.39	14.81	3.14	1.29	1.29	11.39	1.75	9.70
Isobutene, C ₄ H ₈	0.1480	6.756	3068	2869	20,750	19,382	6.0	22.59	28.59	4.0	4.0	22.59	3.42	11.39	14.81	3.14	1.29	1.29	11.39	—	—
n-Pentene, C ₅ H ₁₀	0.1852	5.400	3836	3586	20,712	19,363	7.5	28.23	35.73	5.0	5.0	28.23	3.42	11.39	14.81	3.14	1.29	1.29	11.39	—	—
Aromatic series																					
Benzene, C ₆ H ₆	0.2060	4.852	3751	3601	18,210	17,480	7.5	28.23	35.73	6.0	3.0	28.23	3.07	10.22	13.50	3.38	0.69	0.69	10.22	1.40	7.10
Toluene, C ₇ H ₈	0.2431	4.113	4484	4284	18,440	17,620	9.0	33.88	42.88	7.0	4.0	33.88	3.13	10.40	13.53	3.34	0.78	0.78	10.40	1.27	6.75
Xylene, C ₈ H ₁₀	0.2803	3.567	5250	4980	18,650	17,760	10.5	39.52	50.02	8.0	5.0	39.52	3.17	10.53	13.70	3.32	0.85	0.85	10.53	1.00	6.00
Miscellaneous gases																					
Acetylene, C ₂ H ₂	0.0697	14.344	1499	1448	21,500	20,776	2.5	9.41	11.91	2.0	1.0	9.41	3.07	10.22	13.50	3.38	0.69	0.69	10.22	—	—
Naphthalene, C ₁₀ H ₈	0.3384	2.955	5854	5654	17,298	16,708	12.0	45.17	57.17	10.0	4.0	45.17	3.00	9.97	12.96	3.43	0.56	0.56	9.97	—	—
Methyl alcohol, CH ₃ OH	0.0846	11.820	868	768	10,259	9,078	1.5	5.65	7.15	1.0	2.0	5.65	1.50	4.98	6.48	1.37	1.13	1.13	4.98	6.72	36.50
Ethyl alcohol, C ₂ H ₅ OH	0.1216	8.221	1600	1451	13,161	11,929	3.0	11.29	14.29	2.0	3.0	11.29	2.08	6.93	9.02	1.92	1.17	1.17	6.93	3.28	18.95
Ammonia, NH ₃	0.0456	21.914	441	365	9,668	8,001	0.75	2.82	3.57	—	1.5	3.32	1.41	4.69	6.10	—	1.59	1.59	5.51	15.50	27.00
Sulfur, S*	—	—	—	—	3,983	3,983	1.0	3.76	4.76	1.0	—	3.76	1.00	3.29	4.29	SO ₂	—	—	3.29	—	—
Hydrogen sulfide, H ₂ S	0.1733	5.770	647	596	7,100	6,545	1.5	5.65	7.15	1.0	1.0	5.65	1.41	4.69	6.10	1.88	0.53	0.53	4.69	4.50	45.50
Sulfur dioxide, SO ₂	0.0476	21.017	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Water vapor, H ₂ O	0.0766	13.063	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Air	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Gasoline	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.40	7.60

*Carbon and sulfur are considered as gases for molar calculations only.

Combustion Calculations:

First define the following energy quantities,

- Sensible heat, h_g ,
heat which when added or removed causes a change in temperature.
- Latent heat, λ
heat given off by a vapor condensing to liquid, or,
gained by a liquid to evaporate, without a change in temperature.
- Heat content or enthalpy, h
The total energy of a substance, the sum of latent heat and sensible heat minus that contained at an arbitrary set of conditions chosen as the basis or zero point.
- Gross heating value, h_{vg}
The total heat obtained from complete combustion of a fuel which is at 60°F when combustion starts, and combustion products which are cooled to 60°F before the quantity of heat released is measured. It is also called total or higher heating values.
- Net heating value, h_{v_n}
The gross heating value minus latent heat of vaporization of water (at 212°F equals 970.3 Btu/lb) formed by the combustion of the hydrogen in the fuel. For a fuel containing no hydrogen, the net and gross heating values are the same.
- Available heat, h_a
The gross heat minus the sensible heat carried away by the dry flue gases and minus the latent and sensible heat carried away in water vapor contained in the flue gases. The available heat represents the net quantity of heat remaining for useful heating. Figure 2 shows the available heat from the complete combustion of various fuels at various flue gas temperature.
- Specific heat, C_p
Specific heat is defined as the amount of heat required to raise 1 gm of a substance 1°C.

Now consider the incinerator shown in Figure 3. From the energy conservation law:

$$\text{Heat in} = \text{Heat out} + \text{Heat lost}$$

The heat content, H , can be found from

$$H = C_p(T - T_0)$$

where T is the fuel temperature and T_0 is a reference temperature chosen arbitrarily. In the gas industry, the reference tem-

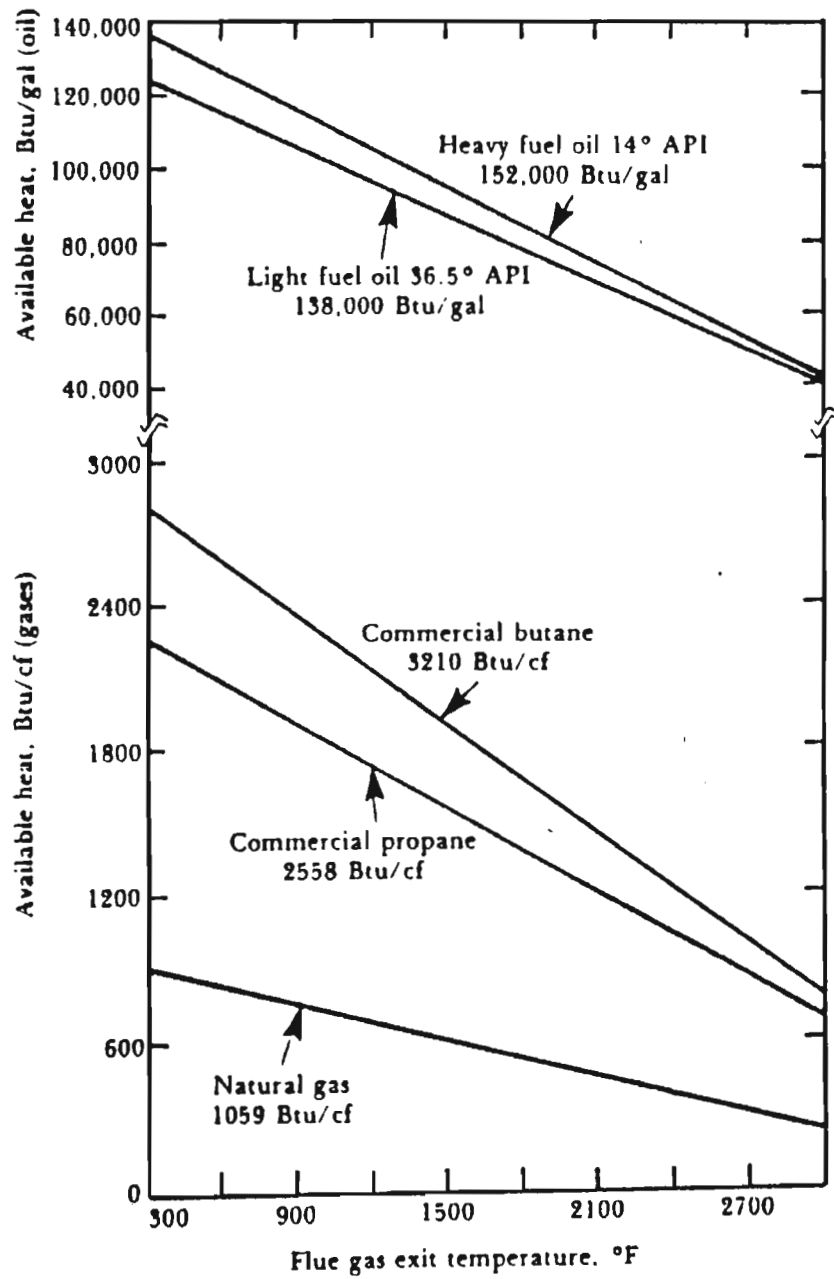


Fig. 4.2. Available Heat for Some Typical Fuels.

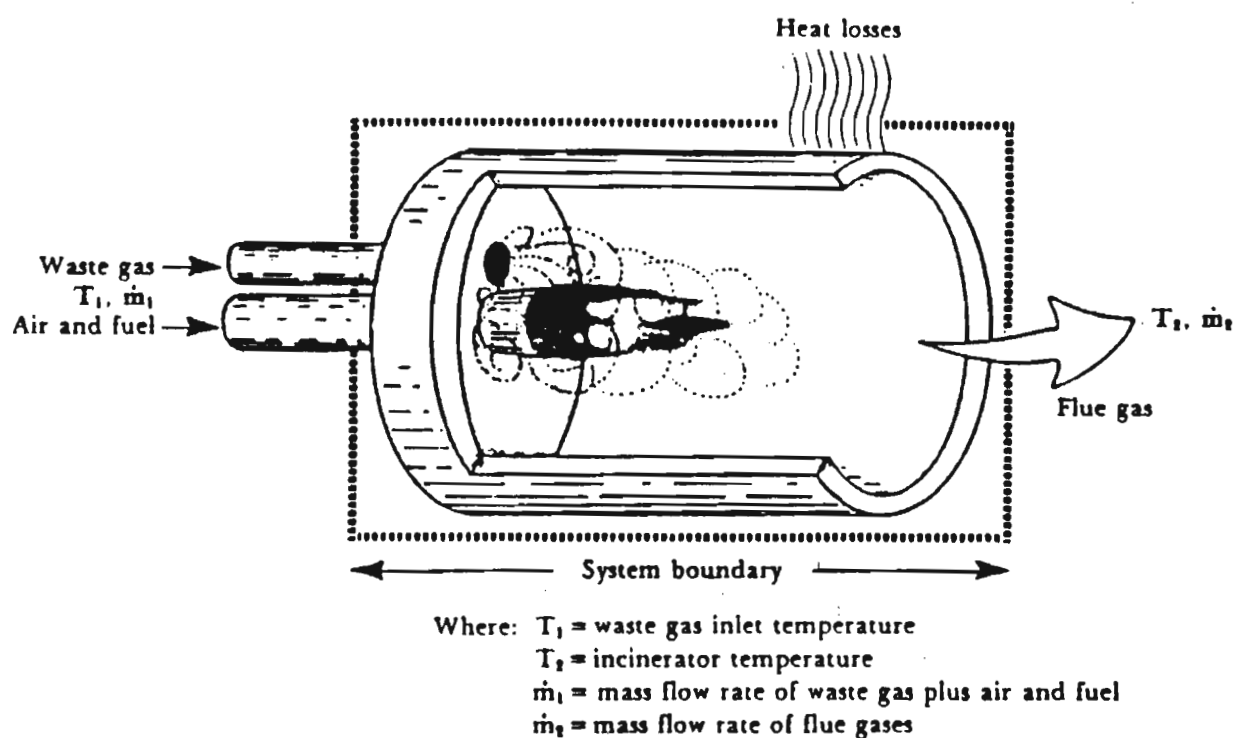


Fig. 4.3. Energy Balance in Thermal Incinerator.

perature is normally 16°C (60°F). So the change in the enthalpy across the incinerator is

$$\Delta H = [C_{p2}(T_2 - T_0) - C_{p1}(T_1 - T_0)]$$

If an average value of specific heat, $\overline{C_p}$ is known,

$$\Delta H = \overline{C_p} (T_2 - T_1)$$

This is a reasonable approximation, since for most incineration systems waste gases are considered to be essentially air. Average specific heat of air is 1088 J/Kg°R (0.26 Btu/lb°F).

Then the heat rate, q , can be found by multiplying ΔH by the mass flow rate, \dot{m}

$$q = \dot{m} \Delta H = \dot{m} \overline{C_p} (T_2 - T_1)$$

Heat lost is usually found as percentage of the heat rate. It often known by experience. If assuming no heat losses, the amount of fuel required can be obtained when knowing the available heat of the fuel, h_a , so

$$\text{amount of fuel needed, } Q_{\text{gas}} = \frac{q}{h_a}$$

Types of Incinerators:

In the thermal conversion of pollutants, two types of incinerator are often used. These are direct flame incinerator and thermal incinerator. Direct flame incinerator, as the name implies, is a method by which the waste gases are burned directly in a combustor, with or without the aid of additional fuel such as natural gas. Direct flame incineration is used only when combustibles in waste gas contribute a significant portion (more than 50%) of the total energy required for combustion.

The major disadvantage of direct flame incineration is the high flame temperature, about 2500°F. At these temperatures, nitrogen oxides may formed causing a pollution problem. An example of direct flame incineration is the flare.

Thermal incinerators are used when combustible pollutants is quite low. As a rule of thumb, a stoichiometric mixture of hydrocarbon and air has a heat of combustion of roughly 100 Btu/scf (3725 KJ/m³). A waste gas with a heating value of 85 - 90 Btu/scf (3150 - 3350 KJ/m³) can be burned directly without the

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auxiliary fuel. When the heating value of the waste gas is in the range 1-20 Btu/scf (40 - 750 KJ/m³) thermal incineration may be used.

Figure 4 shows the ground flare and the smokeless flare tip as an example of direct flame incinerator.

Figure 5 shows a typical thermal incinerator while Figure 6 and Figure 7 illustrate the detail design of different thermal incinerators.

Most flared are elevated, located at 5 to 100 m above ground level. The following equation can be used to find the flare height, H,

$$H = \frac{\sqrt{\dot{Q}}}{e} - 20 D$$

where \dot{Q} is the energy release rate in watt.

D is diameter of the flare.

e is constant, between 320 for continuous exposure of personnel to 550 for exposure of equipment and structure.

To eliminate smoke formation, production of long-chain hydrocarbons and inhibit polymization of the hydrocarbons, steam is usually injected into the flare. The required amount of steam, m_s , can be estimated from the following equation

$$\frac{m_s}{m_f} = 0.1 + 4.15 \frac{m_{usat}}{m_f}$$

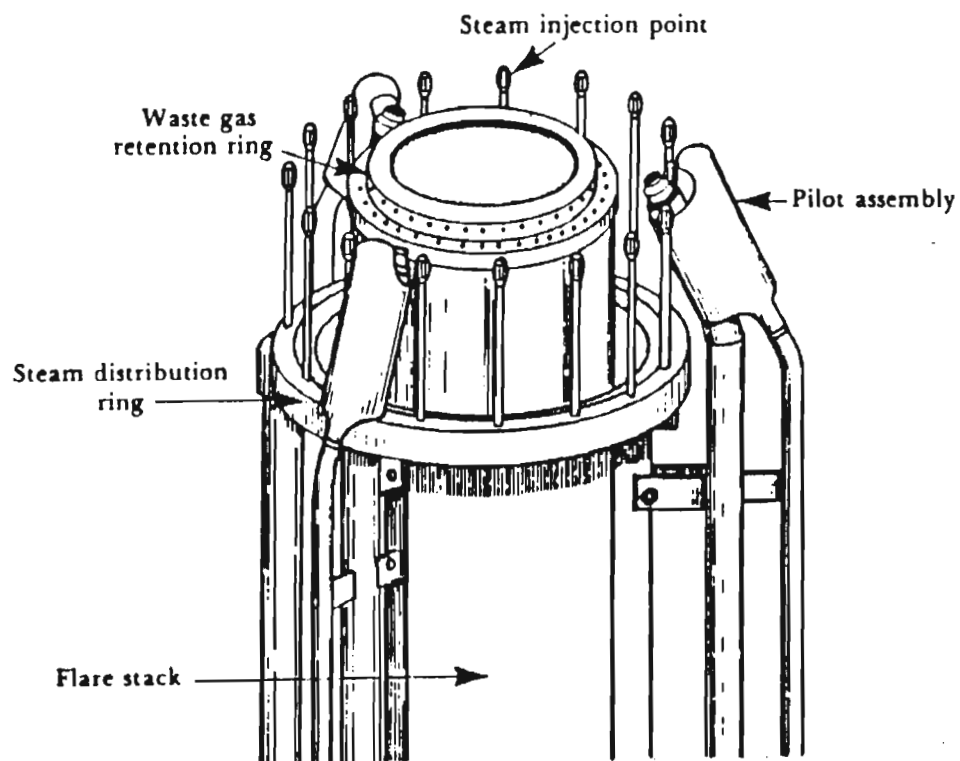
where m_f is the mass of fuel mixture

m_{usat} is the mass of unsaturated hydrocarbons in the fuel.

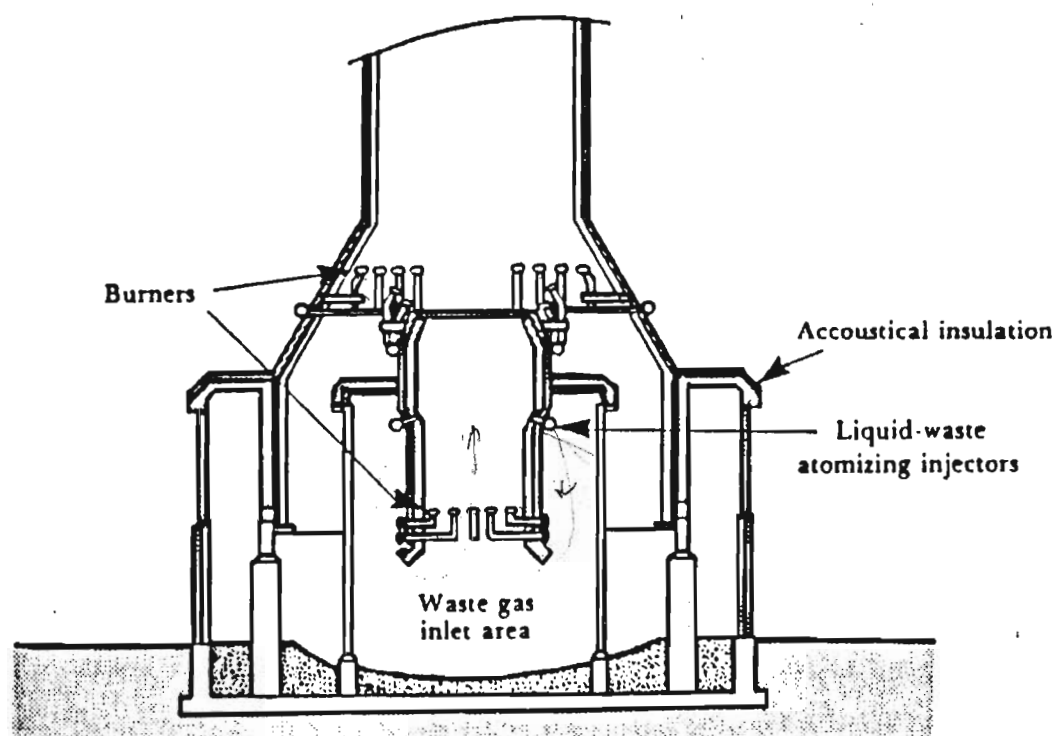
4.3.2 Catalytic Processes

In catalytic conversion processes, a waste gas (pollutant) is passed through a catalyst bed. The catalyst is a substance which causes or speeds a chemical reaction without participating in the reaction. It causes the combustion to proceed at a faster rate and lower temperature. Catalytic incinerators operating in a 370-480°C (700-900°F) can achieve the same efficiency as a thermal incinerator operating between 700-820° (1300-1500°F). This can result in a 40-60% fuel saving. Consider the reaction





Smokeless flare tip.



Ground flare.

Fig. 4.4. Types of Direct Flame Incinerators.

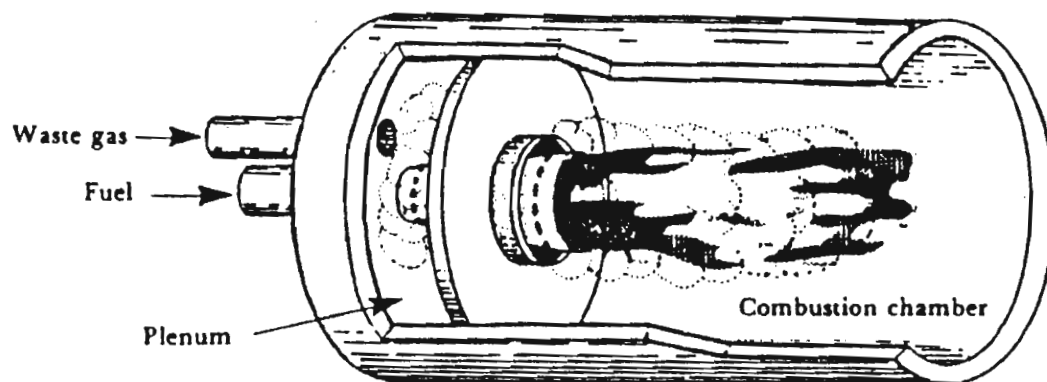
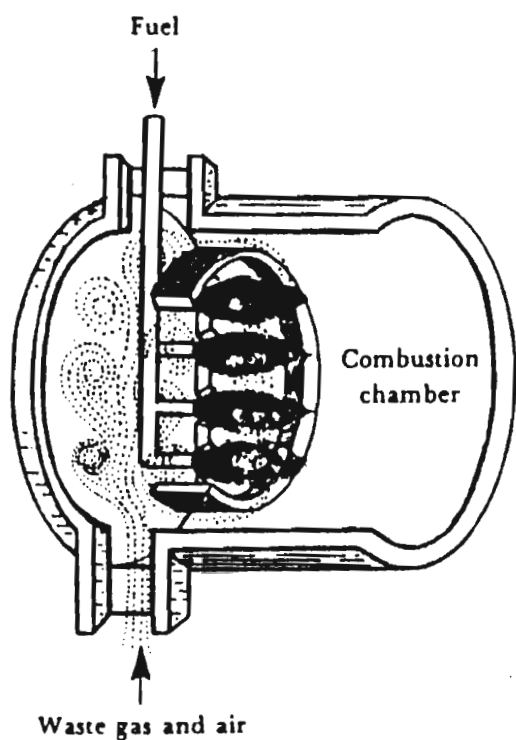
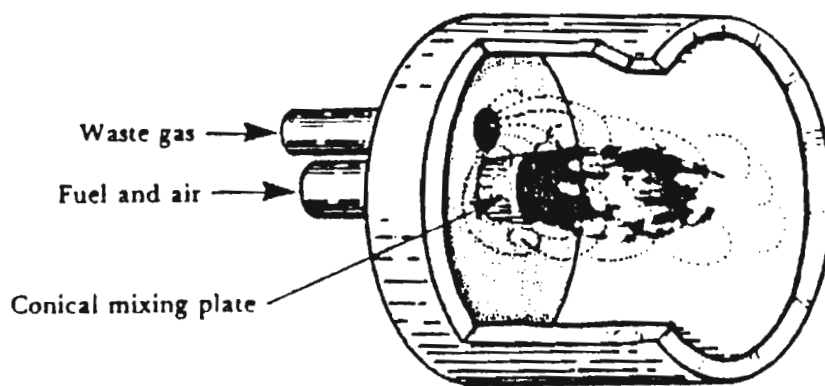


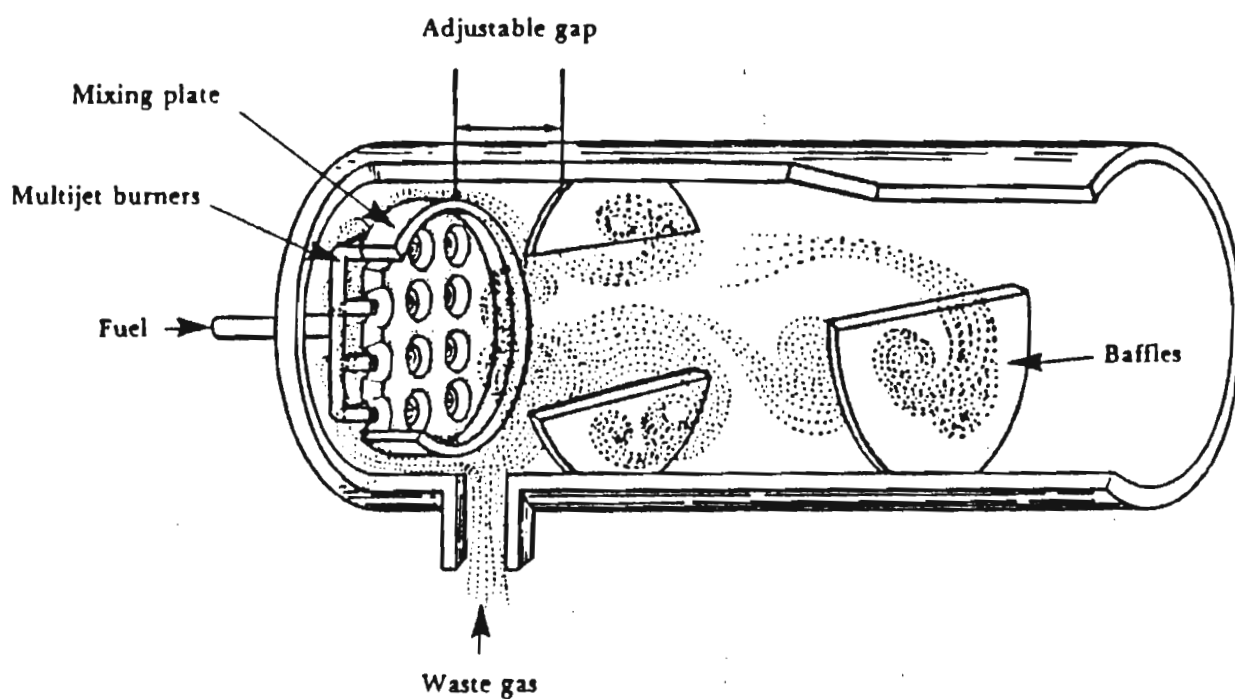
Fig. 4.5. Typical Thermal Incinerator.



Distributed (line) burner.

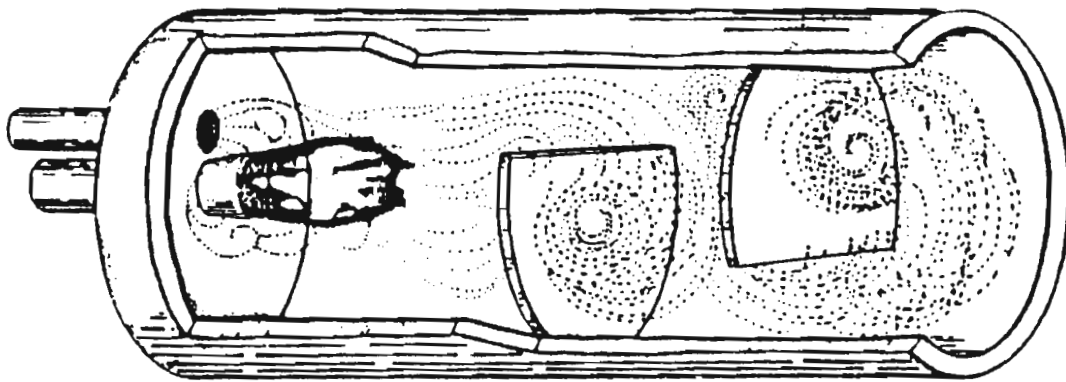


Discrete burner.

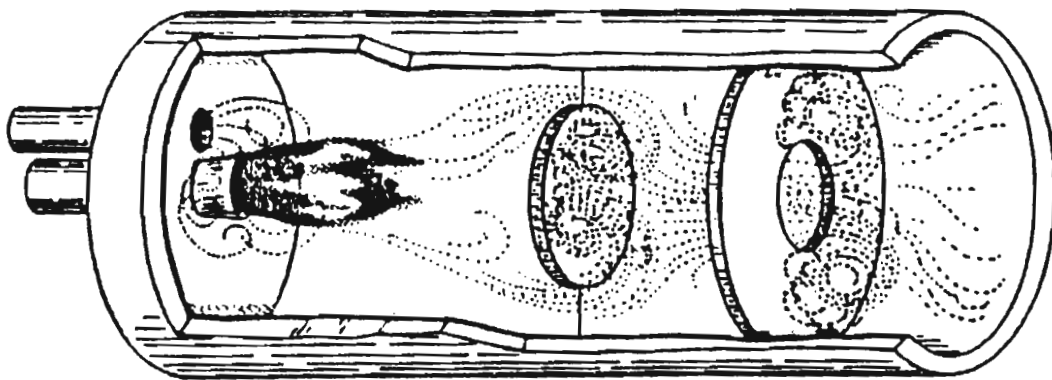


Multijet burner.

Fig. 4.6. Types of Thermal Incinerator Burners.



Bridge wall baffle.



Ring and disc baffle.

Fig. 4.7. Typical Baffle Arrangements used in Thermal Incinerators.

the reaction rate can be given by the change per unit time of the concentration of any reactant, hence

$$\text{reaction rate} = \frac{d[A]}{dt} = -\frac{a}{b} \frac{d[B]}{dt} = \frac{a}{c} \frac{d[C]}{dt} = \frac{a}{d} \frac{d[D]}{dt}$$

Alternatively, reaction rate may be expressed in the following general form

$$r = K \phi(C_i)$$

Where $\phi(C_i)$ is a function of concentration.
K is called reaction rate constant.

The rate constant generally varies with the reaction temperature according to Arrhenius law

$$K = A e^{-E/RT}$$

Where A is constant called frequency factor
E is the activation energy of the reaction
R is the gas constant.

The rate constant for natural gas is given by the following relation

$$K = 1.65 \times 10^{12} \text{ Exp}(-\frac{206}{8.315T}) \text{ , sec}$$

where T is in Kelvin

At 1000K, only 3% decrease in the activation energy will result in an increase in the reaction constant >51%. While a 5% decrease, increase the reaction rate 70%. So the reduction in the activation energy will accelerate the reaction significantly. As illustrated in Figure 8 catalyst reduces the activation energy remarkably. This is the important contribution of a catalyst in promoting, fasting and accelerating a chemical reaction.

Also the reaction rate constant changes little with temperature at low activation energy and drastic changes occur at high activation energy. Consider the following rate constants; K_L the low activation energy reaction rate constant and K_h the high activation energy reaction rate constant,

$$K_L = 10^{12} \exp\left(-\frac{20,000}{R_T}\right)$$

$$K_h = 10^{12} \exp\left(-\frac{300,000}{R_T}\right)$$

where

R is gas constant equals 8.315 J/g mole K and T is tem-

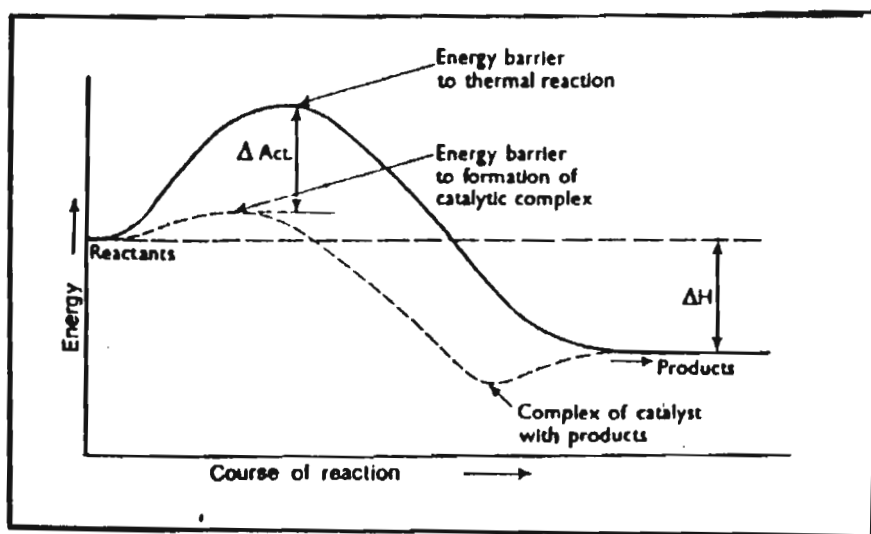


Fig. 4.8 Activation Energy of Catalyzed and Non-catalyzed Chemical Reactions.

perature in K. The following changes in K are obtained for the temperature 1000, 1500 and 2000 K:

Temp, K	K_L	K_h
1000	9.02×10^{10}	2.14×10^{-4}
1500	2.01×10^{11}	3.58×10^{-4}
2000	3.0×10^{11}	1.46×10^{-4}

So with a relatively low activation energy, the value of K increases simply by a factor of 10. While with high activation energy, K altered by roughly 8 order of magnitude. Generally it is correct to say, when the activation energy is reasonably small (e.g. <50,000 J/g mole), the rate constant K is fairly insensitive to temperature. For activation energies greater than this (say >100,000 J/g mole), the rate constant is extremely sensitive to temperature variations.

Table 6 below shows a comparison between direct flame, thermal and catalytic incineration systems. The table shows that catalytic combustion may be the economical choice. It also offer the lower thermal operation where nitrogen oxides can not be formed.

Table 6. Conversion Processes,

Method	Operating temp, °F	Equipment Cost \$/scfm	Annual fuel \$/1000 scfm
Direct flame	2,500 +	5 - 10	0 - 20
Thermal	1,000 - 1,500	1.75 - 10	0 - 7.50
Catalytic	600 - 900	1.75 - 5	0 - 4.50

Catalytic reactions are either homogeneous or heterogeneous. Homogeneous reactions occur throughout the bulk of the catalyst, while heterogeneous reactions occur only on the surface of the catalyst. Catalytic converters are of heterogeneous type. As in thermal processes, CO_2 and H_2O are the products of complete catalytic combustion.

Heterogeneous catalytic reactions proceeds through the following steps:

- Diffusion of reactants from the bulk into the catalytic surface.
- Adsorption of reactants on the surface.
- Reaction (oxidation) step
- Desorption of products
- Diffusion of products from the catalyst surface into the bulk.

Noble metals are commonly used for oxidation reactions. Platinum and palladium are often used. They exhibit high oxidation activity at low temperatures and are stable at high temperature and are chemically inert.

Catalytic materials are sometime coated onto a cheaper support materials, such as alumina, silica alumina, nickel-chromium or ceramics. Figure 9 shows a schematic diagram of a catalytic incinerators. It consists of

- preheat section
to heat the pollutants upto the operating temperature.
- burner
to ignite the flame, same as in thermal incinerator
- catalyst bed
to ensure conversion of the pollutants.
- heat recovery section (optional)

Catalytic materials are subjected to the following operating problems:

- fouling: depsoition of particulate matter
- poisoning: either fast or slow poisoning
fast poisoning is caused by phosphorus bismuth, arsenic, antimony and mercury. Slow poisoning includes zinc, lead and tin.
- suppressants: tolerable poisoning caused by sulphur and halogen compounds.
- deterioration: gradual loss of the catalyst material causes by erosion, attrition, and vaporization.
- thermal aging: loss of catalyst activity due to high temperature.

The major advantage of catalytic incinerators against thermal incinerators is that complete combustion can be achieved at much lower temperatures. The reduction in the operating temperature reduces the fuel cost and the cost of construction. The only disadvantages is the reduction or loss of catalyst activity. Hence the requirement of catalyst treatment and/or replacement.

4.3.3 Problems

- 1- The waste gas from an industrial process at 450°K contains 1450 ppm of hydrocarbons and 90 ppm of carbon monoxide. After treatment in an afterburner at 900°K the concentrations of hydrocarbons and carbon monoxide are found to be 105 ppm and 280 ppm, respectively. What is the conversion efficiency based on hydrocarbons alone?
- 2- Methane (CH_4) is to be burned in 150 percent stoichiometric air. Write and balance the combustion equation, and determine the air-fuel ratio required.
- 3- Determine the stoichiometric air-fuel ratio for the combustion of formaldehyde.

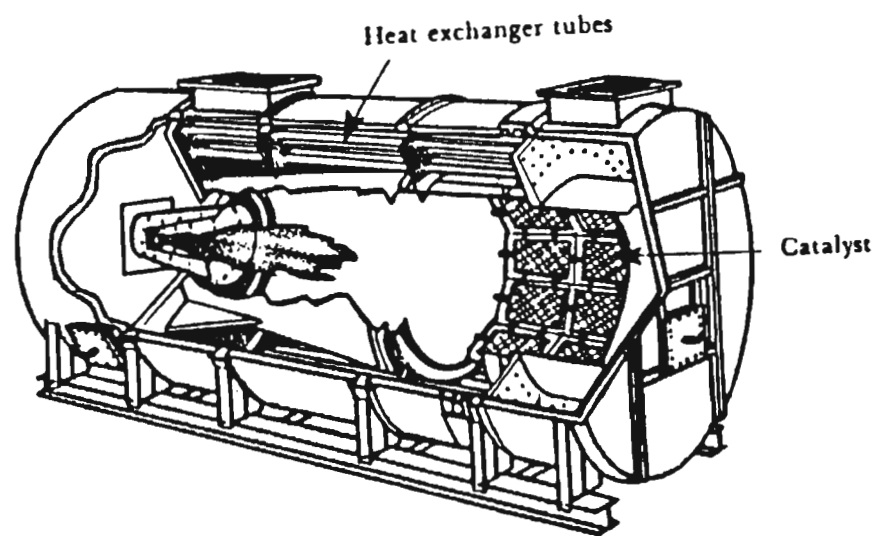


Fig. 4.9. Catalytic Incinerator.

- 4- Emissions from a paint baking oven are controlled by a thermal oxidizer. The unit has a diameter of 1.5 m (5 ft) and is 3.5 m (12 ft) long. The exhaust from the oven is $3.8 \text{ m}^3/\text{s}$ (800 scfm). The oxidizer uses $0.14 \text{ m}^3/\text{s}$ (300 scfm) of natural gas and operates at a temperature of 760°C (1400°F). If all the oxygen necessary for combustion is supplied from the process stream (no outside air added), what is the residence time of the gases in the chamber?
- 5- The exhaust from a meat smoke house contains obnoxious odors and fumes. The company plans to incinerate the 5000 acfm exhaust stream. What quantity of natural gas is required to raise the waste gas stream from a temperature of 90°F to the required temperature of 1200°F ? The gross heating value of natural gas is 1059 Btu/scf and assume no heat losses.
- 6- A natural-gas-fired circular afterburner is to be designed to incinerate the contaminants discharged from a meat smokehouse and thus eliminate visible emissions and odor. The maximum rate of discharge from the smokehouse is 1200 scfm of gas at 180°F . (Note that the volume rate at 180°F has been corrected to standard conditions of 60°F and 1 atm.) Assume that the contaminated gas has approximately the properties of air, no heating value is assigned to the contaminants due to their low concentration, and a temperature of 1200°F will eliminate the odors. The natural gas supplied to the incinerator is 90 percent methane and 10 percent ethane by volume with a lower heating value of 980 Btu/ft³. The fuel is supplied with 20 percent excess air, with the fuel entering at 60°F and the combustion air entering at 70°F . Also assume that 10 percent of the energy released by combustion of the fuel appears as a heat loss to the surroundings. Determine (a) the mass flow rates and volume flow rates of the combustion air and fuel, (b) the required throat or burner diameter in feet, (c) the large chamber diameter in feet, and (d) the residence time in the large chamber in seconds.

4.4 ABSORPTION

Absorption is a term used to describe the transfer of a gaseous component from gas phase into a liquid phase. In air pollution control, absorption refers to the removal of gaseous pollutants from a process stream by dissolving them in a liquid.

The following are some important terms often used in absorption:

Absorbent: The liquid (usually water) which absorbs the gaseous pollutants.

Absorbate or solute: The gaseous pollutant that is absorbed in the liquid, e.g. SO_2 , H_2S ...etc.

Carrier gas: The inert portion of the gas stream, usually air, from which pollutants are removed.

Interface: The contact area of gas phase and liquid phase.

Solubility: The capability of a gas to be dissolved in a liquid.

Equilibrium: The state where the net transfer of mass and energy is zero.

Steady state: The state where there is no change in mass or energy with respect to time.

Mass transfer operation: The transfer of mass due to the difference in concentration.

Absorbers or wet scrubbers are the devices used to absorb gaseous contaminants. Wet scrubbers are also used to remove particulate matter from gas streams. The optimum removal of gaseous pollutants by an absorber can be accomplished by:

- 1- Providing a large interfacial contact area.
- 2- Providing good mixing between gas and liquid phases.
- 3- Allowing sufficient residence or contact time between the phases.
- 4- Ensuring a high degree of solubility of the pollutant in the absorbent.

Absorption Theory

When two phases of different solute concentrations are brought in contact, the mass transfer between these phases are given by

$$N_A = K_c (C_g - C_{gi})$$

where N_A mass flux of component A, $\text{K mole/m}^2\text{s}$

K_c mass transfer coefficient, m/s

C_g concentration of A in the gas phase, K mole/m^3

C_{gi} concentration of A in the gas-liquid interface, K mole/m^3 .

The concentration in the liquid-side interface is C_{li} . It is in equilibrium with C_{gi} . Figure 10 shows a typical absorption gas-liquid interface condition.

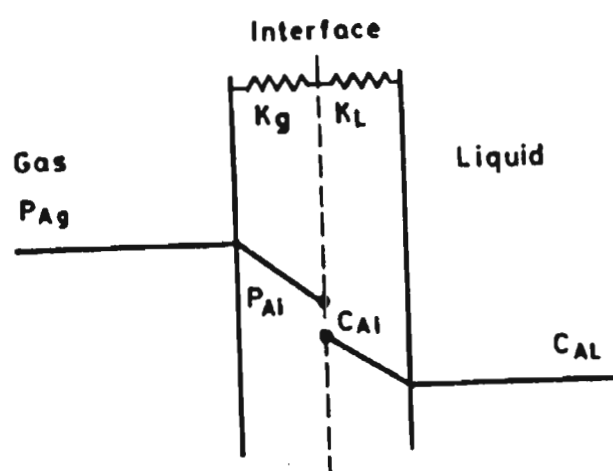


Fig. 4.10. Typical Gas-Liquid Interface.

The mass transfer coefficient can be obtained by assuming a model for the gas-liquid interface. The following are examples of some of those models often used:

1- Film mass-transfer theory

A fictitious laminar film next to the boundary is assumed. In this film, only molecular diffusion is assumed to be occurring. This film has resistance to mass transfer proportional to its thickness, δ_f , so

$$K_c (C_g - C_{gi}) = \frac{D_{AB}}{\delta_f} (C_g - C_{gi})$$

then $K_c \propto D_{AB}$

2- Penetration theory

A fluid eddy that has a uniform concentration in the turbulent core is assumed to sweep to the interface and undergo unsteady state diffusion. Then the eddy is swept away to the eddy core and other eddies are swept to the interface and stay for a random amount of time. A mean interface renewal factor S is

defined by $K_c = \sqrt{D_{AB} S}$. So $K_c \propto D_{AB}^{0.5}$

3- Boundary-Layer theory

The presence of a steady-laminar layer at the interface is assumed. This is most appropriate for fluid passing solid sur-

face. $K_c \propto D_{AB}^{2/3}$.

In absorption, the film theory is often used. For low or moderate solubility of gases, Henry's law is used to express the equilibrium solubility of gas liquid system. Henry's law is given as:

$$P_i^* = H_i x_i$$

where

P_i^* partial pressure of solute at equilibrium.

x_i mole fraction of solute in the liquid

H_i Henry's law constant, (pressure/mole fraction).

A more useful form of Henry's law can be obtained by dividing the previous form by the total pressure,

$$y_i^* = H_i^* x_i$$

where

y_i^* mole fraction in the gas phase, $y_i^* = P_i^*/P$

$H_i^* = H_i/P$, (mole fraction in vapor/that in liquid)

Table 7 below lists the Henry's constants for some gases in water at various temperatures.

In applying Henry's law, two restrictions have to be observed, the low solute concentrations and non-reacting and non-dissociating air-liquid absorption systems.

Absorption Phenomenon

A mathematical expression will be developed here to describe the absorption phenomenon. This form will be used to determine the proper absorber size at the working conditions. It is also used to predict how a change in operating conditions affects absorber performance.

As mentioned before, the film theory is the most acceptable form often used in absorption. In this model, a solute molecule to be absorbed pass through the following steps (as shown in Figure 10):

- 1- transport from bulk to the gas film
- 2- diffusion through the gas film
- 3- passing the interface
- 4- diffusion through the liquid film
- 5- transport and mixing into the bulk liquid.

The theory assume complete mixing in the gas and liquid bulk phases and the intrerface is at equilibrium with respect to molecules transferring in or out. The gas concentration is expressed in partial pressure while liquid concentration is usually given in gmole of solute/m³ of liquid. So concentration in the gas phase changes from P_{Ag} in the bulk to P_{Ai} at the interface. The liquid concentration changes from C_{Ai} at the interface to C_{Al} in the bulk. The rate of mass transfer is then equal to the amount of molecule A transferred is proportional to the driving force in both sides of the film, i.e.

$$N_A \propto (P_{Ag} - P_{Ai}) \quad \text{or} \quad N_A = K_g (P_{Ag} - P_{Ai})$$

and

Table 7. Henry's Law Constants for Various Gases in Water.

(1 atm = 101.33 kN/m²)

$$p_a = H_a x_a$$

where p_a = partial pressure of the solute a in the gas phase, atm x_a = mole fraction of solute a in the liquid phase, mole fraction H_a = Henry's law constant, atm/mole fraction $H_a \times 10^{-4}$, atm/mole fraction

$T, ^\circ\text{C}$	Air	CO ₂	CO	C ₂ H ₆	H ₂	H ₂ S	CH ₄	NO	N ₂	O ₂
0	4.32	0.0728	3.52	1.26	5.79	0.0268	2.24	1.89	5.29	2.55
10	5.49	0.104	4.42	1.89	6.36	0.0367	2.97	2.18	6.68	3.27
20	6.64	0.142	5.36	2.63	6.83	0.0483	3.76	2.64	8.04	4.01
30	7.71	0.186	6.20	3.42	7.29	0.0609	4.49	3.10	9.24	4.75
40	8.70	0.233	6.96	4.23	7.51	0.0745	5.20	3.52	10.4	5.35
50	9.46	0.283	7.61	5.00	7.65	0.0884	5.77	3.90	11.3	5.88
60	10.1	0.341	8.21	5.65	7.65	0.103	6.26	4.18	12.0	6.29
70	10.5		8.45	6.23	7.61	0.119	6.66	4.38	12.5	6.63
80	10.7		8.45	6.61	7.55	0.135	6.82	4.48	12.6	6.87
90	10.8		8.46	6.87	7.51	0.144	6.92	4.52	12.6	6.99
100	10.7		8.46	6.92	7.45	0.148	7.01	4.54	12.6	7.01

$$N_A \propto (C_{Ai} - C_{AL}) \quad \text{or} \quad N_A = K_L (C_{Ai} - C_{AL})$$

where

K_g is the mass transfer coefficient for gas film.

K_L is the mass transfer coefficient for liquid film.

The mass transfer coefficients, K_g and K_L , represent the flow resistance the solute encounters in diffusing through the gas and liquid films respectively. The interfacial concentrations, P_{Ai} and C_{Li} , are fictitious quantities that can not be measured. If a straight equilibrium line is assumed between P_{Ai} and P_A^* and between C_{Ai} and C_A^* as shown in Figure 11, the following relations are then obtained:

$$N_A = K_{og} (P_{Ag} - P_A^*)$$

$$N_A = K_{oL} (C_A^* - C_{AL})$$

where K_{og} is the overall mass transfer coefficient based on gas phase

K_{oL} is the overall mass transfer coefficient based on liquid phase.

From the geometry of Figure 11,

$$\begin{aligned} (P_{Ag} - P_A^*) &= (P_{Ag} - P_{Ai}) + (P_{Ai} - P_A^*) \\ &= (P_{Ag} - P_{Ai}) + H(C_{Ai} - C_{AL}) \end{aligned}$$

Substituting for the concentration difference the equivalents (flux/coefficient) gives

$$\frac{N_A}{K_{og}} = \frac{N_A}{K_g} + H \frac{N_A}{K_L} \quad \text{OK} \quad \frac{1}{K_{og}} = \frac{1}{K_g} + \frac{H}{K_L}$$

Similarly, the relation between the overall mass transfer coefficient in the liquid phase, K_{oL} , and the individual mass transfer coefficients in gas and liquid phases, K_g and K_L , are obtained to be:

$$K_{oL} = \frac{1}{K_L} + \frac{1}{H K_g}$$

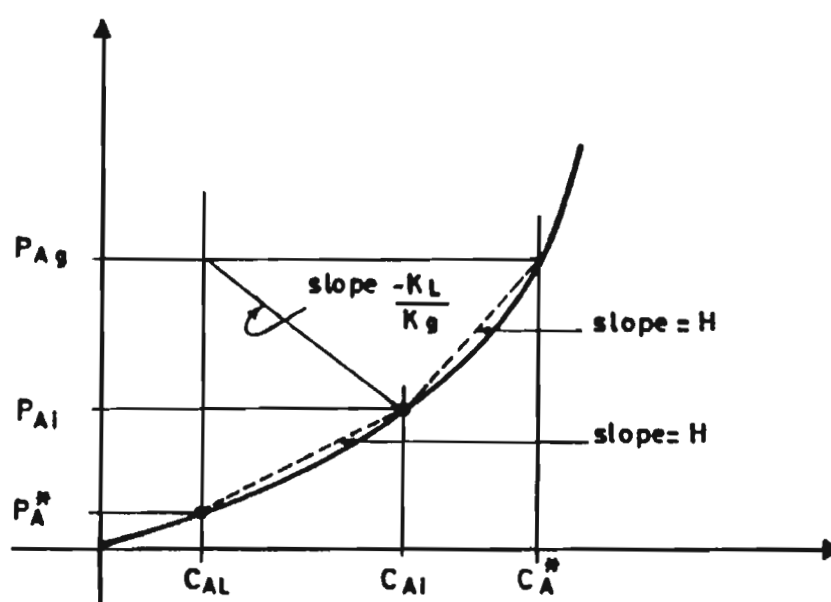


Fig. 4.11. Overall Concentration Differences.

From the previous equations the following facts are noted:

- 1- The rate of mass transfer is dependent on the concentration departure from equilibrium in either the gas phase or the liquid phase. The larger those concentration differences are, the greater the rate of mass transfer. If equilibrium is ever reached ($P_{Ag} = P_A^*$ or $C_{AL} = C_A^*$) absorption stops and no net transfer occurs.
- 2- If Henry's law constant is very small, which means the gas is very soluble in the liquid, then $K_{og} \approx K_g$ and absorption is said to be gas film control. The major resistance to mass transfer is in the gas phase.
- 3- If on other hand H is very large, then $K_{ol} \approx K_l$ and the mass transfer is liquid film controlled. Most air pollution systems are gas phase controlled since the liquid is chosen so that the solute will have a high degree of solubility.

Mass transfer coefficient are measured experimentally and reported either:

- 1- in an empirical relationship based on a function of the liquid flow or gas flow or slope of the equilibrium line.
- 2- or correlated in terms of a dimensionless number, usually either Reynolds or Schmidt Number.

They are also often expressed as $K_{og}a$, K_la and K_ga , where "a" represent the surface area available for absorption per unit volume of the column. This allows an easy determination of the column area required to accomplish the desired separation.

Absorption Design

Consider the absorber in Figure 12 where the polluted gas enters the bottom of the tower and flows upward. Liquid flows downward. Gas and liquid are brought in contact on special design surface either on trays or on packing materials. Define the following:

x mole fraction of solute in liquid,

$$X = \frac{x}{1-x} \text{ solute free basis mole fraction}$$

y mole fraction of solute in inert gas,

$$Y = \frac{y}{1-y} \text{ solute free basis mole fraction}$$

L_m liquid flow rate, gmole/hr

G_m gas flow rate, gmole/hr

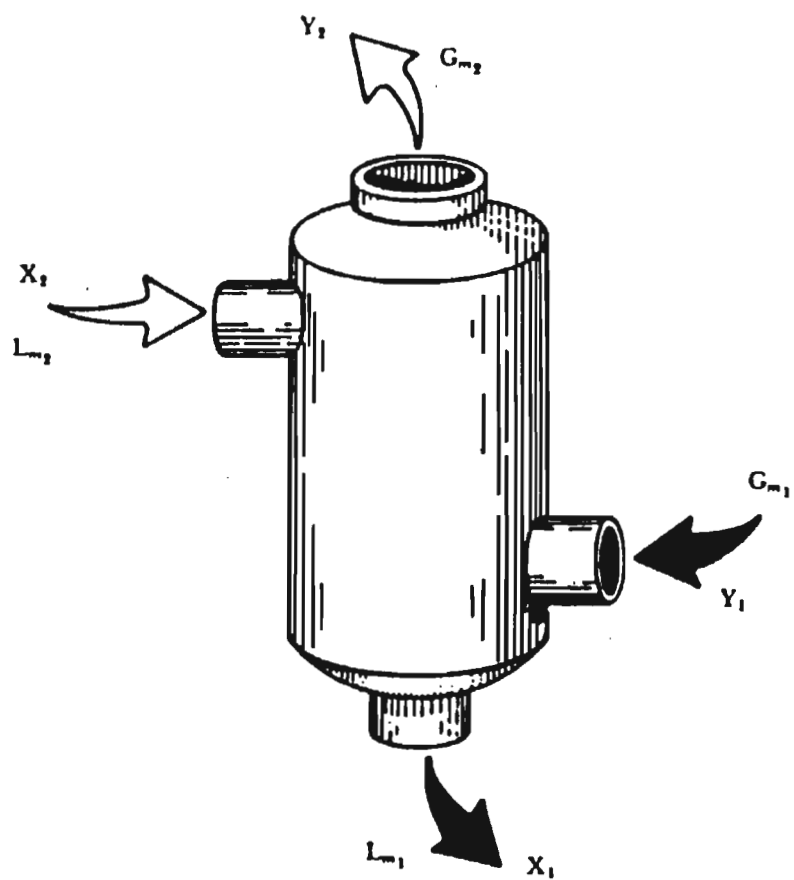


Fig. 4.12. Material Balance for Countercurrent Flow Absorber.

So from the mass conservation principle:

$$G_{m1} + L_{m2} = G_{m2} + L_{m1}$$

$$Y_1 G_{m1} + X_2 L_{m2} = Y_2 G_{m2} + X_1 L_{m1}$$

where subscript 1 refers to the bottom of the absorber column and 2 refers to the top of the column.

If constant gas and liquid flow rates are assumed, then

$$G_m(Y_1 - Y_2) = L_m(X_2 - X_1)$$

$$\text{and } Y_1 - Y_2 = \frac{L_m}{G_m}(X_2 - X_1)$$

— 4.15 is 1.5 times $\frac{L}{G}$

This is a straight line equation. It is called an operating line. It has a slope of L_m/G_m , liquid to gas ratio. By definition it passes through the top and bottom points of the column. Figure 13 shows a plot of this line with the equilibrium curve on X-Y diagram.

In most of absorption design, G_m and Y_1 are set by the process condition, i.e. they are known. Value of Y_2 is specified by the minimum acceptable standard. Also X_2 is known or can be assumed to be zero if there is no recycling of liquid. So by plotting these data on an equilibrium diagram, the minimum amount of liquid required to achieve the required outlet concentration, Y_2 , can be determined. This is done by the following steps:

- 1- Locate point (X_2, Y_2) on the equilibrium diagram, let it to be point A. ($X_2 = 0$ for pure solvent, Y_2 is the required mole fraction of pollutants in the exit gas).
- 2- At the minimum liquid rate, the inlet gas concentration of solute, Y_1 , is in equilibrium with the outlet liquid concentration of solute, X_{\max} . So find point B on the equilibrium curve at Y_1 .
- 3- Line AB represent the minimum operating line, and its slope is $(L_m/G_m)_{\min}$. By knowing G_m , the minimum liquid flow rate can be found by multiplying the slope by gas flow rate, i.e. $(L_m/G_m)_{\min} \times G_m$.

Generally, the actual liquid flow rates are specified at 25 to 100% greater than the required minimum typical absorber operation is 50%, i.e. 1.5 times the minimum liquid-to-gas ratio. So by knowing $(L_m/G_m)_{\text{actual}}$, the actual operating line can be found. Figure 14 shows the minimum and the actual operating lines.

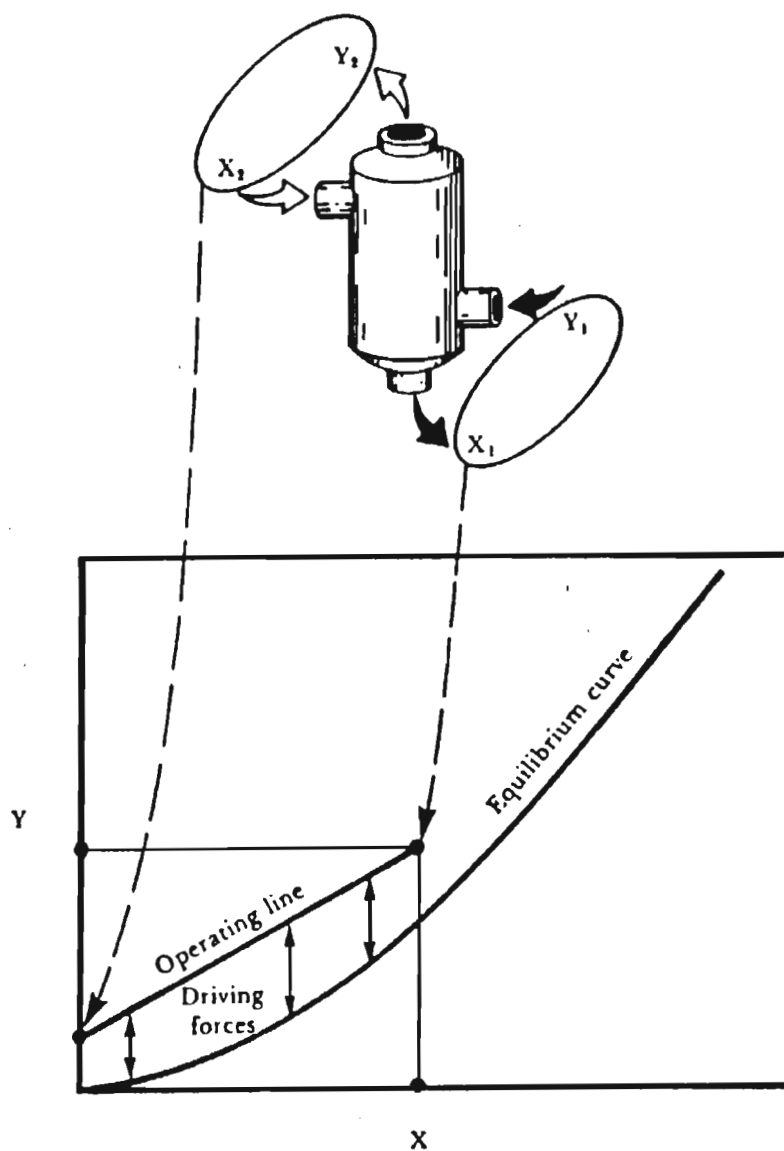


Fig. 4.13. Typical Operating Line Diagram.

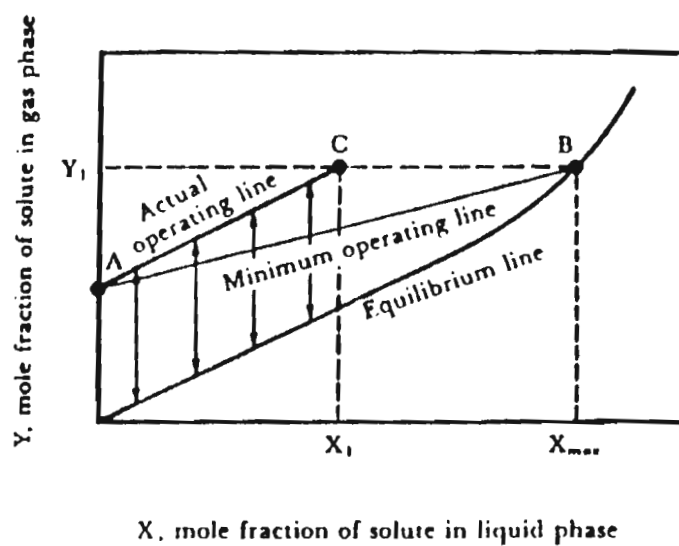


Fig. 4.14. Graphical Determination of Liquid Flow Rate.

Determination of Packed Column Diameter:

Gas velocity is the main parameter affecting the size of the packed column. At a specified gas and liquid flow rates, decreasing the diameter of the column will increase the velocity. If the gas flow rate is gradually increase, a point will be reached where the liquid flowing down over the packing begins to be held in the void spaces between the packing. This gas to liquid flow ratio is termed the loading point. The pressure drop over the column begins to increase and the degree of mixing between the phases decreases. A further increase in gas velocity will cause the liquid to completely fill the void spaces in the packing. The liquid forms a layer over the top of the packing and no more liquid can flow down through the tower. The pressure drop increases substantially and mixing between the phases is minimal. This condition is referred as flooding and the gas velocity at which it occurs is the flooding velocity. By using large diameter, this effect would be eliminated. However, as the diameter increases, the cost of the tower increases.

Normally, packing column diameter is chosen at a certain percentage of the flooding velocity. A typical operating range of the gas velocity through the column is 50 to 75% of the flooding velocity.

A common and simple procedure to estimate the flooding velocity is to use a generalized flooding and pressure drop correlation. Figure 15 shows the Sherwood Correlation which is based on the physical properties of the gas and liquid stream and the tower packing characteristics. The procedure to determine the tower diameter is as follows:

- 1- Calculate the value of the abscissa

$$\frac{L}{G} \left(\frac{\rho_g}{\rho_L} \right)^{0.5}$$

where, L, G liquid and gas flow rates

ρ_g, ρ_L gas and liquid densities

- 2- Use Figure 15, to find ϵ at the flooding line.

- 3- Find G^* from the value of ϵ as

$$G^* = \left[\frac{\epsilon \rho_g \rho_L g_c}{F \phi \mu_L} \right]^{0.5}$$

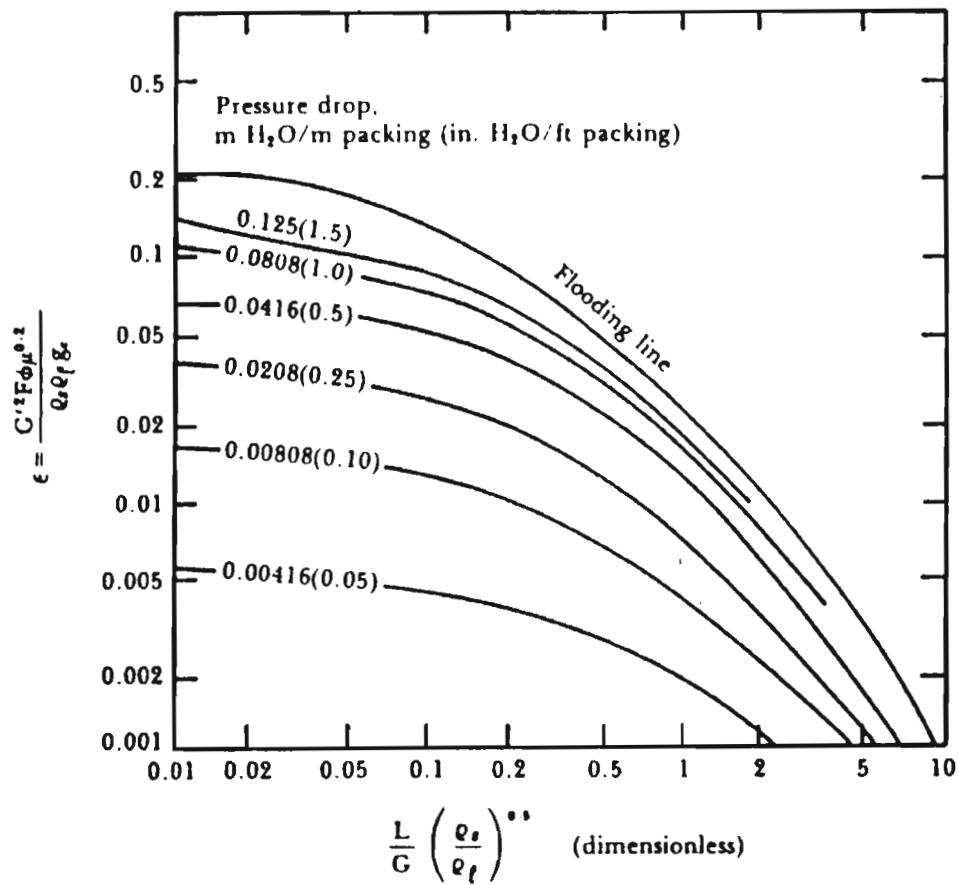


Fig. 4.15. Generalized Flooding and Pressure Drop Correlation.

Where: F = packing factor given in Table 8 for different types of packing.

ϕ = ratio of specific gravity of the scrubbing liquid to that of water.

μ_L = viscosity of liquid (for water = 0.8 centipoise)

G^* = mass flow rate of gas per unit cross sectional area of column at flooding, g/s.m^2 (lb/s.ft^2).

ρ_L = density of the absorbing liquid, kg/m^3 (lb/ft^3)

ρ_g = density of the gas stream, kg/m^3 (lb/ft^3)

g_c = gravitational constant = 9.82 m/s^2 (32.2 ft/s^2)

4- G^* at operating is a fraction of G^* at flooding.

$$G^*_{\text{operating}} = (f)(G^*_{\text{flooding}})$$

5- The cross sectional area of column A is calculated from:

$$A = \frac{G}{G^*_{\text{operating}}}$$

6- The diameter of the column is obtained from:

$$d_r = \left(\frac{4A}{\pi}\right)^{0.5} = 1.13 A^{0.5}$$

Determination of the Packed Column Height:

Conducting a material balance on a differential height of a tower and using the film theory yield the familiar form of tower height equation:

$$Z = \frac{G^*}{K_g a P} \int_{Y_2}^{Y_1} \frac{dY}{(1-Y)(Y-Y^*)}$$

where

Z = height of packing, m

a = interfacial contact area, m^2

Table 8. Packing Data.

Packing	Size (in.)	Weight (lb/ft ³)	Surface area, a (ft ² /ft ³ packing volume)	Void fraction (%)	Packing factor, F (ft ² /ft ³)
Raschig rings (ceramic and porcelain)	½	52	114	65	580
	1	44	58	70	155
	1½	42	36	72	95
	2	38	28	75	65
	3	34	19	77	37
Raschig rings (steel)	½ × 1/32	77	128	84	300
	1 × 1/32	40	63	92	115
	2 × 1/16	38	31	92	57
Berl saddles (ceramic and porcelain)	¼	55	274	63	900
	½	54	155	64	240
	1	48	79	68	110
	2	38	32	75	45
Intalox saddles (ceramic)	¼	54	300	75	725
	½	45	190	78	200
	1	44	78	77	98
	2	42	36	79	40
Intalox saddles (plastic)	1	6.00	63	91	30
	2	3.75	33	93	20
	3	3.25	27	94	15
Pall rings (plastic)	5/8	7.0	104	87	97
	1	5.5	63	90	52
	2	4.5	31	92	25
Pall rings (metal)	5/8 × 0.018 thick	38	104	93	73
	1½ × 0.03 thick	24	39	95	28
Tellerettes	1	7.5	55	87	40
	2	3.9	38	93	20
	3	5.0	30	92	15

P = tower pressure, kPa

This equation can be divided into two parts,

- 1- $G/K_a P$ = height of a transfer unit, m, (HTU)
- 2- Integral part \Rightarrow number of transfer unit, dimensionless, (NTU)

$$\text{so} \quad Z = \text{HTU} \times \text{NTU}$$

The height of transfer unit and the number of transfer unit can be evaluated based on the overall gas and liquid film coefficients. They are usually given by the absorber manufacturer and evaluated experimentally by pilot units. However, there are some empirical correlations often used to estimate HTU and NTU. Normally, HTU is ranged from 0.3 to 1.2 m (1-4 ft). Colburn diagram presented on Figure 16 is often used to find NTU with m as the slope of equilibrium line.

Alternatively, the tower height can be estimated from the following approximate equation

$$H_{tOG} = H_{tG} + \left(\frac{mG}{L} \right) H_{tL}$$

This equation permits the evaluation of the overall height of a transfer unit in terms of gas-phase and liquid-phase transfer heights H_{tG} and H_{tL} .

The gas-phase and liquid-phase transfer heights have been correlated over a wide range of experimental data. Generalized equations for H_{tG} and H_{tL} are given below.

$$H_{tG} = \frac{\alpha (G')^\beta}{(L')^\gamma} \left(\frac{\mu_G}{\rho_G D_G} \right)^{0.5}$$

where H_{tG} is the height of a gas transfer unit, in feet; L' is the superficial liquid flow rate, in lb/hr.ft²; and G' is the superficial gas flow rate, in lb/hr.ft². In addition, α , β and γ are packing constants (see Table 9) and the quantity $(\mu_G/\rho_G D_G)$ is the Schmidt number for the gas phase. Also

$$H_{tL} = \phi \left(\frac{L'}{\mu_L} \right)^\eta \left(\frac{\mu_L}{\rho_L D_L} \right)^{0.5}$$

where H_{tL} is the height of the liquid transfer unit, in feet, and μ_L is the liquid viscosity, in lb/ft.hr. In addition, ϕ and η are packing constants (see Table 10). Likewise, $(\mu_L/\rho_L D_L)$ is the Schmidt number for the liquid phase. The Schmidt number in either case is a dimensionless value.

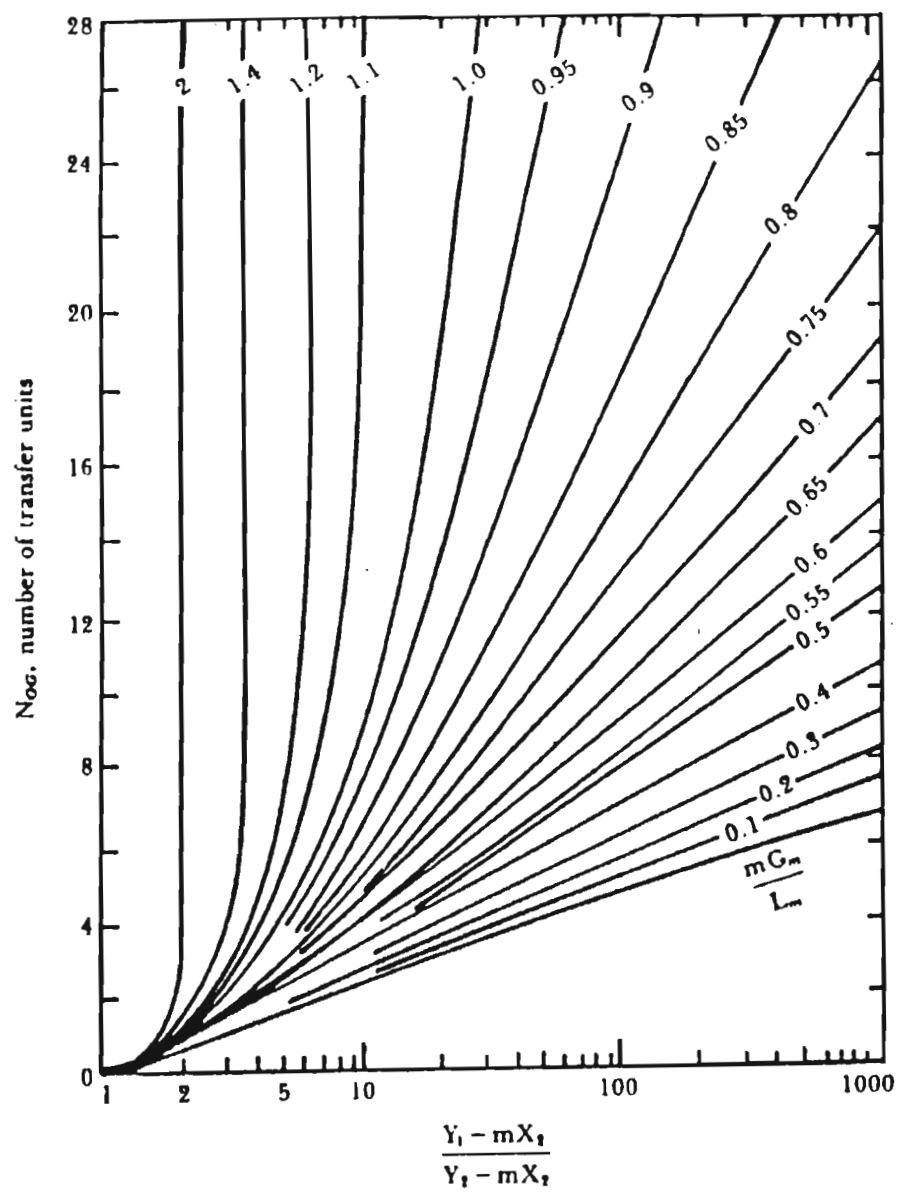


Fig. 4.16. Colburn Diagram.

Table 9. Constants for use in Determining Gas-Phase Height of Transfer Unit.

PACKING	α	β	γ	GAS-FLOW RATE	LIQUID-FLOW RATE
				(lb/hr-ft ²)	(lb/hr-ft ²)
Raschig rings					
$\frac{3}{4}$ in.	2.32	0.45	0.47	200-500	500-1500
1 in.	7.00	0.39	0.58	200-800	400-500
	6.41	0.32	0.51	200-600	500-4500
$1\frac{1}{2}$ in.	17.30	0.38	0.66	200-700	500-1500
	2.58	0.38	0.40	200-700	1500-4500
2 in.	3.82	0.41	0.45	200-800	500-4500
Berl saddles					
$\frac{1}{2}$ in.	32.40	0.30	0.74	200-700	500-1500
	0.81	0.30	0.24	200-700	1500-4500
1 in.	1.97	0.30	0.40	200-800	400-4500
$1\frac{1}{2}$ in.	5.05	0.32	0.45	200-1000	400-4500
Partition rings					
3 in.	6.50	0.58	1.06	150-900	3000-10,000
Spiral rings (stacked, staggered)					
3-in. single spiral	2.38	0.35	0.29	130-700	3000-10,000
3-in. triple spiral	15.00	0.38	0.60	200-1000	500-3000

SOURCE: R. E. Treybal. *Mass Transfer Operations*. New York: McGraw-Hill, 1968.

Table 10. Constants for use in Determining Liquid-Phase Height of Transfer Unit.

PACKING	ϕ	η	L' RANGE
			(lb/hr-ft ²)
Raschig rings			
$\frac{3}{4}$ in.	0.00182	0.46	400-15,000
$\frac{1}{2}$ in.	0.00357	0.35	400-15,000
1 in.	0.0100	0.22	400-15,000
$1\frac{1}{2}$ in.	0.0111	0.22	400-15,000
2 in.	0.0125	0.22	400-15,000
Berl saddles			
$\frac{1}{2}$ in.	0.00066	0.28	400-15,000
1 in.	0.00588	0.28	400-15,000
$1\frac{1}{2}$ in.	0.00625	0.28	400-15,000
Partition rings			
3 in.	0.0025	0.09	3000-14,000
Spiral rings (stacked, staggered)			
3-in. single spiral	0.00009	0.28	400-15,000
3-in. triple spiral	0.0116	0.28	3000-14,000

SOURCE: R. E. Treybal. *Mass Transfer Operations*. New York: McGraw-Hill, 1968.

Table 11. Pressure Drop Constants for Tower Packing.

PACKING TYPE	m	n	L' RANGE
			(lb/hr-ft ²)
Raschig rings			
$\frac{1}{2}$ in.	139.00	0.00720	300-8,600
$\frac{3}{4}$ in.	32.90	0.00450	1800-10,800
1 in.	32.10	0.00434	360-27,000
$1\frac{1}{2}$ in.	12.08	0.00398	720-18,000
2 in.	11.13	0.00295	720-21,000
Berl saddles			
$\frac{1}{2}$ in.	60.40	0.00340	300-14,100
$\frac{3}{4}$ in.	24.10	0.00295	300-14,400
1 in.	16.01	0.00295	720-78,800
$1\frac{1}{2}$ in.	8.01	0.00225	720-21,600
Intalox saddles			
1 in.	12.44	0.00277	2520-14,400
$1\frac{1}{2}$ in.	5.66	0.00225	2520-14,400

SOURCE: R. E. Treybal. *Mass Transfer Operations*. New York: McGraw-Hill,

Another empirical correlation for the pressure drop in packing when operating below the load point is

$$\frac{\Delta P}{Z} = 10^{-8} m [10^{(nL'/\rho_L)}] \frac{(G')^2}{\rho_G}$$

where ΔP is in pounds per square feet, Z is in feet, and m and n are packing constants (see Table 11).

Determination of Plate Tower Diameter

Absorption in plate tower occurs in a stepwise or stage process. Plate surface provides the contact area between the gas and liquid. At high gas velocity, liquid drops are entrained by the fast flowing gas causing poor contact of gas and liquid. Entrainment (so called priming) in plate column is analogous to flooding in packed column. It determines the minimum acceptable diameter. This diameter can be determined by empirical equations such as,

$$d = \psi(Q\sqrt{\rho_g})^{0.5}$$

Q is the volumetric flow of gas, m^3/hr

ρ_g is the gas density, Kg/m^3

ψ_g is an empirical value depends on the type of tray and unit used as given in Table 12 below.

ψ_g

Table 12. Empirical constant for the minimum plate tower diameter

Tray	Metric Unit ¹	Engineering Unit ²
Bubble cap	0.0162	0.1386
Sieve	0.0140	0.1198
Valve	0.0125	0.1069

¹ For Q in m^3/hr , ρ in Kg/m^3 gives d in m

² for Q in cfm , ρ in lb/ft^3 gives d in ft .

FDMA 4-14 (P4-33)
Corrosion factor

Trays are normally spaced 45 to 70 cm (18 - 28 inches) apart to allow easy maintenance and cleaning.

Determination of Number of Plates (Trays) in a Tray Column

A simple method to determine the number of theoretical plates required to obtain certain removal duty is the graphical method. This method is illustrated on Figure 17. Also a simple and more accurate method depends on the following correlation. This correlation is valid only if equilibrium and operating lines are straight which is often the case in air pollution control system.

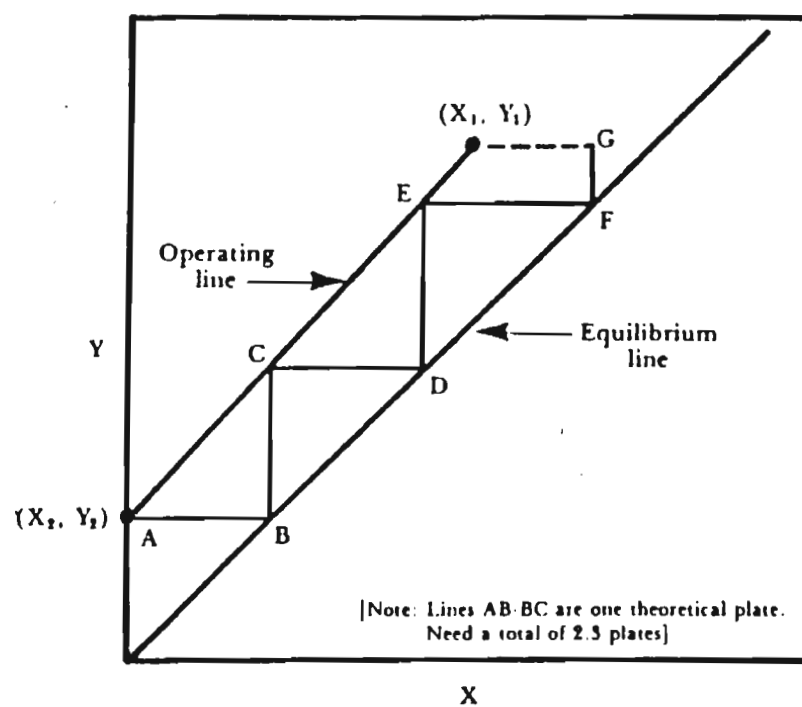


Fig. 4.17. Graphical Determination of the Number of Theoretical Plates.

$$N = \frac{\ln\left[\left(\frac{Y_1 - mX_2}{Y_2 - mX_2}\right)\left(1 - \frac{mG_m}{L_m}\right) + \frac{mG_m}{L_m}\right]}{\ln\left(\frac{L_m}{mG_m}\right)}$$

The theoretical number of plates is found when the gas and liquid leaving the plates are in equilibrium with each other. Large number of plates are required to compensate for the non-equilibrium situation. This is accomplished by assuming (or estimating) the plate efficiency. Usually 80% is used for the plate efficiency. So the actual number of plates is

$$N_a = \frac{N}{0.8}$$

Absorption Equipments:

The following figures illustrate the different types of absorbers used in air pollution control systems.

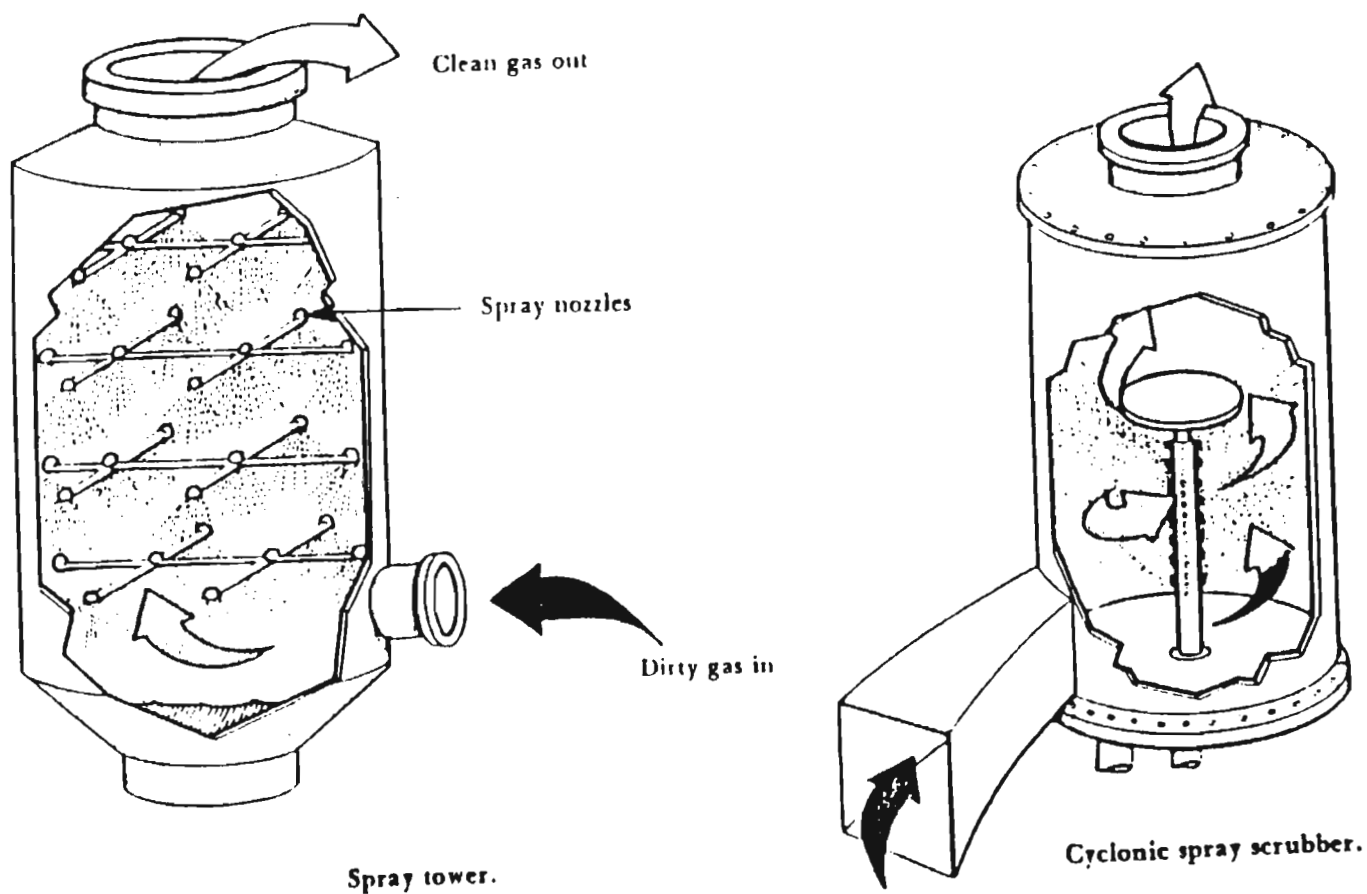
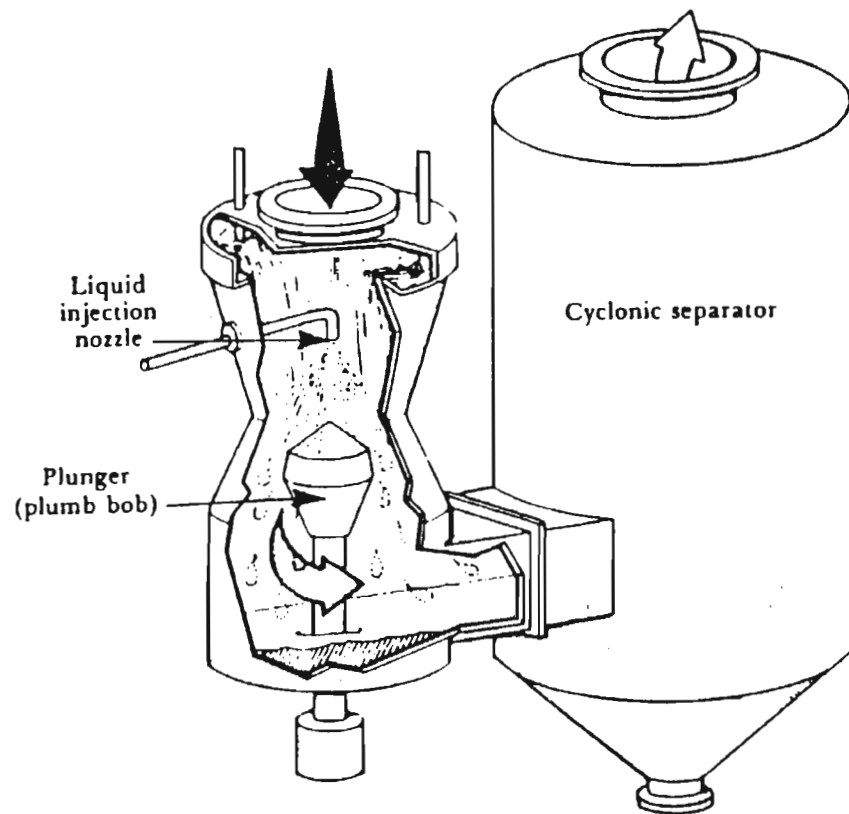
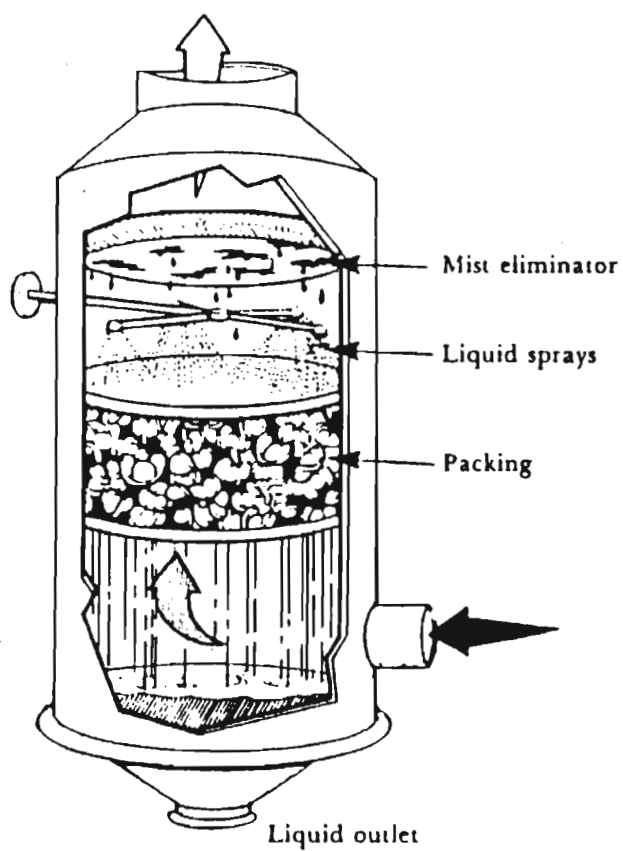


Fig. 4.18. Examples of Absorber Equipments.

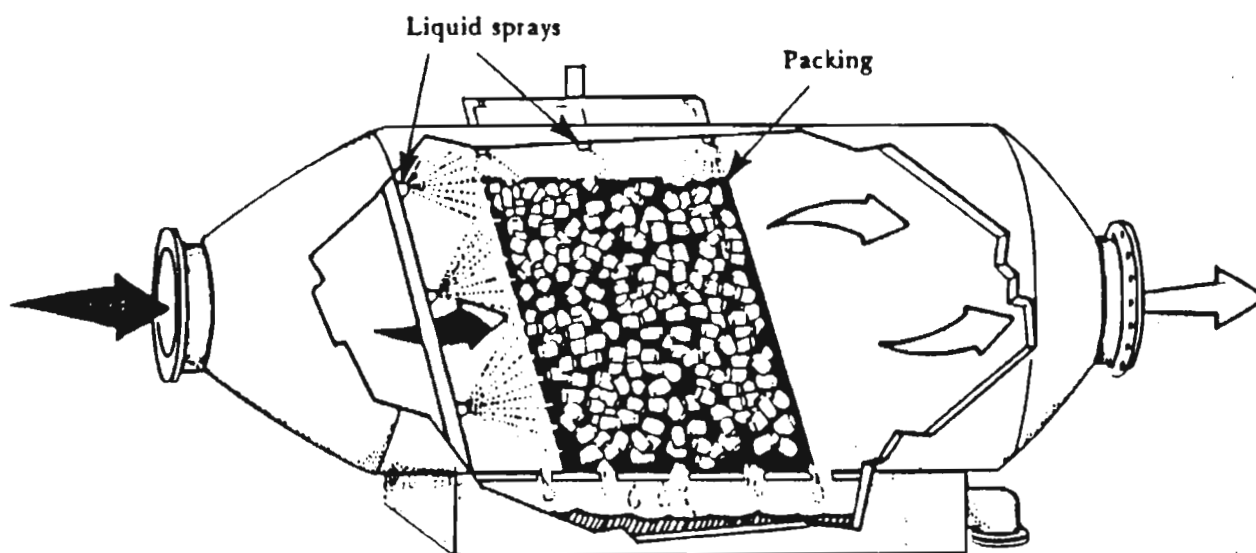


Adjustable throat venturi.

Fig. 4.18. Continued.



Countercurrent packed tower.



Cross flow packed tower.

Fig. 4.18. Continued.

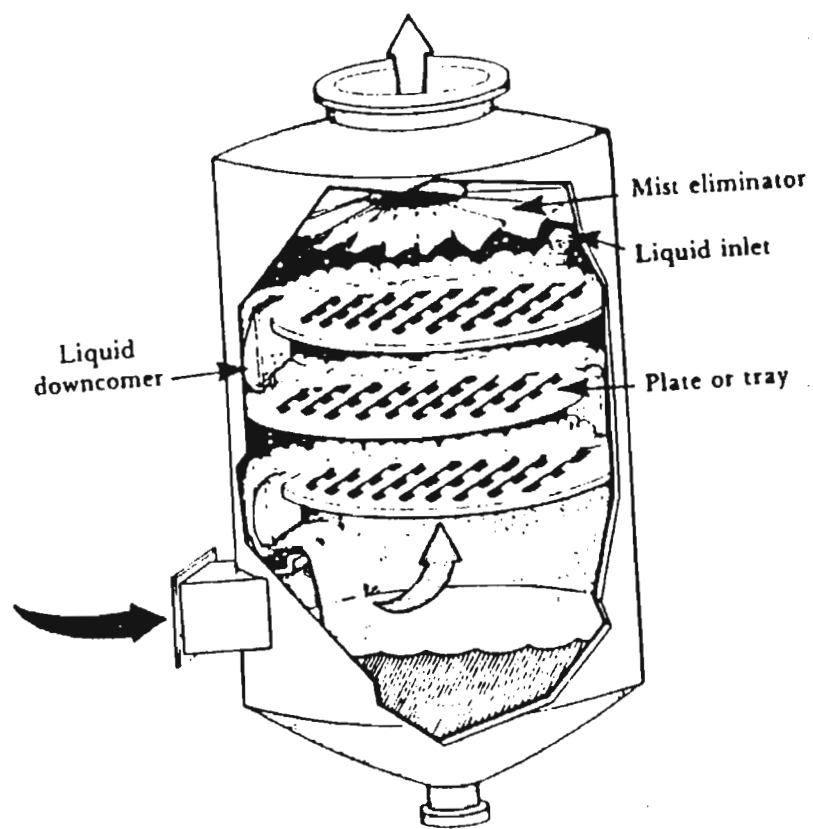


Plate tower.

Fig. 4.18. Continued.

Problems

- 1- Given the following data for the solubility of SO_2 in pure water at 303 K (30°C) and 101.3 kPa (760 mmHg), plot the equilibrium diagram and determine if Henry's Law applies.

Equilibrium data

C_{SO_2} (g of SO_2 per 100 g of H_2O)	$P^*_{\text{SO}_2}$ (partial pressure of SO_2)
0.5	6 kPa (42 mm Hg)
1.0	11.6 kPa (85 mm Hg)
1.5	18.3 kPa (129 mm Hg)
2.0	24.3 kPa (176 mm Hg)
2.5	30.0 kPa (224 mm Hg)
3.0	36.4 kPa (273 mm Hg)

- 2- Using the data and results from Problem 1, compute the minimum liquid rate of pure water required to remove 90% of the SO_2 from a gas stream of 84.9 m³/min (3000 acfm) containing 3% SO_2 by volume. The temperature is 293 K and the pressure is 101.3 kPa.
- 3- For the scrubber in Problem 2, determine the column diameter if the operating liquid rate is 1.5 times the minimum. The gas velocity should be no greater than 75% of the flooding velocity and the packing material is two-inch ceramic Intalox saddles.
- 4- From pilot plant studies of the absorption system in Problem 2, it was determined that the H_{OG} for the SO_2 -water system is 0.829 m (2.72 ft). Calculate the total height of packing required to achieve the 90% removal. The following data are given:

$$m = 42.7 \frac{\text{kg mole } \text{H}_2\text{O}}{\text{kg mole air}}$$

$$G_m = 3.5 \frac{\text{kg mole}}{\text{min}}$$

$$L_m = 3672 \frac{\text{kg}}{\text{min}} \times \frac{\text{kg mole}}{18 \text{ kg}} = 204 \frac{\text{kg mole}}{\text{min}}$$

$$x_2 = 0 (\text{no recycle liquid})$$

$$Y_1 = 0.03$$

$$Y_2 = 0.003$$

- 5- For the condition described in Problem 2, determine the minimum acceptable diameter if the scrubber is a bubble cap tray tower. The trays are spaced 0.53 m (21 inches) apart.
- 6- Calculate the number of theoretical plates required for the scrubber in Problem 5, using the same conditions as in Problem 4. Estimate the total height of the column if the trays are spaced at 0.53 m intervals and assume an overall tray efficiency of 70%.
- 7- Derive the following equation

$$Z = \frac{G}{K_g a P} \int_{Y_2}^{Y_1} \frac{dy}{(1-Y)(Y-Y^*)}$$

- 8- Derive the following equation

$$H_{OG} = H_{tG} + \left(\frac{mG_m}{L_m} \right) H_{tL}$$

- 9- A packed tower is to be designed to remove 95 percent of the ammonia from a gaseous mixture of 8 percent ammonia and 92 percent air, by volume. The flow rate of the gas mixture entering the tower at 68°F and 1 atm is 80 lb-moles/hr. Water containing no ammonia is to be the solvent, and 1-in. ceramic rasching ring will be used as the packing. The tower is to operate at 60 percent of the flood point, and the liquid water rate is to be 30 percent greater than the minimum rate. Determine:
 1. The gas-phase flow rates, in pound-moles per hour, for the solute and carrier gas.
 2. The mole ratios of the gas and liquid phases at inlet and outlet, and the required water rate in pound-moles per hour.
 3. The gas and liquid rates, in pounds per hour, for carrier gas, solute gas, total gas, liquid solvent, solute in liquid, and total liquid.
 4. The tower area and diameter.
 5. The pressure drop, in pounds per square inch and inches of water, based on two methods.
- 10- Employing the data and results of problem 9, determine the overall height of a transfer unit, in feet, and the total height of the tower, in feet. Also compute the total pressure drop on the basis of the $\Delta P/Z$ values found by two methods in part 5 of problem 9.

4.5 ADSORPTION

Adsorption is a separation process based on the ability of certain solids to remove gaseous (or liquid) components preferentially from a flow stream. The pollutant gas or vapor molecules present in a waste stream are collected on the surface of the solid material. The solid adsorbing medium is named adsorbent, while the gas or vapor adsorbed is called the adsorbate. Adsorption is a particularly useful technique when:

- 1- the pollutant gas is non-combustible
- 2- the pollutant is sufficiently valuable or highly toxic
- 3- the pollutant is in a very dilute concentration, < 1 ppm.

Adsorption is often classified according to the gas-solid attraction forces. Weak attractional forces are named physical adsorption, physi-sorption. Physical adsorption is a result of intermolecular attractive forces, Van der Waals' forces. Chemical adsorption or chemisorption has strong attraction forces between the adsorbed gas and the adsorbing solid.

Adsorption is an exothermic process. The heat liberated in physical adsorption is in the order of heat of condensation of the vapor, roughly between 2 to 20 KJ/g.mole. Heat liberated during chemisorption is much larger. It is in the order of heat of reaction, roughly between 20 to 400 KJ/g.mole.

Physical adsorption is reversible. By lowering the pressure of the adsorbate or by raising the temperature, the adsorbed gas is readily desorbed without a change in chemical composition. In opposite, chemisorption is irreversible. On desorption, the chemical nature of the chemisorbed gas will have undergone a change. So if either regeneration of the adsorbent or recovery of the adsorbate is desirable, the adsorbing medium must be chosen so that a physical adsorption process controls. For air pollution control purposes, adsorption is not a final control process. Adsorbent after being saturated with adsorbate must either be disposed of and replaced, or the vapors must be desorbed. For these reasons and other physical adsorption is more desirable for air pollution control. Table 13 below summarizes the characteristic of physical versus chemical adsorption.

Table 13. Comparison between chemisorption and physical adsorption.

Releases high heat 10,000 cal/mol	Releases low energy 100 cal/mol
Forms a chemical compound	Dipolar interaction
Desorption is difficult	Desorption is easy
Impossible adsorbate recovery	Easy adsorbate recovery

4.5.1 Theory of Adsorption

Adsorption occurs in three steps.

- 1- diffusion of pollutant from the air stream into the adsorbent surface.
- 2- migration of pollutant from certain area of the adsorbent surface (a few m^2/g) to the adsorbent pores.
- 3- adhesion of pollutant to the surface of the pores (hundreds of m^2/g).

Usually step 3 is fast and can be ignored in determining the adsorbed performance. Step 1 and step 2 are diffusional processes. In step 1, diffusion occurs due to the concentration difference. The rate of mass transferred by this step can be given by the following equation as in the absorption process;

$$N_A = \frac{k_g A_B (p - p_i)}{\rho_B}$$

Where: N_A = rate of mass transfer, kg mol/s
 k_g = local mass transfer coefficient, $\text{kg mol/s.m}^3.\text{Pa}$
 ψ = void area between adsorbent granules, m^3/m^3
 A = surface area of adsorbent, m^2/kg
 p = partial pressure of adsorbate in gas phase, Pa
 p_i = partial pressure of adsorbate at the gas-solid interface, Pa
 ρ_B = bulk density of adsorbent, kg/m^4 .

Diffusion in the pores of adsorbent can be occur by different mechanisms depending on the size of the pore. For large pores, bulk diffusion predominates. Intermolecular collisions are more important than molecule-wall collisions. For small pores, wall collisions are more likely than intermolecular collisions. This is termed Knudson or molecular diffusion. It occurs much slower than dose bulk diffusion for a given pore length. For very

small pores, surface diffusion predominates. Gas molecules can then either migrate along the surface of the solid or jump between adsorption sites. These diffusion mechanisms make the determination of the rates of mass transfer rather difficult. Empirical formulas often used to predict the rate of mass transfer rates. These equations are based on adsorption equilibrium and isotherms which will be discussed next.

Adsorption Equilibrium

At equilibrium, the number of molecules adsorbed equals that desorbed. The adsorbent bed is said to be saturated with vapors and can not adsorb any further vapors. So equilibrium determines the maximum amount of adsorbed vapor at a given temperature and pressure.

Three types of equilibrium graphs are used to describe adsorption systems as follows:

Isotherm: at constant temperature
 Isobar : at constant pressure
 Isostere: at constant amount of vapors adsorbed.

Isotherm is the most common and useful one. Figure 19 is a typical example of an adsorption isotherm. There are many attempts to predict the adsorption isotherms. Polanyi potential is the most useful theory from an engineering view point. Langmuir theory also has been used widely to describe the isothermal adsorption system.

Equilibrium isotherms are classified in five principal forms as shown in Figure 20. These include the following:

1- Type I

It is Langmuir type. It is characterized by the formation of a complete chemisorbed monolayer. It has been observed for microporous adsorbents such as charcoal, silica gel and molecular sieve of few molecular capillaries diameters.

2- Type II

It is characteristic of the formation of multilayers of adsorbates. It is known as BET after Brunauer, Emmett and Teller. It has been observed for nonporous solids.

3- Type III

It is similar to Type II but relatively rare.

4- Type IV and Type V

They reflect capillary condensation since they level off as the saturation pressure of the adsorbate vapor is reached. They exhibit a hysteresis loop when adsorbates are desorbed. They have been observed for porous adsorbents.

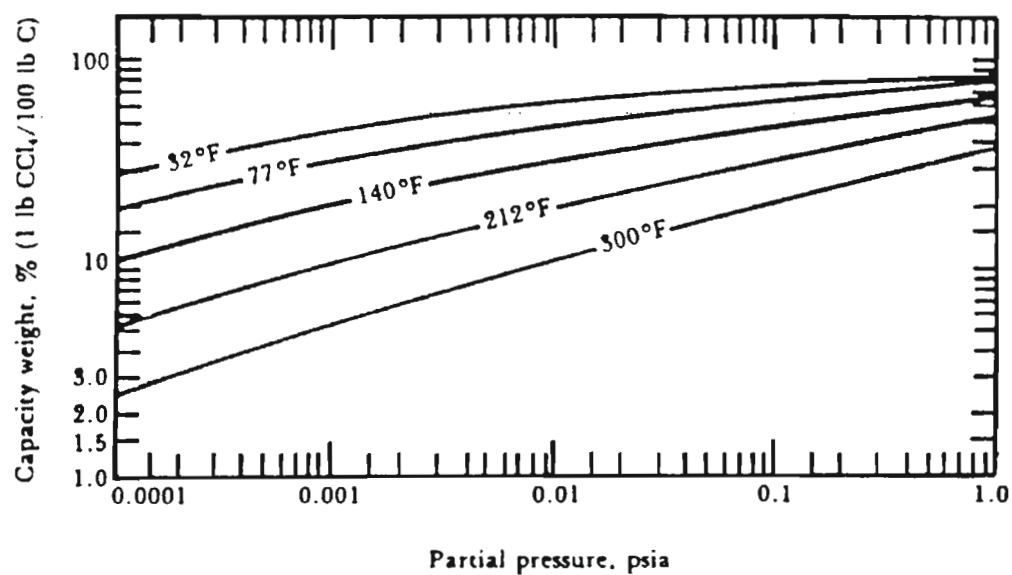


Fig. 4.19. Adsorption Isotherm for Carbon Tetrachloride on Activated Carbon.

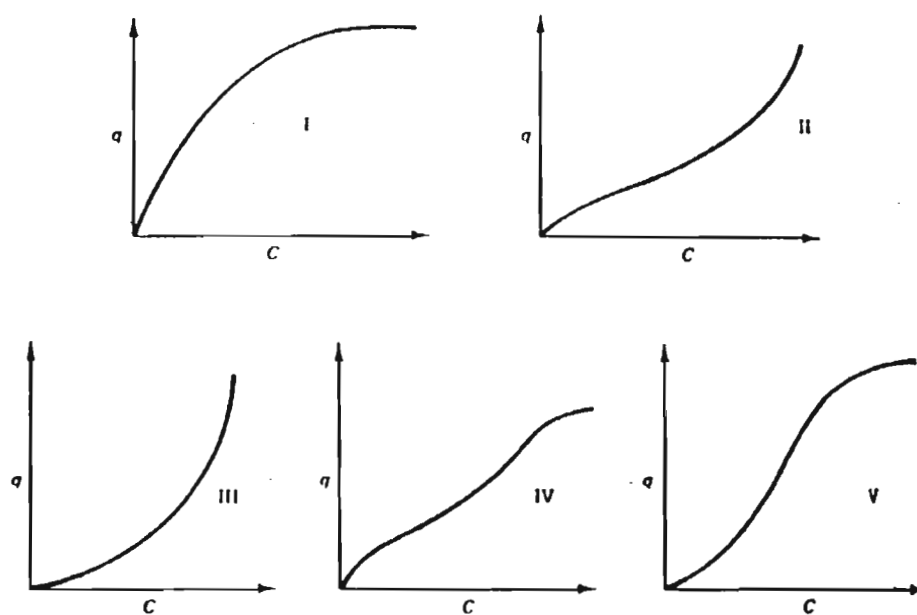


Fig. 4.20. Adsorption Isotherms.

Adsorption Isotherm Models

the Polanyi potential theory states that the adsorption potential is a function of the reversible isothermal work done by the system. So the free energy of adsorption, ΔF , is related to the relative vapor pressure by the following equation.

$$\Delta F = -RT \ln\left(\frac{p^\circ}{p}\right)$$

where R = ideal gas constant
 T = absolute temperature
 p° = vapor pressure of adsorbate
 p = partial pressure at adsorbate

In Langmuir theory, a monolayer is assumed to be adsorbed only. So a molecule can be adsorbed if it strikes an uncovered area of the adsorbent.

The principal assumptions for Langmuir models are

- 1- all the sites of the solid have the same activity for adsorption.
- 2- there is no interaction between adsorbed molecules.
- 3- all of the adsorption occurs by the same mechanism and each adsorbent complex has the same structure.
- 4- one monolayer is only formed on the surface.

The derivation of Langmuir equation is accomplished by finding the rate of the surface coverage, $d\theta/dt$, which is given by

$$\frac{d\theta}{dt} = r_a - r_d$$

where r_a and r_d are rate of adsorption and desorption respectively. The rate of adsorption is equal to

$$r_a = K_a P(1 - \theta)$$

Where P is the system pressure
 θ is the surface coverage
 $(1-\theta)$ is the fraction of bare/surface
 K_a is the rate constant, $K_a = N_0/(2\pi MRT)^{1/2}$
 $(N_0$ is Avogadro's No., M is the molecular weight and R is the gas constant).

The desorption rate is

$$r_d = K_d \theta$$

where K_d is desorption rate constant

$$K_d = K_1 \exp\left(\frac{-E_1}{R_T}\right)$$

So the rate of the surface coverage is equal to

$$\frac{d\theta}{dt} = r_a - r_d = K_a P(1-\theta) - K_d \theta$$

Upon integration

$$\theta = \frac{(K_a/K_d)P}{1+(K_a/K_d)P} \{1 - \exp [-(K_a + K_d)t]\}$$

for equilibrium (t is infinite)

$$\theta = \frac{KP}{1+KP}, \text{ where } K = K_a/K_d$$

if θ is replaced by V/V_m , where V_m is the maximum monolayer capacity, then

$$V = \frac{V_m KP}{1 + KP}$$

for low pressure

$$V = V_m KP$$

Alternatively Langmuir isotherm can be rewritten in the following form

$$\frac{P}{V} = \frac{1}{K V_m} + \frac{P}{V_m}$$

Langmuir equation has no direct application in pollution control system. Instead, Brunauer, Emmett and Teller developed the following equation for multilayer adsorption based on Langmuir's theory. This equation is often known as BET equation.

$$\frac{p}{V(p^\circ - p)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right) \frac{p}{p^\circ}$$

where

V is volume of vapor adsorbed per unit weight of adsorbent

V_m is volume of vapor adsorbed per unit weight with a layer one molecule thick

C is constant dependent on temperature.

A plot of $[p/V(p^\circ - p)]$ versus p/p° gives a straight line with a slope of $(C-1)/V_m C$ and an intercept of $1/V_m C$. Then both C and V_m can be computed.

The plot of $\ln p$ versus $1/T$ at a constant amount of vapor adsorbed is called an isostere adsorption equilibrium. Figure 21 shows an adsorption isostere graph of adsorption of H_2S gas onto molecular sieves. The slope of isostere lines at different amount of adsorbed vapor gives the heat of adsorption.

Figure 22 is called an isobar adsorption equilibrium. It is a plot of the amount of vapors adsorbed versus temperature at a constant pressure.

Another isotherm model is known as Freundlich isotherm. It is a semiempirical equation expressed in the following form

$$q = K(C)^{1/n}$$

where q is the adsorbate uptake per unit weight of adsorbent.
 C is the equilibrium adsorbate concentration
 K and n are constants for the adsorbate adsorbent system.

Adsorbent Materials

Adsorbents are characterized by their surface area, volume and diameters of their pores. The most important chemical differences among adsorbents are in their electrical polarity.

Activated carbon, activated alumina, silica gel and molecular sieve are the most common adsorbent often used in air pollution control. Table 13 below gives some of the important physical properties of these adsorbent.

Table 13. Physical properties of important adsorbents.

	Activated carbon	Activated alumina	Silica gel	Molecular sieve
Surface area (m^2/gm)	1100-1600	210-360	750	-
Surface area (m^2/cm^3)	300-560	210-320	520	-
Pore volume (cm^3/gm)	0.80-1.20	0.29-0.37	0.40	0.27-0.38
Pore volume (cm^3/cm^3)	0.40-0.42	0.29-0.33	0.28	0.22-0.30
Mean pore diameter ($^{\circ}A$)	15-20	18-20		3-9

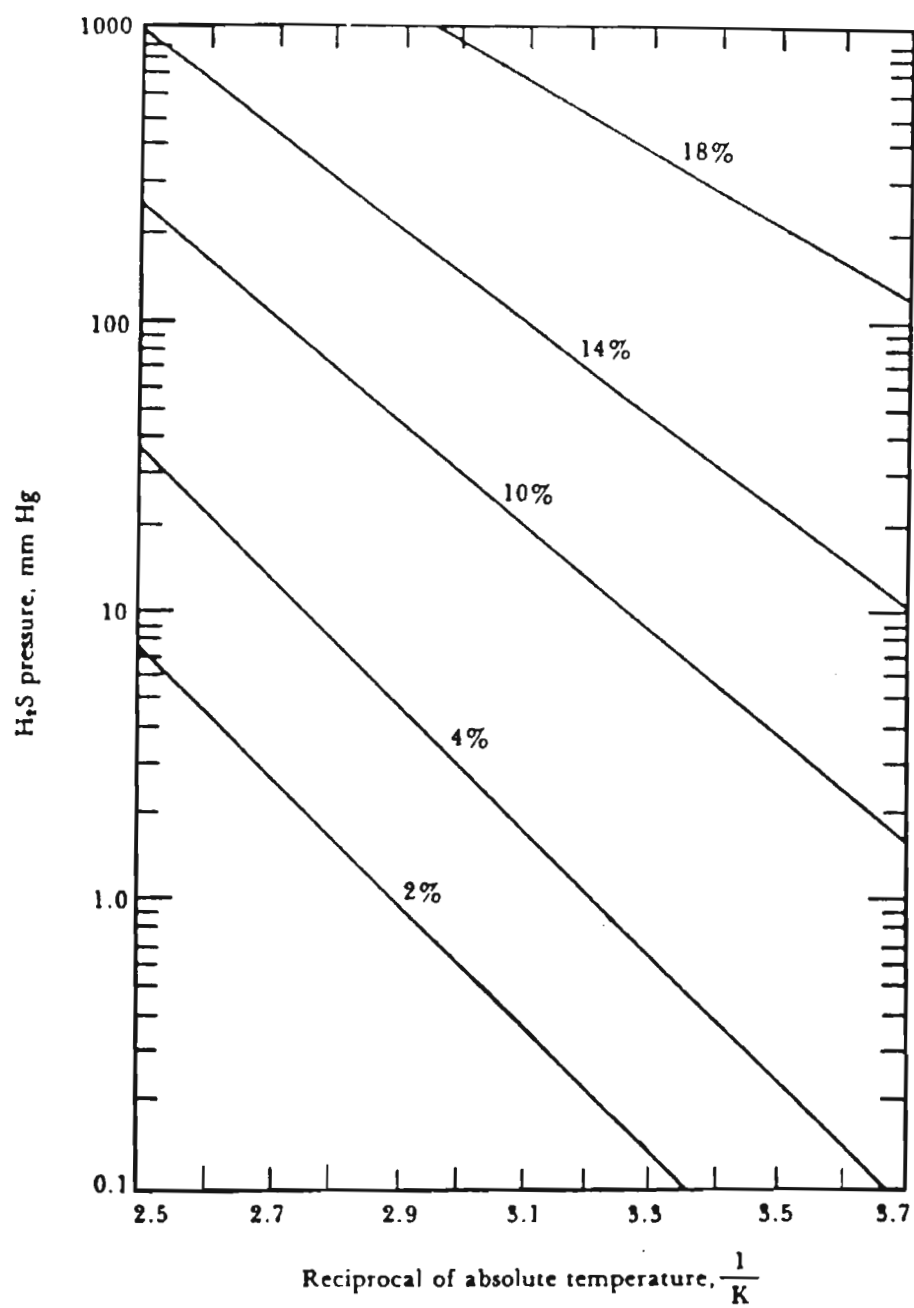


Fig. 4.21. Adsorption Isosteres of H_2S on Molecular Sieve.

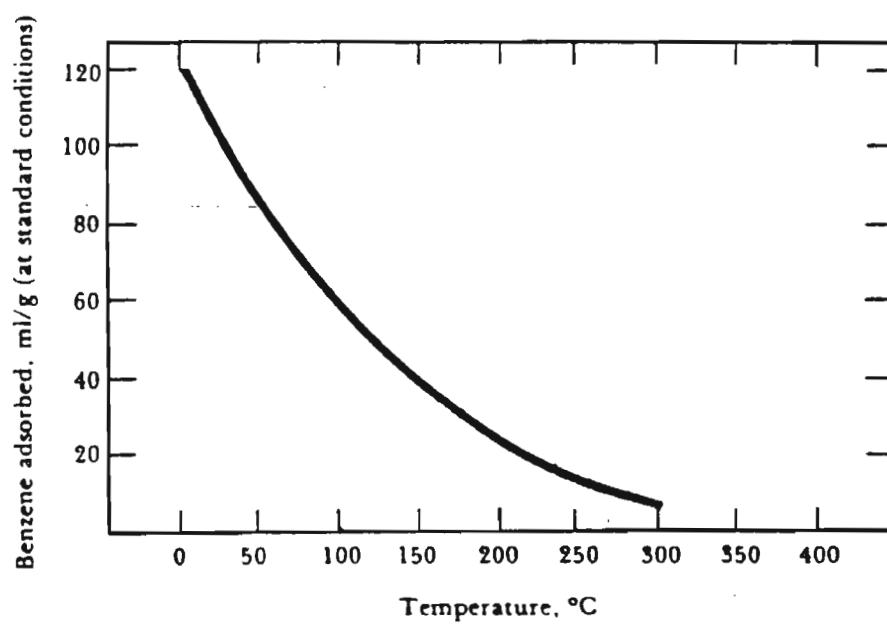


Fig. 4.22. Adsorption Isobar for Benzene on Carbon (Benzene at 10 mmHg).

Adsorption System

Temperature, pressure and gas velocity have different effects on adsorption. For physical adsorption, adsorption ability decreases as the system temperature increases. On opposite, adsorption capacity increases with an increase in the partial pressure of the vapor.

The probability of a molecule to be adsorbed increases at a slower gas velocity. Usually 30 m/min (100 ft/min) is the maximum velocity used for conventional absorbers. A lower limit of 6 m/min (20 ft/min) is requested for avoiding channeling and other flow distribution problems. However, the required gas velocity depends on the absorber diameter and the volumetric flow rate of the contaminant gas.

Gas velocity affects the absorber pressure drop. High pressure drop is expected at high gas velocity. The pressure drop across the bed depends on the depth of adsorbent. The adsorbent depth determines the capability of the adsorbent in gas removal. For shorter bed depth than the required mass transfer zone, MTZ, absorber will be inefficient. The MTZ is estimated from the following relation

$$MTZ = \frac{1}{1 - X_s} D \left(1 - \frac{C_B}{C_s}\right)$$

where

D is the bed depth, m

C_B, C_s is breakthrough and saturation capacity, %.

X_s is degree of saturation in MTZ (usually assumed 50%).

If the total amount of adsorbent is known (from adsorption isotherm), the bed depth can then be found by knowing the adsorber diameter and the adsorbent density. The adsorbent depth is normally found from the pressure drop data. Figure 23 shows the variation of the pressure drop with gas velocity for granular carbon beds. This graph determines the maximum allowable pressure drop in the bed per unit bed length. The adsorbent depth is found from this graph by dividing the used pressure drop by the maximum allowable pressure drop obtained from the graph at the same gas velocity.

Regeneration and sometime replacement of adsorbent is always required to maintain high efficient adsorption. There are four methods often used in adsorbent regeneration. These include

- 1- Thermal Swing

Heat is used to desorb the adsorbate. Steam regeneration is often used.

- 2- Pressure Swing

Reduction of the pressure at constant temperature also allow a desorption of adsorbate.

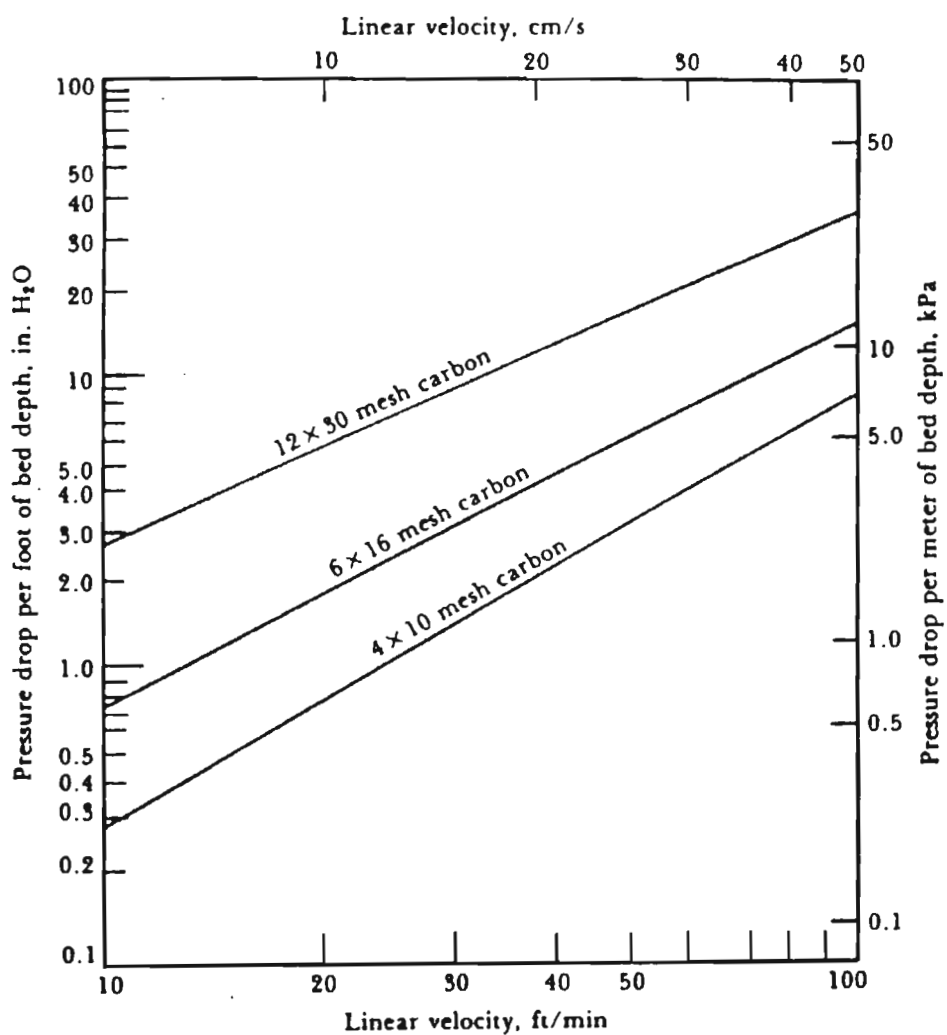


Fig. 4.23. Pressure Drop vs. Flow Rate for Granular Carbon Beds.

- 3- Inert purge gas stripping
Introduction of an inert gas into the adsorbent causes the adsorbate to be stripped into the gas phase.
- 4- Displacement
Adsorbate is adsorbed by other adsorbent material.

Table 14 below gives a comparison between these methods. Evidently steam regeneration is the most effective methods in adsorbent regeneration.

Table 14. Regeneration of one pound of carbon loaded with 20% ether

Regeneration method	Regeneration conditions	Expelled ether (%)
Thermal swing	Heating at 100°C (212°F) for 20 min	15
Pressure swing	Vacuum of 50 mm Hg at 20°C (68°F) for 20 min	25
Combination	Gas circulation at 130°C (266°F) for 20 min	45
Thermal swing	Direct steam at 100°C (212°F) for 20 min	98

Figures 24 to 28 show examples of the adsorbers often used in air pollution industry. these include the following groups

- 1- Conister adsorber, Figure 24
- 2- Fixed-bed adsorbers, Figure 25 and 26
- 3- Fluidized bed adsorber, Figure 27
- 4- Rotating bed adsorber, figure 28

PROBLEMS

- 1- A dry cleaning process exhausts a 15,000 scfm air stream containing 680 ppm carbon tetrachloride. Given Figure 19 and assuming the exhaust stream is at approximately 140°F and 14.7 psia, determine the saturation capacity of the carbon.
- 2- Assume the same conditions as stated in Problem 1. Estimate the amount of carbon that would be required if the adsorber were to operate on a 4-hour cycle. The molecular weight of CCl_4 is 154 lb/lb mole.
- 3- A solvent degreaser is designed to recover toluene from a 3.78 m³/s (8000 acfm) air stream at 25°C (77°F) and atmospheric pressure. The company is planning to use a two bed carbon adsorption system with a cycle time of 4 hours.

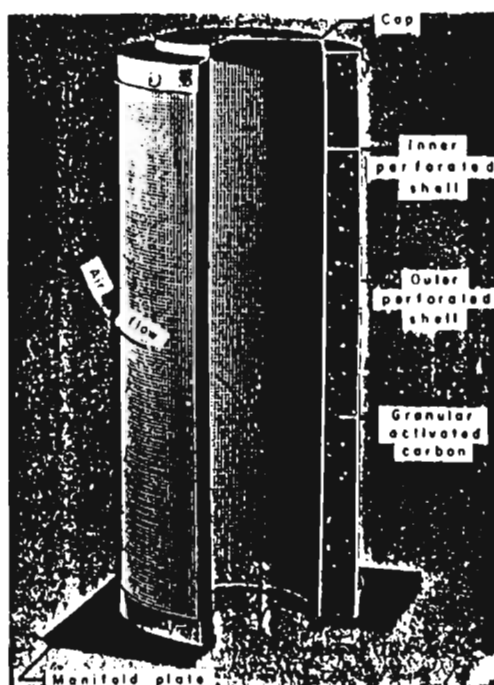


Fig. 4.24. Cylindrical Canister Adsorber.

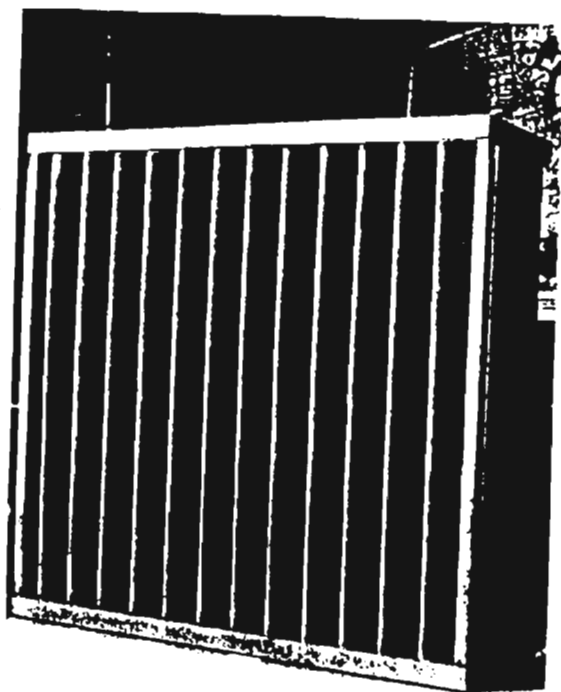


Fig. 4.25. Pleated Cell Adsorber.

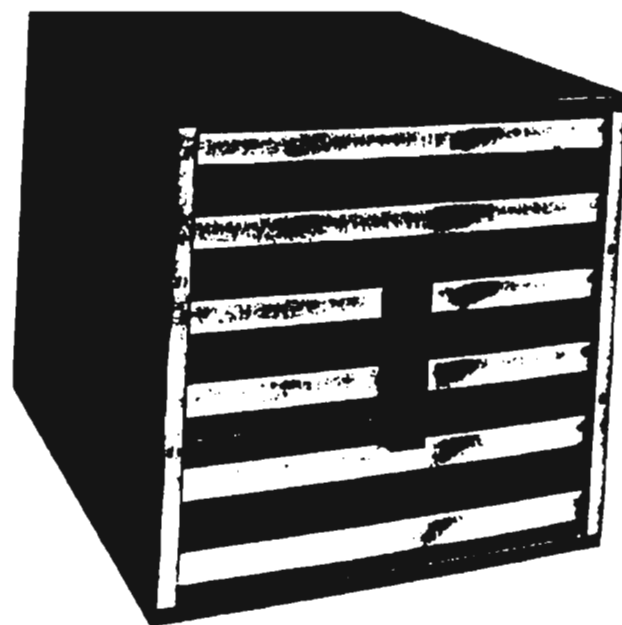


Fig. 4.25. Aggregated Flat Adsorber.

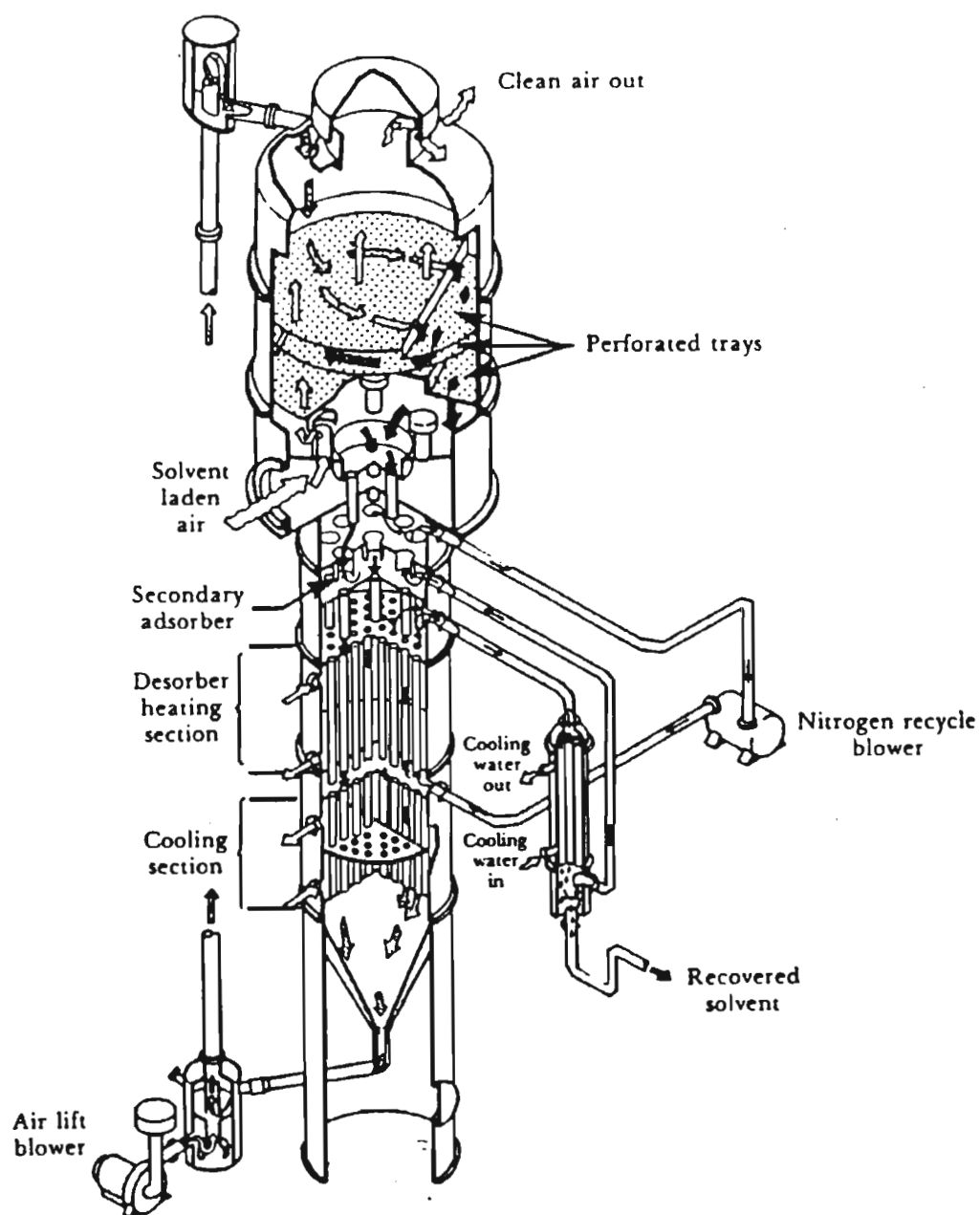


Fig. 4.27. Fluidized Bed Adsorber.

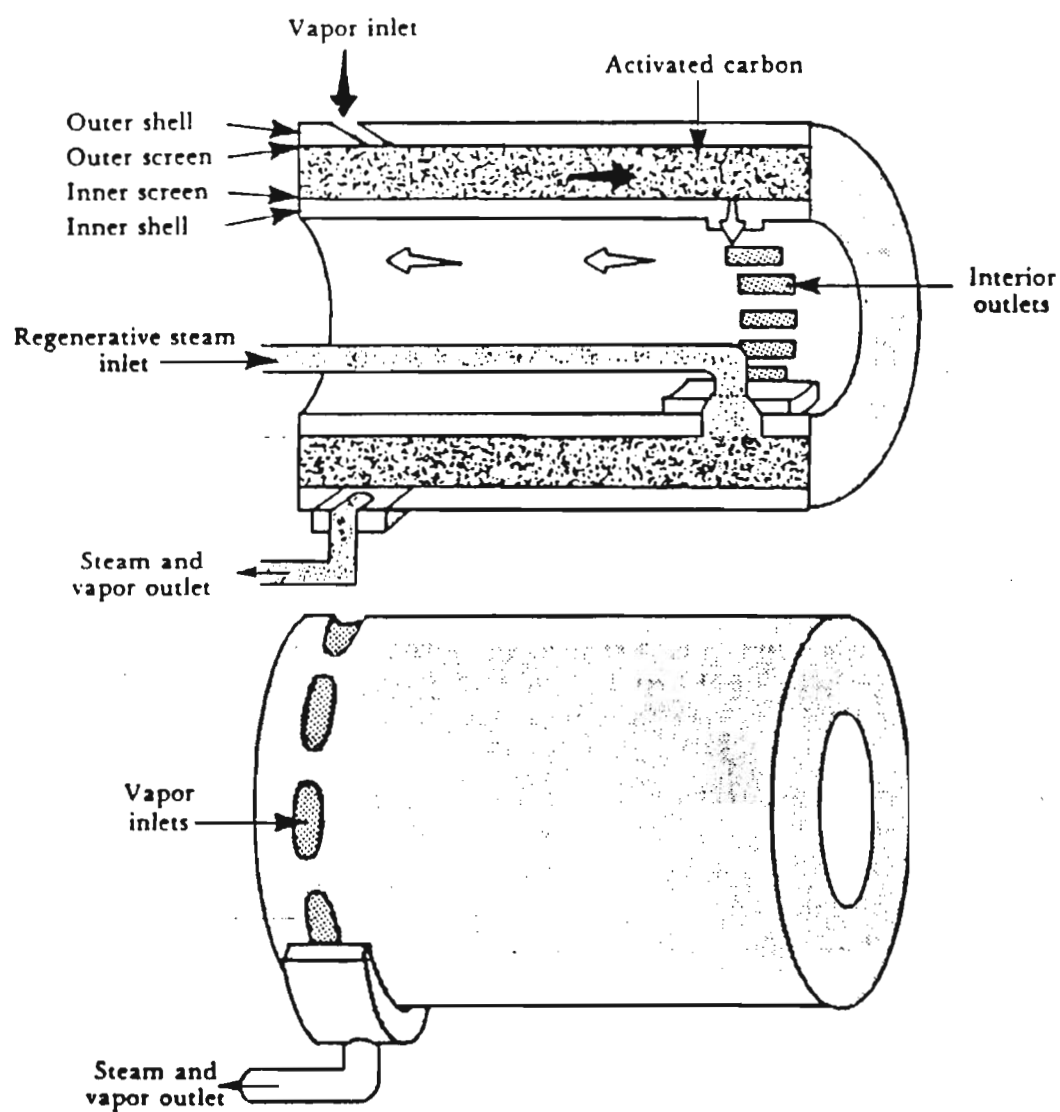


Fig. 4.28. Rotary Bed Adsorber.

The maximum concentration of toluene is kept below 50% of the lower explosive limit for safety purposes. Knowing that the saturation capacity of the carbon is 40% (or 40 kg toluene per 100 kg of carbon) at 0.089, estimate:

1. the amount of carbon required for a 4-hour cycle
2. square feet of surface area required based on a 0.508 m/s (100 fpm) maximum velocity
3. depth of the carbon bed

Given: LEL for toluene = 1.2%
 molecular weight of toluene = 92.1 kg/kg mol
 carbon density = 480 kg/m³ (30 lb/ft³)

- 4- The adsorption of ethane on Linde molecular sieve, type 5A, was studied by Glessner and Myers in 1969 at 35°C. (a) Using the data presented below, determine if the Langmuir equation can be used to model the data. (b) Calculate the total surface area of the solid.

P (mmHg)	Uptake [cm ³ (STP)/g]
0.17	0.059
0.95	0.318
5.57	1.638
12.09	3.613
111.32	24.236
220.87	34.278
300.05	38.340
401.25	41.779
500.18	44.037
602.74	45.693

- 5- Using the data given below for the adsorption of carbon dioxide on type 5A molecular sieve (a) show that the data for 35°C and 55°C can be described by a single characteristic curve as required by the potential theory. (b) Calculate the isosteric heat of adsorption.

T = 35°C		T = 45°C		T = 55°C	
P (mmHg)	Uptake [cm ³ (STP)/g]	P (mmHg)	Uptake [cm ³ (STP)/g]	P (mmHg)	Uptake [cm ³ (STP)/g]
0.028	0.755	0.085	0.935	0.21	1.26
0.15	2.17	0.26	2.06	0.44	2.09
0.35	3.73	0.48	3.16	0.78	3.11
0.62	5.46	0.70	4.16	0.99	3.66
0.92	7.07	0.75	4.28	1.12	3.81
0.94	7.14	-	-	1.18	4.01

6. The adsorption of sulfur dioxide on mordenities was studied by Roux et al. in 1973 at 0°C. (a) Using the data below, determine the Langmuir constants, and (b) calculate the total surface area of the solid. The density of liquid SO₂ at 0°C in the adsorbed phase is 1.43 g/cm³.

PSO ₂ (mmHg)	Uptake (mmoHg)
5	1.75
10	2.20
15	2.40
20	2.62
30	2.75
40	2.85
50	3.00
60	3.05
70	3.12

- 7- The equilibrium adsorption isotherm for nitrogen on silica gel was obtained by Emmette 1954 at -195.8°C. Using the data below, determine the change of spreading pressure as a function of the pressure of nitrogen in the vapor phase. The surface area of the adsorbent (silic gel) is 550 m²/g.

$P_{N_2}(\text{mmHg})$	Uptake [$\text{cm}^3(\text{STP})/\text{g}$]
27.69	60.61
146.15	94.55
200.00	101.82
261.54	115.15
292.31	120.00
361.54	134.55
433.85	157.58

- 8- Ethylene is to be separated from butadiene by flowing the gas mixture through a packed bed of molecular sieve at a temperature of 15°C and a pressure of 1.0 atm. From an analysis of the data it was found that only 20% of the adsorbent surface was covered. Assuming that the Hill-de Boer model can be used to describe the adsorption system, estimate the fraction of surface coverage at a pressure of 10 atm and 15°C .
- 9- Emmett 1954 studied the adsorption of argon on 0.606 g of silica gel at -183°C . Using the BET equation and the data below, calculate the surface area of the adsorbent.

$P(\text{mmHg})$	Volume Adsorbed [$\text{cm}^3(\text{STP})$]
78.46	55.03
176.92	72.73
224.62	80.00
378.46	106.67
432.31	117.58
515.38	138.18
584.62	166.06

The surface area of the adsorbent can be related to the volume of gas adsorbed in the monolayer by the expression

$$S_g = 4.35 \times 10^4 V_m$$

where S_g is the surface area per unit weight of the adsorbent (cm^2/g solid) and V_m is the volume of gas adsorbed in the monolayer (cm^3/g).

- 10- The adsorption of phenol from an aqueous solution onto XAD-8 resin was studied by Farrier et al in 1979. The isosteric heat of adsorption can be expressed by

$$\frac{\Delta H_{st}}{R} = - \left| \frac{\partial(\ln C_f)}{\partial\left(\frac{1}{T}\right)} \right|_q$$

where C_f is the equilibrium concentration and q is the uptake. From the data below, calculate the heat of adsorption at $q = 1.0$ mg of phenol per gram of solid.

Temperature (°C)	q (mg/g solid)	C_f (mg/ml solution)
0	0.5	0.00082
	1.0	0.002
	2.0	0.005
25	0.5	0.0015
	1.0	0.005
	2.1	0.008
75	0.5	0.005
	1.0	0.010
	2.0	0.020

- 11- The adsorption of carbon dioxide on molecular sieve, type 5A, was studied by Blakly and Taylor in 1969 at three different temperatures. (a) Using the data below, determine if the Polanyi potential theory can be used to model the data, and (b) calculate the isosteric heat of adsorption.

Equilibrium Uptake (lb CO ₂ /lb solid)			
P _{CO₂}	T = 32°F	T = 50.9°F	T = 64.4°F
1.0	0.043	0.032	0.024
2.0	0.066	0.048	0.038
3.0	0.078	0.062	0.047
4.0	0.086	0.072	0.055
5.0	0.092	0.080	0.063
6.0	0.098	0.086	0.070
7.0	0.102	0.090	0.076
8.0	0.105	0.093	0.080
9.0	0.108	0.098	0.083

4.6 CONDENSATION

Condensation is the process of reducing a gas or vapor to a liquid by lowering their temperature and/or increasing the pressure. Usually decreasing the temperature is much cheaper than increasing the pressure.

Condensation is considered the best way of recovering a valuable organic gaseous pollutant. It can be used alone as an effective pollution control device if refrigerated fluid is used. However, water and/or air condenser are a valuable preliminary device often used before employing any effective pollution control unit such as absorbers, adsorbers and incinerators.

Condensers are simple and inexpensive devices. They are often called heat-exchangers. Their primary use is to reduce the overall cost of the pollution control system. Before discussing the different types of condensers used in gaseous pollutant control, brief presentation of the thermal properties of pollutants and condensation principles will be given.

Thermodynamic Properties of Pollutants

Table 15 lists some important properties of common pollutants. The relation of vapor pressure to temperature for saturated vapor and the variation of the latent heat of condensation h_{fg} with temperature are important in predicting the condenser performance.

Kalkwarf-Thodos equation is one possible way of expressing the vapor pressure P_p as function of temperature. This equation is given by

$$\ln P_p = \ln P_c - 2.303B \left(\frac{1}{T} - \frac{1}{T_c} \right) + \left(2.67 - \frac{1.8B}{T_c} \right) \ln \frac{T}{T_c} + 0.422 \left(\frac{T_c^2}{P_c T^2} P_p - 1 \right)$$

where T_c, P_c are the critical pressure and temperature

B is constant given by

$$B = \frac{\ln P_c + 2.67 \ln T_b/T_c + 0.422(T_c^2/P_c T_b^2 - 1)}{2.303(1/T_b - 1/T_c) + (1.8/T_c) \ln T_b/T_c}$$

where T_b is the normal boiling temperature (Table 15 gives values of B too).

The latent heat of condensation is listed in Table 15 at the normal boiling temperature. At other temperature, it can be estimated from the following equation

Table 15. Properties of Some Pollutant Gases.

Gas	h_{fg} , kJ/kg	T_b , K	T_c , K	P_c , atm	B , K
Acetaldehyde	570	293	461	54.7	2182
Acetic acid	405	391	594	57.1	3384
Acetone	520	330	510	47.2	2473
Allyl alcohol	684	370	545	55.5	3582
Ammonia	1175	239	405	111.3	1802
n-Butyl alcohol	503	411	583	37.4	3990
Benzene	391	353	562	48.3	2387
Bromine	191	331	584	102	2136
n-Butane	386	272	425	37.7	1765
n-Butyl alcohol	592	391	563	43.6	3786
Carbon disulfide	352	319	552	78	1925
Carbon tetrachloride	194	350	556	45.0	2313
Chloroform	237	334	536	54	2401
Cyclohexane	358	354	553	40.2	2369
n-Decane	252	417	618	20.8	3707
Diethylamine	381	329	496	36.6	2432
Diethyl ketone	380	376	561	36.9	2912
Ethane	489	184	305	48.2	1073
Ethyl acetate	434	305	523	38.0	2730
Ethyl alcohol	855	351	516	63.0	3590
Ethylamine	611	290	456	55.5	2178
Ethyl benzene	339	409	617	35.6	2976
Ethyl chloride	388	285	460	52	1892
Ethylene	483	169	283	50.5	971
1,2-Ethylene chloride	324	355	561	53	2568
Ethyl ether	351	308	467	35.9	2204
Ethyl formate	407	327	508	46.8	2393
Freon 22	232	232	370	48.5	1562
n-Heptane	320	371	540	27.0	2755
n-Hexane	337	342	507	29.3	2439
Hydrogen bromide	218	207	363	84	1265
Hydrogen chloride	443	188	324	81.5	1200
Hydrogen cyanide	880	299	457	53.2	2458
Hydrogen fluoride	1562	188	461	64	368
Hydrogen sulfide	548	213	373	88.9	1336
Isobutyl acetate	309	391	561	31.4	3134
Isobutyl alcohol	578	381	518	42.4	3665
Isopropyl alcohol	667	355	508	47.0	3640
Methane	510	111	190	45.4	562
Methyl alcohol	1100	338	512	79.9	3345
Methyl chloride	428	249	416	65.9	1618
Methyl ethyl ketone	444	353	535	41.0	2688
Methyl formate	470	305	487	59.2	2223
Naphthalene	316	491	748	40.0	3621
n-Octane	306	399	569	24.5	3098
n-Pentane	357	309	470	33.4	2108
Propane	426	231	370	41.9	1432
Propionic acid	414	414	612	53	3880
n-Propyl acetate	336	375	519	33.2	3000
n-Propyl alcohol	688	371	537	51.0	3739
Propylene	418	225	365	45.6	1383
Pyridine	450	388	620	55.6	2748
Sulfur dioxide	389	263	431	77.9	1947
Sulfur trioxide	533	318	491	83.8	2980
Toluene	363	384	592	40.6	2719
Trichloroethylene	240	360	544	49.5	3005
Water	2257	373	647	218.3	3233
Xylene	347	417	640	36.8	3063

$$h_{fg} = h_{fgb} \left(\frac{T_c - T}{T_c - T_b} \right)^{0.38}$$

Condensation Principles

As mentioned before, lowering the temperature or increasing the pressure lead to condensation. At low temperature the kinetic energy of the gas molecules are low. While high pressures cause the molecules to be brought close together. The actual conditions at which a particular gas molecules will condense depends on its physical and chemical properties.

Condensation occurs when the partial pressure of the pollutant in the gas stream equals its vapor pressure as a pure substance at the operating conditions. This can be accomplished by

1. increasing the system pressure (compressing the gas volume) until the partial pressure of the gas equals its vapor pressure.
2. Cooling the gas at fixed pressure until the partial pressure equals its vapor pressure.
3. Both compressing and cooling of the gas until its partial pressure equals its vapor pressure.

Figure 29 illustrates these steps clearly. This figure is called P-T diagram. Detail discussion of its significance can be found in physical chemistry texts and elementary thermodynamics books.

However, temperature is the only process variable which governs the effectiveness of a condenser. Increasing the pressure is very costly and rarely used in industrial condensers. At the operating pressure, the outlet temperature from the condenser determines the maximum removal efficiency. The collection efficiency for the removal of a gaseous pollutant can be given by

$$\eta = 1 - \frac{\dot{m}_2}{\dot{m}_1}$$

where \dot{m} is the mass flow rate of pollutant or in term of the pollutant concentration,

$$\eta = \frac{P}{P - P_2} \left(1 - \frac{M P_2}{R T_1 C_1} \right)$$

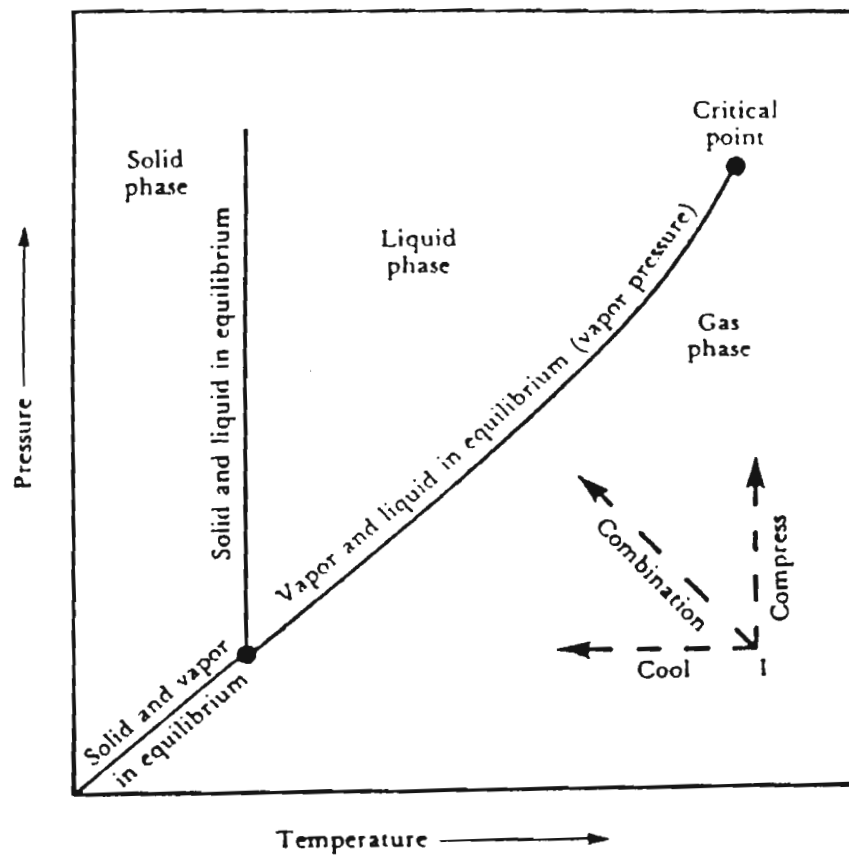


Fig. 4.29. Typical P-T Diagram.

Types of Condensers

Condensers fall in two groups, contact and surface condensers. In the contact condensers, the coolant and the vapor stream are physically mixed. Figure 30 shows three types of contact condensers. These are spray, jet ejector and barometric condensers.

No contact is allowed between the coolant and the gas stream in surface condensers. Surface condensers are often named shell and tube heat exchangers. Figure 31 and 32 show examples of a single pass and two multipass exchangers.

Condensers Performance

As the vapor stream passes through the condenser, both its temperature and its compositions are changing. So simultaneous heat and mass are transferred. A basic heat balance equation can be written for condensation in the following form,

$$q = \dot{m} \bar{C}_p (T_{g1} - T_d) + \dot{m} H_v = L \bar{C}_p (T_{L2} - T_{L1})$$

where

- q is the heat transfer rate
- \dot{m} is mass flow rate of vapor
- L is mass flow rate of coolant
- \bar{C}_p is average specific heat of gas or liquid
- T is temperature
(subscript g for gas, L for liquid & d for dew point)
- H_v is heat of condensation or vaporization

In a surface condensers, heat is transferred from the vapor to the coolant through a heat exchange surface. The rate of heat transfer depends on

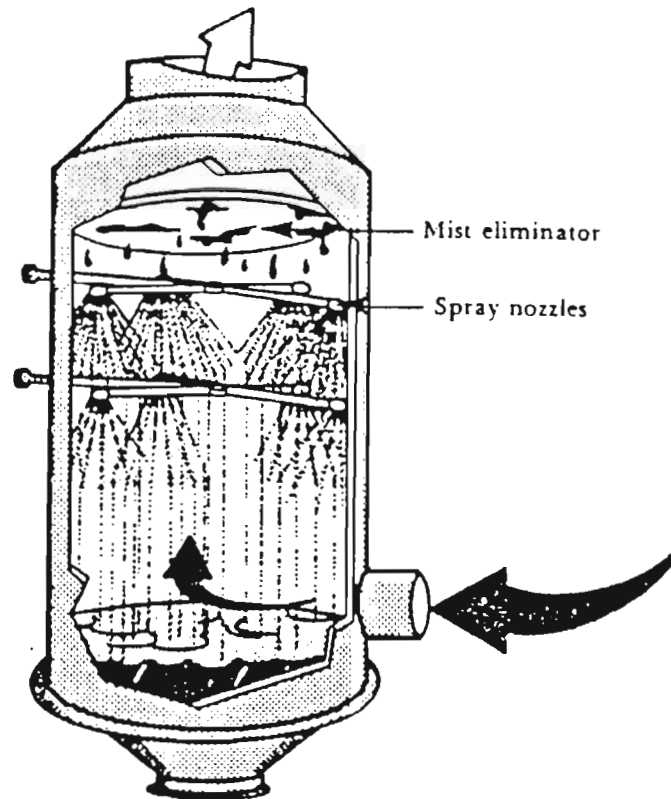
- 1- the available surface area, A
- 2- the resistance to heat transfer, (so called overall heat transfer coefficient, U)
- 3- the mean temperature difference between vapor and coolant, ΔT_m .

This mathematically expressed by

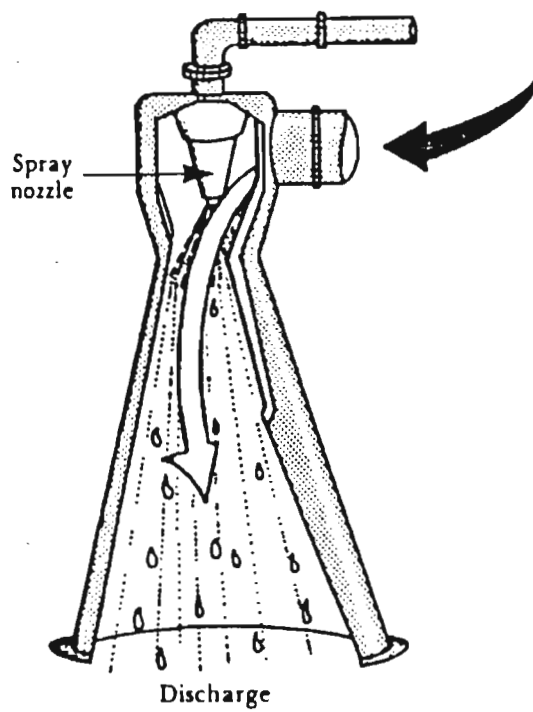
$$q = U A \Delta T_m$$

The overall heat transfer coefficient represents the total resistance that heat experience while being transferred. Figure 33 shows these resistances around a cooling tube. Mathematically these resistance are given by the following relation

(a) spray contact condenser



(b) jet ejector condenser



(c) barometric condenser

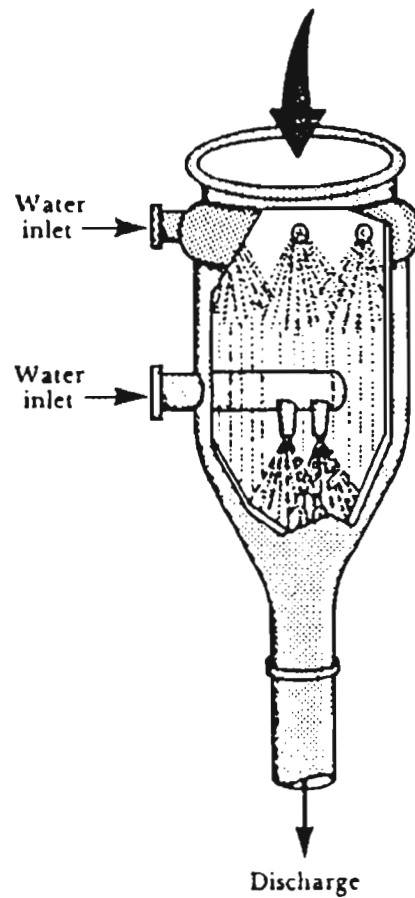


Fig. 4.30. Direct Contact Condensers.

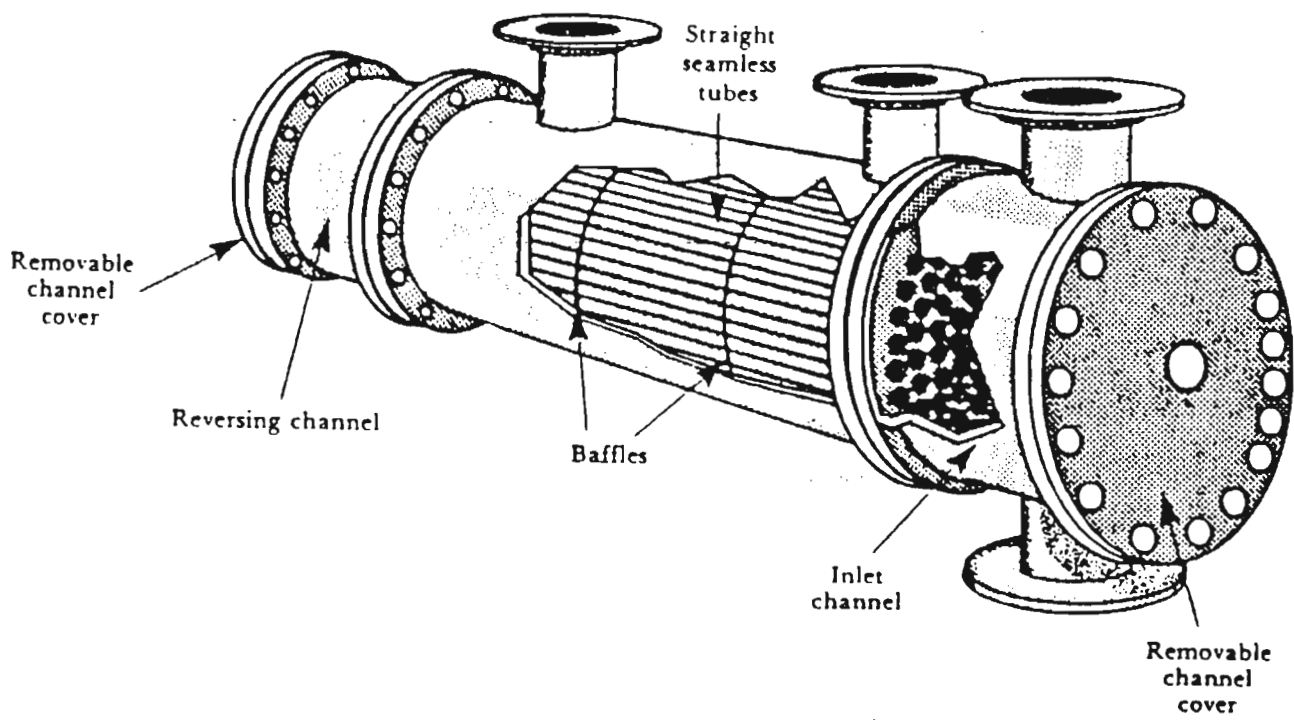
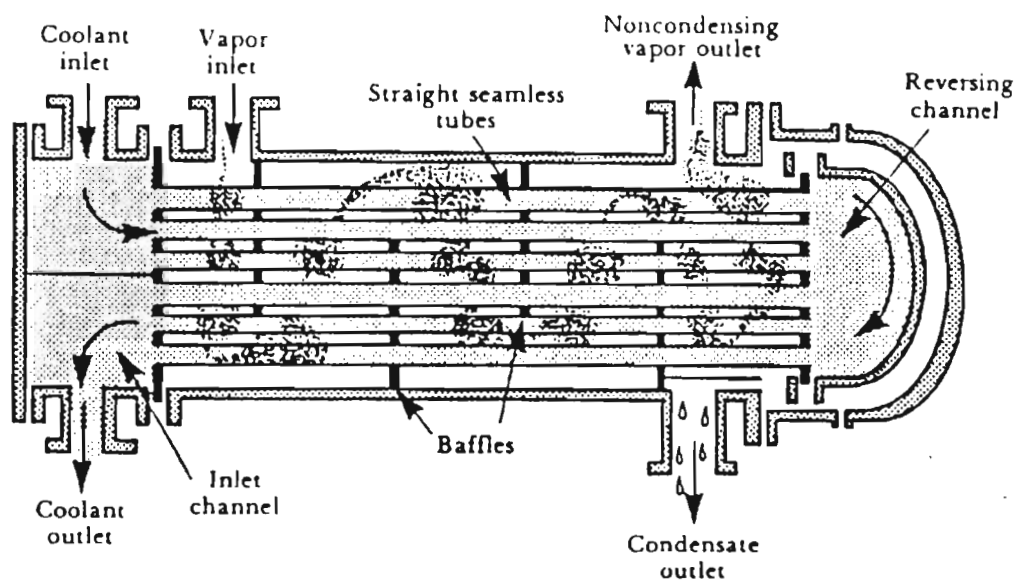


Fig. 4.31. Single-Pass Surface Condensers.

1-2 parallel flow exchanger



2-4 exchanger

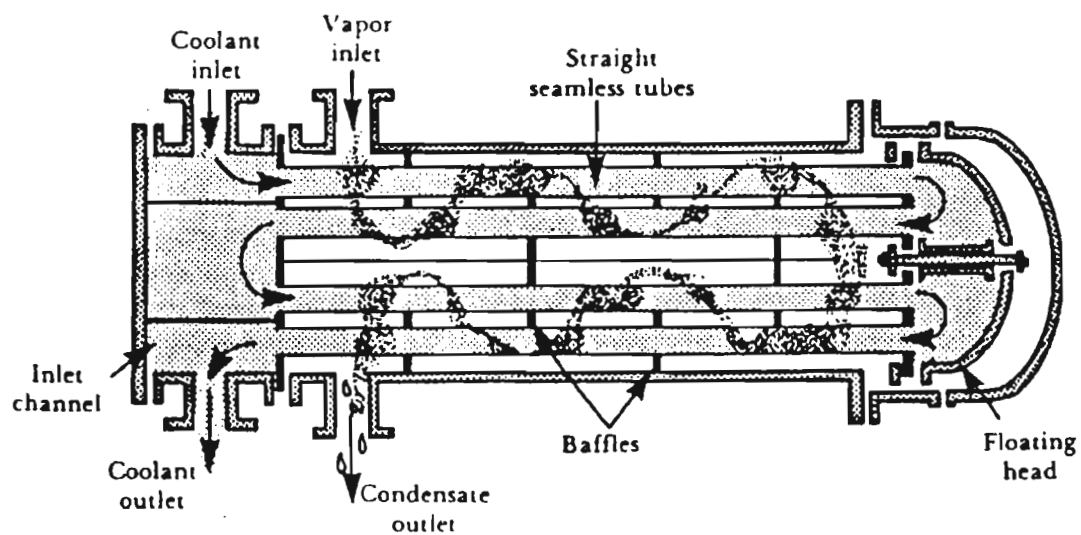


Fig. 4.32. Multipass Surface Condensers.

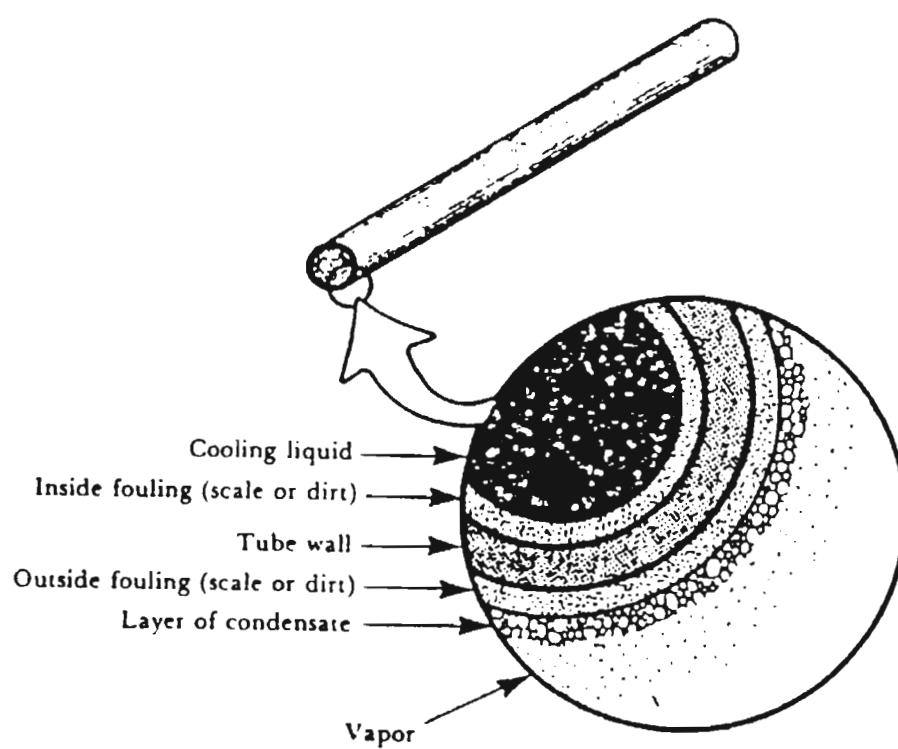


Fig. 4.33. Resistances to Heat Transfer Around A Cooling Tube.

$$\frac{1}{U} = \frac{1}{h_o} + \frac{r_o}{r_i} \frac{1}{h_i} + \frac{r_o}{K} \ln \frac{r_o}{r_i} + \frac{1}{h_{fi}} + \frac{1}{h_{fo}}$$

where,

h_o, h_i are film coefficient for outside and inside surface.

r_o, r_i are outside and inside tube radius.

K is the thermal conductivity of the tube

h_{fi}, h_{fo} are fouling factors on the inside and outside walls.

for usual applications, K is large and r_o/r_i is close to unity so

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_i} + \frac{1}{h_{fi}} + \frac{1}{h_{fo}}$$

This relation can be further simplified if ignoring the fouling factors,

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_i}$$

Many empirical equations are given for estimating the values of the film coefficients, h_i and h_o . Among these are the following

$$h_i = 0.023 \frac{K}{D} Re^{0.8} Pr^{1/3} \left(\frac{\mu_{mb}}{\mu_w} \right)^{0.14}$$

$$h_o = C \frac{K}{D} Re^n Pr^{1/3}$$

where K is the thermal conductivity of the tube

D is the tube diameter

Re is Reynolds number, $Re = \rho v d / \mu$

Pr is Prandtl number, $Pr = C_p \mu / K$

μ_{mb} is fluid viscosity at the mean bulk temperature

μ_w is fluid viscosity at the tube wall temperature

Equation for h_i is valid for $Re > 10,000$, $0.7 < Pr < 17,000$ and length/diameter ratio $L/D > 60$. The constants C and n in h_o equation have the following values according to the value of Re :

Re	C	n
1 - 4	0.989	0.330
4 - 40	0.911	0.385
40 - 4,000	0.683	0.466
4,000 - 40,000	0.183	0.618
40,000 - 250,000	0.0266	0.805

Table 16 below gives typical values of the overall heat transfer coefficient that can be used for preliminary condenser design only. Actual heat transfer coefficient must be known for accurate design. This may require numerous data from actual running systems.

Table 16 Typical Overall Heat Transfer Coefficient
in Tubular Heat Exchangers

Condensing vapor* (shell side)	Cooling liquid (tube side)	U (Btu/°F.ft ² .hr)
Alcohol vapor	Water	100 - 200
High boiling hydrocarbons (vacuum)	Water	20 - 50
Low boiling hydrocarbons	Water	80 - 200
Organic solvents	Water	100 - 200
Organic solvents with high percent of non- condensables present	Water or brine	20 - 60
Naptha	Water	50 - 75
Stabilizer reflux vapors	Water	80 - 120
Sulfur dioxide	Water	150 - 200
Tall oil derivatives vegetable oil vapors	Water	20 - 50
Steam	Feedwater	400 - 1000

*Note: for water-water (liquid-liquid) heat exchanger (no phase change) the values for U range between 200-250.

For counter-flow, the mean temperature difference is the logarithmic mean of the temperature differences at each end of the heat exchanger,

$$\Delta T_m = \frac{(T_{hi} - T_{co}) - (T_{ho} - T_{ci})}{\ln(T_{hi} - T_{co}) / (T_{ho} - T_{ci})}$$

where subscripts h,c for hot and cold fluid and i,o for inlet and outlet.

PROBLEMS

- 1- Compute the pressure and latent heat of condensation of saturated octane vapor at 20°C.
- 2- In a rendering plant, tallow is obtained by removing the moisture from animal matter in a cooker. Exhaust gases from the cookers contain essentially steam, however, the entrained vapors are highly odorous and must be controlled. Condensers are normally used to remove most of the moisture prior to incineration, scrubbing, or carbon adsorption.

The exhaust flow rate from the continuous rendering cooker is 20,000 scfm at 250°F. The exhaust gases are 95% moisture with the remaining portion consisting of air and obnoxious organic vapors. The exhaust stream is sent first to a shell-and-tube condenser to remove the moisture and then to a carbon adsorption unit. If the coolant water enters at 60°F and leaves at 120°F, estimate the required surface area of the condenser. The condenser is a horizontal, countercurrent flow system with the bottom few tubes flooded to provide subcooling.

- 3- A 1-2 heat exchanger is to cool a stream of 1.0 m³/s of air at 100 to 30°C using a stream of water entering at 20 and leaving at 40°C. The water velocity inside the pipes is 1.0 m/s; the film coefficient on the outside tube surface is 500 W/m².K. The tubes are 1.0 cm inside diameter with a wall thickness of 1.0 mm. The thermal conductivity of the tube-wall material is 175 W/m.K; there is a fouling factor of $h_{fi} = 1000 \text{ W/m}^2\text{.K}$ on the inside surface, and no fouling factor on the outside surface ($h_{fa} = \infty$).
 - (a) Compute the overall heat-transfer coefficient.
 - (b) How many tubes are required and what length of tube is required?

4.7 CONTROL OF SO₂ EMISSIONS

Sources of Sulphur Oxides

More than 25 million tons of sulphur oxides are emitted into the atmosphere annually from manmade sources. Power plants are responsible for over than 60% of total emissions. Petroleum refining, copper smelters, industrial boilers and transportation are the other major sulphur oxides sources.

Sulphur is naturally found in coal, oil and natural gas with a composition varying from 0.1 to over 5%. Figure 34 shows the percentage of sulphur in the world crude oil. Table 17 gives the sulphur content of important Saudi oil and natural gas fields.

Table 17. Saudi Oil and Natural Gas Sulphur Contents.

A) Typical Oil Fields and Sulphur Contents

Field	Sulphur wt%
Safaniya	3.0
Zuluf	1.45
Marjan	2.62
Berri	1.34
Khursaniyah	2.23
Ain Dar	1.63
Uthmaniya	1.83

B) Typical Gas Fields and H₂S Content

Field	H ₂ S wt%
Dammam	2.0
Jawb	0.58
Lawhah	0.3 - 1.3
Maharah	0.20
Marjan	0.0 - 4.2
Shaybah	0.30
Abqaiq	20.5
Berri	19.8
Ghawar	0.0 - 3.6
Kidan	0.0 - 43.1
Qatif	7.2

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Sulphur Content of Crude Oil

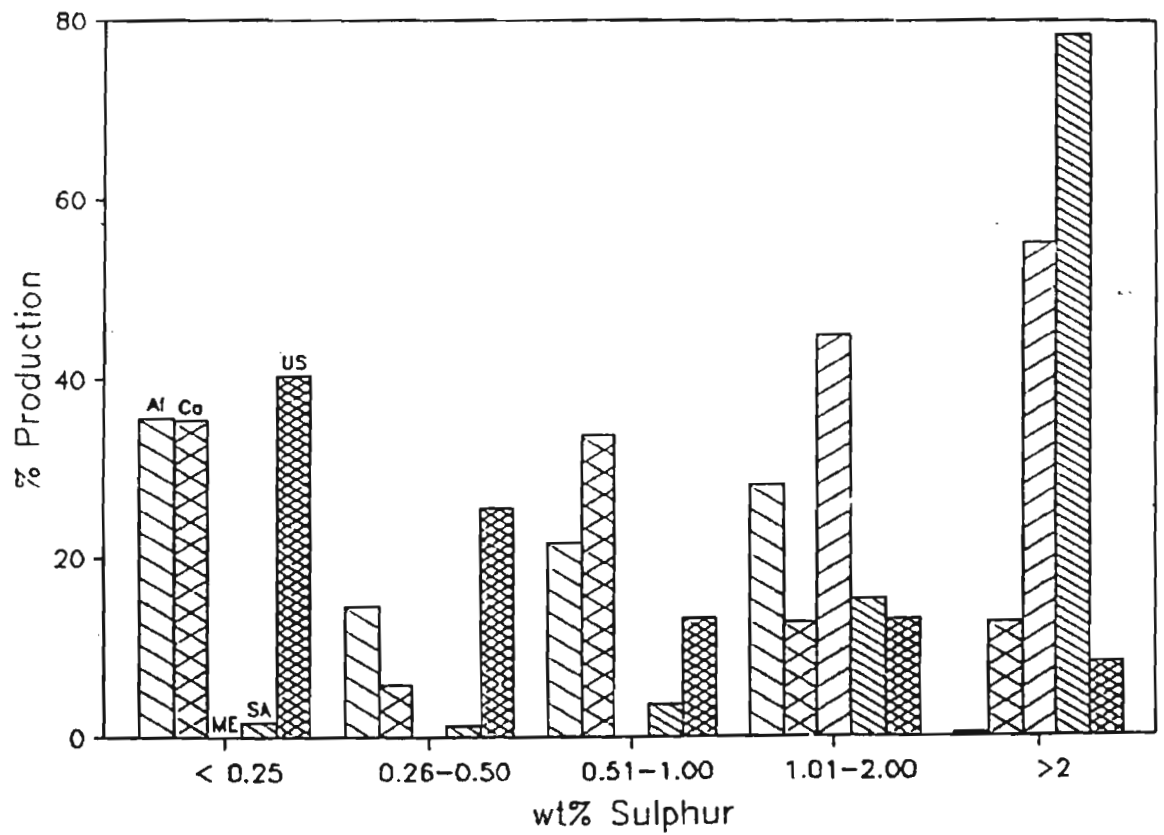


Fig. 4.34. Percentage Distribution of Sulphur in the World Crude (Af: Africa, Ca: Canada, ME: Middle East, SA: South America, US: United States).

Approximately 95% of all sulphur oxides emitted from combustion processes are in the form of sulphur dioxide, SO_2 . The SO_2 concentration in the large cities typically ranges from 0.01 to 0.1 ppm (30 to 300 $\mu\text{g}/\text{m}^3$) for 1 hour average time. The clean troposphere SO_2 concentration is 1 to 10 ppb. The ambient air quality standard for SO_2 are presented on Table 18. Some

Table 18 SO_2 Ambient Air Quality Standards.

Average time	Standard
Annual	80 $\mu\text{g}/\text{m}^3$ (0.03 ppm)
24 hour	365 $\mu\text{g}/\text{m}^3$ (0.14 ppm)
3 hour	1300 $\mu\text{g}/\text{m}^3$ (0.5 ppm)

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table 2-1
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countries like the United State regulates the potential SO_2 sources from certain industry. For example, for the coal-fired units, the standard required at least 90% reduction of potential SO_2 emissions and limits the SO_2 emission rate to 1.2 lb/ 10^6 Btu input, or requires at least a 70% reduction of and limits the emission rate to 0.6 lb/ 10^6 Btu. Table 19 shows the emission factors of some SO_2 emitting industry that need to fulfil the regulations. The US Federal performance standards for SO_2 are presented in Table 20.

By these regulations, a power plant of 250×10^6 Btu/hr capacity cannot have SO_2 emissions exceeding 1.2 lb/ 10^6 Btu. Also the plant is required to reduce the SO_2 emission by 90%. If the plant's emissions are less than 0.6 lb/ 10^6 Btu then only 70% scrubbing is required.

Table 19. Emission Factors for SO₂ from Stationary Sources.

Source or Process	Emission Factor (SO ₂)
1. Fuel combustion	
Coal	19S g kg ⁻¹ (assumes 5% of sulfur remains in ash) ^a
Natural gas	6.4 kg (10 ⁶ m ³) ⁻¹
Process gas	45.6C kg (10 ⁶ m ³) ^{-1b}
Fuel oil	19.8S kg (10 ³ l) ^{-1a}
Gasoline-powered engine	1.1 kg (10 ³ l) ⁻¹ (assumed sulfur content of 0.07%)
Diesel-powered engine	5 kg (10 ³ l) ⁻¹ (assumed sulfur content of 0.3%)
2. Nonferrous primary smelters	
Several important metallic ores, such as copper, lead, and zinc, occur as sulfides. The natural metal ores are usually mixed with large amounts of worthless rock. The process of removing the worthless rock, concentrating the metallic ore, and finally driving off the sulfur (as SO ₂) is called smelting. For example, for copper and lead the important reactions are	
$\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2$ $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$	
Exit SO ₂ concentrations with moderate control are often as high as 8000 ppm.	
Copper smelting—primary	625 g kg ⁻¹ of ore
Lead smelting—primary	330 g kg ⁻¹ of ore
Lead smelting—secondary cupola	32 g kg ⁻¹ of metal charged
Lead smelting—secondary reverberatory and sweat furnaces	75 g kg ⁻¹ of metal charged
Zinc smelting—primary	265 g kg ⁻¹ of ore
3. Sulfuric acid plants	
Sulfuric acid is essentially made by burning elemental sulfur with a controlled amount of excess air, producing SO ₂ , and then catalytically oxidizing the SO ₂ to SO ₃ , and finally absorbing SO ₃ in water to yield H ₂ SO ₄ . The heart of the sulfuric acid plant is the converter in which SO ₂ is catalytically converted to SO ₃ in a fixed bed. The ultimate SO ₂ remaining after the final absorption step (and thus emitted from the plant if uncontrolled) depends on the operation of the converter. Exit gas concentrations of SO ₂ vary from 2000 to 3500 ppm.	
	Range: 10–35 g kg ⁻¹ of 100% acid produced
4. Pulp and paper mills	
In pulping, wood is reduced to fiber, bleached, and dried in preparation for making paper at the paper mill. Most pulp mill processes use some type of cooking liquor to dissolve lignins in the wood and free the wood fibers. To make this process economical, spent cooking liquor is recovered, usually by some process involving combustion. It is primarily in recovery processes that particulate matter, odorous sulfur compounds (H ₂ S and organic sulfides), and SO ₂ are produced.	
Kraft type—recovery furnace	2.2–6.7 g kg ⁻¹ of air-dried pulp
Sulfite type—recovery furnace	20 g kg ⁻¹ of air-dried pulp (assumes 90% recovery of SO ₂)

^aS = percent sulfur by weight.

Table 20. US Federal Source Performance Standards
for SO₂.

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Source Category	Affected Facilities	Maximum Emissions
Fossil-Fueled Steam Generators	Coal- and Oil-Fired Boilers	Solid Fuel: 2.2 g SO ₂ /10 ⁶ cal (1.2 lb SO ₂ /10 ⁶ Btu)* Liquid Fuel: 1.4 g SO ₂ /10 ⁶ cal (0.8 lb SO ₂ /10 ⁶ Btu)
Sulfuric Acid Plants	Process Equipment	2 Kg SO ₂ /10 ⁶ cal (4 lb SO ₂ /ton H ₂ SO ₄) 0.074 kg acid mist/mton H ₂ SO ₄ (0.15 lb acid mist/ton H ₂ SO ₄)
Petroleum Refineries	Refinery Process Equipment including waste-heat boilers and fuel gas combustors	Fuel gas max H ₂ S: 230 mg/dry Std M ³ (0.10 grain/dry Std ft ³)
Primary Copper Smelters	Roaster, Smelting Furnace Copper Converter	0.065% SO ₂ by vol
Primary Zinc Smelters	Roaster, Sintering Machine	0.065% SO ₂ by vol
Primary Lead Smelters	Sintering Machine, Dross Reverberatory Furnace, Electric Smelting Furnace and Converter	0.065% SO ₂ by vol
Petroleum-Refinery Sulfur Recovery Plants	Claus Plants	0.025% SO ₂ by vol (with incineration) or 0.030% by vol reduced sulfur compounds and 0.0010% by vol H ₂ S (reduction only)

Formation of SO_2

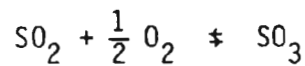
The overall reaction for the formation of SO_2 from sulphur in fossil fuels is



The reaction is highly exothermic with a heat release of 296,800 KJ/Kg mole (127,700 Btu/lb mole) at 25°C. Small amount of sulphur trioxide SO_3 is formed in the combustion reaction, usually in the ratio of SO_2/SO_3 40:1 to 80:1.

Sulphur dioxide is a colorless gas that when cooled and liquified is used as a bleach, disinfectant, refrigerant or preservative. SO_2 can form sulfates (SO_4^{--}) and sulfiles (SO_3^{--}) when oxidized in the atmosphere. SO_3 is not stable. It forms sulphoric acid in the presence of water. The approximate SO_2 life time in the atmosphere is 40 days as compares to few hours for SO_3 .

The equilibrium conversion of SO_2 to SO_3 and vice versa can be given by the following reaction



with an equilibrium constant K_p defined as

$$K_p = \frac{P_{\text{SO}_3}^3}{P_{\text{SO}_2} (P_{\text{O}_2})^{1/2}}$$

that has the following values at different temperature

T, K	K_p
298	2.6×10^{12}
500	2.6×10^5
1000	1.8
1500	3.8×10^{-2}
2000	5.6×10^{-3}

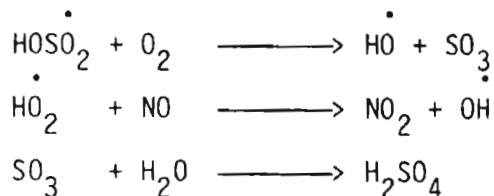
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table 7-2
K. Wark

So at low temperatures, high SO_3 concentrations are predicted. SO_2 dominates at high temperatures.

The photooxidation of SO_2 is not important since a light of wavelength below 218 nm is required for SO_2 photooxidation. Such wavelength do not penetrate to the troposphere to provide sufficient energy for photodissociation of SO_2 . One of the most important reaction for SO_2 oxidation in the atmosphere is



followed by the following chain reactions



Impact of SO₂ Pollution

Sulphur oxide is a nonflammable, nonexplosive colorless gas that causes a taste sensation at concentration from 0.3 to 1.0 ppm in air. Above 3.0 ppm the gas has a pungent, irritating odor. Table 21 shows the effects of SO₂ at various concentrations.

Table 21 Effects of SO₂ at Various Concentrations.

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K. Wark
Table 1-5

CONCENTRATION	EFFECT
0.03 ppm, annual average	1974 air quality standard, chronic plant injury
0.037-0.092 ppm, annual mean	Accompanied by smoke at a concentration of 185 µg/m ³ , increased frequency of respiratory symptoms and lung disease may occur
0.11-0.19 ppm, 24-hr mean	With low particulate level, increased hospital admission of older persons for respiratory diseases may occur. Increased metal corrosion rate
0.19 ppm, 24-hr mean	With low particulate level, increased mortality may occur
0.25 ppm, 24-hr mean	Accompanied by smoke at a concentration of 750 µg/m ³ , increased daily death rate may occur (British data); a sharp rise in illness rates
0.3 ppm, 8 hr	Some trees show injury
0.52 ppm, 24-hr average	Accompanied by particulate, increased mortality may occur

Aerosols of sulphuric acid and other sulphates are 30 to 50% of the total suspended particulate matter in urban air. So they contribute significantly to the reduction in visibility.

Moreover, major fractions of the sulphate in the urban air have effective size of less than 2 µm, with the peak in the size distribution around 0.2 to 0.9 µm. Since the visible wavelength range of the electromagnetic spectrum is roughly from 0.4 to 0.8

μm , the presence of aerosols of this type can cause a pronounced reduction in visibility.

Sulphur dioxide also helps in the formation of acid rain which is primarily consists of sulphuric (H_2SO_4) and nitric acid (HNO_3). Sulphuric acid comprises 40 to 60% of acid rain. The natural acid concentration in rain water is less than $10 \mu\text{g/L}$. Acid concentration of above $40 \mu\text{g/L}$ were detected. The rain pH is normally close to 7. As low as 3.7 to 4.0 pH rainwater were found due to high acid concentrations.

Acid rain causes the following effects:

- 1- acidification of the natural water sources
- 2- leaching of soil nutrients.

Acid rain and other sulphur containing materials are responsible for the major damage to materials. Sulphur oxides generally accelerate metal corrosion. In urban atmosphere, corrosion rates are 1.5 to 5.0 times the rates in rural environments.

Methods of Control

Most of SO_2 emissions are from combustion of fossil fuels. So the use of low-sulphur fuel is considered one of the potential method for SO_2 emissions reduction. Natural gas, liquified natural gas (LNG), low sulphur oil and low sulphur coal are among the possible fuel alternatives. As seen in Tables 17 and 19, low sulphur ($<1 \text{ ppm}$) fuel are hard to find. Natural gas of low sulphur content if economically feasible provides better solution. LNG can only use for small industry.

Increasing the stack height can help in lowering the ground level concentrations. Chimneys as high as 1250 ft have been used. This may be considered as an acceptable solution for some geographical location. In places where drastic changes in weather occur, this technique may not work.

The remaining processes for sulphur emission control can be grouped in the following categories:

- 1- fuel desulphurization
- 2- flue-gas desulphurization.

Sulphur normally present in coal as organic and inorganic compounds. The inorganic compound is known as pyrite, FeS_2 . It can be removed by physical separation methods since it present as discrete particles. The removal of organic sulphur is more complex and requires costly chemical processes, e.g. coal gasification or conversion of coal to synthetic oil or solid material.

Two chemical processes for coal cleaning are under development. These are microwave desulphurization and hydrothermal

desulphurization. In microwave desulphurization, coal is crushed then heated for 30 to 60 seconds by exposure to microwaves. Mineral sulphur selectively absorbs this radiation forming hydrogen sulphide gas, H_2S . The H_2S is usually reduced to elemental sulphur by the Claus process. Another microwave process adds calcium hydroxide $[Ca(OH)_2]$ to crushed coal. The organic sulfur converts to calcium sulfite ($CaSO_3$) when exposed to this radiation. The coal is washed with water to remove the $CaSO_3$ and other impurities. As much as 70% of the sulfur can be removed by the microwave process.

In hydrothermal desulfurication coal is crushed and mixed with a solution of sodium and calcium hydroxides $[NaOH$ and $Ca(OH)_2]$. When this mixture is heated to $275^\circ C$ in a pressurized vessel, most of the pyritic sulfur and 20 to 50% of the organic sulfur is converted to sodium and calcium sulfities (Na_2SO_3 and $CaSO_3$). The coal is rinsed to remove the sulfites and the water is processed to recycle the sodium and calcium hydroxides. This process is an expensive but effective method for removing sulfur from coal.

Desulphurization of crude oil can be accomplished by commercially available processes. These can be fallen in two groups

I- Liquid Absorption - Oxidation Process

1. Ferrox process
2. Gluud process
3. Manchester process
4. Stretford process
5. Takahax process
6. Tylox process
7. Perox process
8. Giammorco-Vetrocoke process
9. Lacy-keller process
10. Townsend process
11. Shell sulfolane process
12. Freeport sulphur process
13. haines process

II- Direct Oxidation Process

14. Modified Claus process
15. Pan American process

Flue-Gas Desulphurization (FGD) Processes

Combustion processes emit large amounts of SO_2 for 15% excess air, coal combustion of 4% sulphur emits a flue gas with 0.35% SO_2 while combustion of fuel oil of 2% and 5% sulphur emit 0.12% and 0.31% SO_2 respectively. These SO_2 concentration of the flue gas must be lowered to reduce its environmental impact. Figure 35 shows the possible pathways for SO_2 removal.

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A. KOHL

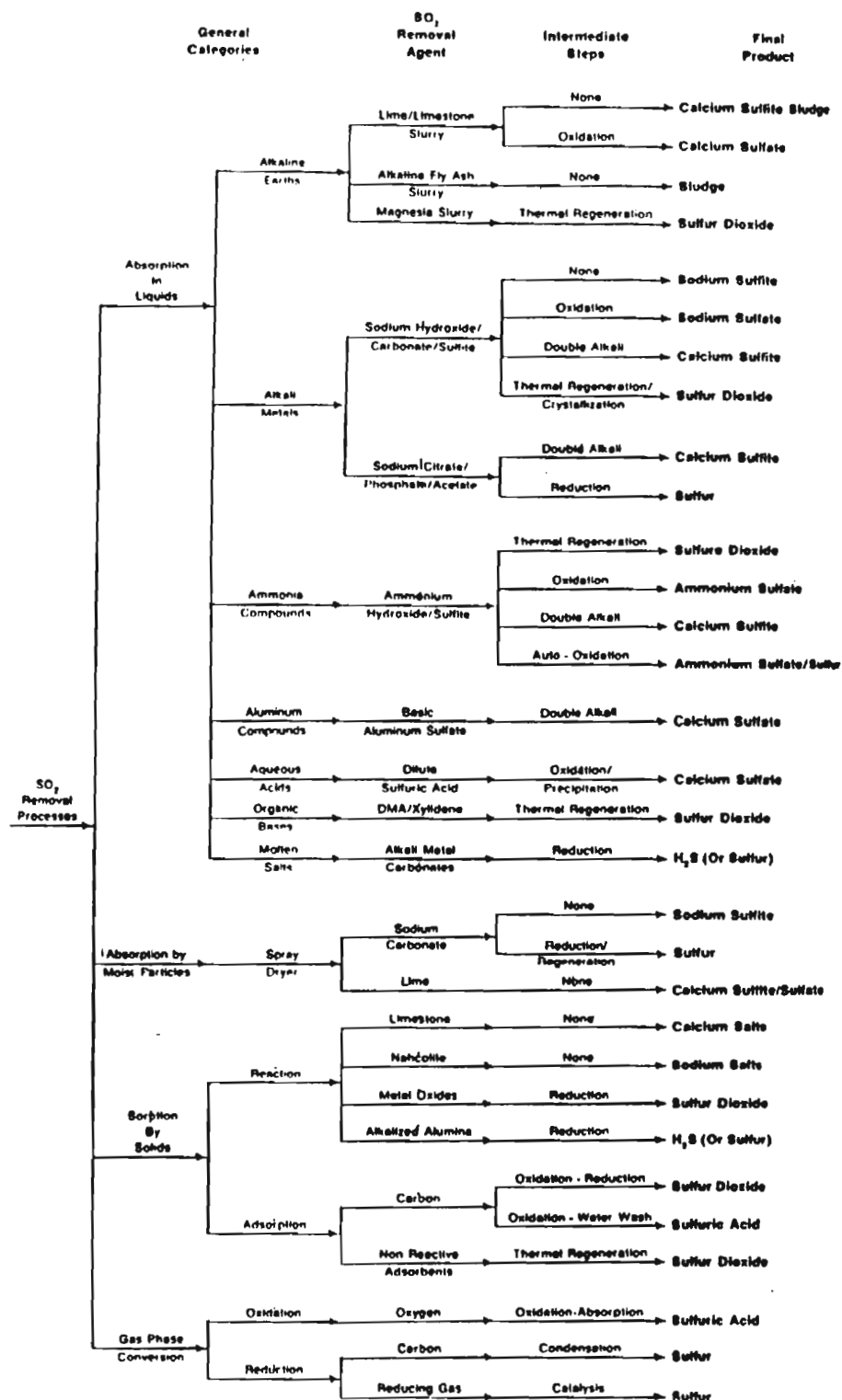


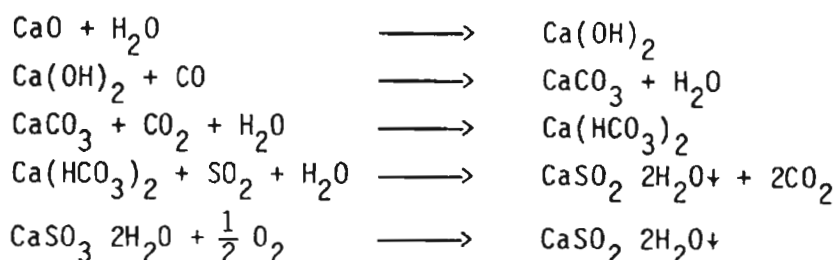
Fig. 4.35. Categorization of SO_2 Removal Processes.

The commercial flue gas desulphurization processes can be divided into two categories; wet and dry. Wet desulphurization processes are either throwaway or regenerative. throwaway processes are those in which a solid waste product is formed which must be discarded. In regenerative processes, the removal agents can be continually regenerated in a close-loop system. Table 22 gives some descriptions of these processes. The following are some highlights on the operation of important SO₂ desulphurization processes.

Nonregenerative FGD Processes

1. Lime Scrubbing

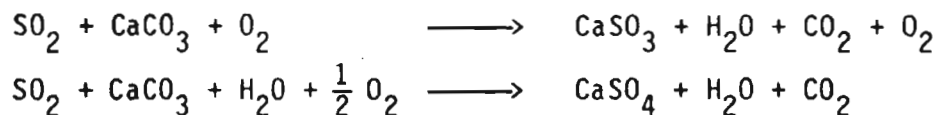
Lime (CaO) 90% pure is added to water to make an alkaline slurry. The alkaline slurry is sprayed in an absorber and reacts with the SO₂ in the flue gas according to the following reactions:



The precipitated calcium sulphite (CaSO₃) and calcium sulphate (CaSO₄) are removed as sludge for landfilling and disposing. Figures 36A and 36B show two possible lime scrubbing system. The first one used a scrubber and absorber for both particulate and SO₂ emission control. Figure 36B consists of an electrostatic precipitator for particulate emission control and a mobile bed absorber for SO₂ emission control.

2. Limestone Scrubbing

In limestone scrubbing, an alkaline slurry made from limestone (CaCO₃) reacts with SO₂ in the flue gas according to the following reactions



Calcium sulphate (CaSO₄) and calcium sulphite (CaSO₃) are removed as sludge. Two major differences between lime and limestone scrubbing are their uses of feed preparation equipment and their liquid to gas ratios. Limestone is generally cheaper than lime.

In limestone scrubbing, limestone is reduced in size by crushing it in a ball mill to small pieces less than 200 mesh. Limestone is then slaked with water in a slurry supply tank. Figure 37 shows a limestone scrubbing system. It consists of a

Table 22. Description of Some SO₂ Removal Processes.

PROCESS GENERICS	PROCESS OPERATIONS	ACTIVE MATERIAL	KEY SULFUR PRODUCT
A. Throwaway scrubbing processes			
1. Lime or limestone	Slurry scrubbing	CaO, CaCO ₃	CaSO ₃ /CaSO ₄
2. Sodium	Na ₂ SO ₃ solution	Na ₂ CO ₃	Na ₂ SO ₄
3. Double alkali	Na ₂ SO ₃ solution, regenerated by CaO or CaCO ₃	CaCO ₃ /Na ₂ SO ₃ or CaO/NaOH	CaSO ₃ /CaSO ₄
4. Magnesium-promoted lime/limestone	MgSO ₃ solution, regenerated by CaO or CaCO ₃	MgO/MgSO ₄	CaSO ₃ /CaSO ₄
B. Regenerative scrubbing processes			
1. Magnesium oxide	Mg(OH) ₂ slurry	MgO	15% SO ₂
2. Sodium	Na ₂ SO ₃ solution	Na ₂ SO ₃	90% SO ₂
3. Citrate	Sodium citrate solution	H ₂ S	Sulfur
4. Ammonia	Ammonia solution, conversion to SO ₂	NH ₄ OH	Sulfur (99.9%)
C. Dry processes			
1. Carbon adsorption	Adsorption at 400°K, reaction with H ₂ S to S, reaction with H ₂ to H ₂ S	Activated carbon/H ₂	Sulfur
2. Spray dryer	Absorption by sodium carbonate or slaked lime solutions	Na ₂ CO ₃ /Ca(OH) ₂	Na ₂ SO ₃ /Na ₂ SO ₄ or CaSO ₃ /CaSO ₄

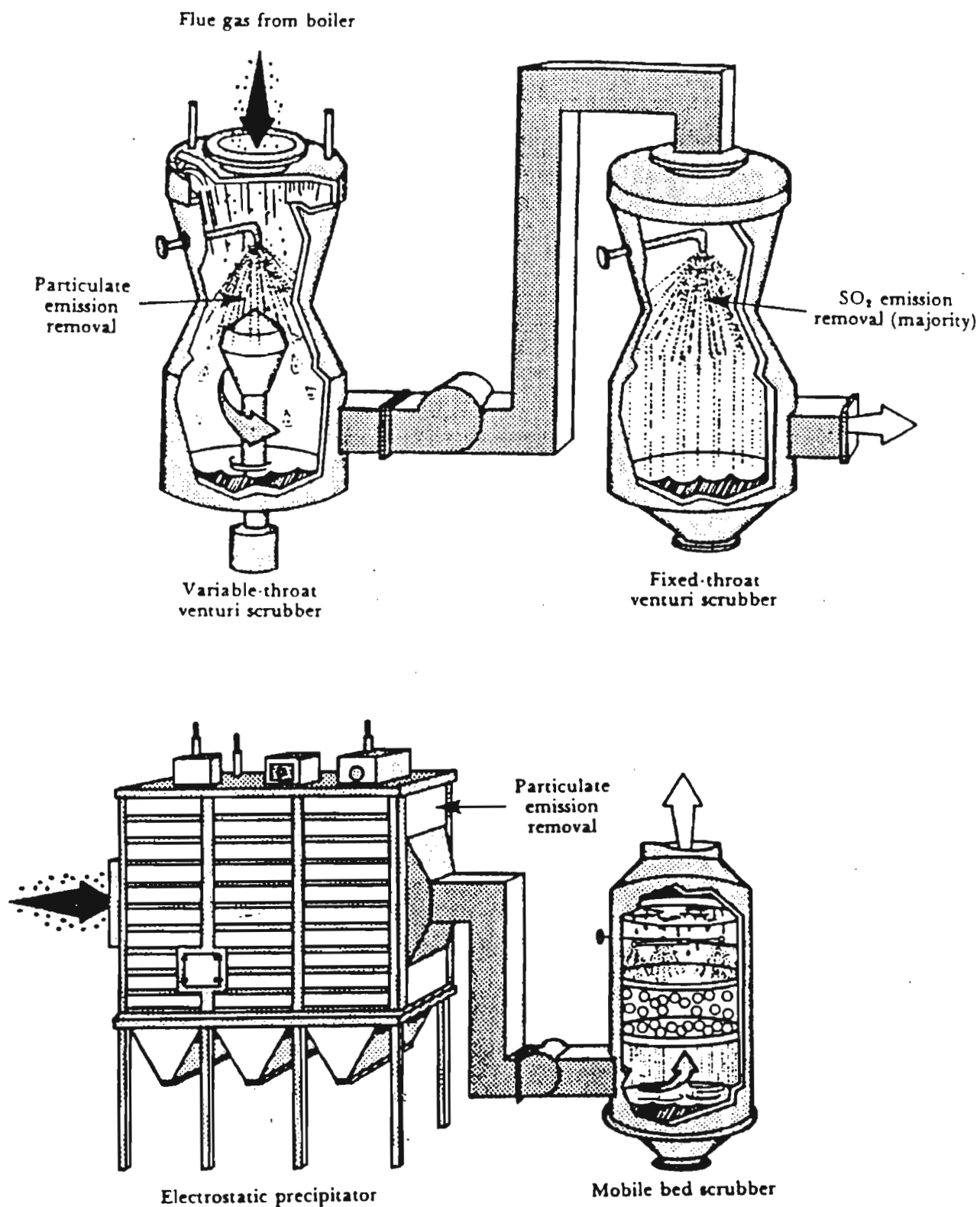


Fig. 4.36. Lime Scrubbing Systems

- a) Venturi Scrubber.
- b) Electrostatic Precipitator and Mobile Scrubber.

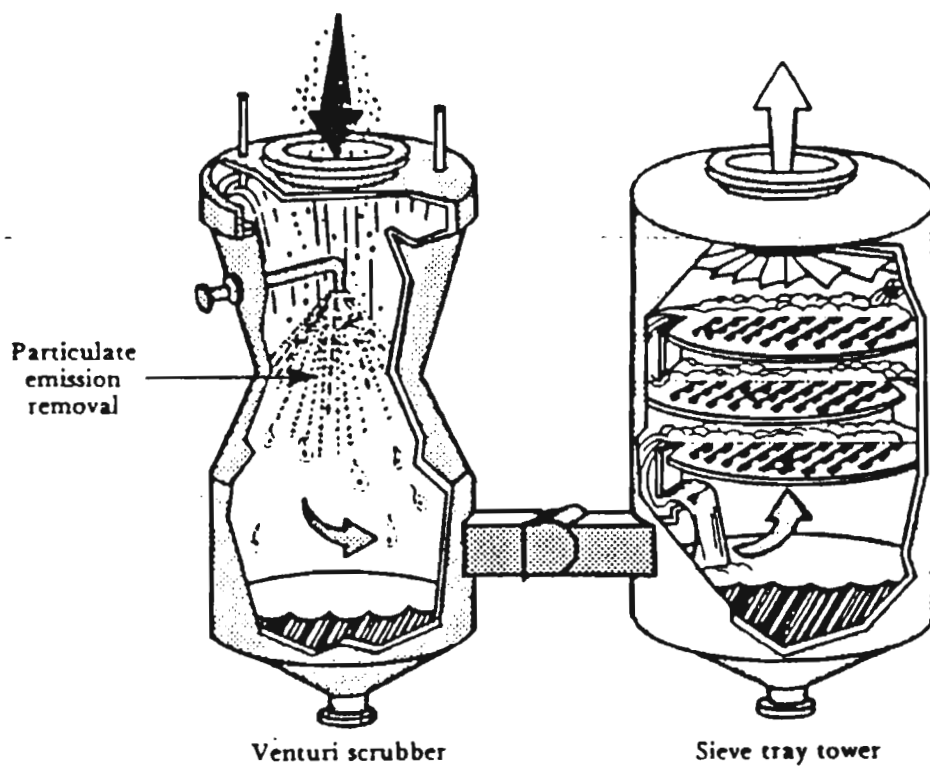


Fig. 4.37. Limestone Scrubbing System.

venturi scrubber for particulate emission control and a sieve tray absorption tower for SO_2 emission control.

To increase the SO_2 removal efficiency, magnesium sulphite is added to the limestone slurry. The power consumption may also be decreased by as much as 50%. Fine particulates can also be removed by this system.

A recent modification of limestone scrubbing includes the additional of adipic acid. Adipic acid is a crystalline powder derived from petroleum. It is non toxic acid, used as food additives. The addition of adipic acid slightly increases the slurry's initial acidity and prevents it from becoming highly acidic. High acidity limits the amount of SO_2 that can be absorbed.

Forced oxidation is also under investigation to solve the calcium sulphite precipitation. The objective of forced oxidation is to use air to oxidized the calcium sulphite into calcium sulphate which can grows to a larger crystal size, so easily to filtered.

3. Double Alkali Scrubbing

In this process, two alkali sprays are used to remove SO_2 from the flue gas. A sodium solution absorbs SO_2 followed by absorbent regeneration. The spent absorbent is reacted with a lime or limestone alkali slurry. Calcium sulphites and sulphates are precipitated and discarded as sludge. The regenerated sodium solution is returned to the absorber. The double alkali process has reduced plugging and scaling problems in the absorber since sodium compounds are very soluble. A general schematic of a double alkali scrubbing system is shown in Figure 38.

Particulate matter is removed prior to scrubbing in the absorber by an electrostatic precipitator or venturi scrubber. This is done to prevent any fly ash erosion to the absorber internals and to prevent any appreciable oxidation to the sodium solution in the absorber due to catalytic elements in the fly ash.

The sodium solution is usually a mixture of sodium carbonate (soda ash, Na_2CO_3), sodium sulphate (Na_2SO_3) and sodium hydroxide (caustic soda, NaOH). Sodium solution is consumed by SO_2 absorption forming sodium bisulphite (NaHSO_3), sodium sulphate (Na_2SO_4) and sodium bicarbonate (NaHCO_3) according to the following reactions:

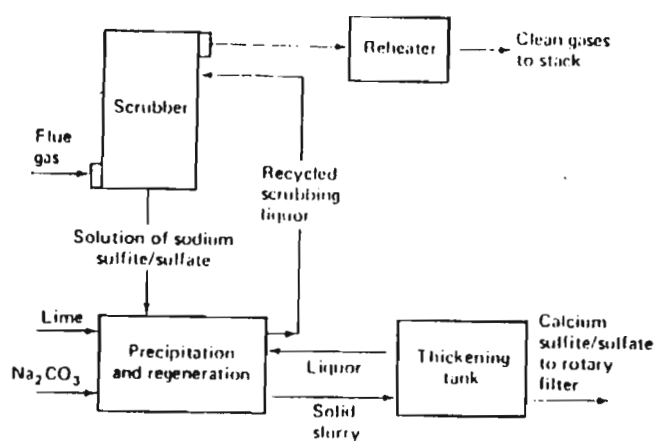
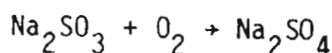
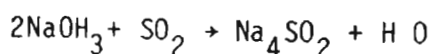
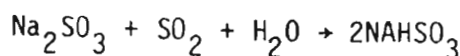
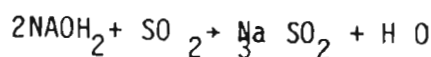
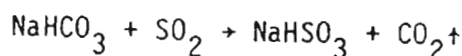
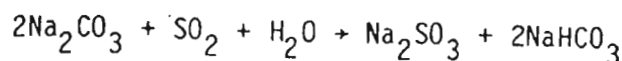
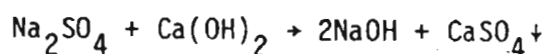
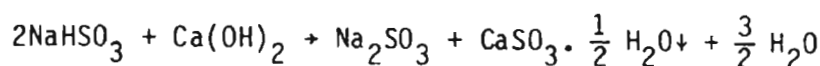


Fig. 4.38. Schematic Diagram of Double Alkaline Scrubbing Process.



The sodium regeneration can be simplified by the following reactions:

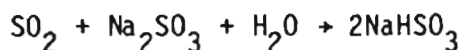


Additional sodium is added to the regenerated solution in the form of soda ash or caustic soda.

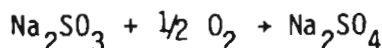
Renewable FGD Processes

1. Wellman-Lord Process

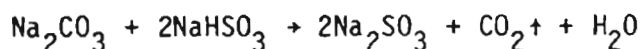
SO_2 is absorbed by aqueous sodium sulfite solution forming a solution of sodium bisulfite. The solution is sent to an evaporator-crystallizer where sodium sulfite and concentrated SO_2 gas are produced. Sodium sulfite is recycled to the absorber and concentrated SO_2 is converted to a saleable product; usually sulfuric acid or elemental sulfur. Flue gas from the boiler is pretreated prior to entering the absorber. Particulate matter is removed by an electrostatic precipitator, fabric filter, or a wet scrubber. A small venturi scrubber removes any additional particulate matter, chlorides and sulfur trioxide. Flue gas is then sent to the absorber where SO_2 gas is absorbed according to the following reaction:



Some oxidation occurs in the absorber forming sodium sulfate which is unreactive with SO_2 gas:



The formation of sodium sulfate depletes the supply of sodium sulfite available for scrubbing. This can be made up by adding sodium carbonate to the scrubbing slurry to combine with sodium bisulfite according to the following chemical reaction:



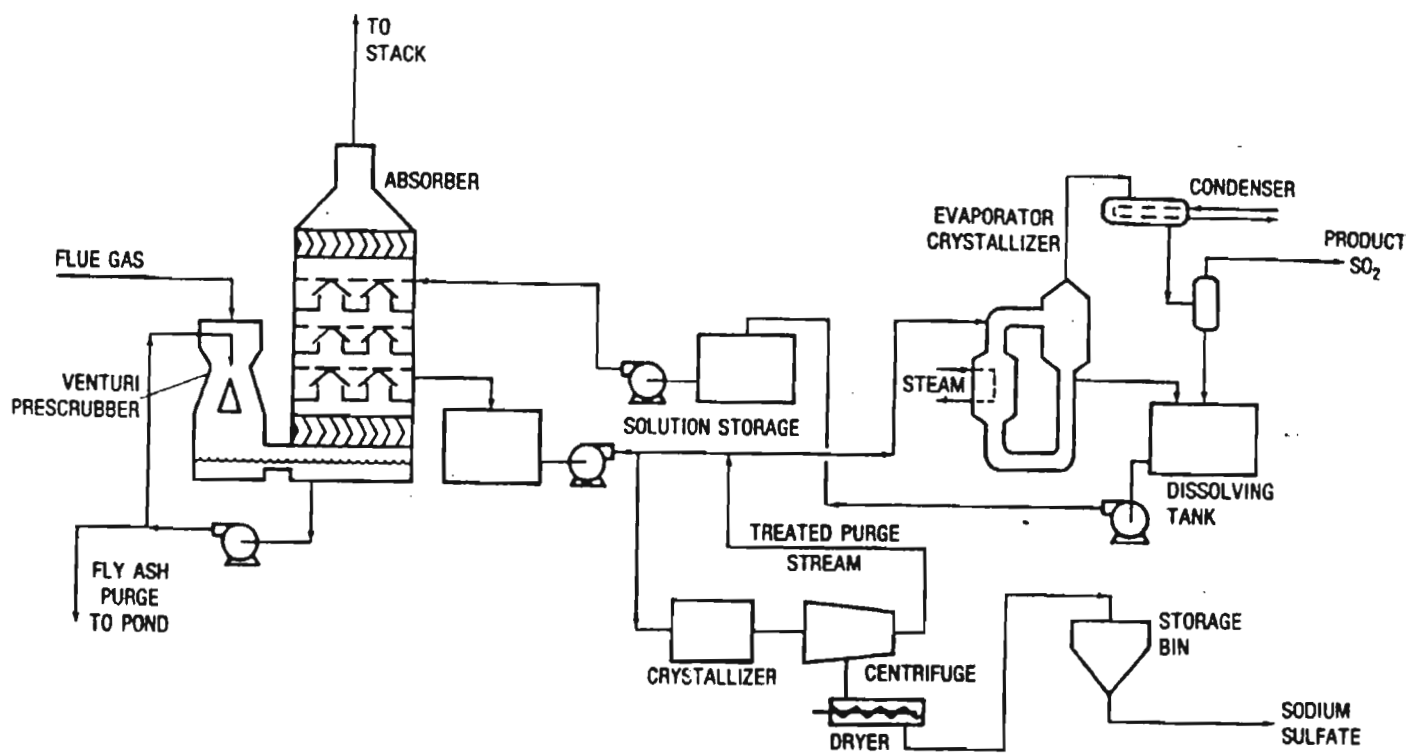
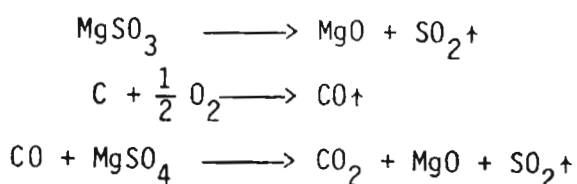


Fig. 4.39. Simplified Flow Diagram of the Wellman-Lord SO₂ Removal Process.

MgO regeneration in calciner



A process schematic diagrams is shown in Figure 40.

3. Citrate Process

The absorbent used is an aqueous solution containing approximately 190g of citric acid and 80g of sodium carbonate per liter, and is capable of absorbing 10 to 20g of sulfur dioxide per liter.

Flue gases containing 1 to 3 percent of sulfur dioxide are first freed of particulate matter, then cooled to about 120°F, and subsequently contacted countercurrently with the citrate solution in an absorption tower. The loaded solution is reacted with hydrogen sulfide in a stirred, closed vessel, and elemental sulfur is precipitated. The sulfur slurry flows to a thickener, and the thickener underflow is centrifuged to separate the sulfur from regenerated citrate solution which, together with the thickener overflow, is returned to the absorption tower. The sulfur cake is heated in an autoclave. Liquid sulfur is separated from the residual citrate solution, which is also returned to the system.

Two-thirds of the molten sulfur product is converted to hydrogen sulfide to be used for solution regeneration.

Dry SO₂ Emission Control Systems

In the dry FGD, the flue gas containing SO₂ is contacted with an alkaline material to produce a dry waste product for disposal. Table 23 below summarizes the features of the possible dry FGD processes.

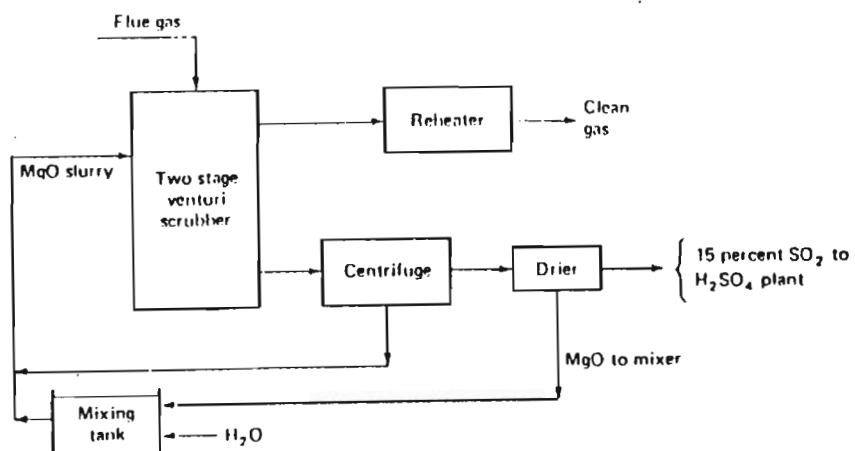


Fig. 4.40. Simplified Schematic Diagram of the Magnesium Oxide Flue Gas Desulphurization.

Table 23. Dry-flue Gas Desulphurization Processes.

Process	Sorbents used	SO ₂ emission removal efficiency (%)	Particulate emission removal efficiency (%)	Development status
Spray dryer with a baghouse or ESP	Sodium carbonate Lime Limestone	60-90	99+	Three utility boilers (400- 500 MW) to be started up 1981, 1982, 1983. Two industrial boilers on line.
Dry injection with a bagh- house or ESP	Sodium carbonate Sodium bicarbonate Nahcolite	60-90	99+	No commercial installation planned as of 1980.
Combustion of coal/limestone mixture with a low NO _x burner	Limestone pellet Lime	75-80	99+*	EPA currently funding pilot tests on small industrial boiler.

* Note: a baghouse or ESP is used for particulate emission control.

PROBLEMS

1. A new power plant is being designed to burn coal having a 3 percent sulfur content and a heating value of 11,000 Btu/lb. What is the minimum efficiency that a sulfur dioxide removal system can have for the plant to comply with an emission standard of 1.2 lb/10⁶ Btu?
2. A new power plant is designed to burn coal with a 4.1 percent sulfur content and a heating value of 10,800 Btu/lb. What is the minimum efficiency that a sulfur dioxide removal system can have in order for the plant to comply with an emission standard of 1.2 lb/10⁶ Btu?
3. A No.5 fuel oil having a maximum sulfur content of 2.0 percent and a heating value of 148,000 Btu/gal is being considered as a fuel for an industrial boiler. If the specific gravity of the oil is 0.953, what is the minimum efficiency required of a sulfur dioxide scrubber system in order for the plant to meet an emission standard of 0.8 lb/10⁶ Btu for a new plant?

4. Consider an initial gaseous mixture which contains 25000 ppm of SO_2 and 60 ppm of SO_3 , plus 3.0 percent by volume of O_2 . If the temperature is 1000°K , estimate the equilibrium concentrations of SO_2 and SO_3 based on thermodynamic considerations alone. The pressure is 1 atm.
5. Limestone (CaCO_3) is used in a throwaway limestone scrubbing system for a powerplant burning coal containing 3.60 percent sulfur and 7.70 percent ash. The SO_2 removal efficiency must be 85 percent to meet federal emission standards for SO_2 . Determine (a) the stoichiometric pounds of limestone required per pound of sulfur in the coal, (b) the pounds of limestone required per ton of coal if 30 percent excess limestone is used, (c) the pounds of sludge produced per ton of coal if the sludge is 60 percent water and 40 percent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, plus ash.
6. A 500-MW electric power plant burns coal having 4.0 percent sulfur and a heating value of 11,500 Btu/lb. The plant thermal efficiency is 33 percent and the ash content of the coal is 6.5 percent. Determine (a) the required SO_2 removal efficiency if the federal SO_2 emission standard is satisfied, (b) the tons of limestone (CaCO_3) required per day if the limestone scrubbing slurry contains 30 percent excess limestone, and (c) the tons per day of sludge produced (including ash) by the throwaway process if the sludge is 60 percent water and 40 percent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and ash, by weight.

4.8 CONTROL OF NITROGEN OXIDES EMISSIONS

Sources of Nitrogen Oxides

The important stable nitrogen oxides are N_2O (nitrous oxide), NO (nitric oxide), N_2O_3 (nitrogen trioxide), NO_2 (nitrogen dioxide) and N_2O_5 (nitrogen pentoxide). Only N_2O , NO and NO_2 are found in significant amount in the atmosphere. N_2O is a colorless gas that is emitted almost totally by natural sources, bacterial action in the soil and reaction in the upper atmosphere. It is an inert gas often used in anesthesia and commonly referred to as "Laughing gas". It is not considered as an air pollutant.

Nitric oxide (NO) is a colorless gas. Its ambient concentration is below 0.5 ppm. It is produced mainly by fuel combustion at high temperatures. Nitrogen dioxide (NO_2) is emitted in small quantities along with NO and is formed also in the atmosphere by oxidation of NO . Nitrogen dioxide (NO_2) is a reddish brown gas and is quite visible in sufficient amounts. A concentration of 1 ppm of NO_2 probably would be detected by the eye. The sum of NO and NO_2 is designated NO_x . Table 24 shows the global budget of NO_x .

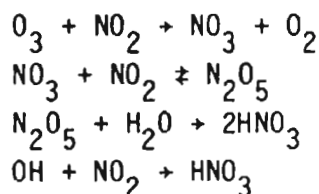
Table 24. Global Budget for NO_x.

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J. H. Seinfeld

Sources	Tg N yr ⁻¹
Fossil Fuel Combustion	21 (14 - 28)
Biomass Burning	12 (4 - 24)
Lightning	8 (2 - 20)
Microbial Activity in Soils	8 (4 - 16)
Oxidation of Ammonia	0 - 10
Photolytic or Biological Processes in Ocean	< 1
Input from the Stratosphere	≈ 0.5
TOTAL	25 - 99
Precipitation	12 - 42
Dry Deposition	11 - 22
TOTAL	23 - 64

Over 90% of all man-made NO_x that enter our atmosphere are produced by the combustion of fuels. About 56% is from automobile. The remainder is from stationary sources. Electric generation account for 35% of the total NO_x emissions. Industrial, commercial and residential utilities contribution is less than 10%.

Nitrogen oxides (NO_x) are an essential part of the nitrogen cycle in nature. Nitrogen dioxide (NO₂) is hydrolyzed to nitric acid in the atmosphere, which in turn is precipitated out as nitrates. These return to the earth's surface as fertilizer for organic growth. Among the possible atmospheric reactions for the formation of nitric acid are:



Nitric acid is a major contributor to acid rain,

It is estimated that the NO_x formed in this natural cycle amounts to 500 × 10⁶ tons/yr.

The actual quantities of NO_x produced by any given industry can be quite large. For example, a 750-MW gas- or coal-fired steam power plant produces around 7500 to 9500 lb of NO_x (NO_x

equivalent) per hour. The total flue-gas flow rate for the plant would be about 80×10^6 scf/hr. From such combustion processes the NO_x is the exhaust stack gas would be 90 percent or more NO , and the rest NO_2 . The type of fuel used can alter the emission rate significantly. Generally, the NO_x emissions, based on the same energy released, increase in the order gas-oil-coal. Table 25 below gives the emission rate based on fuel used.

Table 25. Comparison of the Effect of Fuel Type on Emissions, Expressed as $\text{lb NO}_x/10^9$ Btu Released.

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K. Warik

	Household and Commercial	Industry	Electric Utilities
Natural gas	110	205	375
Fuel oil	80 - 480	480	690
Coal	340	840	840

The US EPA standards of performance for new steam electric power plants are as follows:

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K. Warik

Fuel Type	$\text{lb}/10^6$ Btu	$\text{Kg}/10^6$ kJ	PPM
Gaseous	0.20	0.09	175
Liquid	0.30	0.13	230
Subbituminous coal, shale oil, and fuels derived from coal	0.50	0.21	-
Anthracite or bituminous coal	0.60	0.26	490

(based on 30-day rolling average)

Table 26 gives the emission factors for NO_x from different sources based on the amount of fuel consumed.

Table 26. Emission Factors for Nitrogen Oxides.

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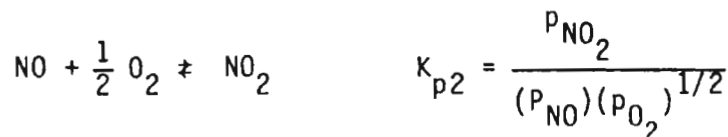
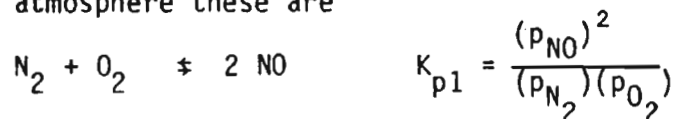
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SOURCE	AVERAGE EMISSION FACTOR
Coal	
Household and commercial	8 lb/ton of coal burned
Industry and utilities	20 lb/ton of coal burned
Fuel oil	
Household and commercial	12 to 72 lb/1000 gal of oil burned
Industry	72 lb/100 gal of oil burned
Utility	104 lb/1000 gal of oil burned
Natural gas	
Household and commercial	116 lb/million ft ³ of gas burned
Industry	214 lb/million ft ³ of gas burned
Utility	390 lb/million ft ³ of gas burned
Gas turbines	200 lb/million ft ³ of gas burned
Waste disposal	
Conical incinerator	0.65 lb/ton of waste burned
Miniciapl incinerator	2 lb/ton of waste burned
Mobile source combustion	
Gasoline-powered vehicle	113 lb/1000 gal of gasoline burned
Diesel-powered vehicle	222 lb/1000 gal of oil burned
Aircraft:conventional	23 lb/flight per engine
fan-type jet	9.2 lb/flight per engine
Nitric acid manufacture	57 lb/ton of acid product

Formation of NO_x

There are two sources of nitrogen which contribute to the formation of oxides of nitrogen in combustion reactions. The inevitable source in fuel-air reactions is the air itself, which contains molecular nitrogen and oxygen in a molar ratio of roughly 3.75:1. In addition, evidence indicates that fuels which contain nitrogen in their structure may be responsible for an appreciable fraction of the nitrogen that eventually appears as NO_x. Fuel oil and coal are of primary concern as contributors, since natural gas is essentially free of nitrogen-type compounds. From a theoretical viewpoint, the bond energy of N≡N in molecular nitrogen is much greater than that of a C - N bond in an organic compound. Thus, oxygen should preferentially attack the weaker C - N bond.

Two basic reaction are important in the formation of NO and NO₂ in the atmosphere these are



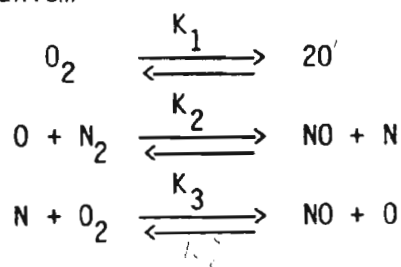
The variation of K_{p1} and K_{p2} with temperature is given in Table 27. Two important facts can be observed from this table. First, equilibrium NO formation increases rapidly with increasing temperature. Below 1000 K, the equilibrium quantity of NO is very small. Above 1000 K, appreciable amounts of NO could be formed. Second, equilibrium constant for the formation of NO_2 decreasing with increasing temperature. So the formation of NO_2 is favored at low temperatures. NO_2 dissociates back into NO at higher temperatures.

Table 27. Equilibrium Constant Values.

Temperature, K	K_{p1}	K_{p2}
300	10^{-30}	10^6
1000	7.5×10^{-9}	1.1×10^{-1}
1500	1.1×10^{-5}	1.1×10^{-2}
2000	4.0×10^{-4}	3.5×10^{-3}

577 + 376
vib 8-4 5-6
K. Wark

Thermodynamic analysis alone can not explain well the amount of NO and NO_2 formed in various combustion systems. Reaction rate information (Kinetics) must be obtained. One of the earliest model for NO formation from the atmospheric nitrogen is put by Zeldovich in 1946. He assumed the formation of atomic oxygen as a precursor to the formation of NO according to the following mechanism



for rich fuel ($\phi > 1.2$), the following reaction is also important



where ϕ is the equivalence ratio of the fuel-air mixture. Generally excess air (lean fuel, $\phi < 1$) is used in all practical combustion processes.

To find a rate of formation for NO, the following assumptions have to be undertaken:

- 1- Atomic oxygen is at equilibrium according to the first reaction of Zeldovich mechanism.

2- Atomic nitrogen is formed and consumed at equal rates due to reactions 2 and 3 of Zeldovich mechanism.

3- Excess air is used.

So the mass balance on nitrogen atoms leads to

$$K_2[O][N_2] + K_3^*[NO][O] - K_2^*[NO][N] - K_3[N][O_2] = 0$$

solving for nitrogen atom concentration, $[N]$

$$\therefore [N] = \frac{[O](K_2[N_2] + K_3^*[NO])}{K_2^*[NO] + K_3[O_2]}$$

from assumption 3, excess air, $K_3[O_3] \gg K_2^*[NO]$

So the rate of NO formation is

$$\frac{d[NO]}{dt} = K_f [N_2] [O_2]^{1/2} - K_b [NO]^2 [O_2]^{-1/2}$$

where K_f and K_b are composite forward and backward rate constants defined as

$$K_f = 2K_1^{1/2}/K_2 \quad \text{and} \quad K_b = 2K_1^{1/2} K_2^* K_3^*/K_3$$

they are equal to

$$K_f = 1.61 \times 10^3 \exp(-135,000/RT), \text{ (cm}^3 \text{ molecules)}^{1/2} \text{ sec}^{-1}$$

$$K_b = 52.9 \exp(-91,600/RT) \quad , \text{ (cm}^3 \text{ molecules)}^{1/2} \text{ sec}^{-1}$$

The previous rate of NO formation is for oxidation of atmospheric nitrogen. It was found that chemically bound nitrogen in hydrocarbon fuel, termed fuel nitrogen, is another major source of NO formation. Figure 41 shows the correlation between NO_x emissions and fuel nitrogen content for liquid fuels burned under fuel lean conditions.

The heterocyclic ring compounds of pyridine, piperidine, and quinoline are the most common fuel nitrogen compounds found in oil. Coal contains both chain and ring nitrogen-bearing compounds. Natural gas is essentially free of such components.

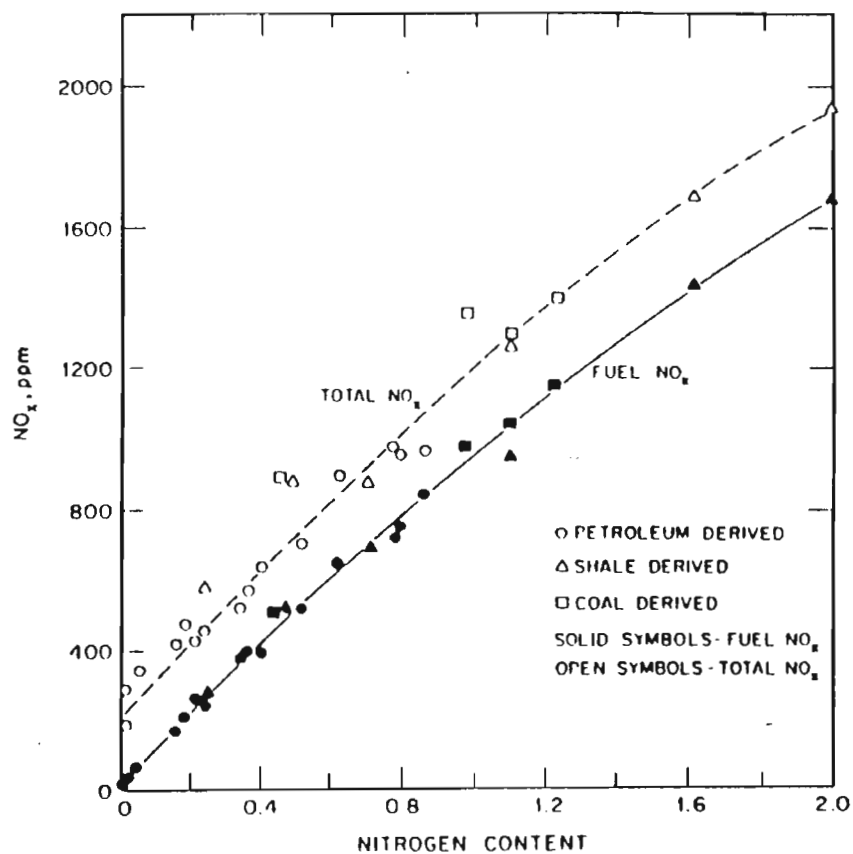


Fig. 4.41. NO_x Emissions from Liquid Fuels
(N_2 in wt%, 5% excess oxygen).

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Fig 3-1
J. H. Seinfeld

The large contribution of fuel nitrogen in the formation of NO is due to the weak bonding energy (~ 940 KJ/2 mole) of nitrogen in the nitrogen bearing organic compounds. Several theories have been proposed for the total NO_x formation. These include:

- 1- The use of cyanide (CN) as an intermediate.
- 2- The release of atomic nitrogen as bonds are broken
- 3- A partial-equilibrium mechanism.

Impact of NO_x Pollution

NO_x emissions are known to cause human health problems and environmental damage. Exposure to nitrogen oxides is believed to increase the risks of acute respiratory disease and susceptibility to chronic respiratory infection. Nitrogen dioxide (NO_2) contributes to heart, lung, liver and kidney damage. Exposure to high NO_2 concentrations can be fatal. At lower NO_2 levels, 25 to 100 parts per million, acute bronchitis and pneumonia can occur. Eye and skin irritations can result from occasional exposure to low concentrations of NO_2 . Nitrogen oxides are also toxic to vegetation. Reduced growth and plant destruction have been observed as a result of exposure to NO_x emissions.

Probably the most important effect of NO_x is the contribution to photochemical smog. NO_x reacts with hydrocarbons in the presence of sunlight to form photochemical oxidants, or ozone (O_3). Ozone can cause severe damage to the lungs and can aggravate asthma and other respiratory diseases. In addition to ozone, other smog pollutants such as peroxyacetylnitrate (PAN) can cause coughing, eye irritation, headaches, and throat irritation.

Nitrogen oxides also contribute to the global acid rain problem. Through a series of complex reactions, nitrogen oxides can be converted to nitric acid and nitrates which may be deposited in the form of rain and snow. Nearly one-half of the acidity in acid rain is due to nitric acid.

METHODS OF CONTROL

Nitrogen oxides emissions can be reduced by two ways. The primary method is to control over the reaction which produces the pollutant, so called combustion control methods. As a second possibility, the pollutant might be removed after it is formed, so called flue gas treatment methods. Another classification of NO_x control methods is as follows

- 1- Before burning
 - . fuel denitrogenation (denitrification)
- 2- During burning
 - . combustion modification
 - . catalytic combustion

- 3- After burning
 - . flue gas treatment
 - . catalytic emission control

Fuel Denitrogenation

This is aimed for nitrogen from the fuel. Nitrogen can be removed from coal, shale, or heavy fuel oils by liquifying the fuels and mixing with hydrogen gas. The mixture is heated and a catalyst is used to cause the fuel nitrogen to combine with the hydrogen. This reaction produces a cleaner fuel and ammonia as a byproducts.

Combustion Modification

A typical furnace with boiler tube sections is shown in Figure 42. The main sections are the fire wall or water wall tubes, superheater, convection tubes, economizer, and air pre-heater. These boiler sections transfer heat in the furnace to produce steam for generation of electricity or process steam in an industrial plant. The furnace is surrounded by water walls or fire wall tubes. Water fed to the tubes is heated and is turned into steam. Steam is collected in steam drums located in the main convection section of the furnace. Convection tubes are used to covert any water collected in the steam drum back into steam. The superheater is a section of tubes used to superheat the steam to a higher temperature prior to going to the turbine. The economizer is used to heat the feedwater makeup to the boiler. The air pre-heater is used to preheat the air used for combustion. The furnace is designed to use as much of the heat as possible before exhausting flue gas out the stack.

The important factors that control NO_x formation are:

- 1- air-fuel ratio
- 2- combustion air temperature
- 3- extent of combustion-zone cooling
- 4- furnace-burner configurations.

The lower the air-fuel ratio, i.e. low excess air, the lower the NO_x emission. Nitrogen oxides reductions averaging between 16 and 20% are achieved on gas and oil fired utility boilers when the excess air is reduced to a level between 2 and 7%. In coal fired utility boilers, 20% NO_x reductions is achieved if the excess air is reduced to the 20% level. Most of the large boilers today operate excess less than 5%.

The reduction of excess air is easy to implement. It slightly decreases the efficiency of the furnace. Combustion efficiency of coal fired boiler is lowered from 99.5% to 92% when reducing the excess air from 25%. However, there are problems with decreasing the excess air. Low excess air firing can produce

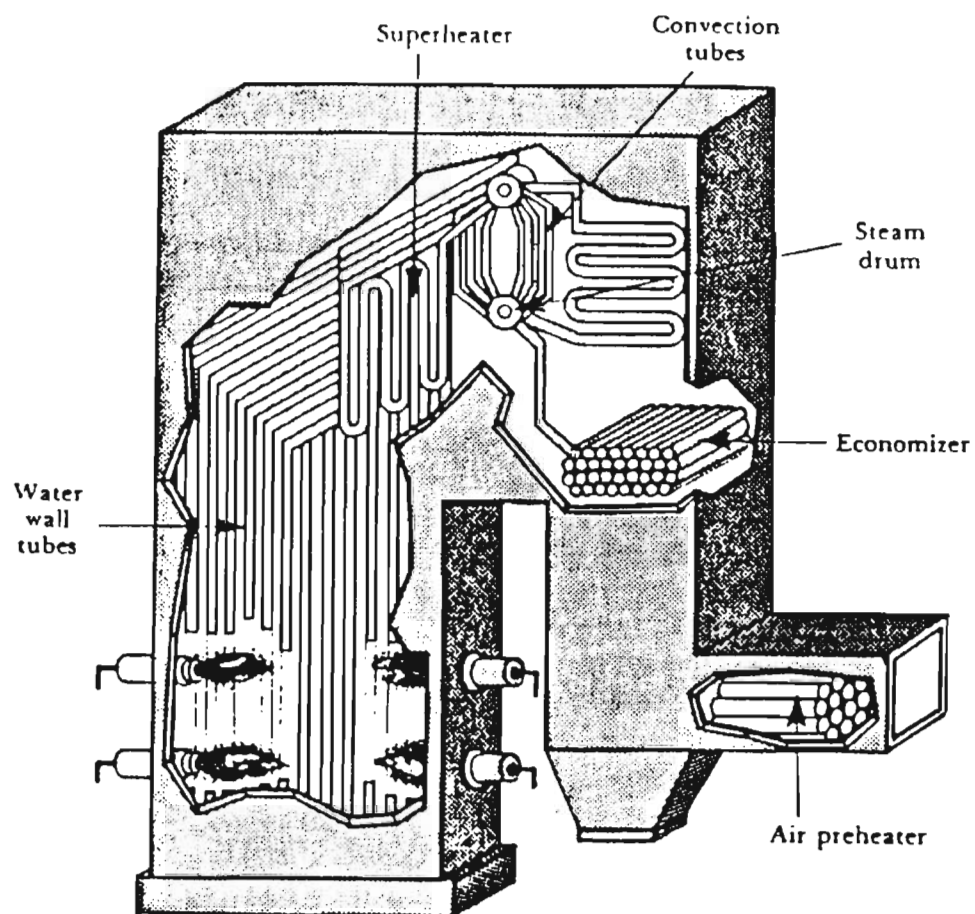


Fig. 4.42. Typical Boiler.

smoke and high carbon monoxide emissions. Also, fouling and slagging of boiler tube surface can occur if various coals and residual oils are burned.

The following are examples of some processes that used in reducing NO_x emissions during the stationary fuel combustion. These methods utilize the prementioned factors that control NO_x emissions.

1- Staged Combustion

Fuel combustion takes place in two stages. In the first stage low excess air is used, near or below stoichiometric conditions. Next, fuel is burned in an excess air conditions, to achieve complete burnout for consuming CO and hydrocarbons left in the first stage. This is accomplished by injecting. Secondary air in the second combustion stage.

Staged combustion reduces NO_x emissions by several factors:

- a- a lack of available oxygen for NO_x formation in the first stage.
- b- the flame temperature is lower in the first stage than that of single stage combustion.
- c- The peak temperature in the second stage is lower.

2- Flue Gas Recirculation, FGR

Flue gas recirculation (FGR) has been used to reduce thermal NO_x emissions from large oil and gas fired boilers. A portion (10 to 30%) of the flue gas exhaust is recycled back into the main combustion chamber by removing it from the stack breeching and mixing it with the secondary air windbox (Figure 43). In order for FGR to be effective in reducing NO_x emissions, the gas must enter directly into the combustion zone. This recirculated gas lowers the flame temperature and dilutes the oxygen content of the combustion air, thus lowering thermal NO_x emissions.

NO_x reduction of approximately 40 to 50% is possible with recirculation of 20 to 30% of the exhaust gas in gas and oil fired boilers. Since FGR is used to reduce thermal NO_x , it is not effective for reducing NO_x emissions generated from burning a high nitrogen content fuel such as coal. At high rates of recirculation (>30%) the flame can become unstable, thus increasing carbon monoxide and hydrocarbon emissions.

Some operational problems can occur using flue gas recirculation. Possible flame instability, loss of heat exchanger efficiency; and for small package boilers, condensation on internal heat transfer surfaces limit the usefulness of gas recirculation.

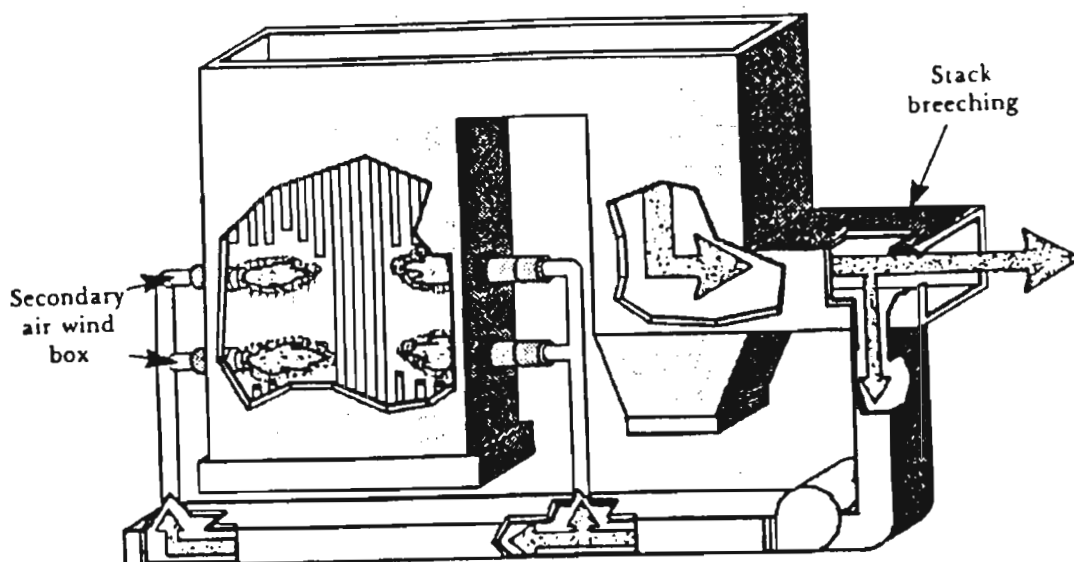


Fig. 4.43. Flue Gas Recirculation.

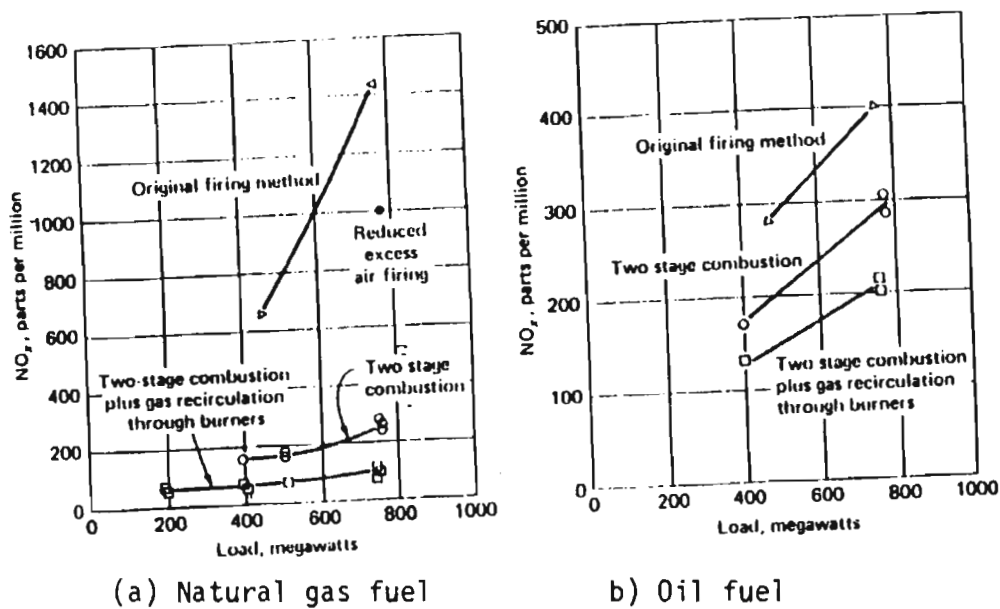


Fig. 4.44. Effect of NO Control Methods.

Figure 44 shows the reduction of NO_x emissions for natural gas and oil fired-boilers used in electric power generation.

3. Low NO_x Burners

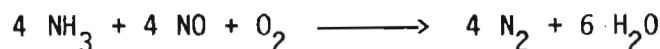
New low NO_x burners have been developed by several manufacturers to reduce NO_x emissions. Burners control mixing of fuel and air in a pattern to keep flame temperature low and dissipate the heat quickly. Some burners are designed to control the flame shape to minimize the reaction of nitrogen and oxygen at peak flame temperatures. Other designs have fuel rich and air rich regions to reduce flame temperature and oxygen availability.

The Dual Registered Low NO_x burner is shown in Figure 45. The mixture of pulverized coal and primary air is controlled to slightly delay combustion of the fuel. The remainder of the combustion air (secondary air) is introduced through two concentric air zones which surround the coal nozzle. The flame produced is elongated compared to the short intense flame produced in a conventional burner. The peak flame temperature is reduced, thus lowering thermal NO_x emissions; and the oxygen available in the flame is lower, thus reducing fuel NO_x emissions. This burner have shown a 40 to 60% reduction in NO_x emissions.

FLUE GAS TREATMENT

1. Exxon Thermal De NO_x Process

Ammonia is injected into the post combustion zone of the boiler to reduce NO_x into molecular oxygen and water according to the following reaction



This reaction is extremely temperature dependent. It successfully takes place at approximately 950°C (1740°F). At higher temperatures (above 1090°C), the ammonia is oxidized to NO_x. At lower temperatures (below 850°C), no reactions occur. Hydrogen shifts the reaction to lower temperatures, to approximately 700°C with H₂:NH₃ ratio of 2:1.

Ammonia is mixed with a carrier gas of air or steam to provide good mixing with the flue gas. This ammonia mixture is injected at various points in the convection and superheater sections of the boiler as shown in Figure 46.

Nitrogen oxides emissions in oil, gas and small coal fired boilers can be reduced more than 60% by using ammonia injection. This process could be used to supplement the NO_x emission reductions accomplished by combustion modifications, when very low levels of NO_x are required.

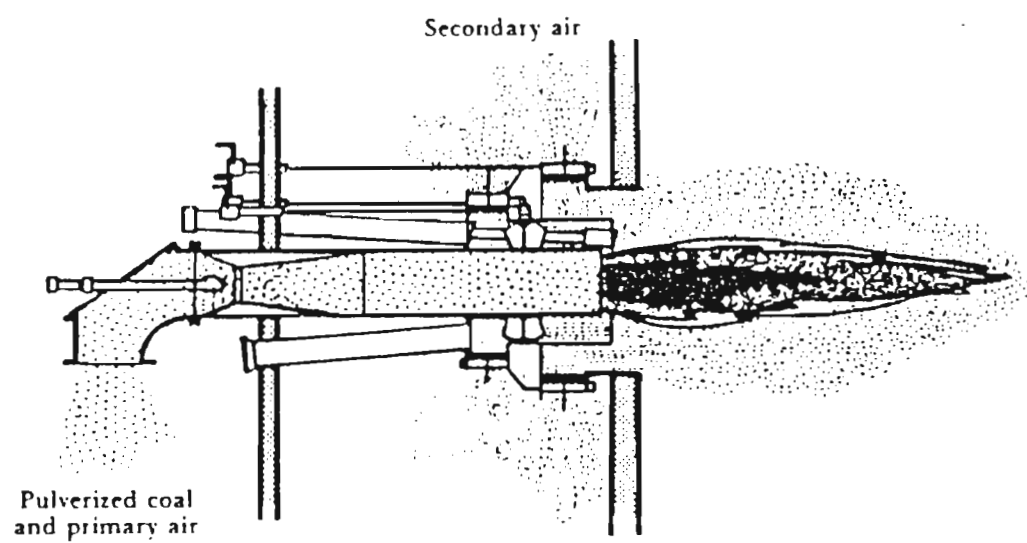


Fig. 4.45. Schematic of a Low NO_x Burner.

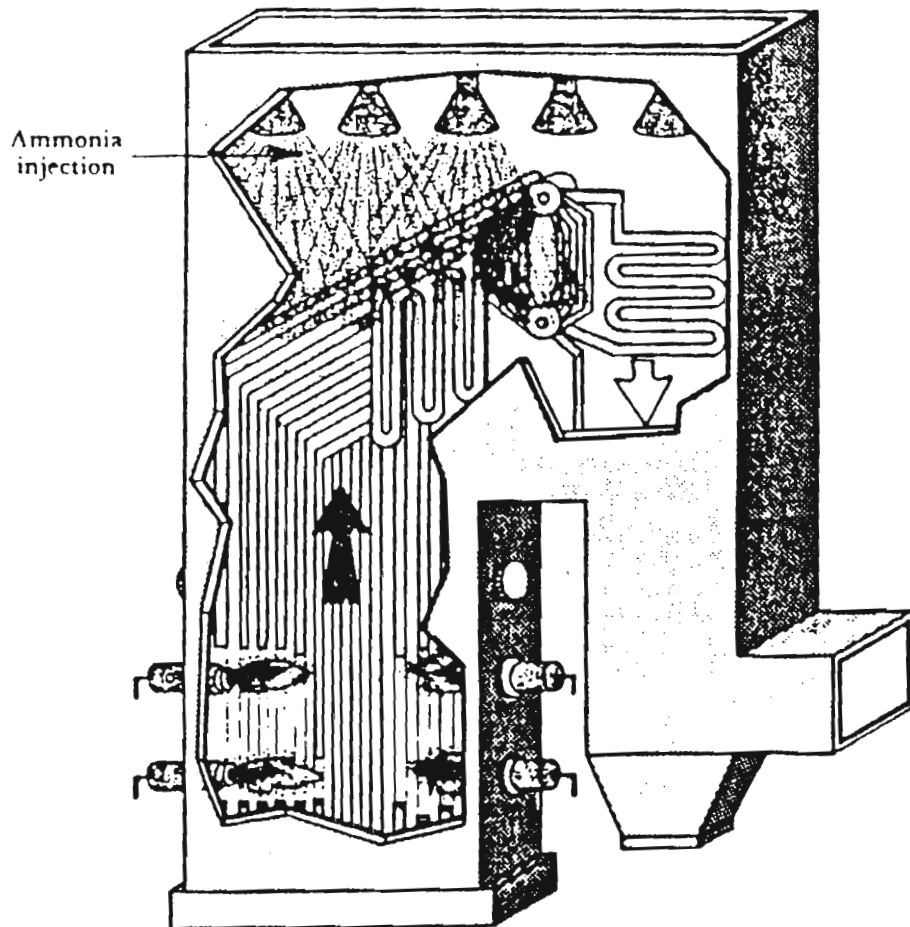
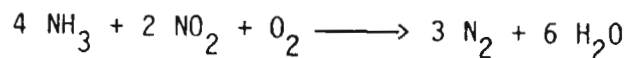
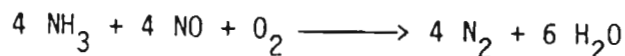


Fig. 4.46. Exxon Thermal De NO_x Process.

2- Selective Catalytic Reduction, SCR

This is a dry process used to reduce NO_x emission from fossil fuel fired boilers to achieve 90% reduction in NO_x emissions. This process is based on the preferential reaction of NH_3 with NO_x rather than SO_2 in the flue gas. The following reactions take place



This process involves injecting NH_3 into the flue gas and passing this mixture through a catalytic reactor (Figure 47). NO_x emissions are reduced to harmless molecular nitrogen (N_2) and water vapor (H_2O). Ammonia is injected on an $\text{NH}_3:\text{NO}$ mole ratio of 1:1 attaining a 90% NO_x emission reduction with less than 20 ppm NH_3 leaving the reactor.

The optimum temperature for successful NO_x reduction in the catalytic reactor is between 300 and 400°C. The reactor is usually located between the boiler economizer and air preheater. A bypass around the economizer is used when temperatures begin to fall below 300°C. The reactor can be located before or after the baghouse or electrostatic precipitator used to collect particulate matter.

A number of materials have been used for catalysts. Initially, a platinum metal on an alumina (Al_2O_3) support was used for NO_x control on gas fired boilers. Sulfur oxides, particularly SO_3 and SO_2 , poison the alumina. Other catalysts must be used which resist SO_x deterioration when burning fuel containing sulfur. Titanium dioxide (TiO_2) and vanadium (V_2O_5) catalysts are resistant to SO_x attack. Therefore, most catalysts on oil and coal fired boilers contain TiO_2 or V_2O_5 . Other active metals including C, CO, Cr, Fe, Mn, Mo, Ni and W have been used as catalysts. The oxides and sulfates of these metals have also been used as catalysts.

Catalyst shape and reactor design vary, depending on the manufacturers' design and the boiler application. Natural gas fired boilers use catalysts made of spherical pellets, rings or cylinders that are packed in a fixed bed reactor. Since high concentrations of particulate matter will plug a fixed bed reactor, a moving bed reactor or a parallel reactor is used on oil or coal fired boilers. In a moving bed reactor or a parallel reactor is used on oil or coal fired boilers. In a moving bed reactor, the catalyst is charged at the top of the reactor and moves down through the vessel while the flue gas passes through the catalyst in a cross flow motion. The spent catalyst is discharged at the bottom of the reactor. Particulate matter is then removed by screening, and the catalyst is regenerated before being returned to the reactor. Parallel flow reactors were designed for use on

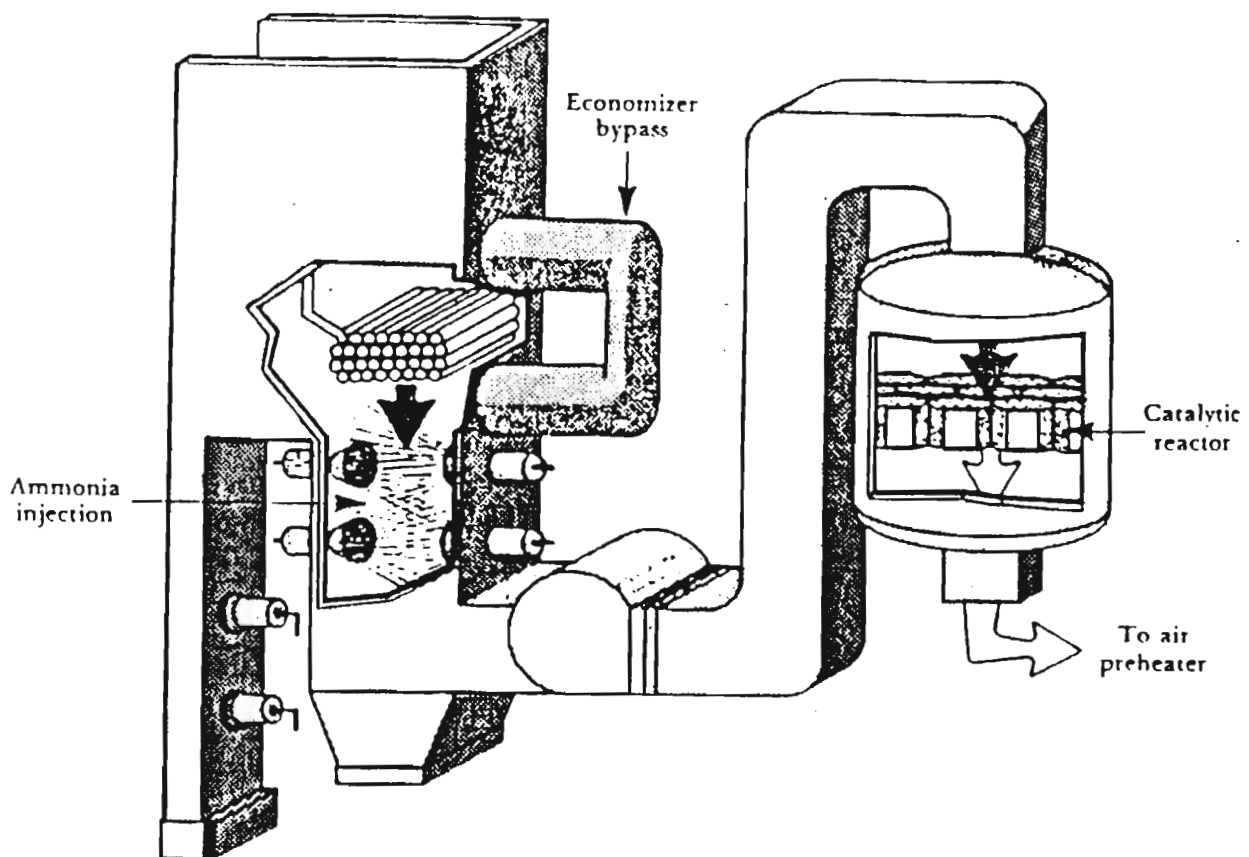


Fig. 4.47. Selective Catalytic Reduction Process.

coal fired boiler flue gas containing a high particulate matter concentration. The flue gas flow is parallel to the catalyst surface. Parallel catalyst shapes are either tubular, honeycomb, or plates. Catalysts are usually made into unit cells that are 12 inches square. These unit cells are stacked into the reactor to form the grids or layers of the catalyst.

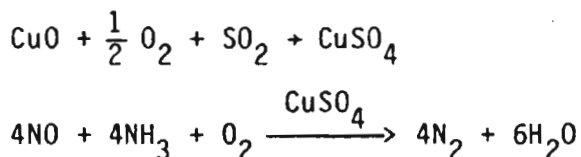
The biggest problem with the SCR process is the formation of solid ammonium sulfates $(\text{NH}_4)_2\text{SO}_4$ and liquid ammonium bisulfate $(\text{NH}_4\text{HSO}_4)$. This problem occurs when using the SCR process on high sulfur oil and coal fired boilers. Ammonia reacts with SO_3 to form corrosive compounds of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 that coat the air preheaters. Increased soot blowing in the furnace and water washing of the air preheaters helps remove these materials.

3- Shell-UOP Process

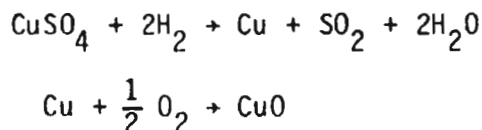
Shell UOP is a dry process that simultaneously removes both NO_x and SO_x emissions. This process can also be designed to remove either compound separately.

The process uses a copper oxide (CuO) catalyst supported on alumina. These catalysts are located in two or more parallel passage reactors as shown in Figure 48. Flue gas containing both NO_x and SO_x is introduced into the reactor where the SO_x reacts with copper oxide to form copper sulfate (CuSO_4). At the same time ammonia is being injected which reacts with the NO_x . The copper sulfate, and to a lesser extent the copper oxide, act as catalysts for the $\text{NO}_x.\text{NH}_3$ reaction.

The following reactions occur in the reactor:



When the reactor catalyst is saturated with CuSO_4 , the flue gas is redirected to a fresh reactor and the spent catalyst is regenerated. Hydrogen is used to regenerate the catalyst by reducing the CuSO_4 to copper and producing a concentrated SO_2 gas stream. The SO_2 gas is then used to produce sulfuric acid or elemental sulfur for commercial sale. The copper in the reactor is oxidized to CuO and the process is ready to be put on line again. The reactions that take place in the reactor during catalyst regeneration are:



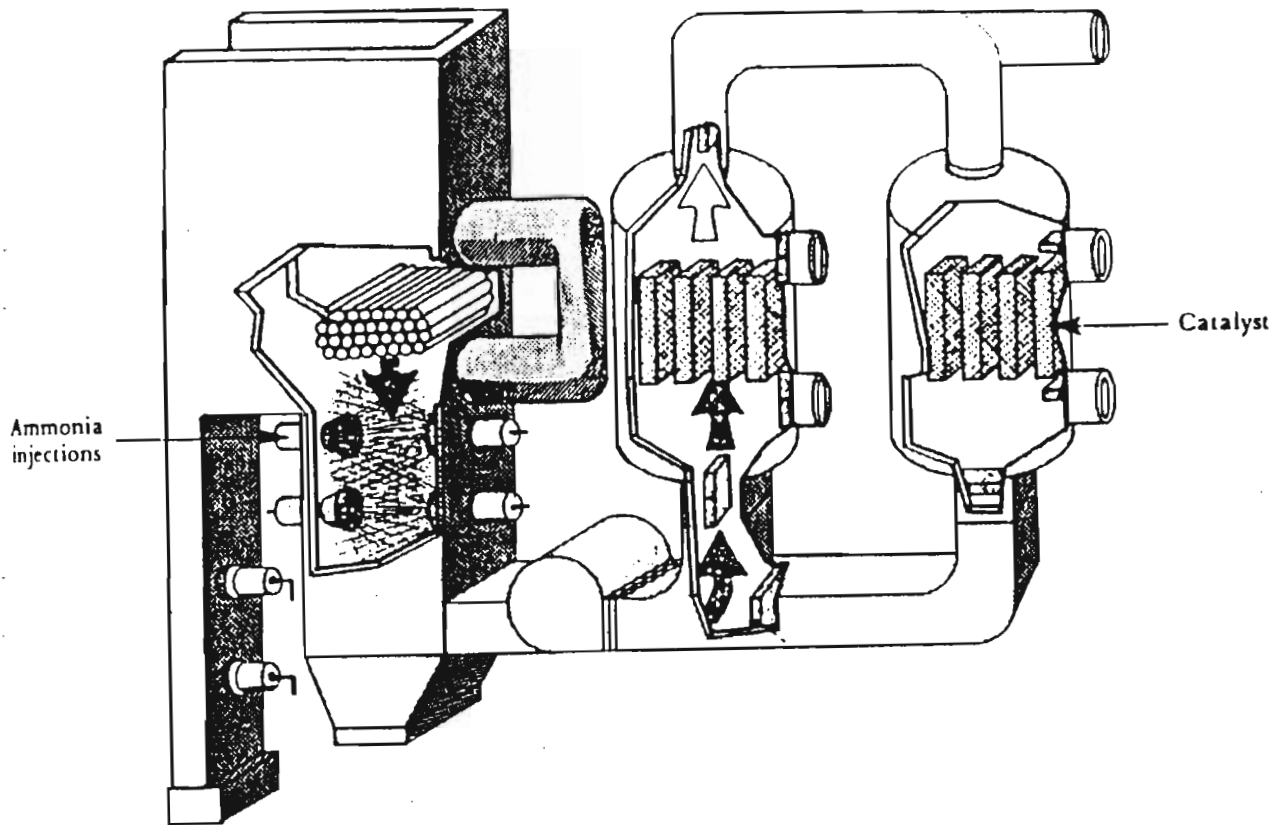


Fig. 4.48. Shell UOP Process.

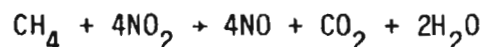
The Shell UOP process can be operated as a NO_x emission reduction process by eliminating the regeneration cycle. The process can be operated as a SO_x emission reduction process by eliminating the ammonia injection.

This system can be designed to use moving packed beds, fixed packed beds, or fluid systems. Shell UOP Inc. has developed a type of fixed bed reactor in which the flue gas flows through open channels called a parallel passage reactor. The catalyst (CuO) is placed between thin layers of wire gauze. Flue gas flows along the catalyst surfaces and the NO_x and SO_x gas diffuses into the catalyst. This design reduces reactor plugging by particulate matter. The NO_x/SO_x emission reduction is achieved in less than one-half second.

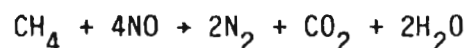
The reactors are operated at temperatures between 350 and 450°C during the NO_x reduction cycle. The pressure drop through the parallel passage reactor is approximately 75 to 150 mm H_2O depending on the gas flow rate and NO_x reduction desired. The ammonia injection rate is one mole of NH_3 injected for one mole of NO_x reduced.

4- Non-Selective Reduction

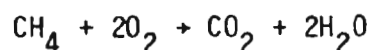
In nonselective reduction the NO_x is converted to N_2 simply by supplying sufficient reactant to reduce the excess oxygen as well. Typical reactants are hydrogen or methane, CH_4 . When methane is used, the overall NO_x reduction reactions are



and



These reactions compete with the methane combustion reaction

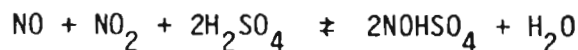


These reactions are highly exothermic. Hence the gas temperature could become quite high as a result of the reduction process. The actual value depends upon the quantity of pollutant reduced. When noble metal catalysts, such as platinum or palladium, are used, the flue-gas temperature must be above some minimum value to ensure ignition. For CH_4 this temperature is around 850°F (730°K). The rate of conversion is high, even with relatively high space velocities. Nonnoble metal catalysts also can be used (such as supported copper oxide).

5- Absorption

The oxides of nitrogen can be absorbed by water, hydroxide and carbonate solutions, sulfuric acid, organic solutions, and molten alkali carbonate and hydroxides. When aqueous alkaline solutions, such as NaOH and MgOH, are used, complete removal requires that one-half of the NO must first be oxidized to NO₂ (or NO₂ gas added to the gas stream). Best absorption occurs when the NO/NO₂ molar ratio is 1:1, which indicates that absorption of the combined oxide, N₂O₃, is the most favorable. The absorption of NO_x by alkaline solutions has been confirmed during desulfurization of power plant emissions by such solutions. In the desulfurization process, apparently about 10 percent of the NO was oxidized to NO₂ before the flue gas reached the scrubber. The scrubber then removed about 20 percent of the total NO_x, in equal parts of NO and NO₂.

The absorption of nitric oxides by strong sulfuric acid has long been known. The compounds formed in this case are violet acid, H₂SO₄.NO, and nitrosyl sulfuric acid, NOHSO₄. The latter is very stable in concentrated acid. The reaction is



Any moisture in the flue gas is picked up by the acid, and this moisture drives the above reaction to the left. This problem area can be reduced by operating at an elevated temperature (>250°F) so that the vapor pressure of water in the solution is equal to the partial pressure of water in the flue gas. The use of sulfuric acid to remove SO₂ and NO_x is currently under active investigation.

NO_x in Internal Combustion Engine

NO formation is favored by high temperatures. So NO is formed primarily in the bulk gases in the cylinder as opposed to within a quench zone near the relatively cold chamber walls.

Figure 49 compares actual exhaust NO, CO, and hydrocarbon concentrations as a function of air-fuel ratio for a typical automobile. The quantity of NO formed depends markedly on the mode of operation of the vehicle. Emissions of NO under varying driving conditions were shown roughly in Table 28. Concentrations are highest during acceleration and cruising, and mass emissions are highest during acceleration, due to the high volume of exhaust gases produced. At low air-fuel ratios both the amount of available O₂ and the flame temperatures are low, resulting in low NO. As the ratio increases, so do the available O₂, flame temperature, and NO concentrations. However, as the air-fuel ratio is increased beyond about 16, the flame temperature and thus the NO begin to decrease owing to dilution of the combustion mixture with excess air.

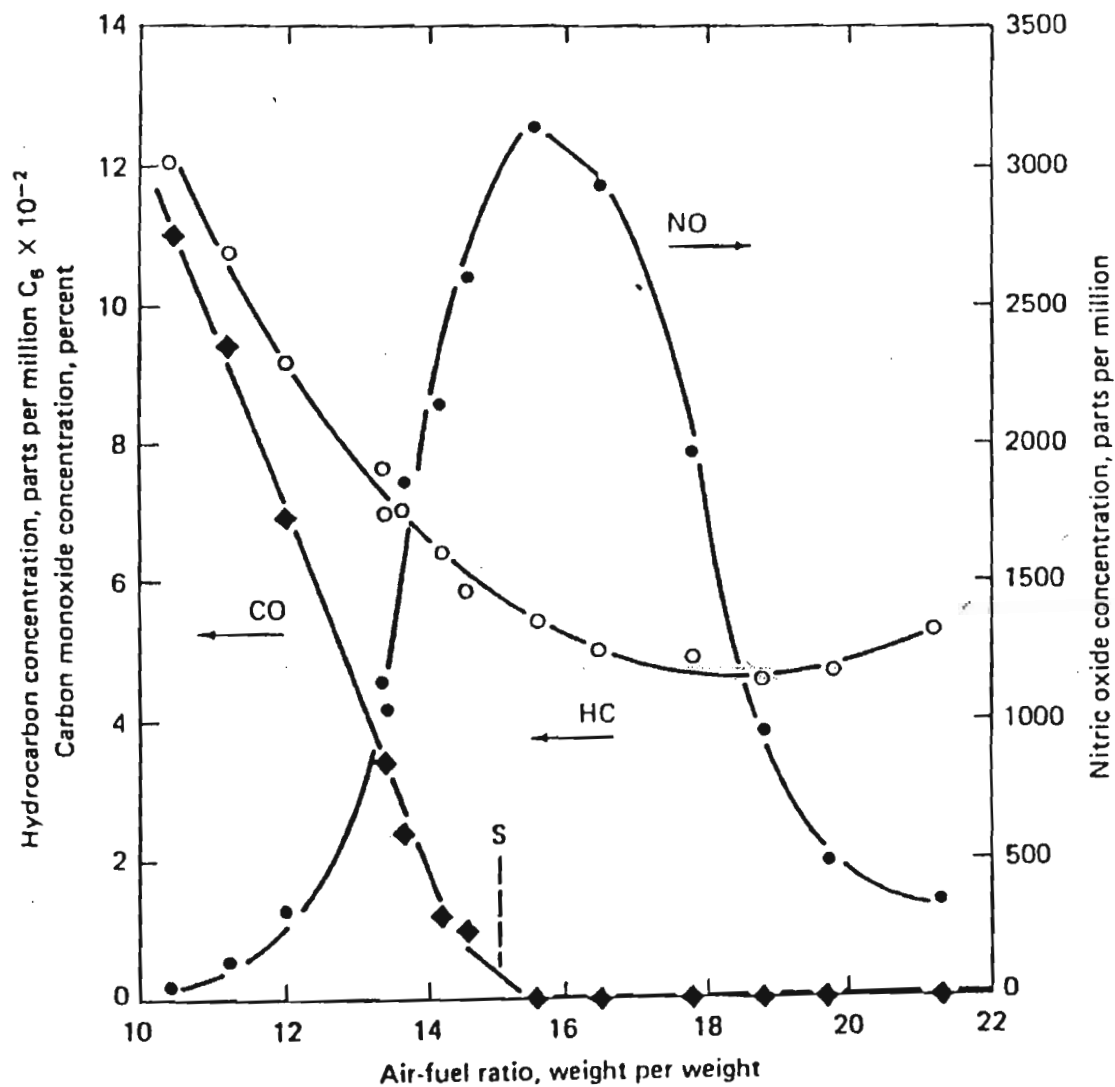


Fig. 4.49. Exhaust Hydrocarbon, CO and NO as a Function of Air Fuel Ratio.

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Table 28. Typical Exhaust Gas Constituents as a Function of Driving Mode.

Pollutant	Idling	Acceleration	Cruising	Deceleration
Carbon monoxide, percent	4-9	0-8	1-7	2-9
Hydrocarbons (as hexane), ppm	500-1000	50-800	200-800	3000-12,000
Oxides of nitrogen, ppm	10-50	1000-4000	1000-3000	5-50

Modifications in conditions that increase the peak temperature or the oxygen concentration in the combustion gases increase the NO concentration in the exhaust. In addition, NO levels are found to be nearer the equilibrium concentration corresponding to the peak cycle temperature and pressure than to the equilibrium concentration at exhaust conditions.

The processes responsible for the production hydrocarbons and nitric oxide in the internal combustion engine are the compressed air-fuel mixture is ignited by the spark plug, and a flame front propagates across the cylinder. As the flame approaches the walls, which are relatively cooler, the flame is quenched, leaving perhaps a very thin layer of unburned or absorbed fuel on the walls and in the crevice between the piston and cylinder wall above the piston ring. During the flame propagation, NO is formed by chemical reactions in the hot just-burned gases. As the piston recedes, the temperatures of the different burned elements drop sharply, "freezing" the NO (i.e., the chemical reactions which would remove the NO become much slower) at the levels formed during combustion, levels well above those corresponding to equilibrium at exhaust temperatures. As the valve opens on the exhaust stroke, the bulk gases containing the NO exit, entraining the unburned hydrocarbons in the wall layers. It is to these processes that we must devote our attention if we wish to reduce both hydrocarbon and NO formation in the cylinder.

The optimum operation for NO_x reduction is either very rich or very lean combustion (assuming that no exhaust gas treatment is employed). Lean operation is effective as a means of reducing NO of formation because the peak cycle temperature decreases as the air-fuel ratio increases. Even though the equilibrium NO levels at the reduced combustion temperatures of lean operation are much higher than desired, the high overall activation energy for NO formation results in a rate of NO formation that declines with temperature much more rapidly than does the equilibrium concentration of NO. As a result, the peak equilibrium NO levels are never attained.

One of the most advantageous means to achieve lean operation is exhaust gas recycle (EGR). The advantages of EGR result mainly from the fact that the air-fuel mixture can be diluted without addition of excess O₂ (from which NO is formed), and that

dilution with exhaust gas results in the introduction into the charge of species, such as CO_2 and H_2O , with higher heat capacities than N_2 .

In general, NO emissions are relatively insensitive to the modifications in the hydrocarbon composition of the gasoline burned. Instead, treatment of exhaust gas are now widely used. Nitrogen oxides had to be reduced to nitrogen and oxygen by the effect of certain catalysts. The presence of lead compounds in the gasoline hindered the use of these catalytic treatment processes due to lead poisoning of the catalysts.

PROBLEMS

1. A 1000-MW power plant may operate with (a) coal with a heating value of 11,000 Btu/lb, (b) fuel oil with a heating value of 18,000 Btu/lb and a specific gravity of 0.86, and (c) natural gas with a heating value of 1000 Btu/scf. If the plant thermal efficiency is 38 percent, determine the NO_x emissions for these three fuel sources, in tons per day, on the basis of emission factors.
2. A residual fuel oil with an average hydrocarbon formula of $\text{C}_{10}\text{H}_{20}$ also contains (a) 0.3 percent and (b) 0.5 percent by weight of nitrogen chemically bound in the fuel. If all of this nitrogen is converted to NO , and the $\text{C}_{10}\text{H}_{20}$ component is burned with 60 percent excess air, calculate the NO concentration in the flue gas, in parts per million, assuming no conversion of nitrogen in the atmospheric air to NO and complete combustion of the hydrocarbon.
3. The NO emission standard in the exhaust gas from an oil-fired unit is roughly 230 ppm. Consider an oil with a formula of $\text{C}_{10}\text{H}_{20}\text{N}_x$. The oil is burned with 50 percent excess air beyond that required to change C and H to CO_2 and H_2O . Assume that 50 percent of the nitrogen bound in the fuel is converted to NO , and no nitrogen (N_2) in the atmospheric air used for combustion is converted. What is the maximum percent by weight of nitrogen permitted in the fuel without exceeding the emission standard?
4. The NO_x emission from a power boiler is $0.65 \text{ lb}/10^6 \text{ Btu}$ input. Assume that the fuel is pure carbon, and that 20 percent excess air is used in the combustion process. Determine the NO_x emitted in parts per million.
5. Determine the concentration in ppb of atomic oxygen that exists at equilibrium for an initial mixture of 97 percent N_2 and 3 percent O_2 by volume and for temperatures of (a) 2000, (b) 2200, and (c) 2400°K.

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