For Environmental Seminar in EiMAS

Introduction of air pollution control

March 10, 2011

Japan Environmental Management Association for Industry (JEMAI)

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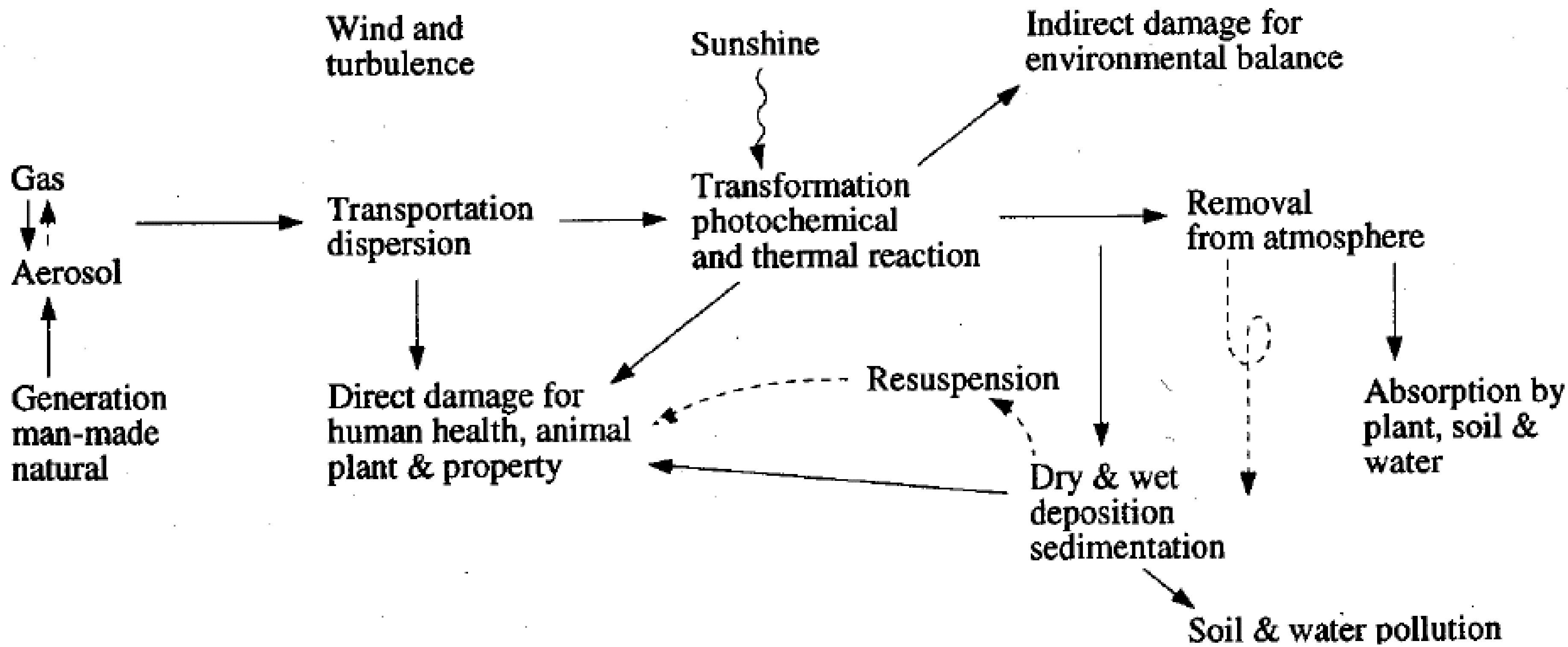
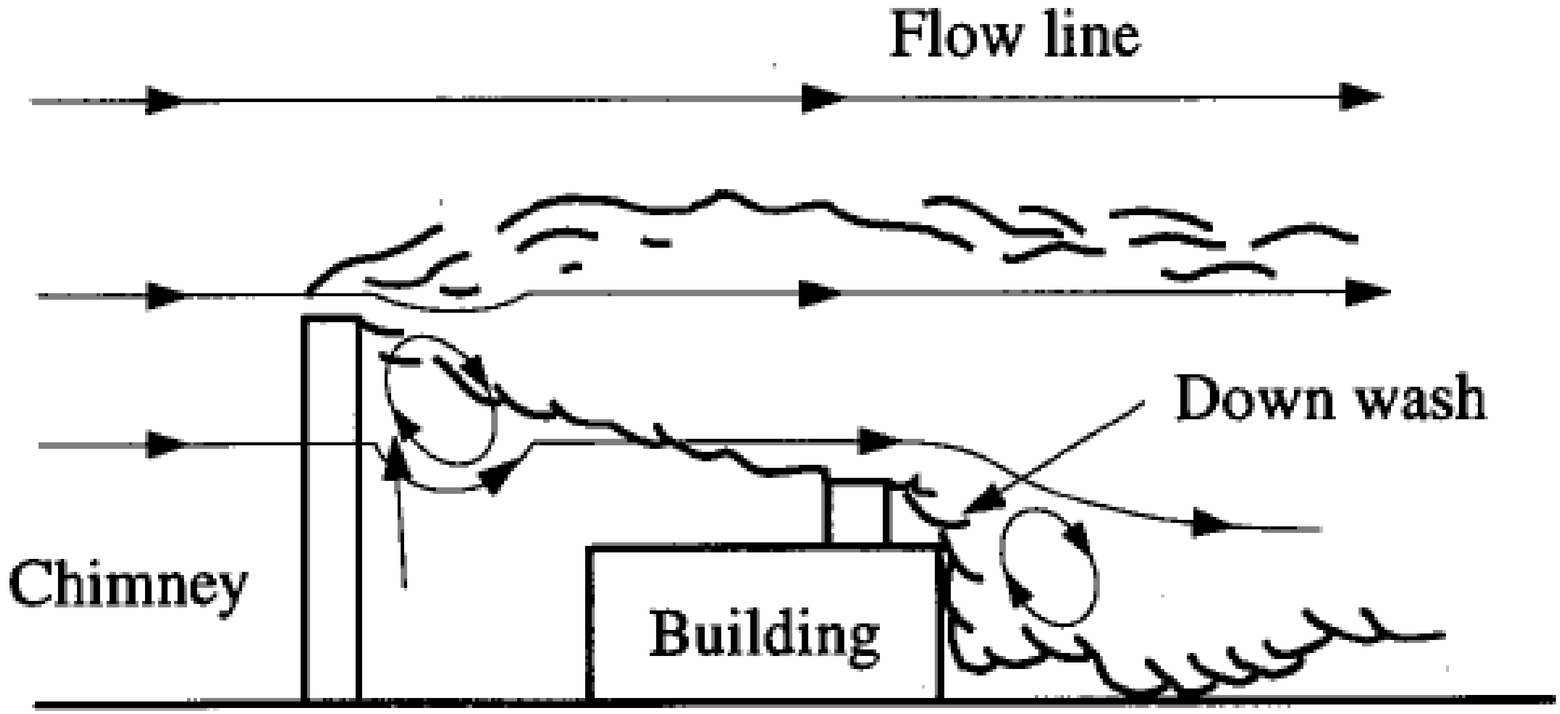
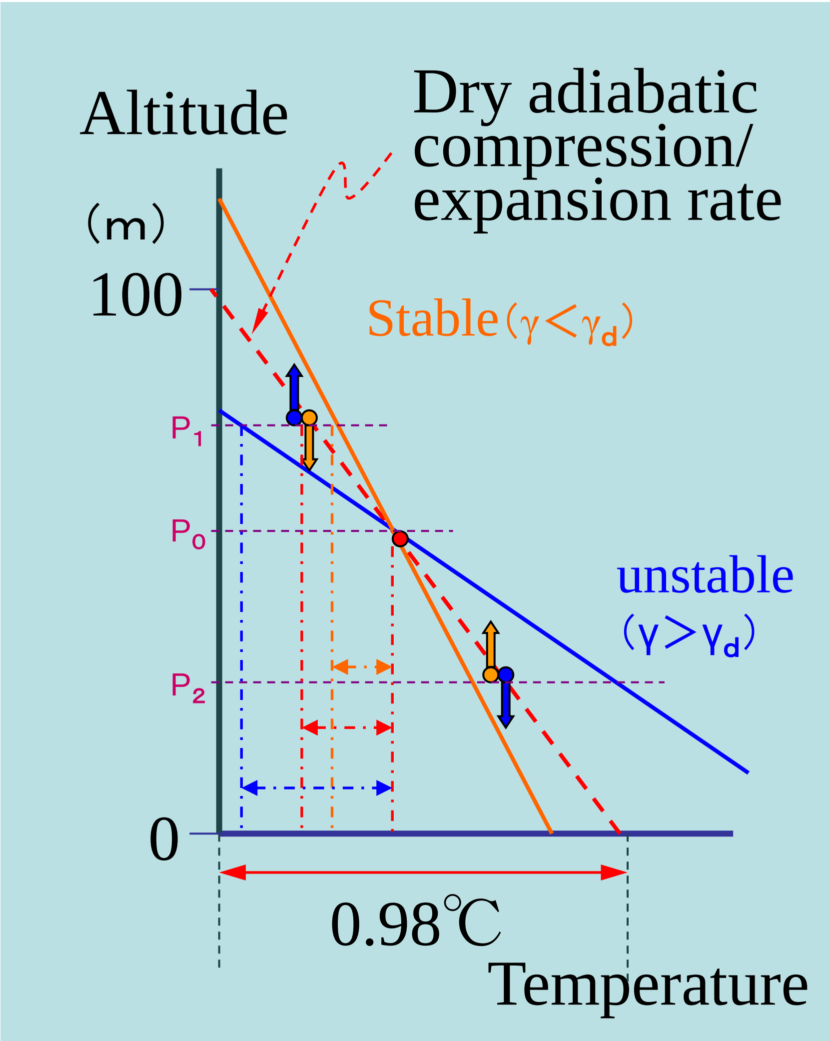
Life cycle of air pollutants



Down wash of smoke behind stuck and building



Theory of air mass movement



●Air mass moves adiabatic up/down.
→up: adiabatic expansion→temp. down
→down: adiabatic compression→temp. up

$$\frac{dT}{dz} = -\gamma_d$$

Dry adiabatic rate γ_d: 0.98℃/100m

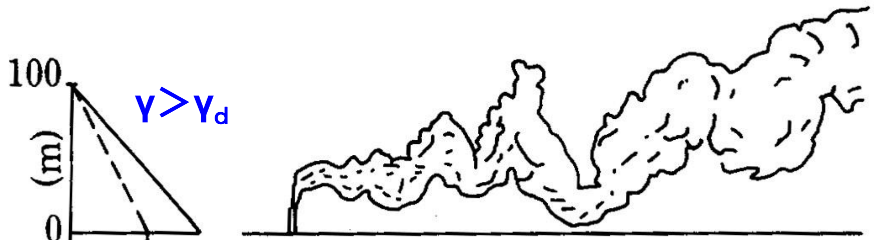
(constant in lower atmosphere)

γ>γd (γ: actual atmospheric temp. inclination)
Temp. of air mass upped becomes higher than ambient air and accelerates its speed.
→ unstable by heat

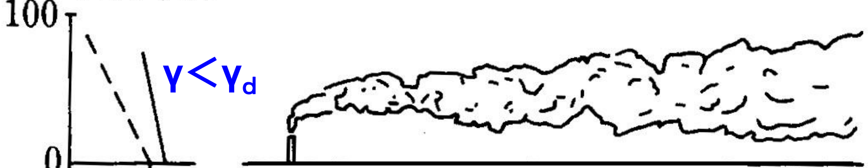
γ<γd
Temp. of air mass upped becomes lower than ambient air and restrains its speed.
→ stable by heat

γ=γd → neutral by heat
(adiabatic distribution)

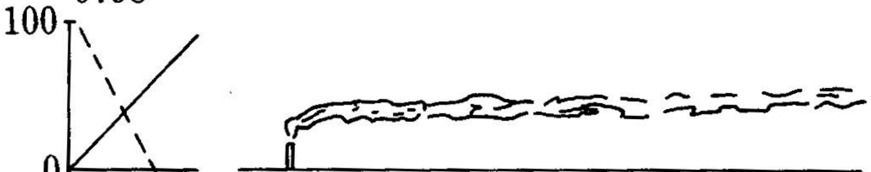
Typical types of smoke plumes and their corresponding temperature profiles



Unstable (Loop shape)

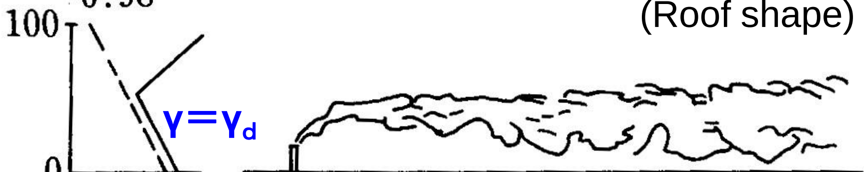


Week stable (Conic shape)



Strong stable (Fan shape)

Lower layer : stable, upper : unstable (Roof shape)



Lower layer : unstable, upper : stable (Smoke shape)

Loop shape : All layer is unstable.

Smoke moves widely up and down. High conc. of smoke appears momentary near emission point. Fine daytime

Conic shape : All layer is neutral or week stable

Smoke diffuses same speed vertically and horizontally. Maximum conc. point appears farther than loop shape.

Fan shape : All layer is strong stable (reverse temp.)

Smoke can not move vertically. Smoke only diffuses horizontally like a fan. Fine nighttime and morning.

Roof shape : Lower layer is stable and upper is unstable

Inclination of temp. changes in reverse. Smoke diffuses upper side of reverse layer. One reason of Smog.

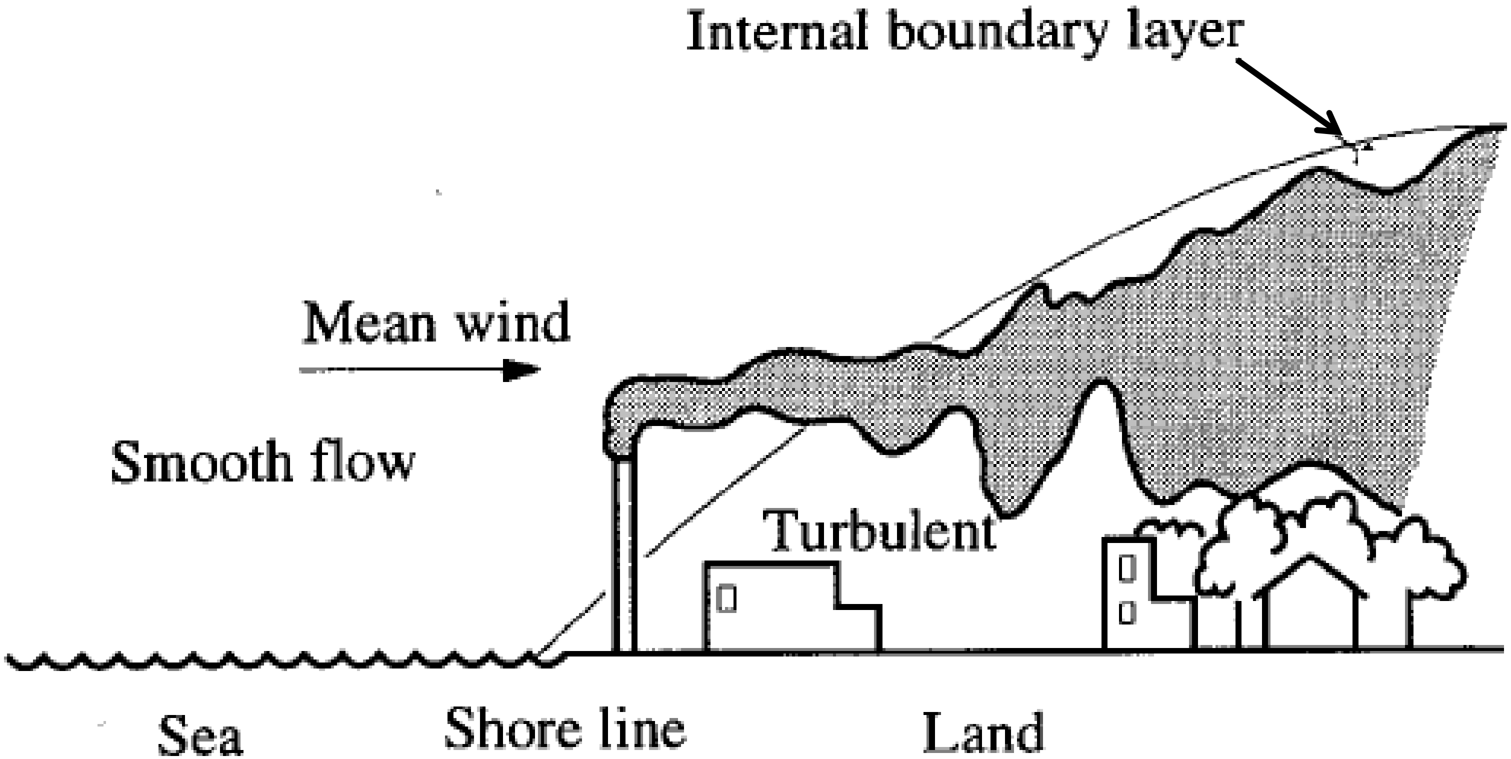
Smoke shape : Lower layer is stable and upper is unstable

Because lower layer is unstable, smoke circulate only in a lower layer. (Fumigation)

Cause of formation and characteristics of surface inversion layer

Name	Cause and characteristics
Geographical inversion of temperature	When air current moves over mountains, because of foehn phenomenon warm air stands over cold air. Basin and/or valley.
Front inversion of temperature.	Because of moving of front cold air exists under warm air. Air pollution becomes serious in case of a stationary front.
Subsidence inversion of temperature	In region of anticyclone, air subsidence causes temp. rise and deep inversion layer is formed during day and night. Photochemical smog appears.
Radiation inversion of temperature	On calm clear night, ground surface is cooled by radiation loss and then strong inversion layer is formed. Smoke from surface is trapped in this layer.
Advection inverse of temperature	This inversion is formed when warm air flows over cold surface. Fog is frequently associated with this type of inversion.

Internal boundary layer formed over land near the sea shore and smoke plume diffusing in the layer



Past Air Pollution in Japan

（Smog : Primary particle)

1966年（神奈川県環境農政部提供）

2001年（川崎市港湾局提供）

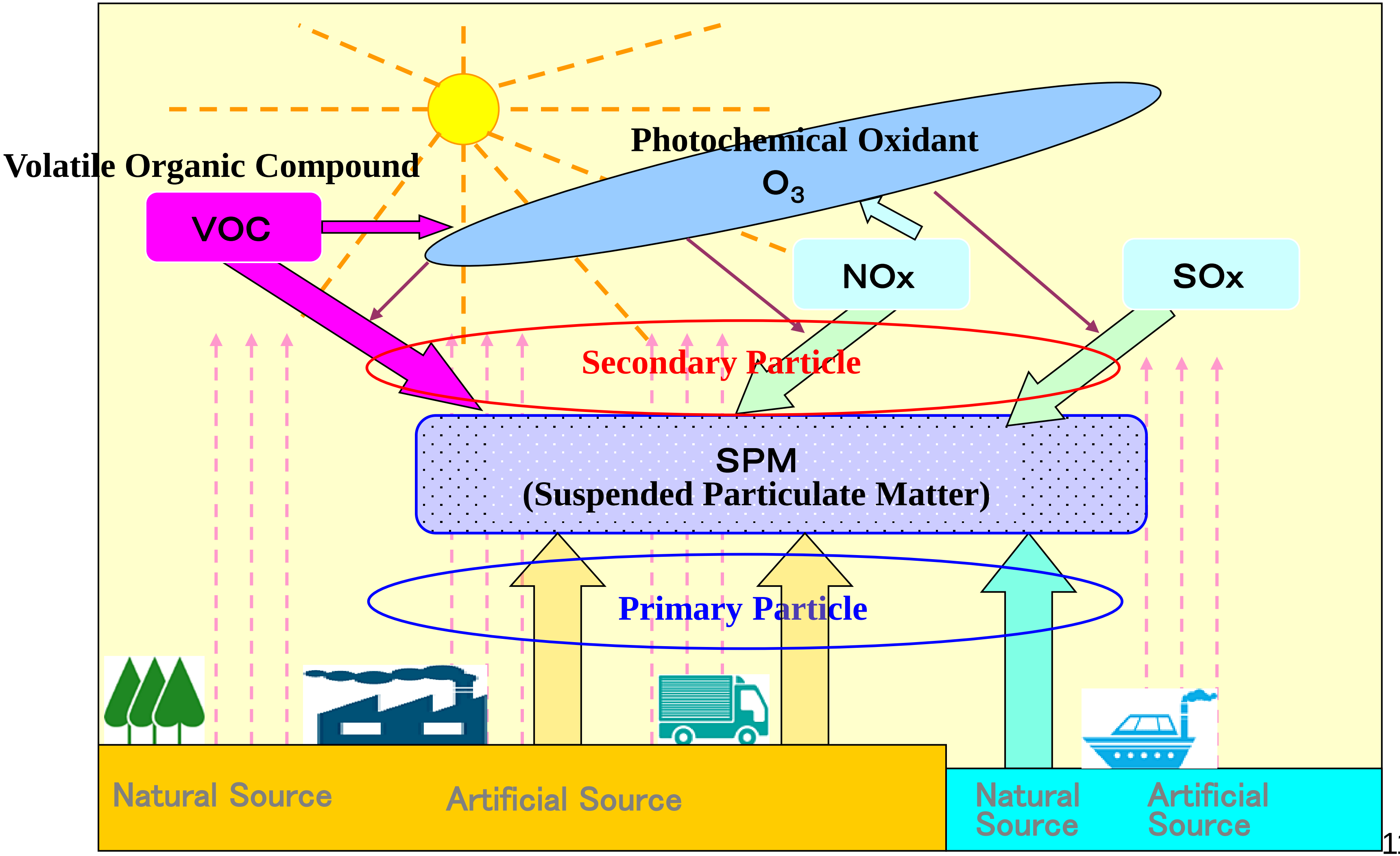
1966 2001

Air Pollution Caused by VOC
(Fume : Secondary Particle)

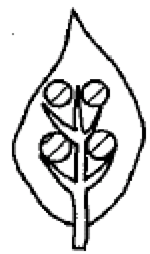
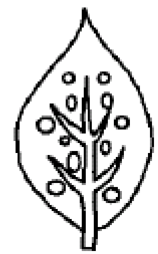
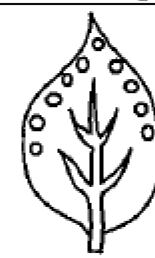
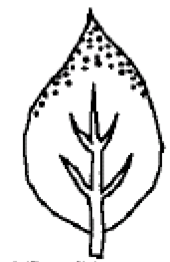
September 3, 2003

September 4, 2003

Reaction of VOC in the Atmosphere



Frequency of appearance of various smoke specks on leaves according to the kind of gas pollutant

	Smoke specks on the leaf periphery and apex.	Inter-vein smoke specks	Point like speck on the whole leaf	Point like specks on the leaf periphery and the apex.	Etiolation on the whole leaf	Etiolation on the leaf apex and at the periphery
						
SO_2	?	+++	+	?	++	+
H_2SO_4 mist	+	+	++	+	+	?
Cl_2	+++	++	+	++	+	++
HCl	++			++		+
HF	+++	?	?	?	+	++
O_3		++	+++	+	++	?
PAN		++				
NO_2	+	+++	++			

(Note) Damage frequency : +++ Very frequently ++ Frequently + Occasional ? Seldom

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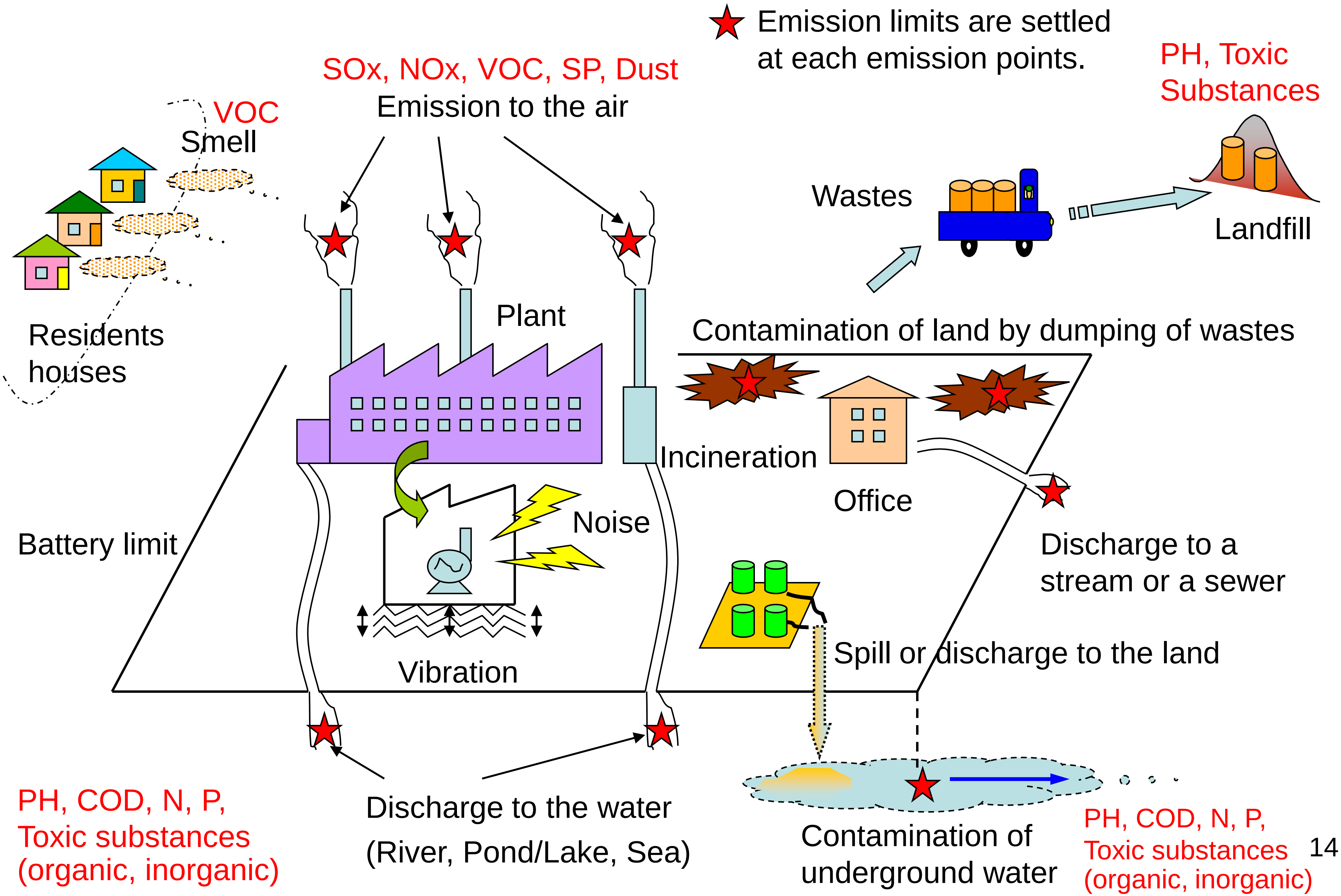
1. Basic theory of pollutant diffusion and their affection
2. Monitoring of pollutants and simulation of their diffusion
3. Characteristics of fuel and sources of pollutants
4. Emission coefficient of SOx and its removal
5. Emission coefficient of Nox and its reduction methods
6. Dust collection method (Electrostatic precipitator)
7. Hazardous gas treatment
8. Absorption methods
9. Adsorption methods

Environmental Aspects caused by Production Activities



Examples

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Characteristics of fuels

Fuel \ Factors	Sulfur content (%)	Specific gravity kg/m^3	Calorific power kcal/l	Exhaust gas Nm^3/l
A heavy oil	0.69	0.84	9390	11.4
B heavy oil	1.82	0.91	9540	12.1
C heavy oil	1.91	0.93	9690	12.2
Light oil	0.40	0.83	9130	11.5
Kerosene	0.004	0.79	8690	10.9
LNG*	0.001	0.71	10498	16.2
Coal**	0.817	1.53	6149	9.1
Firewood**	0.092	0.80	3832	11.4

* /Nm^3

** /kg

(JEA[2], MITI[3])

Examples of Facilities accompanying Fume, Smoke and Dust Emission

Facility	Kinds of emission
Boiler	Cinders, fly ash, fume and smoke
Cement kiln	Clinker dust, dust
Ore calcinating furnace	Metal oxides, fly ash, mineral powder, fume, dust
Blast furnace	Mineral powder, coke powder, slag dust, dust
Ferroalloy furnace	SiO_2 dust, dust
Steel manufacturing open-hearth furnace	Ferrous oxide, dust
Ceramic furnace	Fly ash, dust
Steel converter	Dust
Cement kiln	Dust
Cupola	Dust
Coke oven	Powder, dust
Metal silicon furnace	SiO_2 dust
Carbon black furnace	Dust
Wastes incinerators	Dust, fly ash
Coal carbonization furnace	Tar mist
Sulfuric acid plant	Sulfuric acid mist
Zinc plating	Zinc oxide, ammonium fume
Mineral pulverization, screening, powder disposal transportation equipment	Dust, powder dust
Street paving material disposal furnace	Dust, SiO_2 dust, tar mist

Major Artificial Sources of Pollutants

Substance	Emission source facilities, etc.
SOx	Various types of boilers, chemical plants, diesel cars, vessels, coal heating, etc.
NOx	Various types of combustion facilities, chemical plants, furnaces, automobiles, vessels, aircrafts,home heating, etc.
Suspended particulate (SP) Total suspended particulate (TSP)	Various types of boilers, furnaces, various manufacturing devices accompanying dust generation, automobiles, vessels, aircrafts, civil engineering, stock yard of coal
Hydrocarbons (HC) **VOC**	Petrochemical plant, oil-storage tank, painting and coating, automobiles, vessels, aircrafts, etc.
HCl, Cl_2	Garbage incinerators, HCl manufacturing
HF	Manufacturing facilities of aluminum, glass, phosphate fertilizer, phosphoric acid, fluoric resins, etc.
CO	Automobiles
Offensive odor	Live-stock rasing, food processing, paper and pulpmill, fertilizers, refuse disposal, leather manufacturing, chemical industry

Specific Substances and Related Industries (1/2)

Name of substance	Chemical formula	Related industries
Hydrogen fluoride	HF	Fertilizer industry, ceramic industry, aluminum industry
Hydrogen sulfide	H_2S	Petroleum refinery, gas industry, ammonia industry, pulp mill
Selenium dioxide	SeO_2	Metal refinery, chemical industry
Hydrogen chloride	HCl	Soda industry, plastic process
Nitrogen dioxide	NO_2	Nitric acid manufacture, various industries accompanying combustion
Sulfur dioxide	SO_2	Sulfuric acid production, industries using heavy oil as fuel, metal industry, pulp mill
Chlorine	Cl_2	Soda industry, other chemical industries
Silicon fluoride	SiF_4, Si_2F_6	Fertilizer industry
Phosgene	$COCl_2$	Dyeing industry, organic synthesis
Carbon disulfide	CS_2	Carbon disulfide manufacture, solvent, plant fumigation
Hydrogen cyanide	HCN	Hydrocyanic acid manufacture, iron manufacture, gas industry, chemical industry, electroplating
Ammonia	NH_3	Fertilizer, plating, organic, inorganic drugs, blue print
Phosphorus trichloride	PCl_3	Drug manufacture, phosphorus dichloride
Phosphorus pentachloride	PCl_5	Phosphorus trichloride, phosphorus oxide
Yellow phosphorus	P_4	Phosphorus refinery, phosphorus compound manufacture

Specific Substances and Related Industries (2/2)

Name of substance	Chemical formula	Related industries
Chlorosulfonic acid	HSO_3Cl	Drug manufacture, dyestuffs manufacture
Formaldehyde	HCHO	Formalin manufacture, leather, synthetic resin
Acrolein	$CH_2=CHCHO$	Acrylic acid manufacture, synthetic resin, varnish manufacture
Hydrogen phosphide	PH_3	Phosphoric acid manufacture, phosphoric acid fertilize r manufacture
Benzene	C_6H_6	Petroleum refinery, formalin manufacture, painting industry, organic solvent
Methanol	CH_3OH	Methanol manufacture, formalin manufacture, painting industry, resin industry
Nickel carbonyl	$Ni(CO)_4$	Petrochemistry, nickel refinery
Sulfuric acid (contains SO_3)	H_2SO_4	Sulfuric acid manufacture, fertilizer industry, inorganic chemistry
Bromine	Br_2	Dyes, medicine, agricultural chemicals
Carbon monoxide	CO	Gas industry, metal refinery, internal combustion
Phenol	C_6H_5OH	Tar industry, chemical drug, painting industry, resin industry
Pyridine	C_5H_5N	Pharmaceutical, chemical industry, etc.
Mercaptan	C_mH_nSH	Petroleum, petrochemistry, pharmaceutical, feed manufacture

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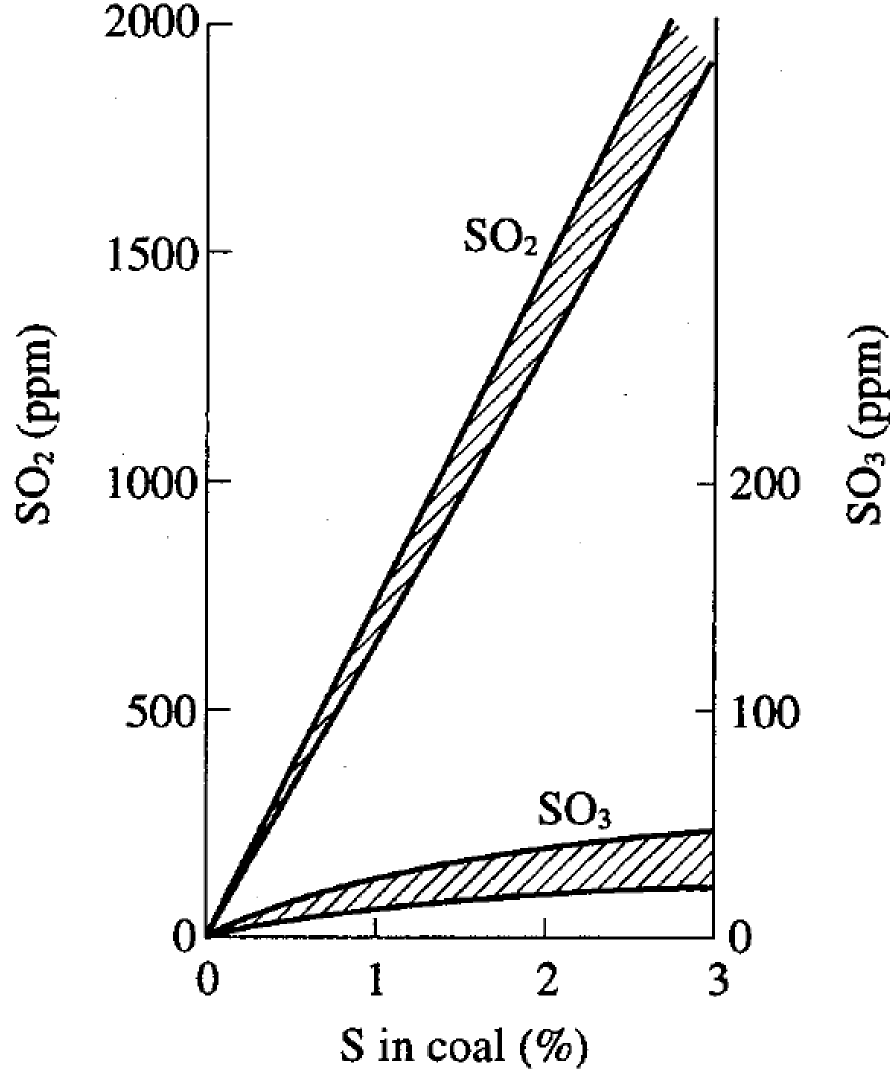
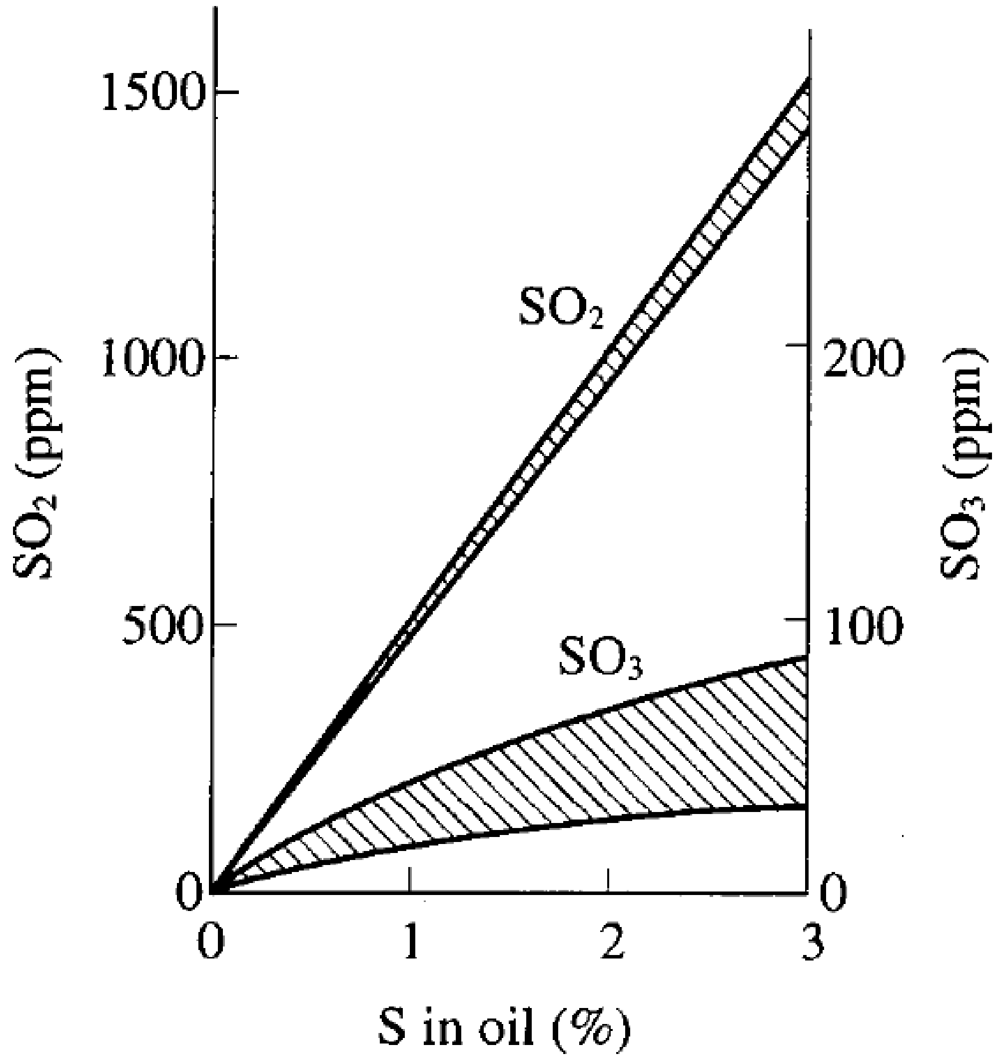
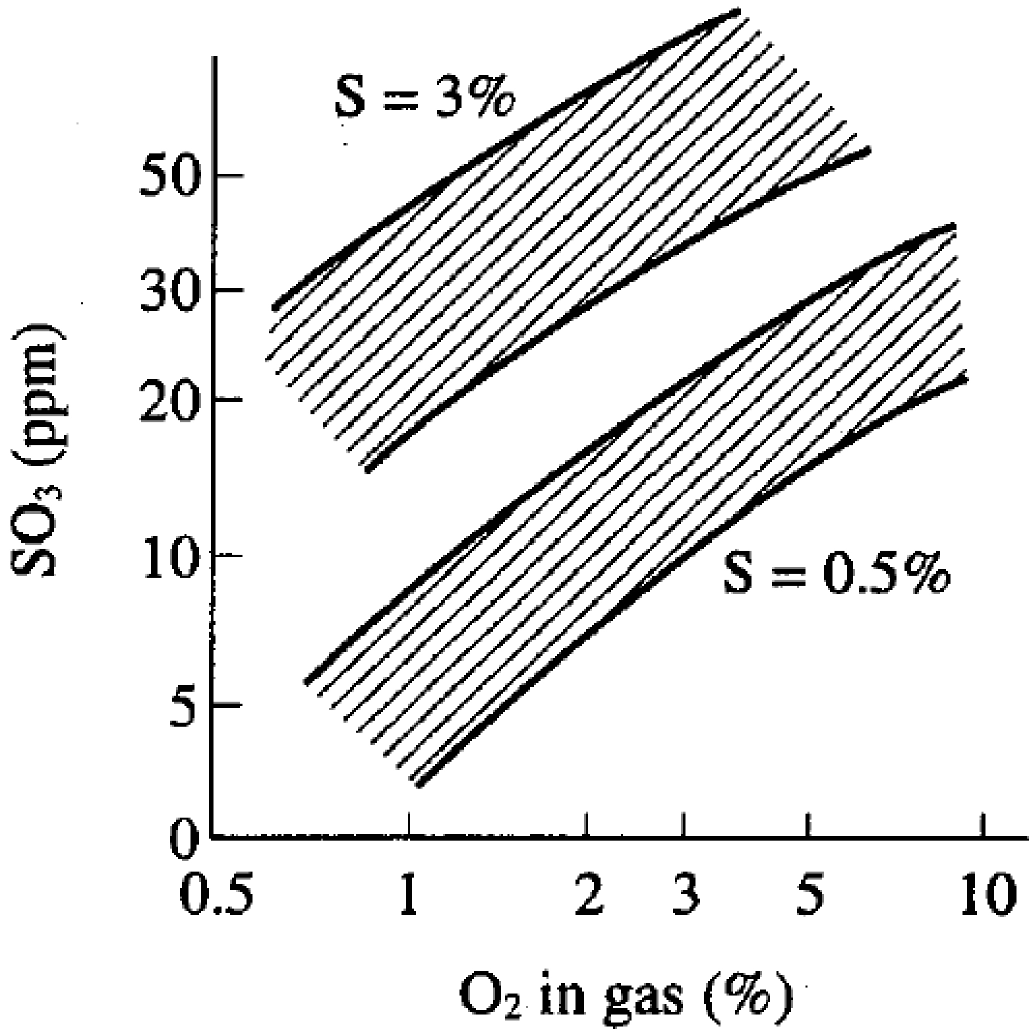
Sulfur content in coal and SOx in combustion gas



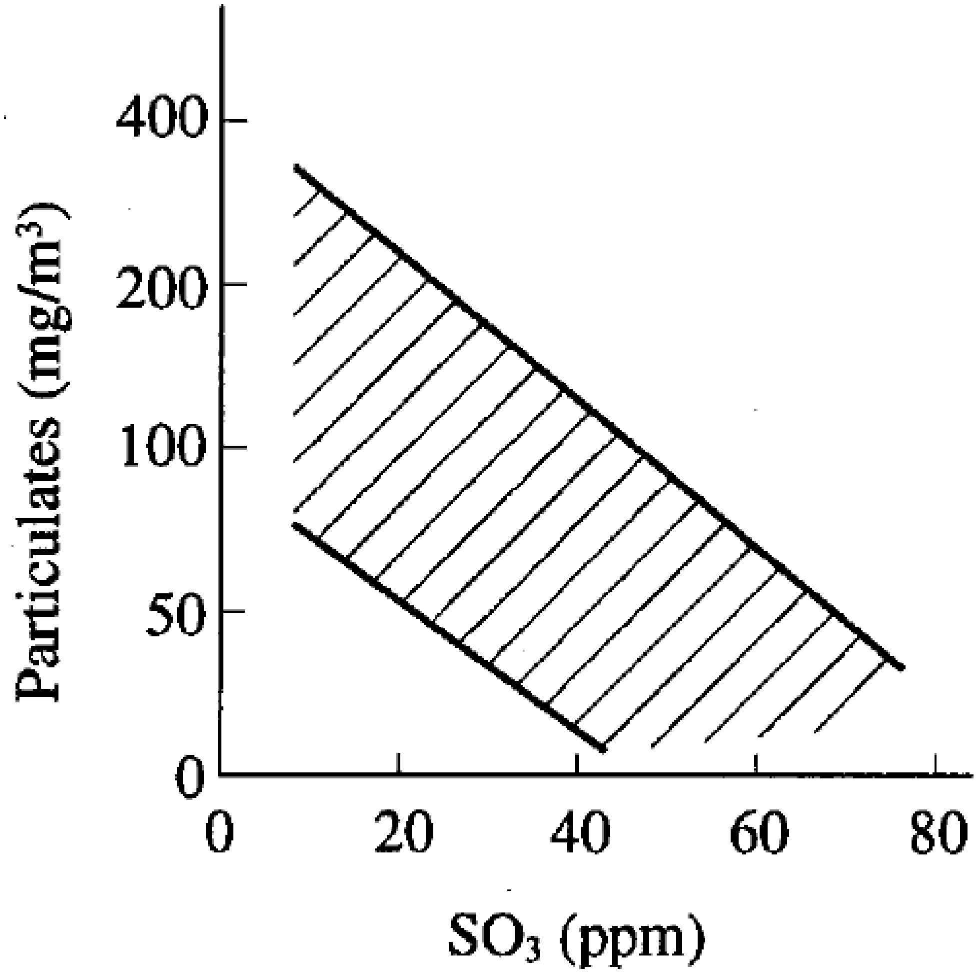
Sulfur content in heavy oil and SOx in combustion gas



Oxygen and SO_3 in heavy oil combustion gas

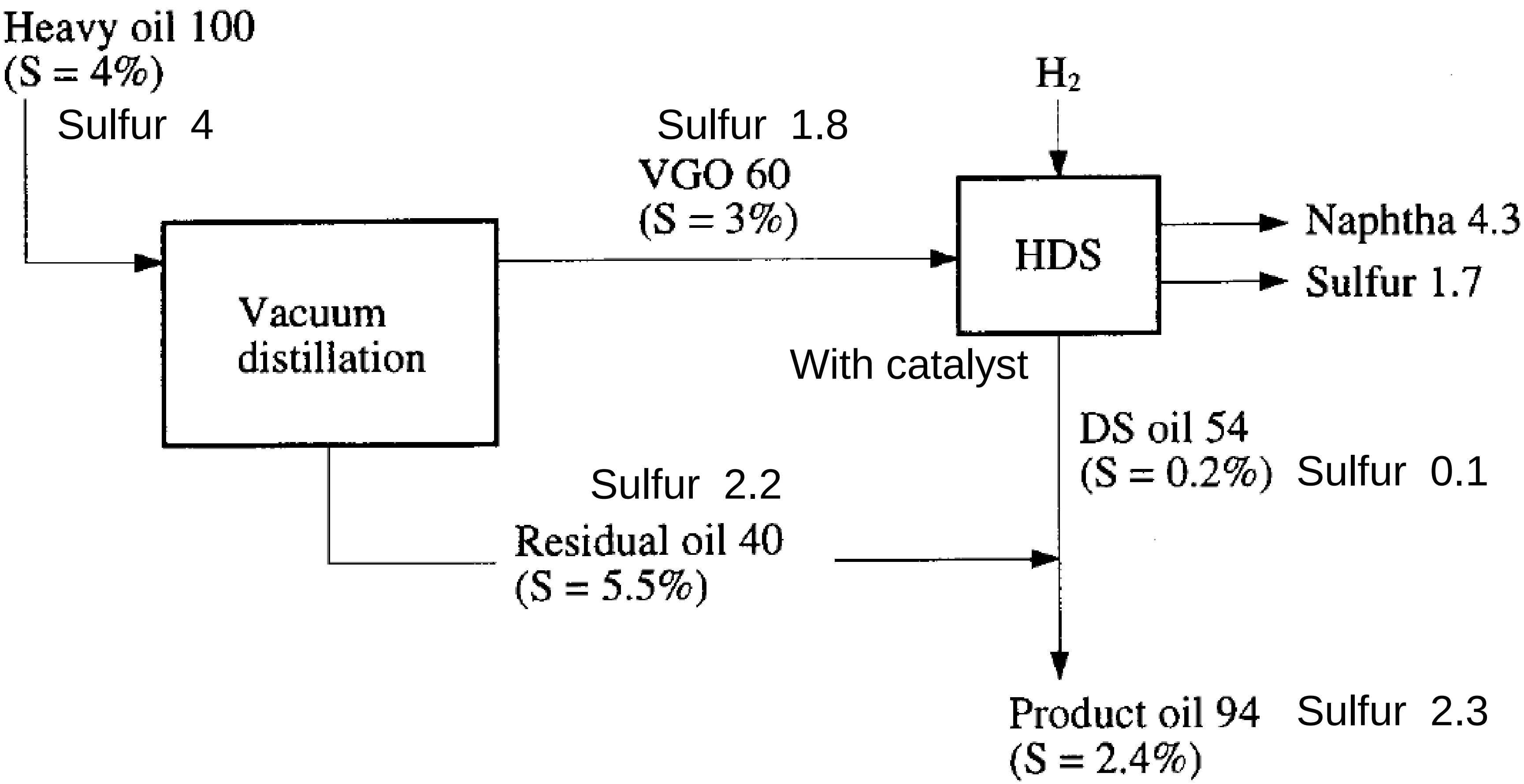


Particulates and SO3 in combustion gas of heavy oil (S=2-3%)

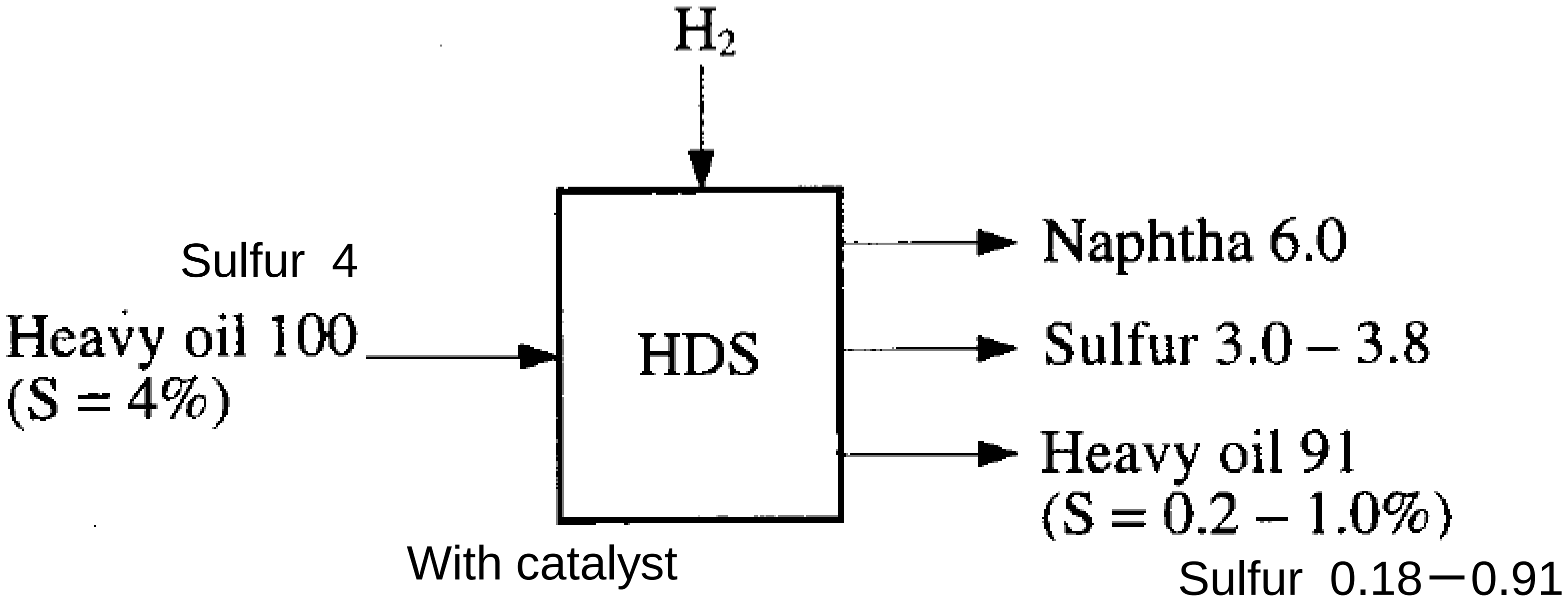


Sulfur removal from fuels

(a) Vacuum gas oil (VGO) hydrodesulfurization (HDS) process



(b) Direct HDS process

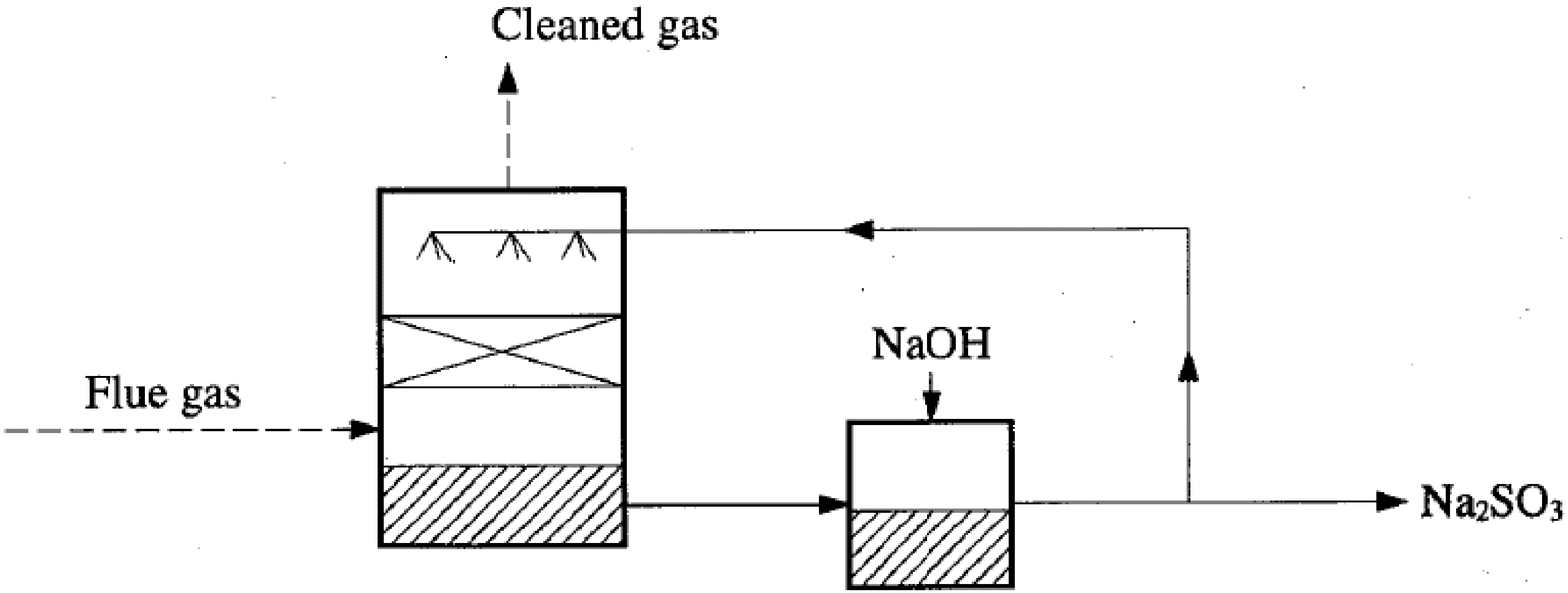


Desulfurization Process

Sodium sulfite recovery process

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$$
$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$
$$Na_2SO_3 + 1/2O_2 = \boxed{Na_2SO_4}$$

Product



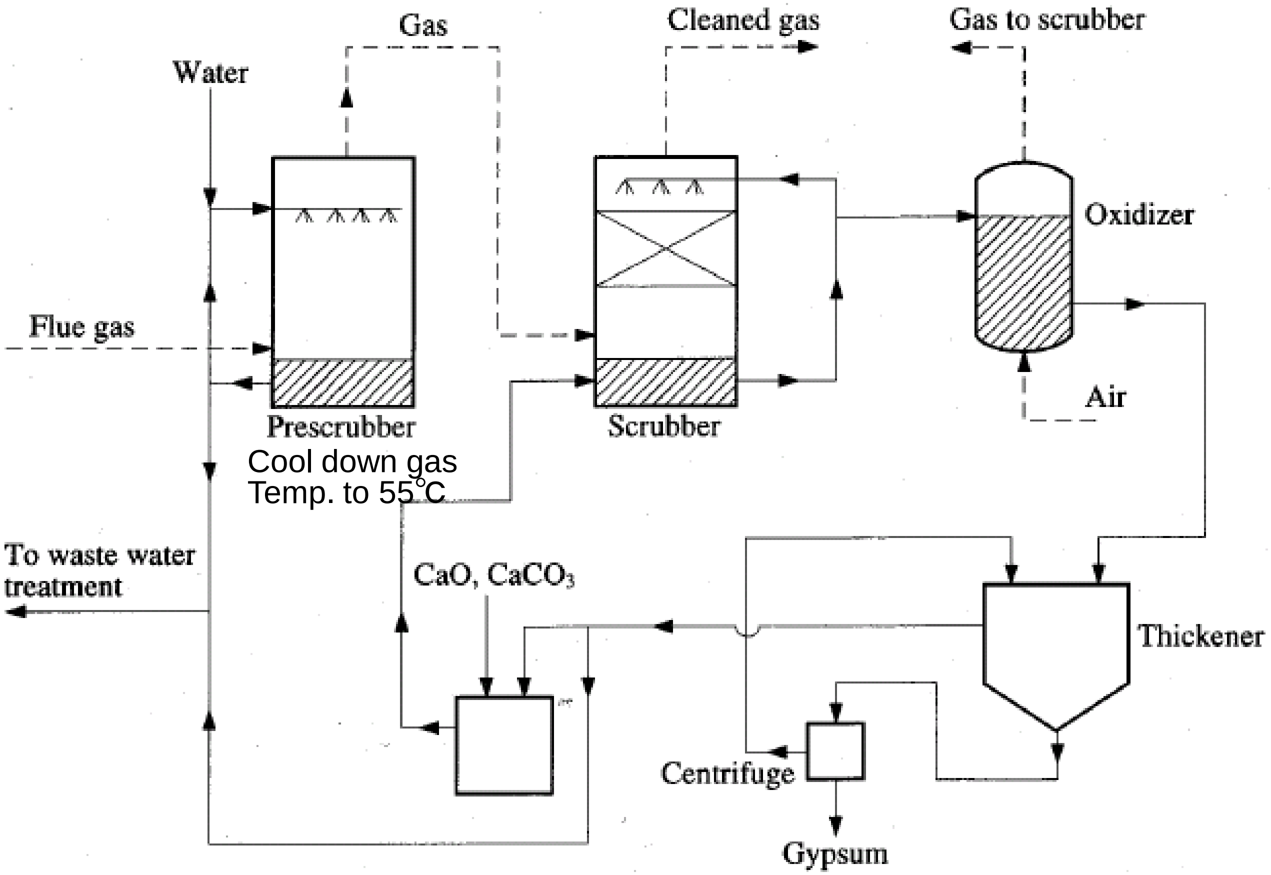
Scrubbing

Desulfurization Process

Flowsheet of lime/limestone-gypsum process (with prescrubber for high purity gypsum production)

$$CaO + SO_2 = CaSO_3$$
$$CaCO_3 + SO_2 = CaSO_3 + CO_2$$
$$CaSO_3 + 1/2O_2 + 2H_2O = \boxed{CaSO_4\ 2H_2O}$$

Product

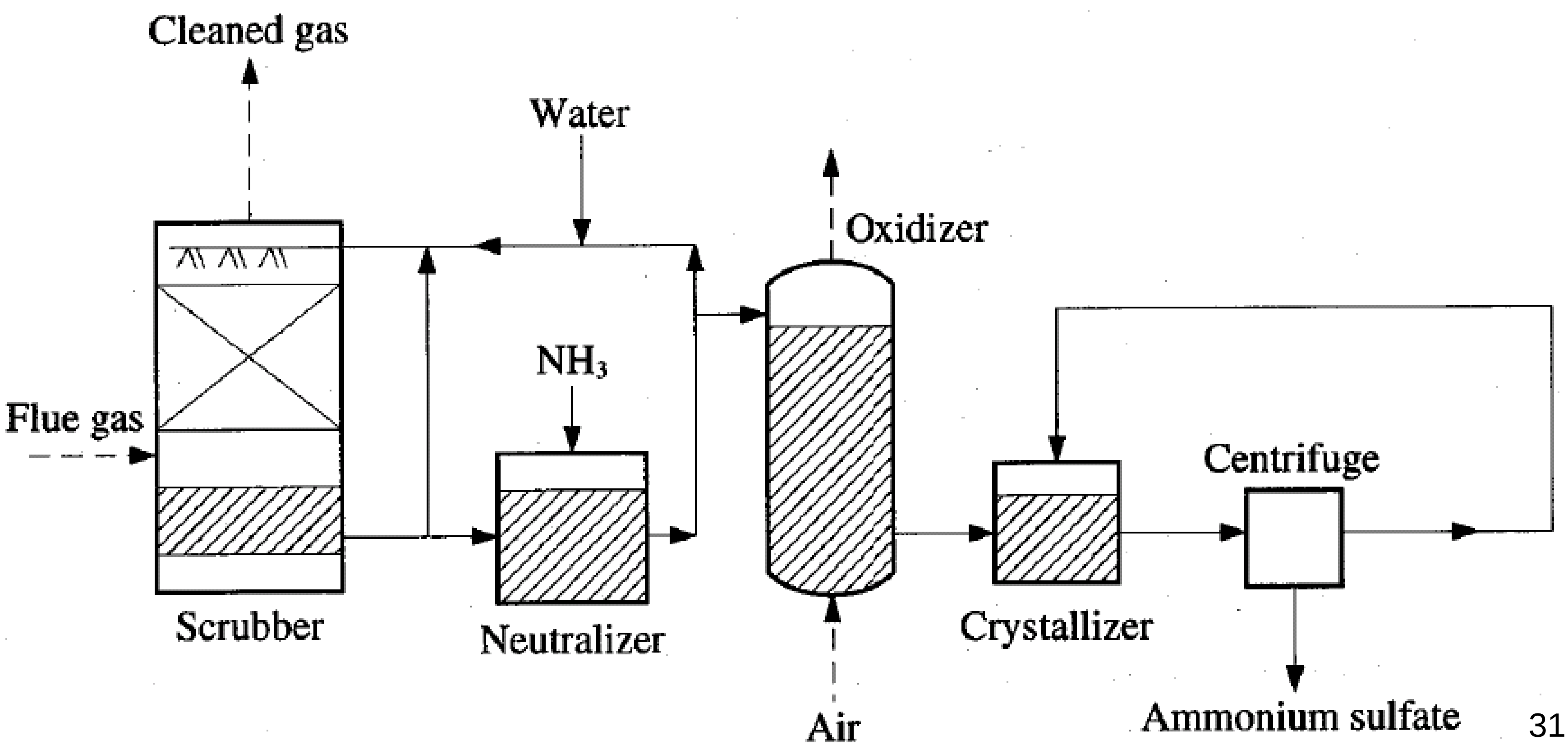


Desulfurization Process

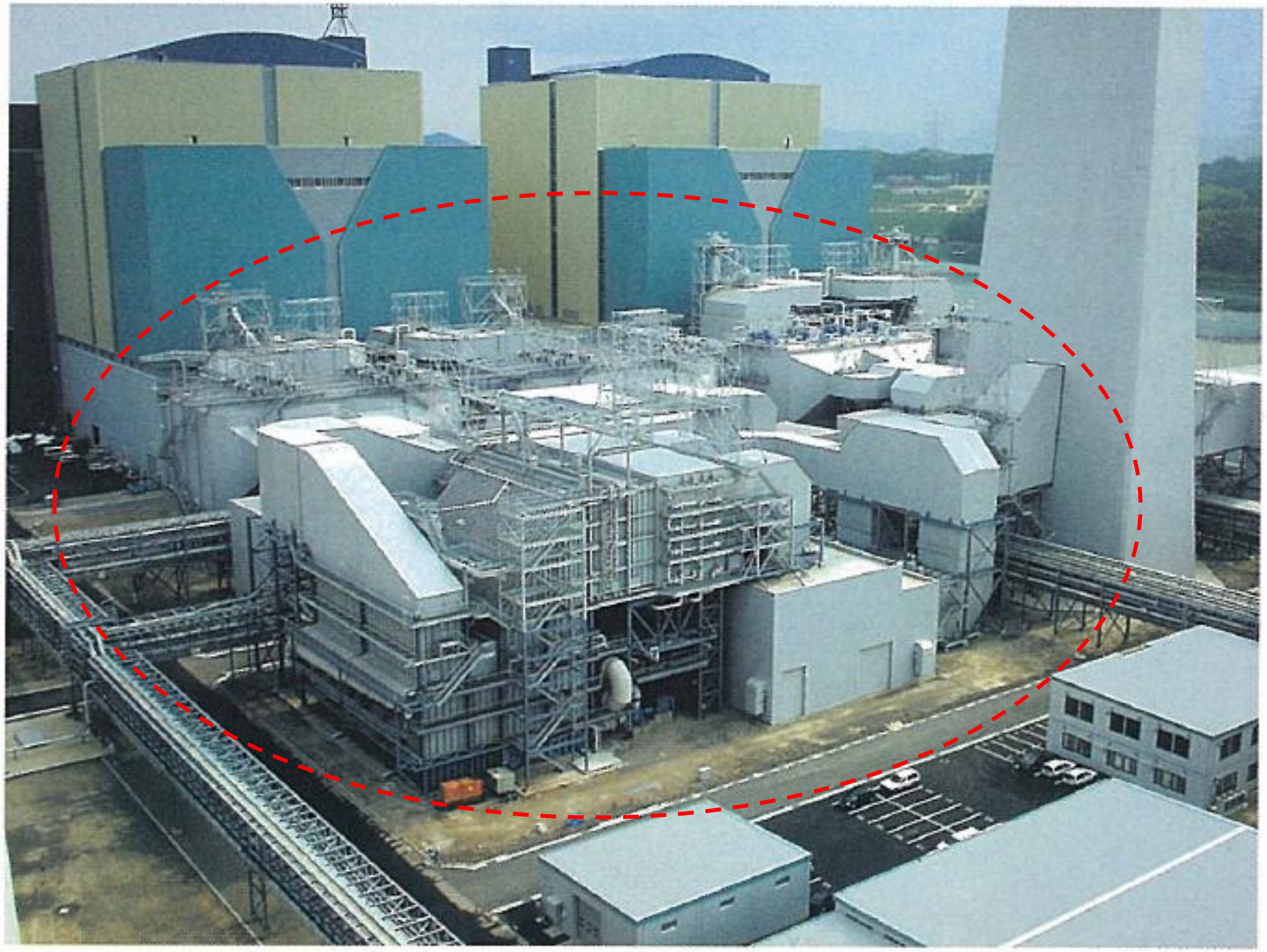
Ammonia scrubbing for ammonium sulfate production

$$(NH_4)_2SO_3 + SO_2 + H_2O = 2NH_4HSO_3$$
$$NH_4HSO_3 + NH_3 = \boxed{(NH_4)_2SO_3}$$

Product



Desulfurization Equipment



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Emission coefficient of NOx from kinds of fuels

Town gas	0.5 - 1.6 $kg/10^3\ m^3$
LPG	1.3 - 2.0 kg/ton
Kerosene	1.3 - 2.0 kg/k*l*
Heavy oil	2.5 - 4.0 kg/k*l*

Emission coefficient of NOx from facilities

Unit: NO_2 converted kg/10^8kcal

Facilities \ Fuel	C heavy oil	B heavy oil	A heavy oil	Kerosene	Light oil	LNG	Coal
Power generation boiler	58.29	57.89	32.21	26.71	13.91	23.31	75.43
Industrial boiler	40.96	41.72	23.21	19.25	10.02	16.38	53.01
Diesel power generation	752.9	711.1	398.9	318.2	410.2	-	-
Gas turbine	160.5	151.6	85.0	67.8	87.4	75.3	-
Gas generating furnace	50.32	47.53	26.66	21.26	27.41	23.61	64.33
Iron ore pellet incinerator	46.28	43.71	24.52	19.56	25.21	21.72	-
Coke oven	273.0	257.8	144.6	115.4	148.7	128.1	349.0
Air-heating stove for blast furnace	77.36	79.82	43.83	35.87	46.30	30.74	-
Petroleum heating furnace (iso)	42.86	44.22	24.28	19.87	25.65	17.14	-
Brick burning furnace (series)	213.5	201.7	113.1	90.24	116.3	100.2	273.0
Cement firing furnace (dry system)	119.6	112.9	63.35	50.53	65.15	56.11	-
Ceramics firing furnace (series)	95.12	89.84	50.39	40.20	51.82	44.63	121.6
Glass melting furnace (series)	256.5	242.3	135.9	108.4	139.8	120.4	327.9

(JEA[(2)], MITI[(3)])

SOx and NOx emission coefficient from cars

Kinds of cars*	SOx emission coefficient g/No. of car·km	NOx emission coefficient g/No. of car·km
Passenger car	0.032	1.255
Light passenger car	0.021	0.267
General truck	1.214	5.454
Small truck	0.042	2.427
Light truck	0.034	0.524
Bus	0.502	6.158

* Average of Japanese cars. (JEA[2])

Engine load ratio by ship operating mode (JEA[2])

Unit: %

Engine Mode	Diesel	Turbine
Full	85	100
Standby full	52	65
Half	10.6	20.5
Slow	5.3	15
Dead slow	3.6	13

Empirical formula of exhaust coefficient for ships (JEA[2])

Diesel engine using heavy oil A

Quantity y	Power x	Formula
1 NOx (Nm^3/h)	x (ps/h)	$y = 1835x^{1.125} \times 10^{-3}$
2 Fuel consumption (kg/h)	x (ps/h)	$y = 0.15x + 25.24$
3 Exhaust (Nm^3/h)	x (ps/h)	$y = 5.05x + 490.96$

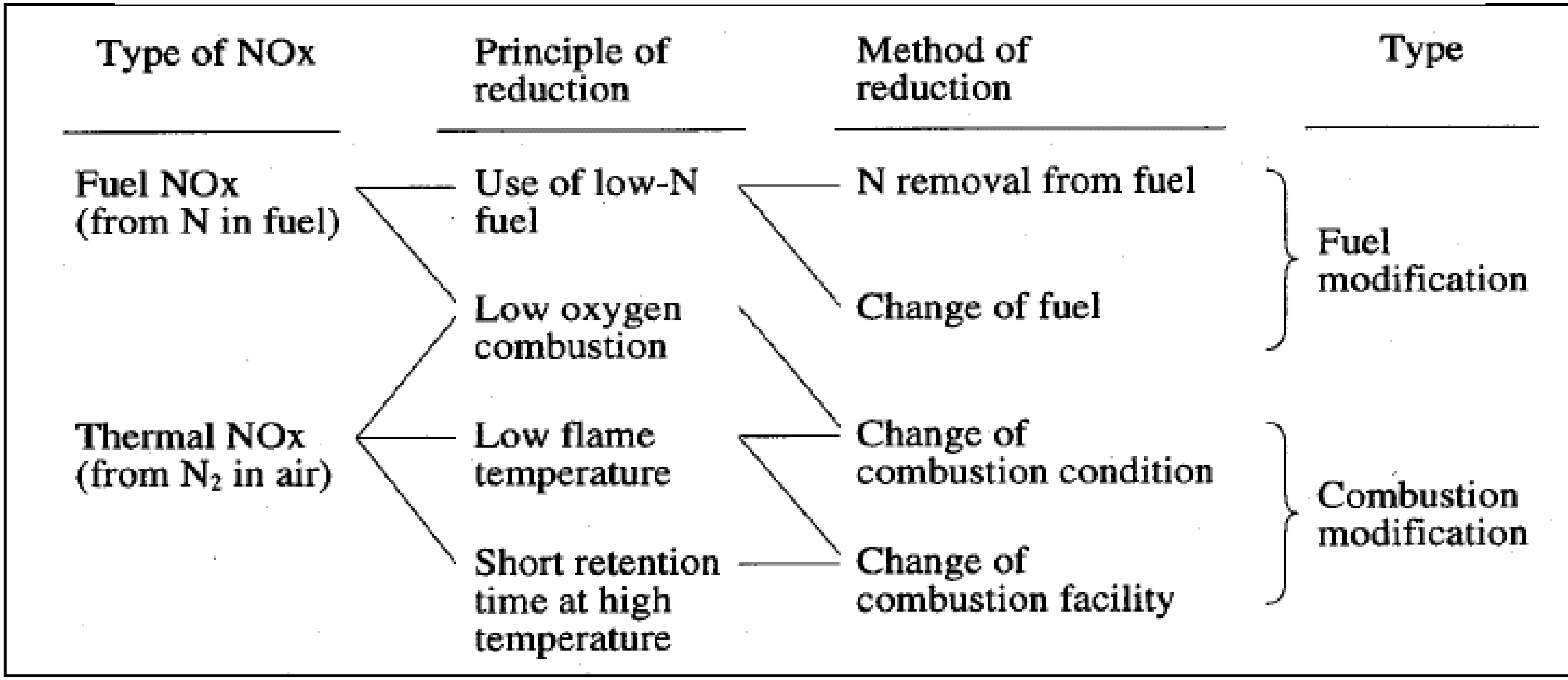
Emission amount of NOx from an airplane engine

Unit:Nm^3/s

Airplane type / Mode	DC-8	B-747	B-737	NAMC-YS-11
Idle	0.211	0.827	0.061 to 0.085	0.028 to 0.034
Approach	2.441	6.506	0.630 to 0.805	0.200 to 0.201
Climb	9.403	52.589	–	–
Take off	14.382	94.063	3.100 to 3.5	0.552

Note: The number in the table is amount from an engine, so that total amount of NOx from an airplane is obtained by multiplying numbers of engine.

Principles and methods of NOx reduction



NOx Concentration in Combustion Gas (ppm)

	Gas N = 0%	Oil N = 0.1 - 0.5%	Coal N = 1 - 3%
Without CM	200 - 300	300 - 500	500 - 1000
With CM	50 - 100	80 - 200	200 - 400

(CM : combustion modification)

The great majority of NOx comes from combustion of fossil fuels, and almost all of it is in the form of NO at the time of occurrence. Some part of NOx generated by combustion is called fuel NOx results from the reaction of nitrogen in the air at a high temperature, and is therefore called thermal NOx.

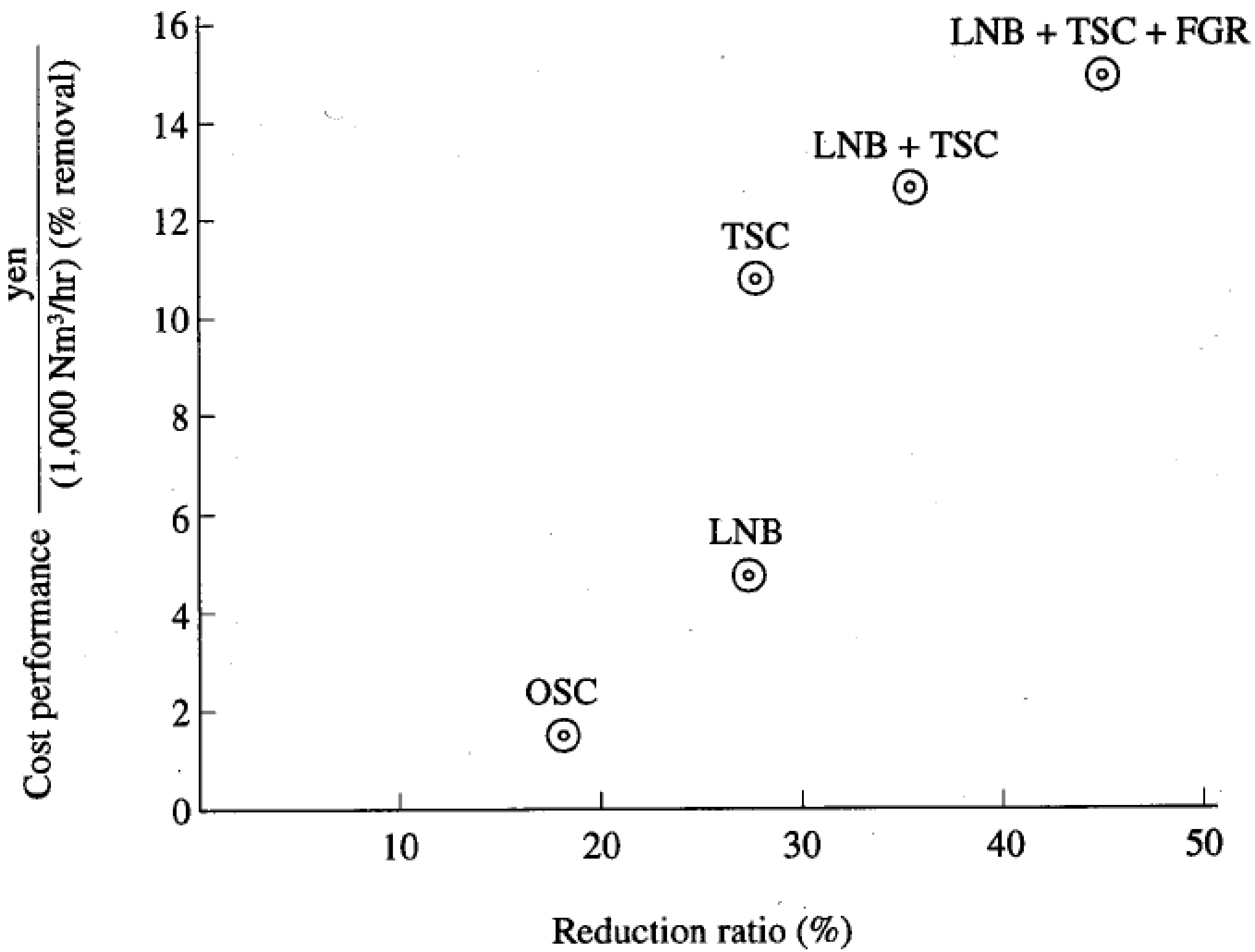
Investment cost for combustion modification

Control technique	Cost (yen/Nm^3/hr)
LNB + TSC + FGR	657
LNB + FGR	491
TSC + FGR	475
LNB + TSC	480
TSC	292
LNB	129
OSC	26
Mean	467

* Including change of burner tip.

LNB : low NOx burner
TSC : two-stage combustion
FGR : flue gas recirculation
OSC : off-stoichiometric combustion

Cost performance of NOx control techniques applied to boilers



NOx reduction method

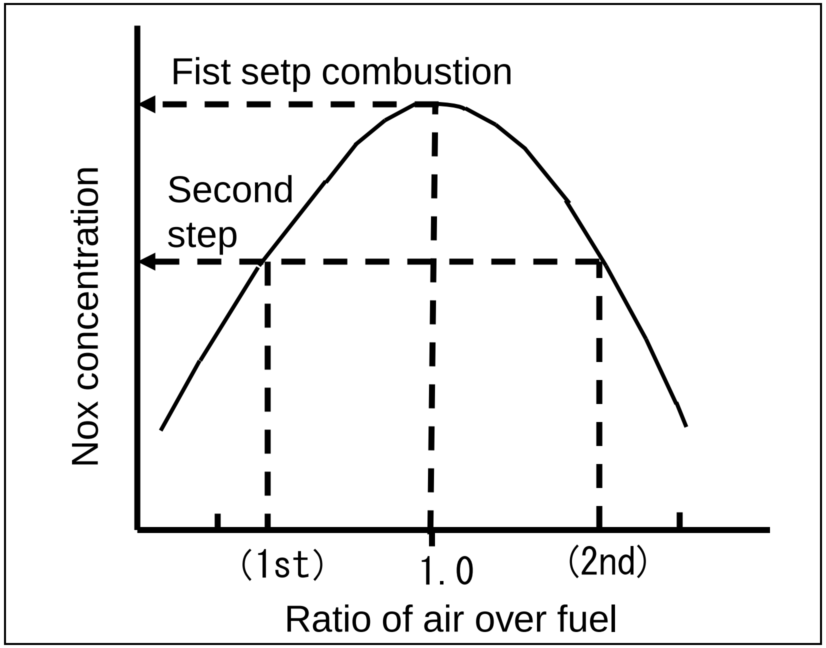
Removal of NOx

Basics of NOx reduction

- Change low N containing fuel
  (Heavy oil→ligh oil、LNG)
- Low O_2 combustion
- Low temperature combustion
  (→control ratio of air and fuel)
- to shorten combustion time at high temperature

Denitrization－Ammonia catalytic denitrization method

- Temp. 300～400℃ (decompose to N_2&H_2O)
  $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
  $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$
- Composition of catalyst：vanadium , Tungsten, Molybdenum oxide,Titanium oxide
- Shape of catalyst: sand, Honeycomb , plate
- Shape of catalyst：high effeciency, no byproduct, easy operation, no waste water

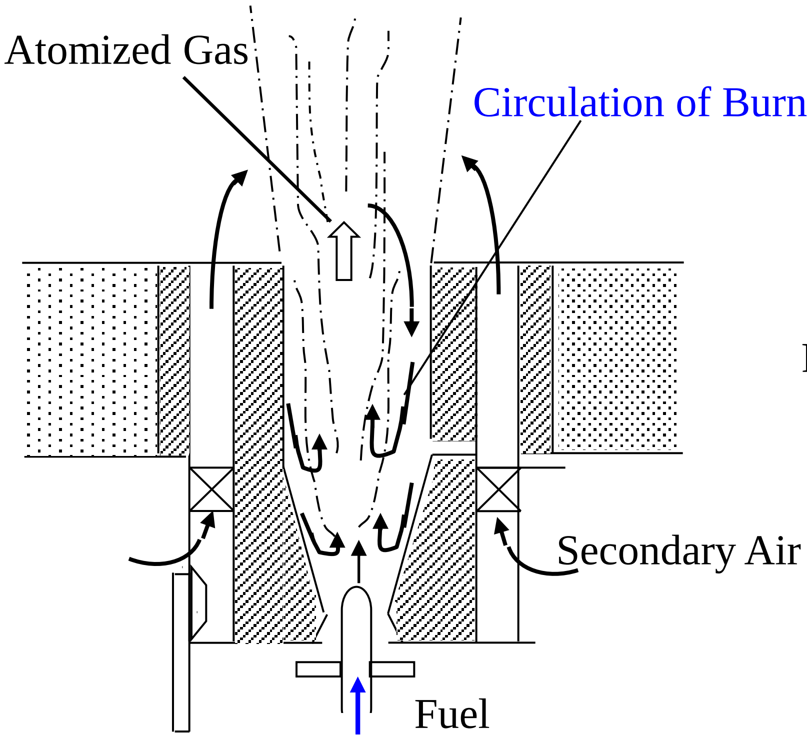


Relationship between ratio of air over fuel and conc. of NOx

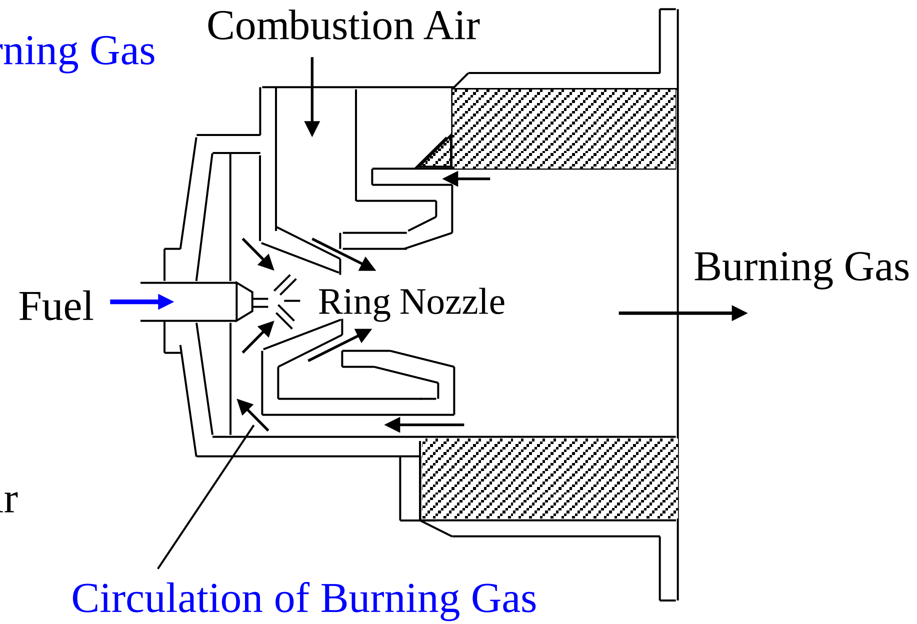
<Theory of second step combustion>

- Ratio of air over fuel < 1 → lack of O_2
  → to reduce Nox generation
- Ratio of air over fuel > 1 → Supply of much excess of air → to reduce Nox generation

Examples of Self-Recycling Low NOx Burner



(A)



(B)

Denitrization of selective contacted reduction

$$4\ NO + 4\ NH_3 + O2 \xrightarrow{\textbf{Catalyst}} 4\ N_2 + 6\ H_2O$$

$$6\ NO_2 + 8\ NH_3 \longrightarrow 7\ N_2 + 12\ H_2O$$

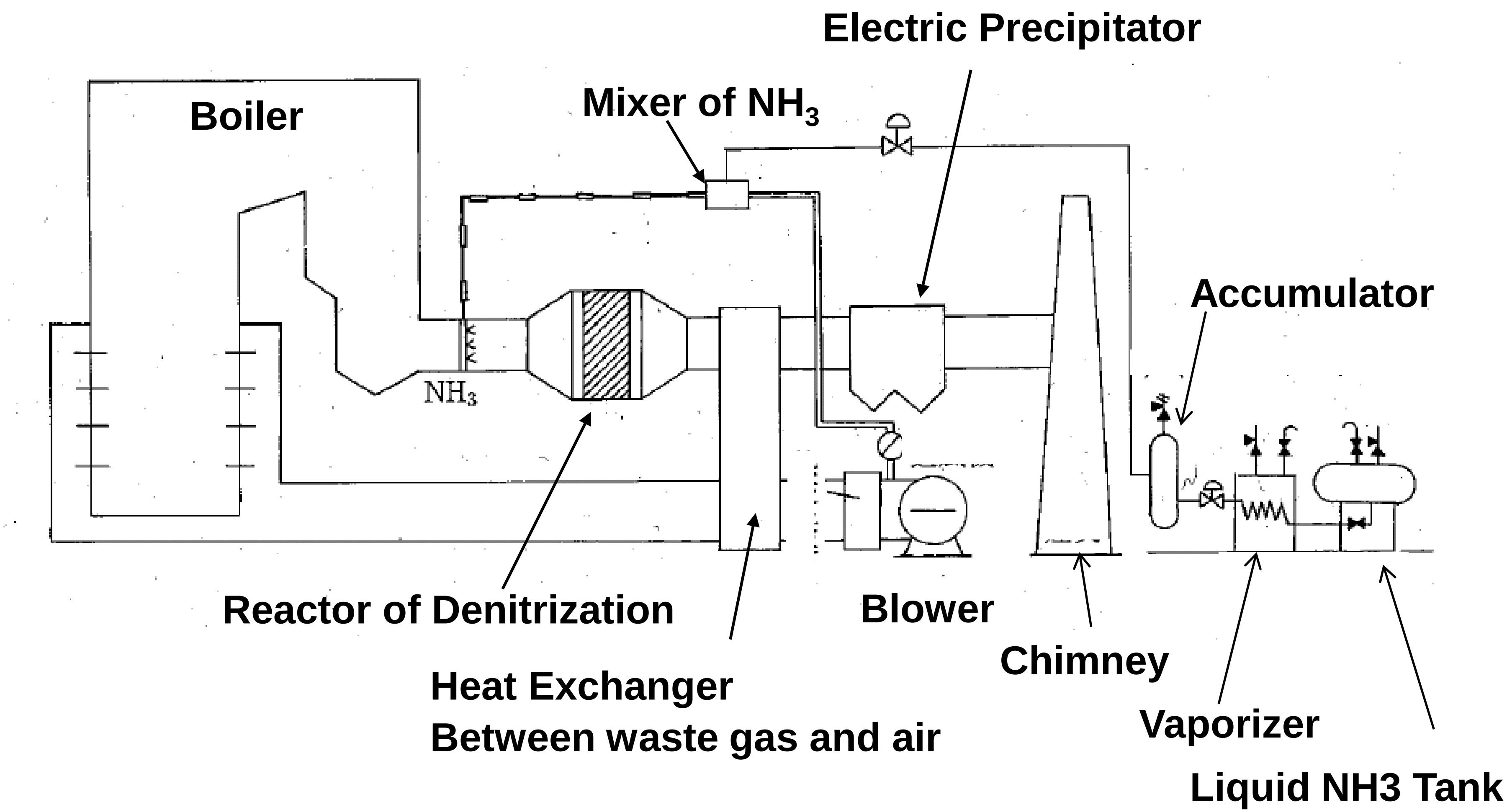
$$NO + NO_2 + 2\ NH_3 \longrightarrow 2\ N_2 + 3\ H_2O$$

Temperature: **300 ℃ ～ 400 ℃**

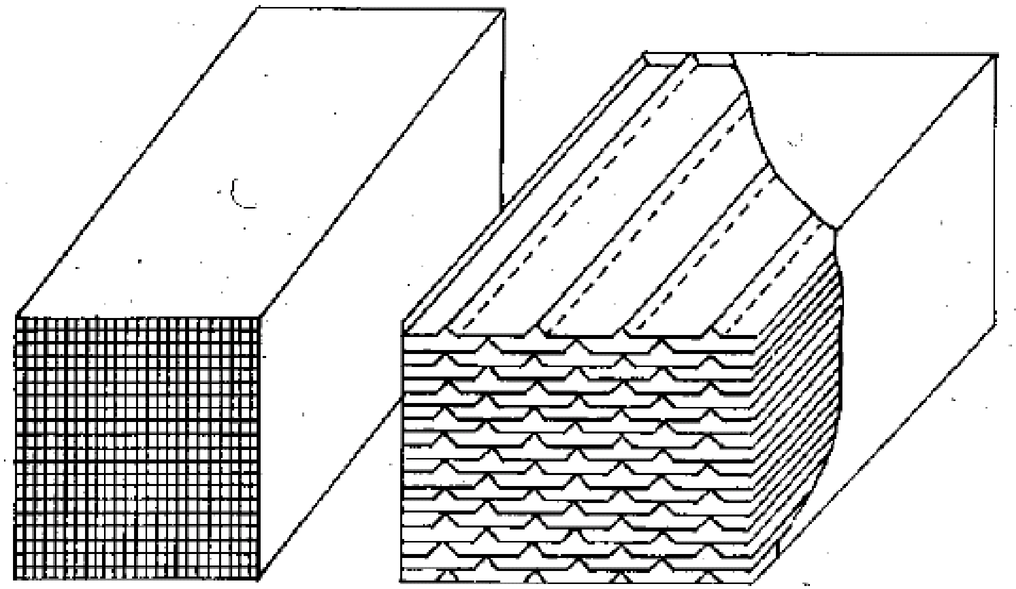
Catalyst : vanadium , Tungsten, Molybdenum oxide,

Titanium oxide

Typical flow of Denitrization of waste gas from a boiler

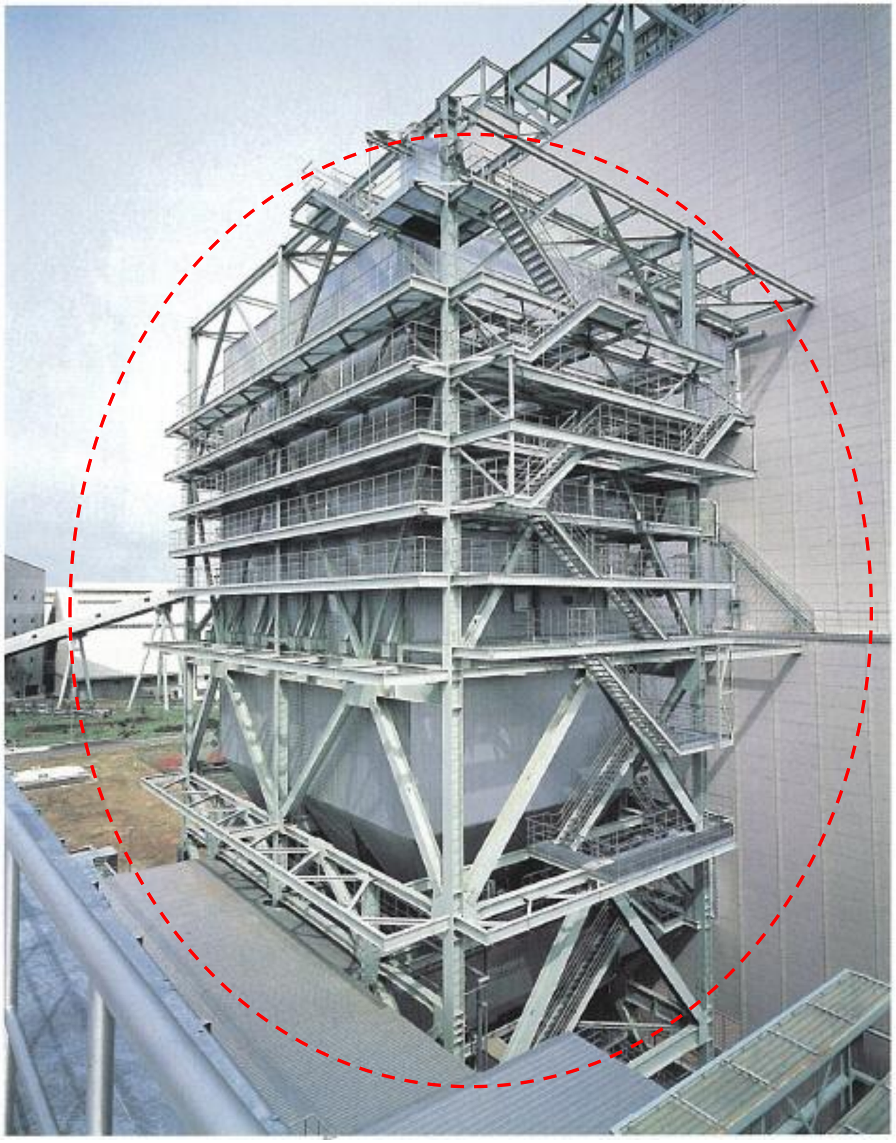


Typical structures of Denitrization Catalysts



Honey-comb Type **Plate Type**

Denitrization Equipment



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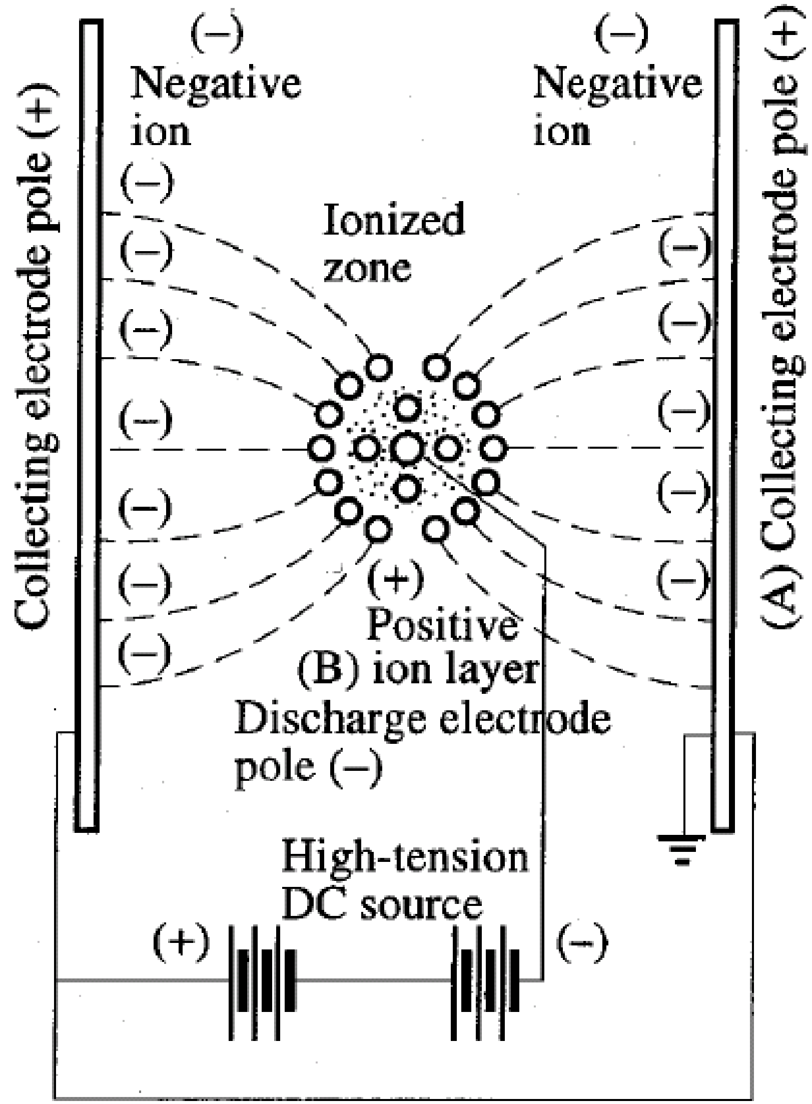
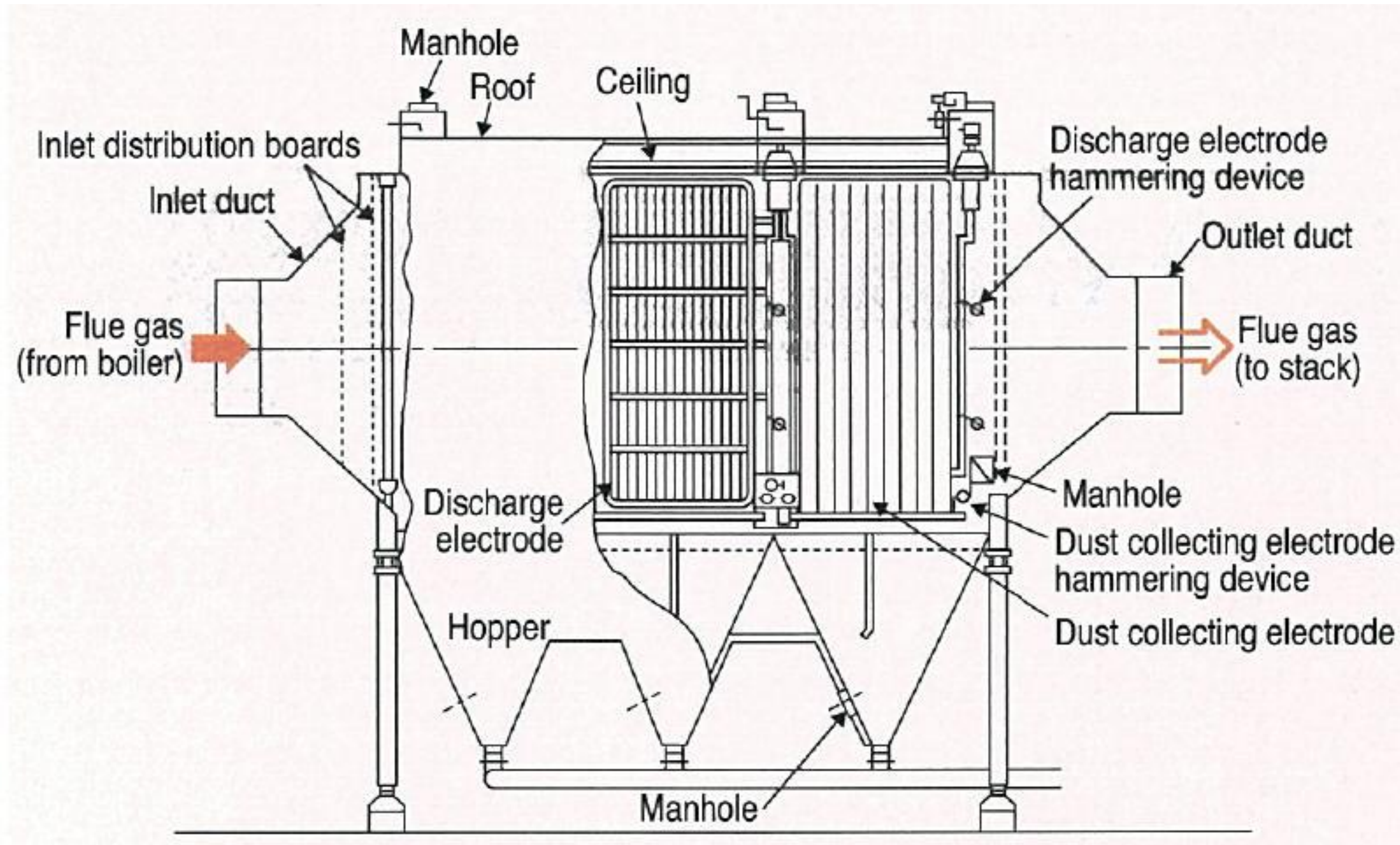
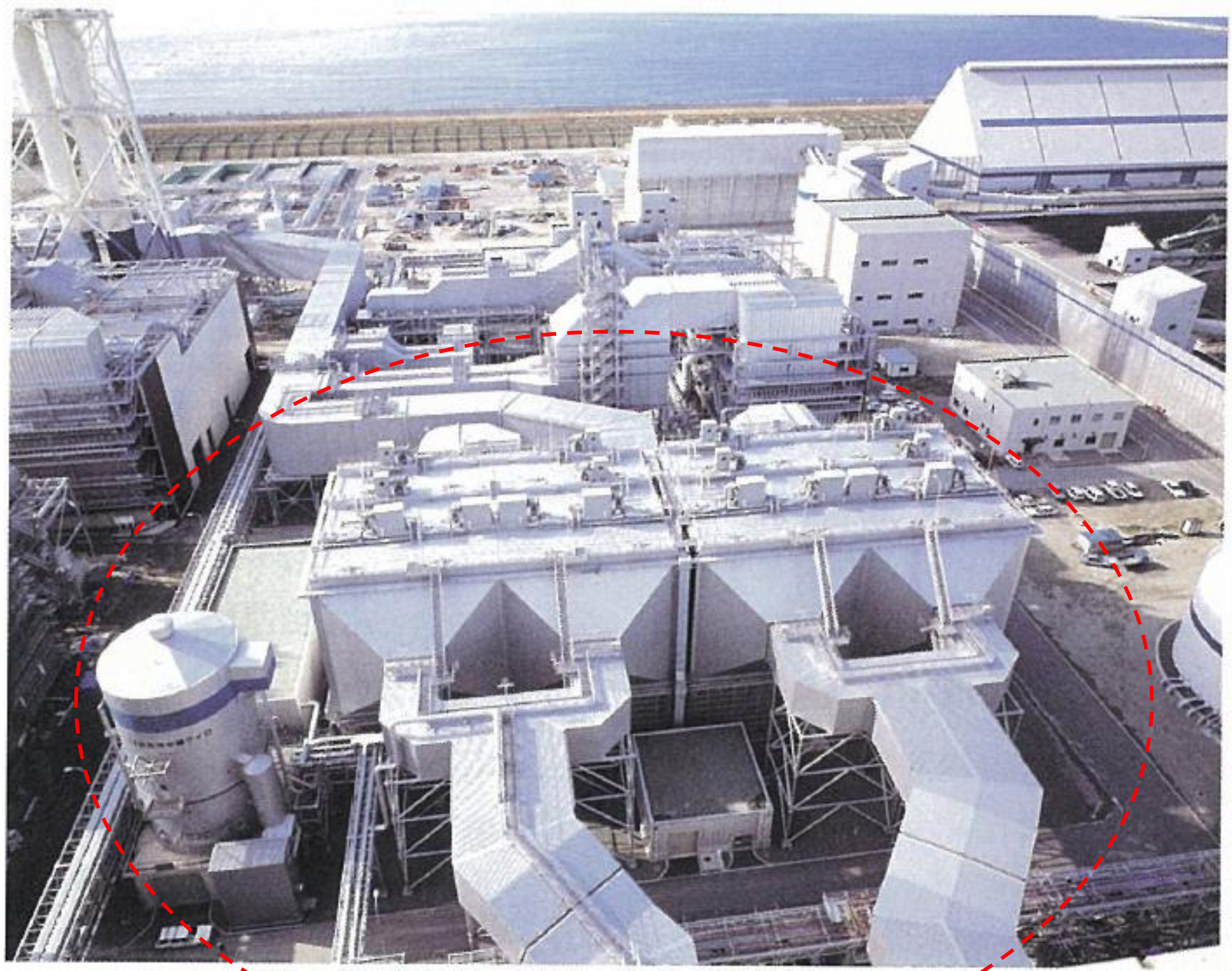
Electric field in an electrostatic precipitator (plate type)



Electrostatic Precipitator



Electrostatic Precipitator



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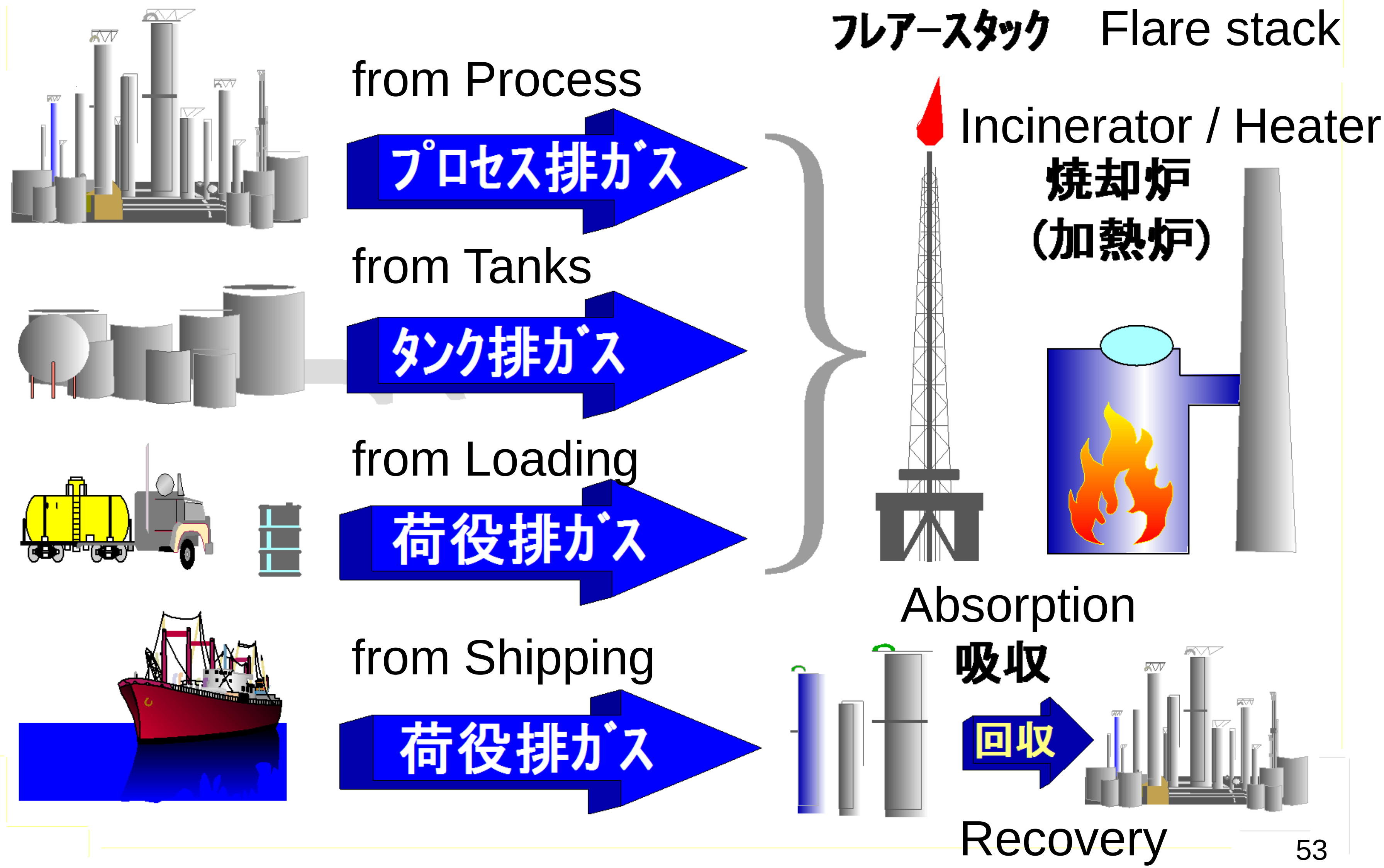
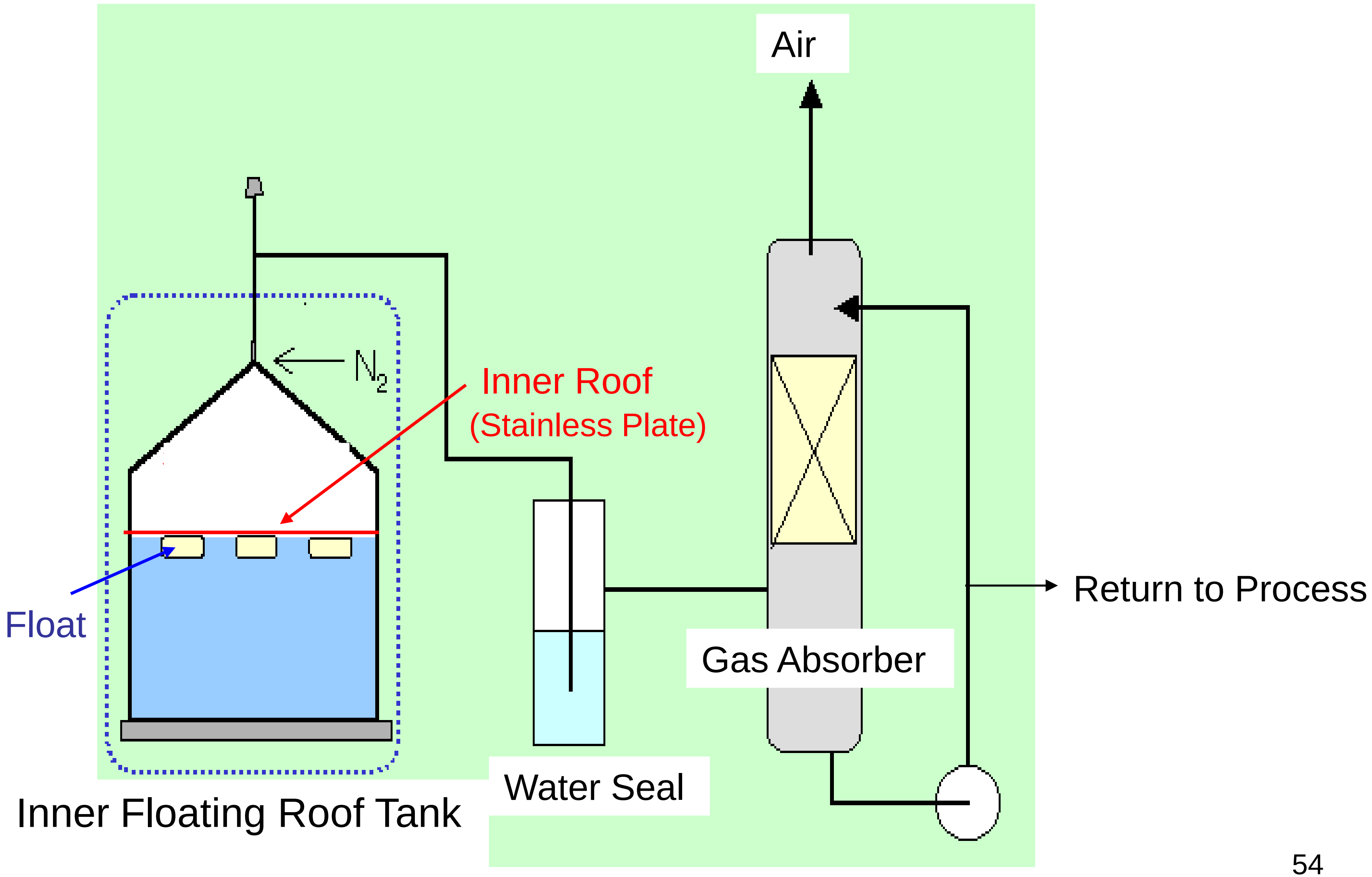
1. Basic theory of pollutant diffusion and their affection
2. Monitoring of pollutants and simulation of their diffusion
3. Characteristics of fuel and sources of pollutants
4. Emission coefficient of SOx and its removal
5. Emission coefficient of Nox and its reduction methods
6. Dust collection method (Electrostatic precipitator)
7. Hazardous gas treatment
8. Absorption methods
9. Adsorption methods

Waste Gas Treatments



Waste Gas Recovery system from a Tank



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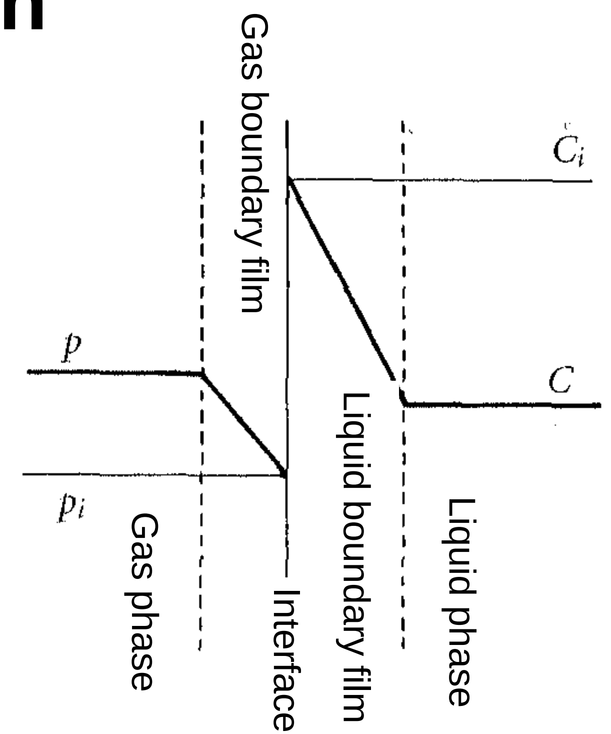
Treatment of Various Gases with Absorption Process

Treatment of Hydrogen Chloride

Hydrogen chloride (HCl) is a colorless, irritating gas, which fumes in moist air. It is readily soluble in water; the solution is highly acidic and strongly corrosive to metals.
Water scrubbing is most extensively used to remove hydrogen chloride, but an alkaline solution is also employed as the absorbent to enhance absorption efficiency.

Process		Outline
Absorption	Water scrubbing	Because of the high solubility in water, a high absorption efficiency can be achieved by increasing the liquid/gas ratio. The spent absorbent solution may be discharged after neutralization, or hydrogen chloride may be recovered from it.
	Absorption with Alkali	A caustic soda solution or a slurry of slaked lime is used as the absorbent when an especially high absorption efficiency is required. Reaction formulae : $NaOH + HCl = NaCl + H_2O$ $Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$

Theory of gas absorption



＜Double film thoery＞

Two boundary film :Vapor side and liquid side,

to reduce diffusion velosity

- Gas phase film coefficient of mass k_G
- Liquid phase film coefficient of mass k_L

Driving force of diffusion：
difference of pressure and concentration

＜ Film coefficient of mass and Total coefficient of mass＞

Gas phase diffusion velocity = Liquid phase diffusion velocity
NA: Mass transfer amount by unit time

$N_A=k_G(p-p_i)=k_L(C_i-C)$ （Stable condition, mass transfer amount）

$N_A=K_G(p-p_i)=K_L(C_i-C)$ （Alternate with total coefficient of mass）

k_G & k_L: impossible to measure
→ alternate with Gas phase total coefficient of mass K_G and Liquid phase total coefficient of mass K_L

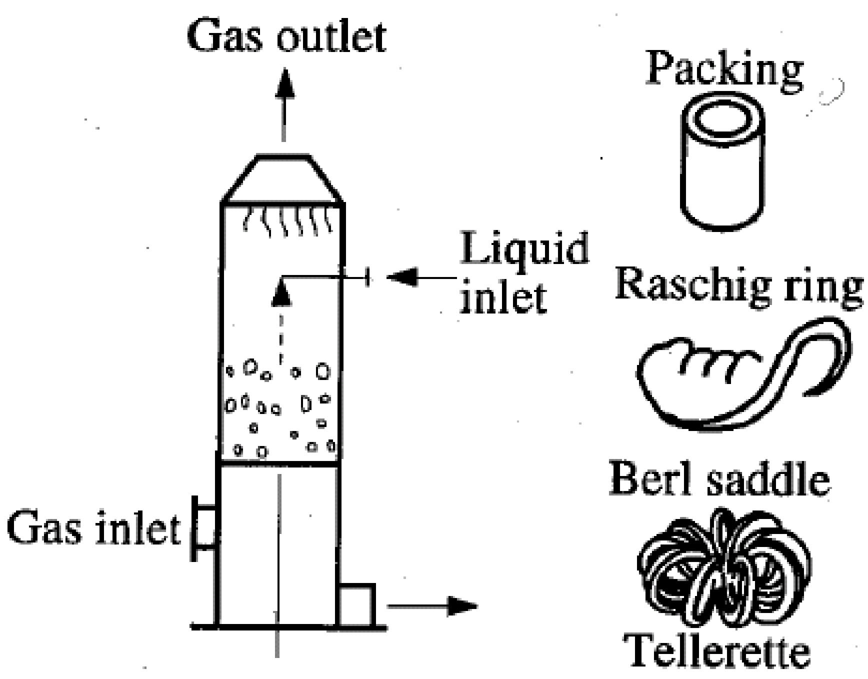
Selection of gas absorption equipment

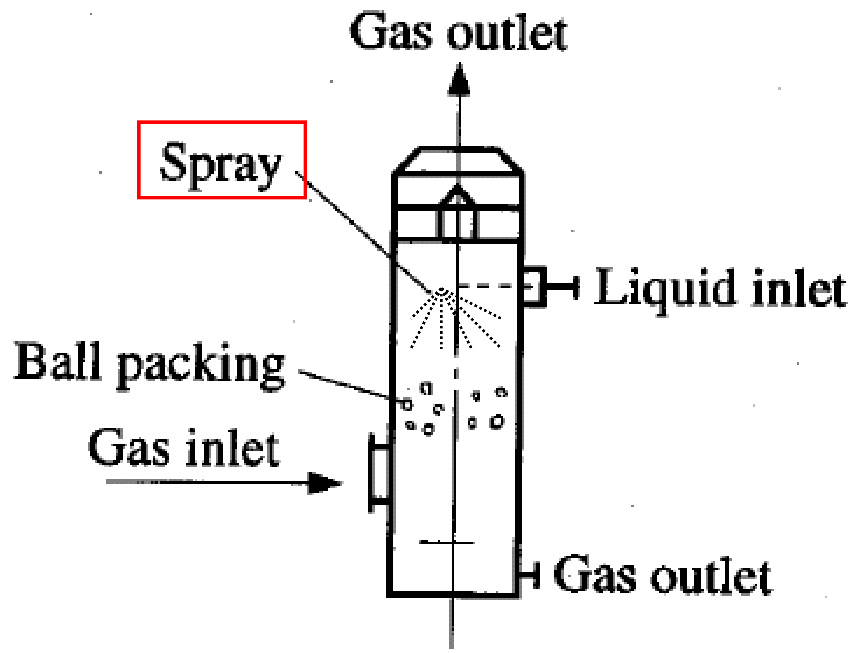
＜Gas phase control and liquid phase control＞

Gas absorbed		Suitable type of equipment	
Low solubility gas	Control by liquid phase coefficient	Equipment to reduce liquid phase resistance	Gas diffusion type equipment
			Perforated plate column Bubble cap column Jet scrubber
High solubility gas	Control by gas phase coefficient	Equipment to reduce gas phase resistance	Liquid diffusion type equipment
			Packed tower Spray tower Venturi scrubber Floating bed scrubber Wetted-wall tower Cyclone scrubber Cross contact flow type

Types of absorption towers (1/6)

Liquid dispersion type



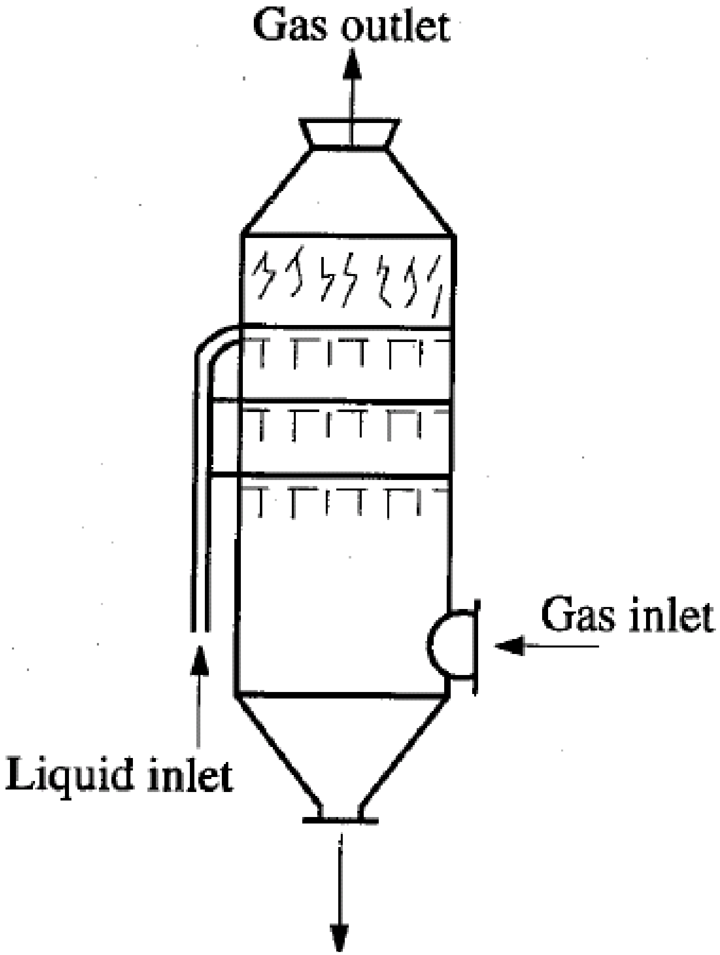


Packed tower

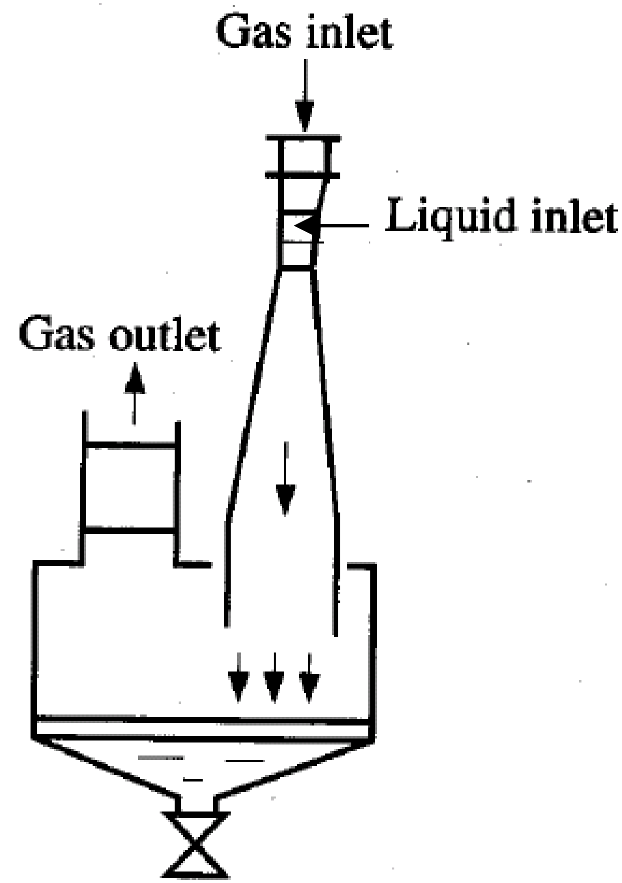
Turbulent
contact absorber

Types of absorption towers (2/6)

Liquid dispersion type



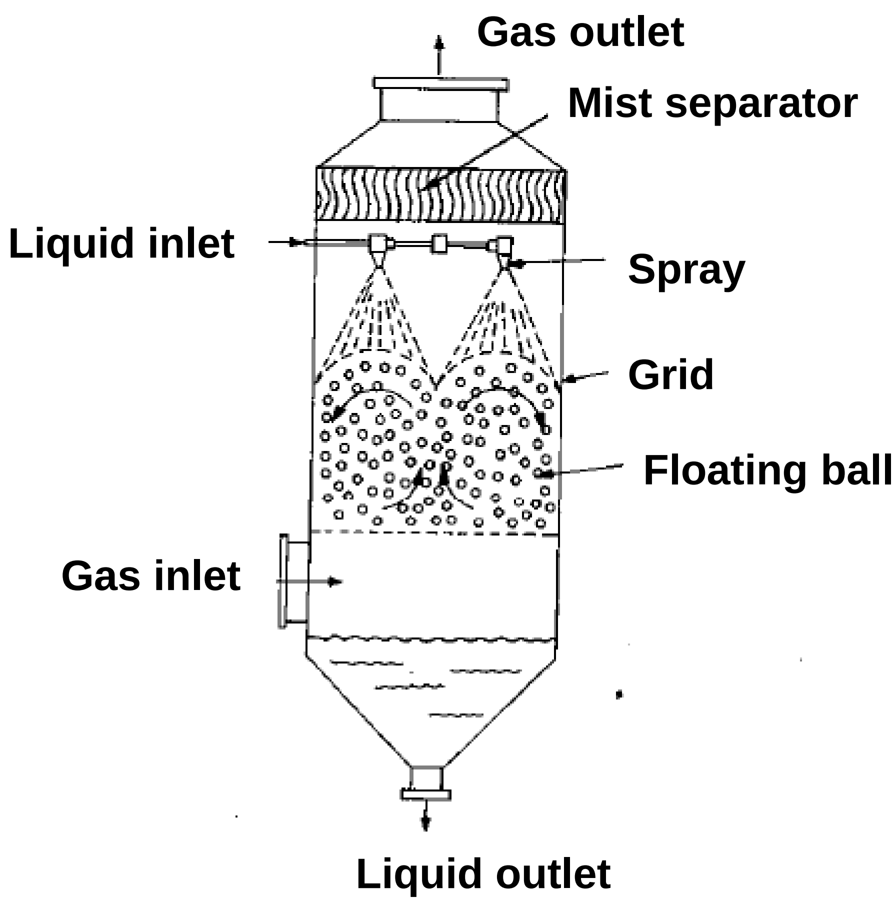
Spray tower



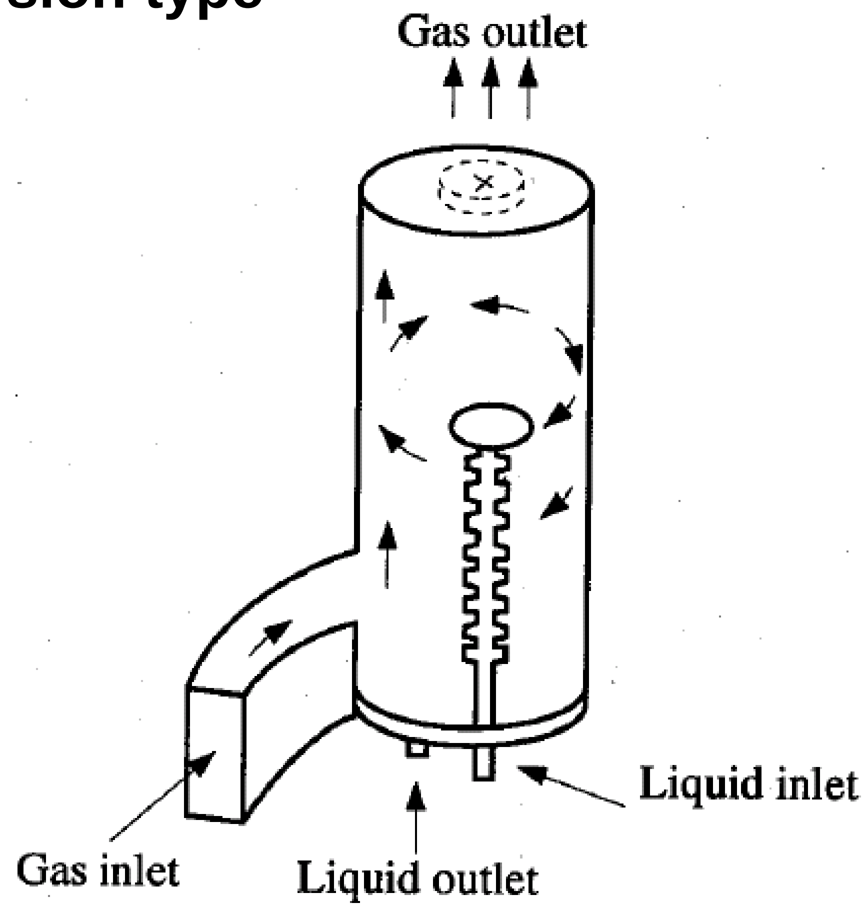
Venturi scrubber

Types of absorption towers (3/6)

Liquid dispersion type



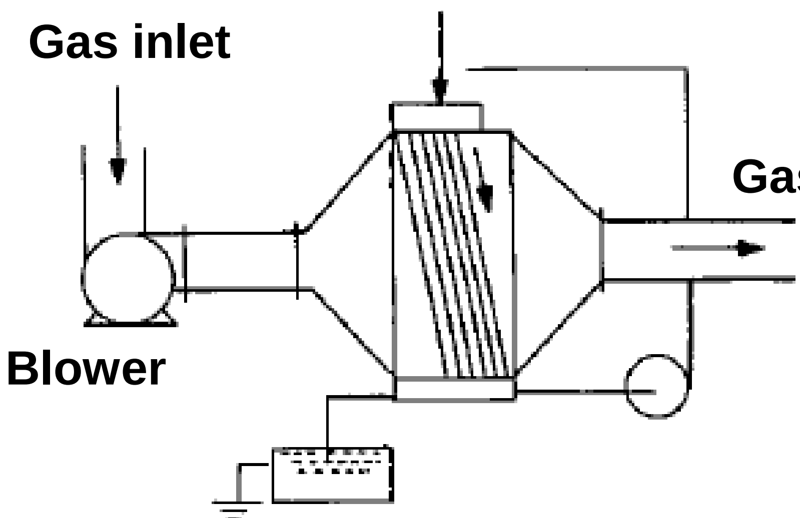
Floating bed scrubber



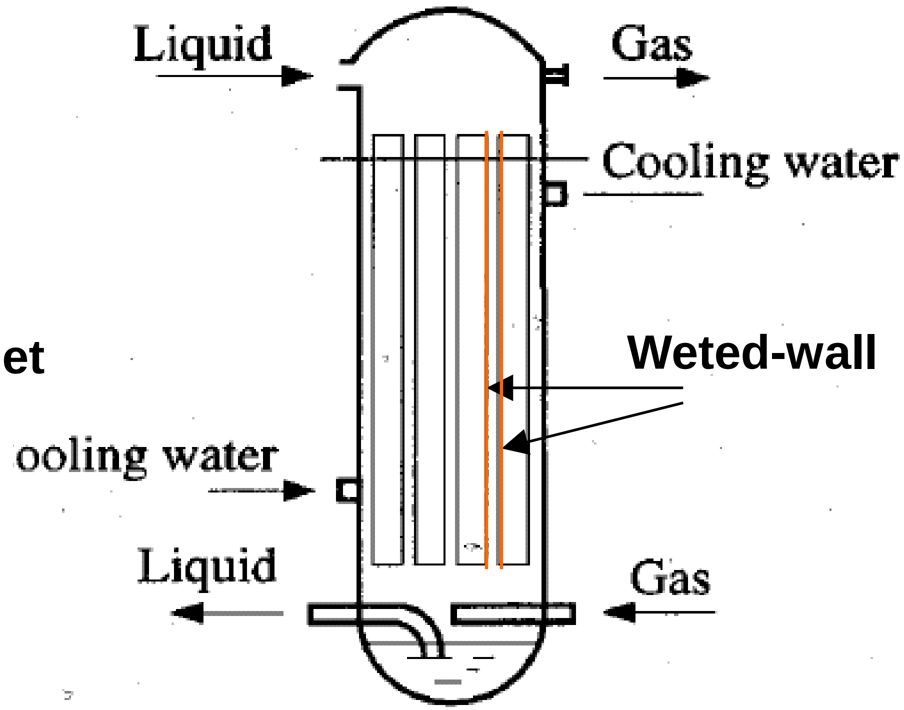
Cyclone scrubber

Types of absorption towers (4/6)

Liquid dispersion type



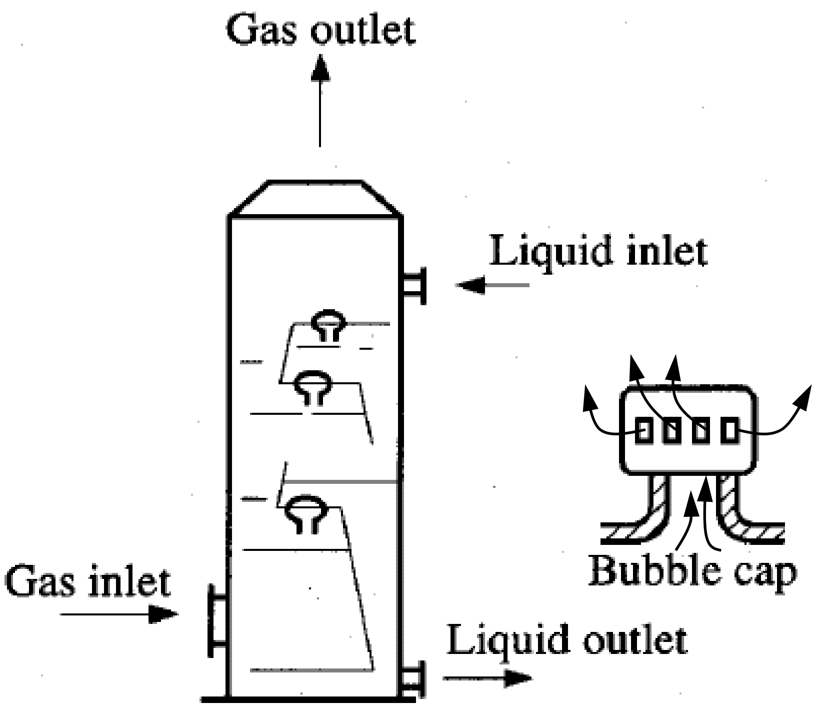
Cross contact flow type



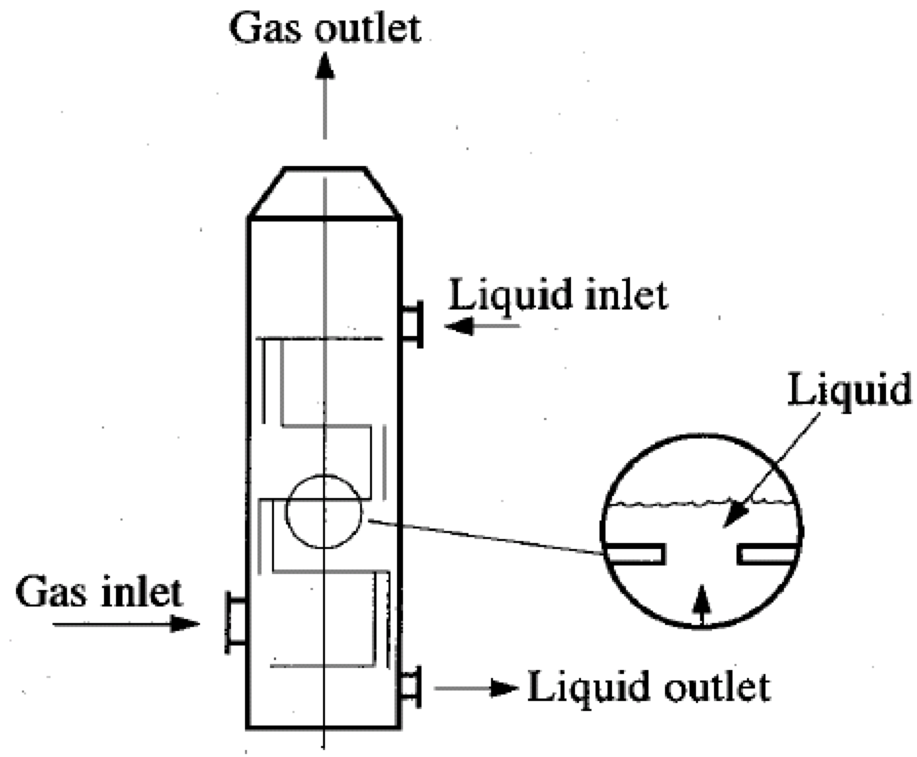
Weted-wall tower

Types of absorption towers (5/6)

Gas dispersion type



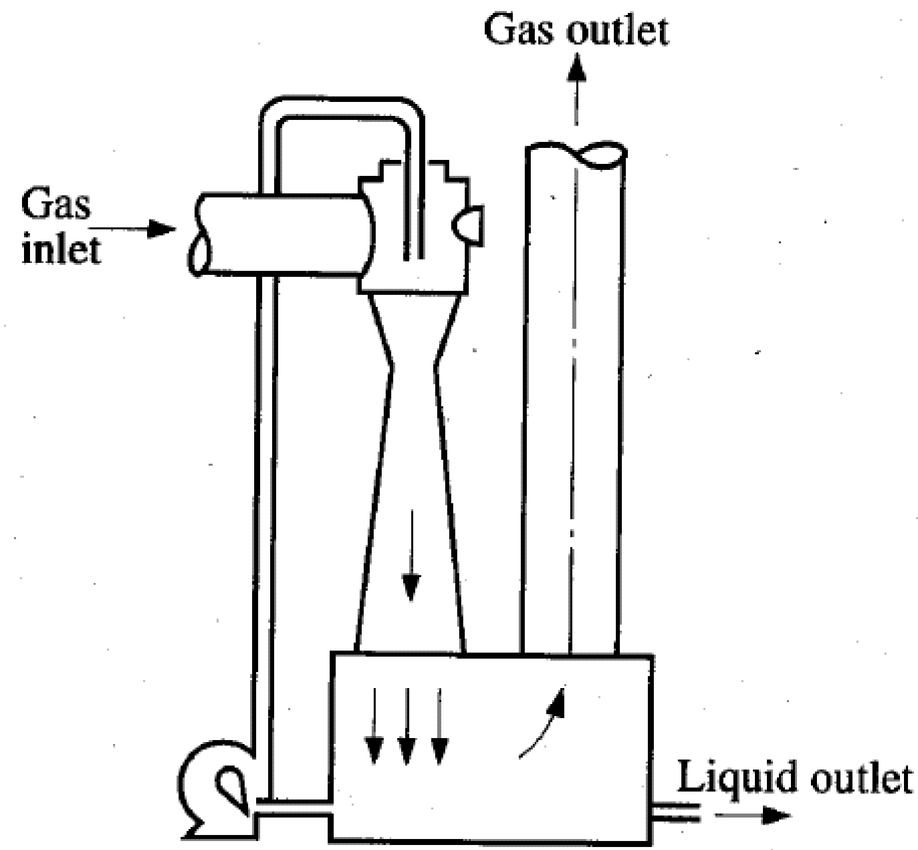
Bubble cap column



Perforated plate column

Types of absorption towers (6/6)

Gas dispersion type



Jet scrubber

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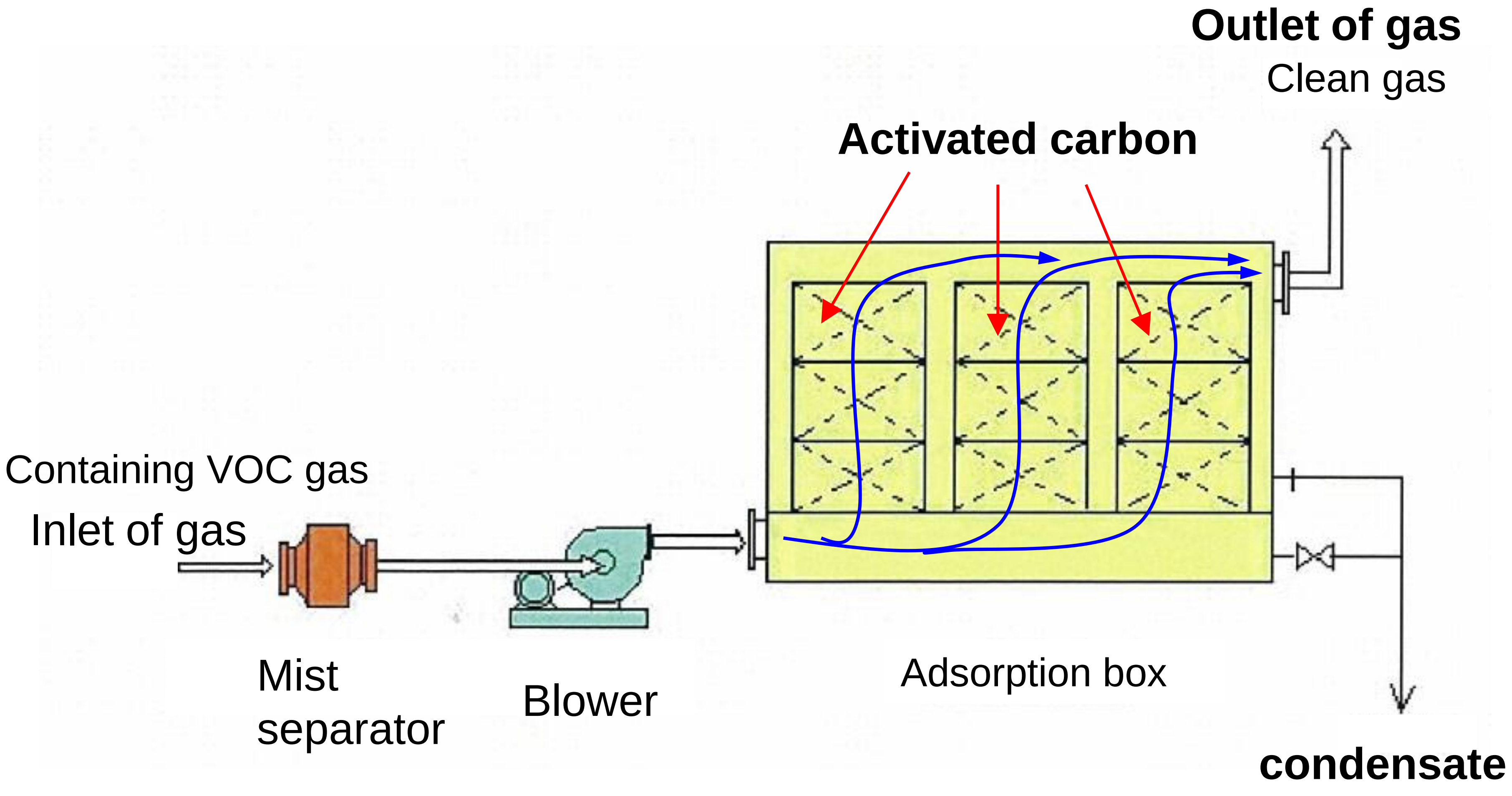
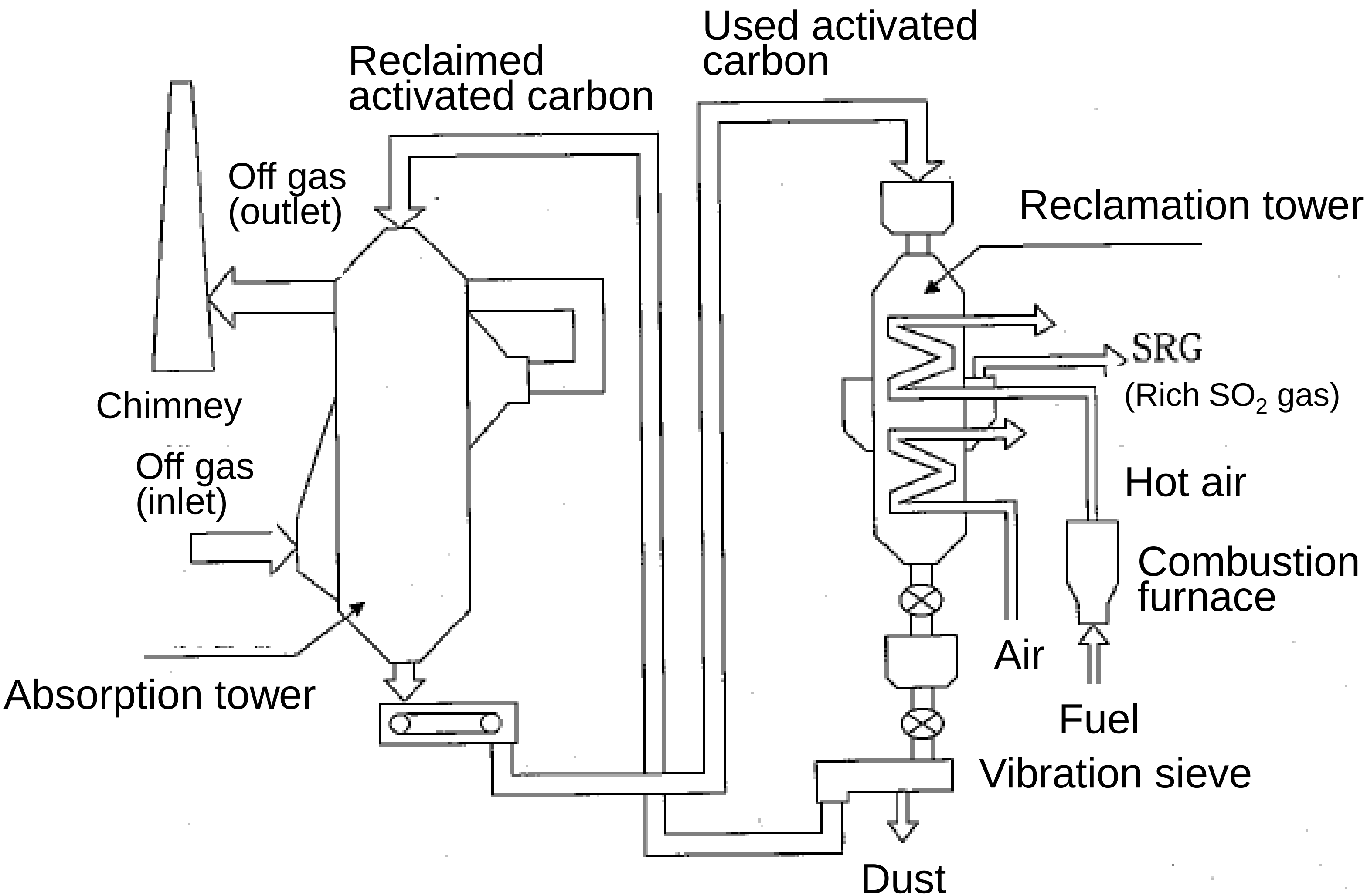
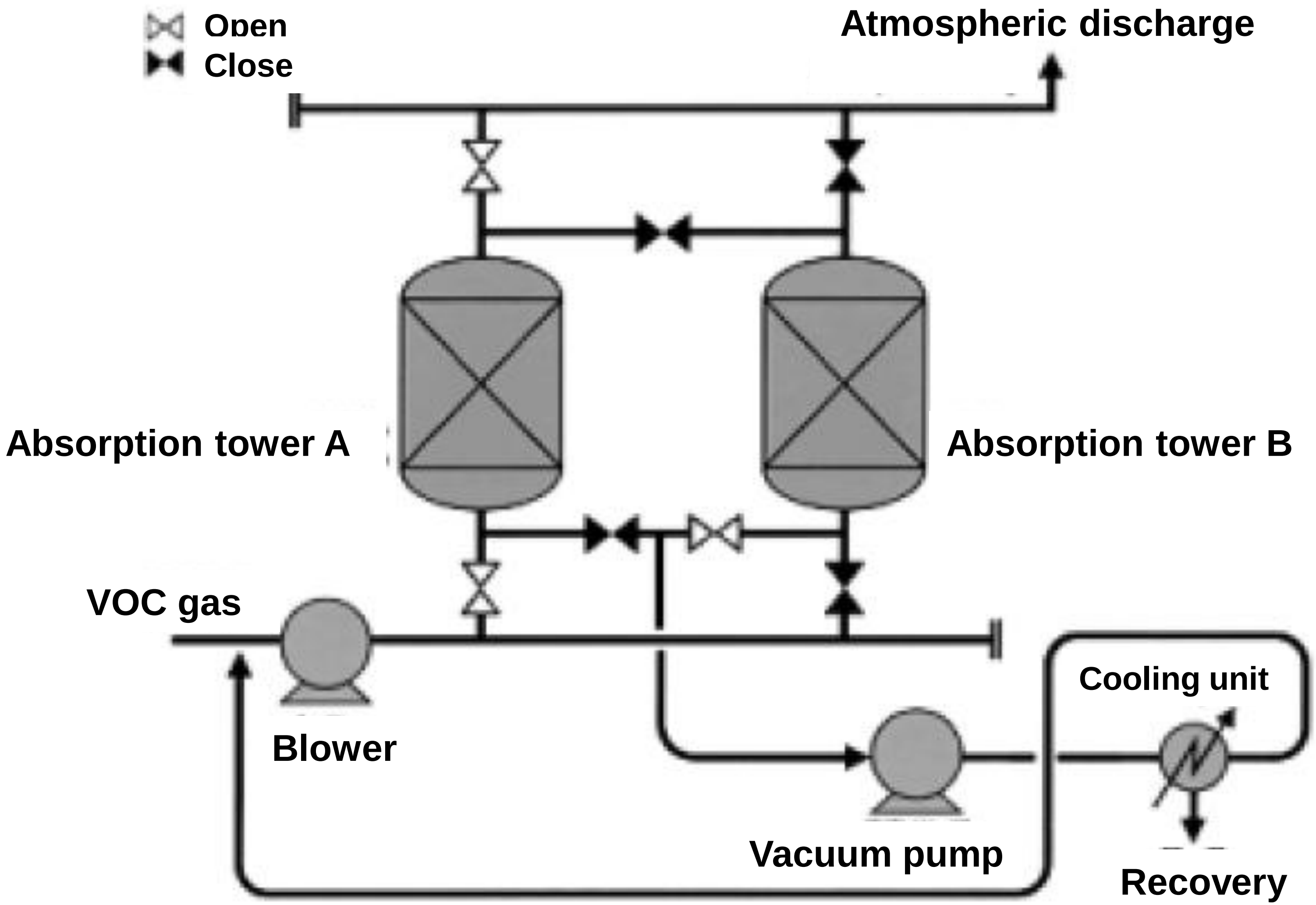
Adsorption with activated carbon



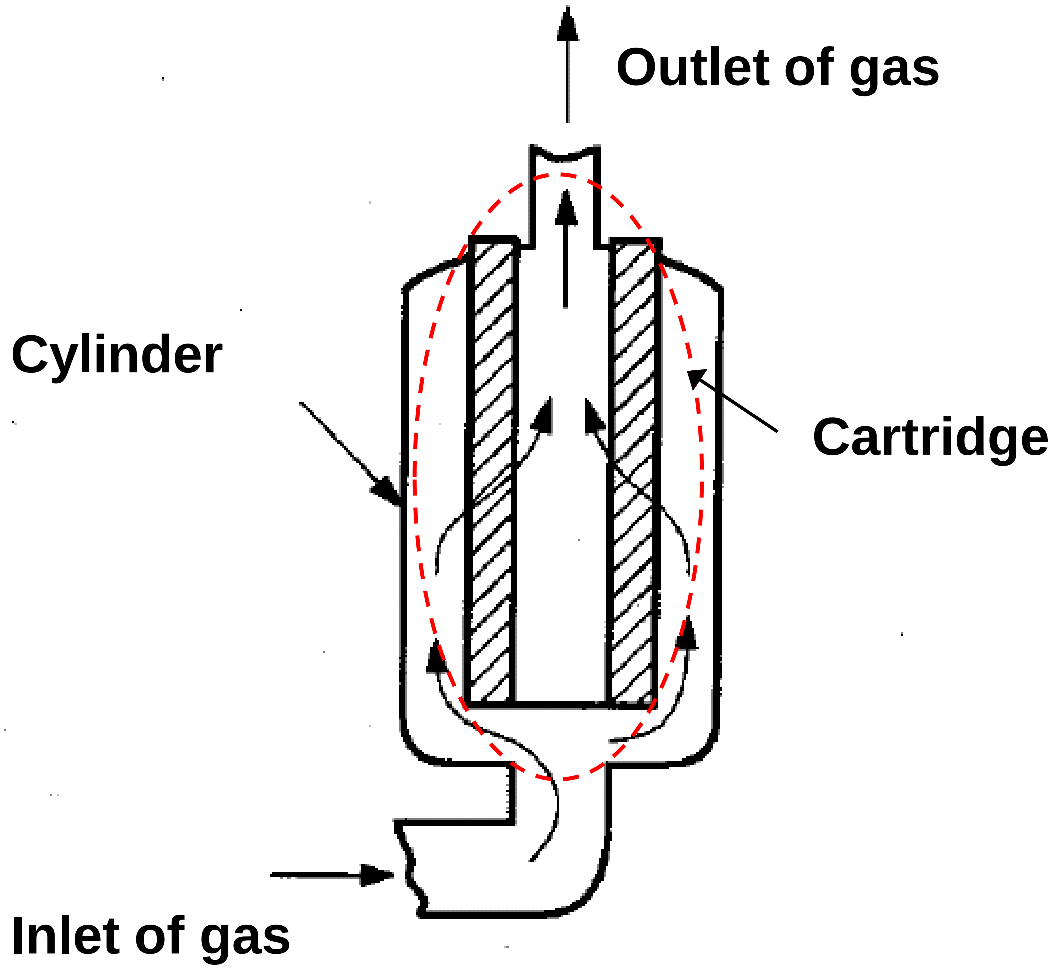
Activated carbon recycle process



Pressure swing process



Cartridge type Adsorption with activated carbon



Thank you for your attention !!

JEMAI