Ministry of the Environment, Japan
環境省

Instructions for Power Point of Air pollution Control Technology

- Thermal Power Plant
- Glass Manufacturing Industry
- Steel Industry
- Fertilizer Manufacturing Industry

March 2005

Supervised by Environmental Cooperation Office, Global Environment Bureau,
Ministry of the Environment, Government of Japan
監修　環境省地球環境局環境保全対策課環境協力室

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Preface

Recently、air pollution has become a serious in developing countries with a background of rapid urbanization and industrialization. Technologies for measuring and reducing pollutants at their sources have not been prevailed widely in these developing countries, making the implementation of effective air pollution control measures difficult.

Japan itself experienced extremely severe industrial pollution in its period of rapid economical growth, but has achieved remarkable results in air pollution control through the effort of both government and industry.

Much of the know-how regarding atmospheric environmental conservation measures developed through the course of this achievement is expected to be useful for developing countries.

In the 1995 fiscal year, therefore, Ministry of the Environment, Government of Japan, started preparing countermeasures manual to meet the needs of developing countries for each type of major industry, to disseminate air pollution control measures. In 1997, technical manuals for thermal power generation industry and iron and steel industry are prepared. In 2001, technical manuals for glass manufacturing industry and fertilizer manufacturing industry are prepared.

In 2005, Overseas Environmental Cooperation Center, Japan was entrusted by Ministry of the Environment to prepare the electronic slides (power point) as teaching materials in order to visualize the essentials of the subject matters of above four technical manuals under the examinations of the committee for air pollution control technology, which reviewed the digested information and these formation.

I will be glad if these slides, which are based on experience with measures concerning industrial air pollution control in Japan, prove of some use to people in countries involved in struggling with the same issues and contribute to preserving the global environment. Finally, I greatly appreciate every committee member and an editor of power points for air pollution control technology.

March 2005

Hiromi Mori
Chairman of Board Directors
Overseas Environmental Cooperation Center, Japan

Committee Member for the Preparation of Electronic Information of the Manuals on Air Pollution Control Technology

Committee Members

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Sources of Data

The slides by power point are prepared based on the following manuals.

1. **Thermal Power Plants**
   "Air Pollution Control Measure Technology in Thermal Power Plant, Global Environment Centre Foundation, March1997" under the supervision by Air Quality Management Division, Environment management Bureau, Ministry of the Environment, Government of Japan

2. **Glass Manufacturing Industry**
   "Technical Manual for Air Pollution Control – Glass Manufacturing Industry- EX Corporation , March 2001" under the supervision by Air Quality Management Division, Environment management Bureau, Ministry of the Environment

3. **Steel Industry**
   "Air Pollution Control Measure Technology in Steel Industry, Kitakyushu International Techno-cooperative Association, March 1997 " under the supervision by Air Quality Management Division, Environment management Bureau, Ministry of the Environment, Government of Japan

4. **Fertilizer Manufacturing Industry** ････The manual is not available in English.
   開発途上国の大気汚染問題に係わる固定発生源対策マニュアル、鉄鋼業編、 平成13年3月、財団法人北九州国際技術協力協会（環境省環境管理局大気環境課監修）

   ("Technical Manual for Air Pollution Control – Fertilizer Manufacturing Industry, Kitakyushu International Techno-cooperative Association, March 2001 " , under the supervision by Air Quality Management Division, Environment management Bureau, Ministry of the Environment, Government)

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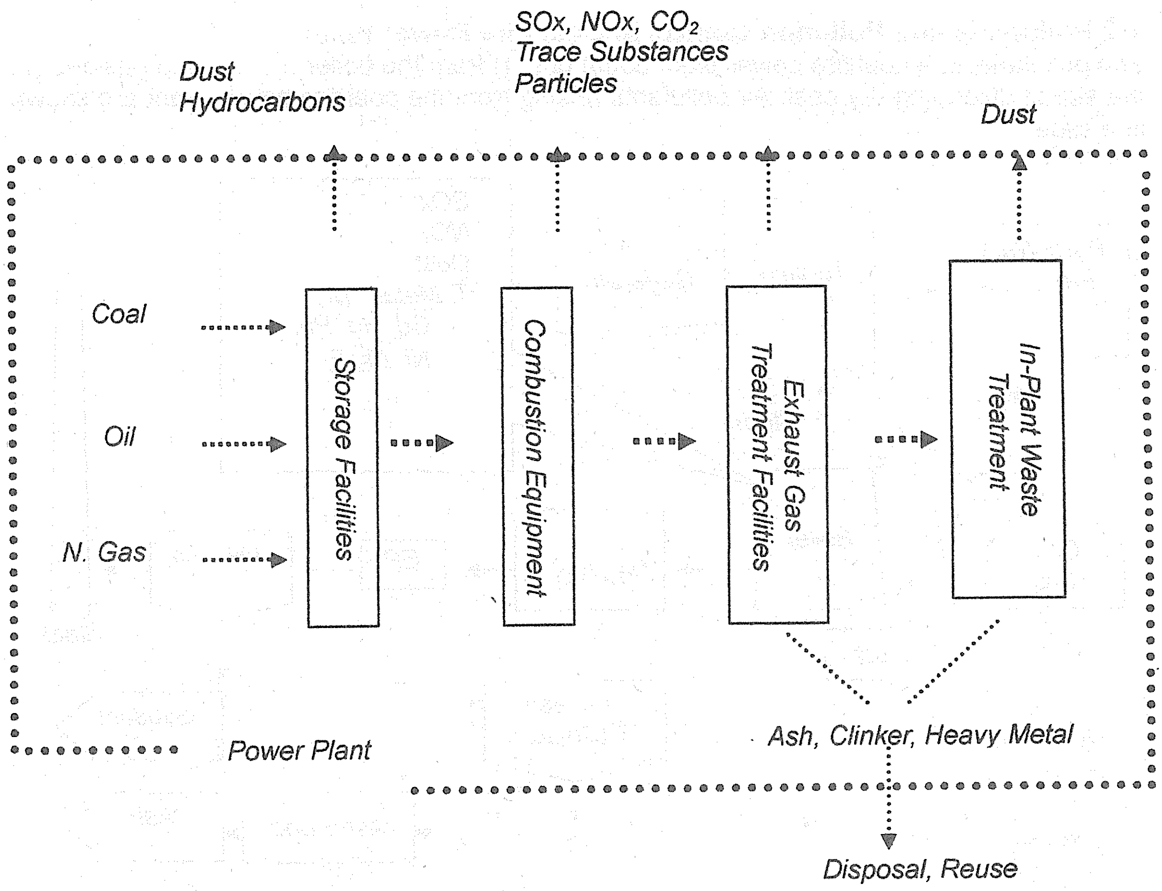
I .Thermal Power Plant

1. Air Pollution in Thermal Power Plant

1-1 Pollutants Emission

In the thermal power plant, coal, oil or natural gas (N Gas) are generally used as fuel for a boiler to drive the turbine generator. In the processes of thermal power, pollutants such as SOx, NOx, CO_2, dust, hydrocarbons, and trace substances are generated and waste materials are reused or disposed as shown in this slide.



Concrete removal methods for these pollutants except CO_2 are described respectively after page 2.

Among the global environmental problems causing worldwide controversy in recent years, "global warming effect" and "acid rain" are associated most intimately with the air pollution problems of thermal power plants.

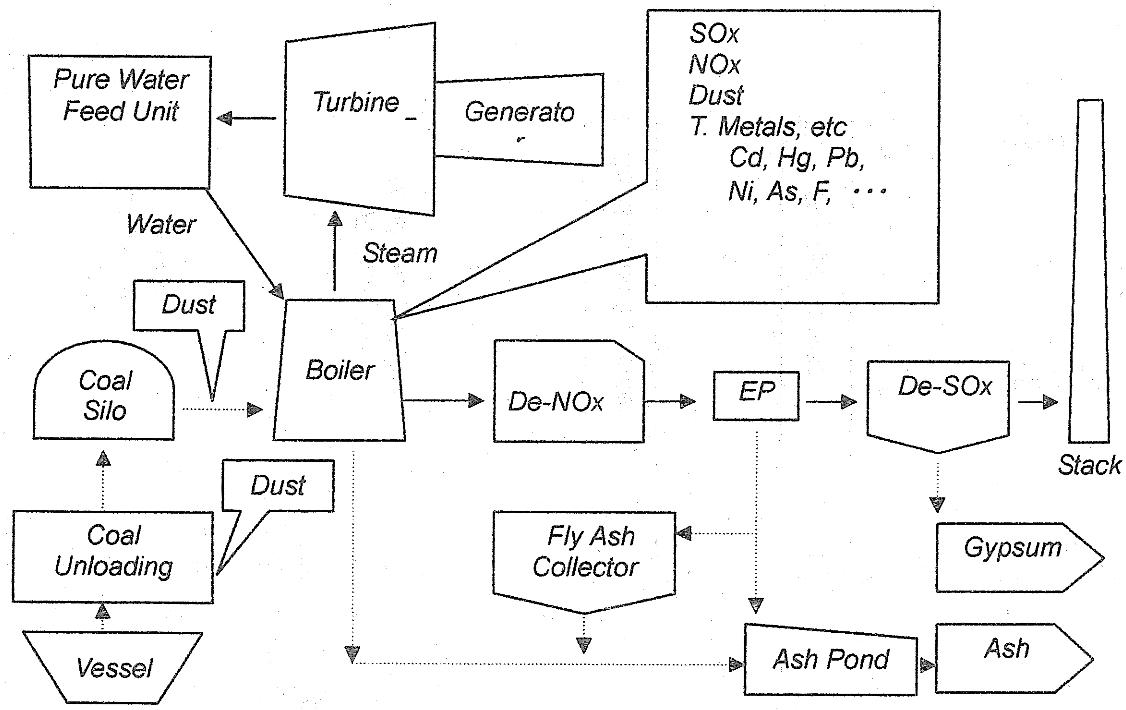
For the controversial global warming, the greenhouse effect gases are carbon dioxide (CO_2), methane (CH_4),nitrous oxide (N_2O), and etc., and it is presumed that CO_2 resulting from fossil fuel combustion has a substantial influence on this problem. This global warming problem has not been clarified yet; its causal relations and measures are not yet perfectly solved scientifically for us to sustain our level of economic activity.

The global warming is an issue that nations will deal with and that emission of green house gases will be lowered or sequestered as envisioned in the Kyoto Protocol.
Regarding the acid rain problem, various countermeasures are described in slides especially in the section of SOx reduction technology.

For the detail information, refer to the pages at P.71~76 (Japanese version) or E.3~8 (English version) of "Air Pollution Control Measure Technology in Thermal Power Plant", Global Environment Centre Foundation, March1997" under the supervision by Air Quality Management Division, Environment management Bureau, Ministry of the Environment, Government of Japan.

1-2 Pollutants and Pollution Control in Coal Fire Power Plant

The pollutants in a coal fire power plant come out (1) from the boiler mainly, and besides (2) the site of unloading dry coal. Air pollutants arising from the coal fire power plant are shown in a slide.



During the handling of coal:
At fuel storage yard, dust scattering during coal unloading and spontaneous combustion of coal particles should be taken into care. These are; coal dust scattering from coal hoist and outdoor coal storage yard, spontaneous combustion in coal storage yard, and coal dust explosion in indoor coal storage yard.

Air pollutants also arise during the transportation from storehouse to boiler and in the pulverizing process.

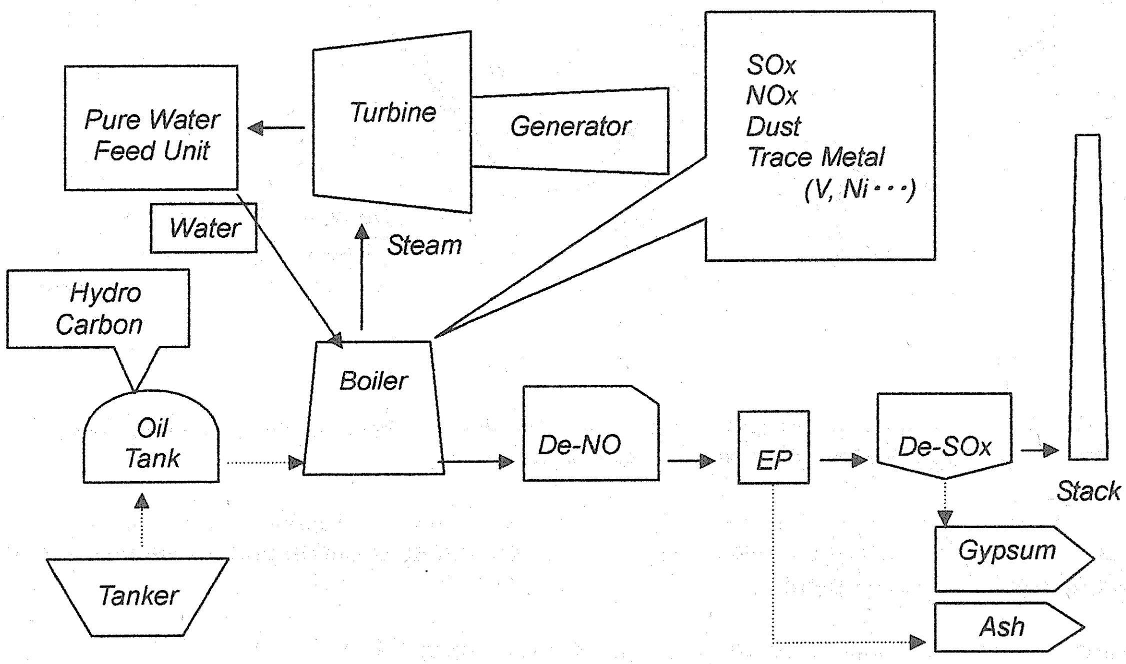
At fuel combustion:
SOx, NOx, dust, trace metals, etc such as cadmium (Cd), mercury (Hg), lead (Pb), nickel (Ni), arsenic (As), fluorine (F), etc. are generated.
The exhaust gas from a coal fire boiler is sequentially led to denitrification equipment,

electrostatic precipitator, desulphurization equipment, and then to stack. The pollutants are recovered as forms of ash and gypsum.

For the detail information, refer to the pages at P. 73~76 or E.4~8.

1-3 Pollutants and Pollution Control in Oil Fire Power Plant

The pollutants in an oil fire power plant come out from (1) the boiler mainly and merely from (2) the oil storage tanks. Air pollutants arising from the oil fire power plant are shown in a slide.



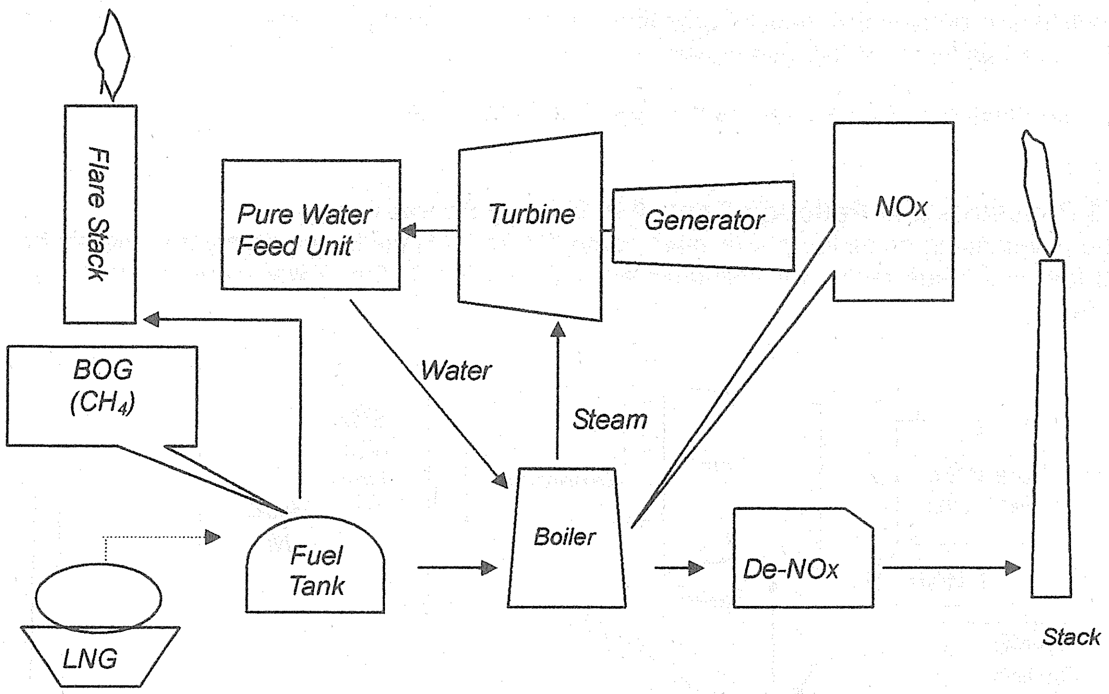
At oil storage yard, vapor from storage tank comes out, of which the compositions are hydrocarbons. During the handling of oil, no air pollutants arise in the processes unlikely coal.At fuel combustion, SOx, NOx, dust, trace metals such as vanadium (V), nickel (Ni), etc. are generated.

The exhaust gas from an oil fire boiler is sequentially led to denitrification equipment, electrostatic precipitator, desulphurization equipment, and then to stack. The removed pollutants are recovered as forms of ash and gypsum.

For the detail information, refer to the pages at P. 73~75 or E.4~8.

1- 4 Pollutants and Pollution Control in Gas Fire Power Plant

The pollutants in a natural gas fire power plant come out from (1) the boiler mainly and merely from (2) fuel tanks. Air pollutants arising from the natural gas fire power plant are shown in a slide which is very simple unlike to coal fire power plant or oil fire power plant.
At oil fuel tank yard, boil –off gas such as methane (CH_4), etc. comes out.



BOG: Boil-off Gas

During the handling of natural gas, no air pollutants arise in the processes unlikely coal. At natural gas combustion, only NOx is generated.

The exhaust gas from natural gas fire boiler is generally led to denitrification equipment and then to stack. No waste materials are generated from the air pollution abatement process at natural gas firing power plant.

For the detail information, refer to the pages at P. 73~76 or E4~8.

2. Measures against Fuel

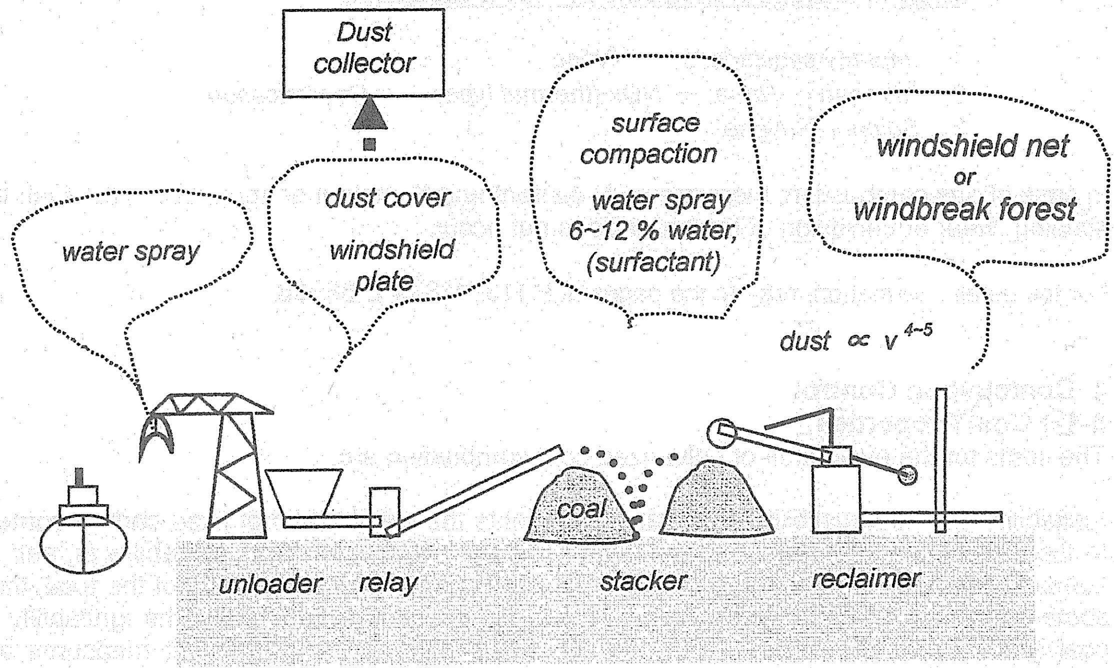
2-1 Coal Fire Power Plant

For construction of a coal fire power plant with outdoor coal storage, a coal dust scattering simulation is carried out in advance in order to predict the amount of coal dust scattering to peripheral areas. The height of windshield fence around the coal storage yard, installation location and the moisture content control for coal are studied, and consequently no coal dust will affect environmental preservation.

Water spraying has the effect of controlling scattering of coal dust by increasing the moisture content in coal. Some coals are highly water repellent and water spraying has only a small dust proofing effect. In this case, the coal dust preventive agent is added.
Windshield fence, windshield net, and windbreak forest are useful to prevent the scattering of dust, because the scattering coal dust volume is said to be proportional to the fourth to fifth power of the average wind velocity (V).

The hermetically sealed conveyer, windshield plate mounted conveyer, dust collector, and surface compaction of storage coal are also effective methods. Recently continuous type unloaders have been popularly employed in view of coal unloading efficiency and environmental measures. For an indoor coal storage, which is not necessary to be concerned with dust as for an outdoor stock pile, the dust collection and ventilating equipment for prevention of coal dust explosion become necessary.

The conceptual figure in the slide shows the coal handling processes, air pollutants sources, pollutants, and pollution control methods.



For the detail information, refer to the pages at P.92~97 or E.27~28.

2-2 Oil and Gas Fuel Power Plants

In case of oil fuel, exhaust gas components that pose environmental problems are nitrogen oxides (NOx), sulphur oxide (SOx), dust and soot and boiler corrosive elements. Residual carbon content is a coke-type carbon residue produced when samples are subject to thermal decomposition with air supply cut. Residual carbon is liable to turn into soot and dust.

Effect of fuel oil properties on exhaust gas quality

1. *Residual Carbon → Soot, Dust → Dust collection*
2. *Nitrogen → NOx → Denitrification*
3. *Sulphur → SOx → Desulphurization*
4. *Ash → Pressure drop, Heat transfer broke,*
   Mechanical Wear, Corrosion → Maintenance

Nitric content amounts to about 0.01~0.6 wt % in the case of heavy crude oil. During combustion, part of the nitric content is exhausted as NOx.

Fuel oil contains sulphur as some form of sulphur compounds or another. When they are burned, they become sulphur oxide (SO_2), and part of it is further oxidized to sulphuric anhydride (SO_3). If the temperature of combustion exhaust gas is lowered below the dew point, SO_3 combines with moisture content within the exhaust gas, becoming sulphuric acid (H_2SO_4), which brings corrosion to steel structure.

Ash is contained in fuel oil, although its volume is small. The ash includes sodium, potassium, iron, silicon, vanadium and nickel. On the occasion of combustion, these attach and accumulate on gas paths, causing the increase of pressure loss, blocking of heat transfer, mechanical wear and chemical corrosion.

Effect of fuel gas properties on exhaust gas quality

1. *Impurity substances・・・・・None*
2. *Nitrogen・・・None → NOx (thermal type) → Denitrification*
3. *Sulphur・・・None*

In case of gas combustion, there are no N content and S content or impurities in the fuel, the staining, wear or corrosion of the boiler does not occur.

For the detail information, refer to the pages at P.113~118 or E.58~66.

3. Combustion Control

3-1-1 Coal Properties

The items for the evaluation of pulverized coal combustion are:

Ignitability and combustibility; Fuel ratio represents the weight ratio of fixed carbon content to the volatile content. Generally, the higher fuel ratio is, the lesser its ignitability is, and its combustion speed also tends to be slow. Volatile content is less than 20% of the total, then some steps for stabilized ignition are necessary. Ignitability index show the ignitability of coal itself. If it is 35 or less, it is generally some ignitability improvement measures are necessary. Button index shows for the possible adhesion of pulverized coal to the burner nozzle, etc. As for coal with a button index of more than 6 or 7, particular steps are necessary to prevent the problems.

Effect of Coal Properties on Pulverized Coal Combustion

Ignitability & Combustibility	*optimum range*	*effects in case of off-spec.*
Fixed-C / volatile content	*<2.5~3.0*	*increase of non-burn loss*
Volatile content	*>20%*	*unstable ignition*
Ignitability Index	*>35*	*hard ignition*
Button Index (viscosity)	*<6~7*	*clogging, adhesion*
Grindability		
Proper size	*50~100μm*	*increase of non-burn loss*
Dryness	*H_2O < 20 %*	*lowering mill performance*
Slagging		
Ash Melting Temp.	*>1,300℃*	*slagging*
Ash Alkaline Ratio	*<0.5*	
Fe_2O_3/CaO	*<0.3~3<*	
S/coal	*<2 %*	
Fouling	*basic content; Na_2O, K_2O, Cl, CaO, S*	*fouling on inner furnace, radiation heating surface*
Wear-out Nature	*quart, Fe_2O_3, S*	*wear of mill, coal tube, heat transfer surface*

Grindability: Pulverized coal firing is generally characterized by combustion state after crushing it into fine particles of 50 to 100 μm, drying them, and burning them. The important point in the firing is to ensure the complete burning within a combustion chamber. In case of off-specification, non-burn loss increases. Much moisture content of 20% or more leads to decline of the mill capacity.

Slagging: coal slagging is a phenomenon, which stems from the melting of coal ash within a boiler furnace, adheres to the radiation heating face of the mill, hardens and accumulates there when it is cooled. Ash melting temperature is judged based on whether the ash melting temperature is higher or lower than the gas temperature near the radiation heating face. Ash higher alkaline ratio means that low-fusing-point oxides and compound salts are liable to be produced, and that the slagging characteristic is considered. If the ratio of Fe_2O_3/CaO in ash is between 0.3 and 3, there is a tendency toward the productions of compounds with a low fusing point. The sulphur produces low-fusing-point complex salt, accelerating the generation of fouling.

Fouling is a phenomenon in which melted ash coagulates to the inner surface of combustion chamber due to the content of Na_2O, or so on.

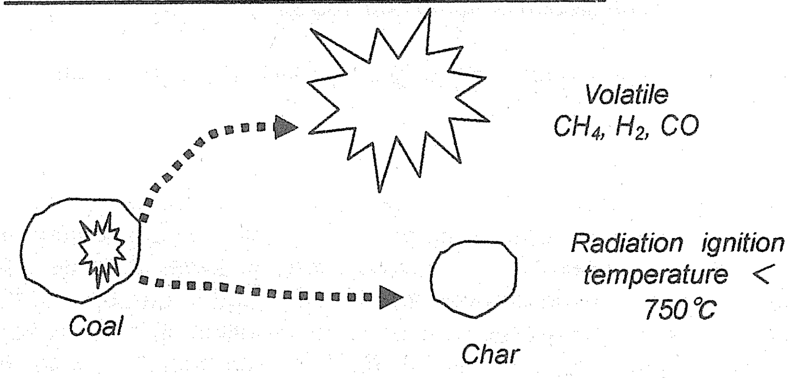
Wear-out nature, which causes abrasion to a mill, tube, heat transfer face, etc., is judged based on analysis values such as quart, so on.

For the detail information, refer to the pages at P107~110 or E.49~54.

3-1-2 Coal combustion

In suspended combustion in the form of pulverized coal, its ignition time and combustion time are extremely shortened, and its burner combustion becomes possible, as if it were heavy oil or gas fuel. In pulverized coal combustion, the primary combustion range is chiefly the combustion range of volatile content such as CH_4, H_2 and CO. The second combustion range is primarily the combustion range of char. The speed of combustion of char is extremely slow, compared with that of volatile matter. Accordingly the combustion time of char accounts for about 80 to 90% of total combustion time. Using a normal pulverized coal combustion boiler, a radiation ignition temperature of 750℃ or less is empirically known as causing virtually no combustion-related problems.

Combustion Mechanism of Pulverized Coal



To complete combustion of fuel, more surplus air than theoretical air volume (air ratio of 1.2 to 1.25 for high volatile content bituminous coal) is necessary. Therefore, various methods have been employed to reduce the NOx as shown in a slide. Among these methods, combustion control itemized No. 1 to 4 in a slide is possible by means of changing operation method.

1. *Reduction of surplus air ratio (high volatile coal; 1.2~1.25)*
2. *Lowering combustion air temp. (normally 250~350 ℃)*
3. *Two stage combustion (1st burner + 2nd burner)*
4. *Recycling exhaust gas ($<$20~30%)*

The inner-furnace denitrification method is to reduce, in combustion chamber, NO which was generated in the same combustion chamber, by means of hydrocarbon. This process is composed of two stages. To validate this process, at first stage, (1) the atmospheric temperature must be higher than the hydrocarbon decomposition temperature (about 900℃), (2) oxygen must be present, (3) the volume of reduction-use hydrocarbon to be used for mixture (fuel) must be more than the chemical equivalent of existing oxygen. The second stage is to arrange for the complete incineration of non-combustion portions. For this, (1) the atmospheric temperature must be higher than the reaction temperature of the non-burned portions, (2) the sufficient volume of oxygen for the complete incineration of the non-burned portions must be supplied.

5.Inner-furnace denitrification

1st Process
— *furnace $>$900℃ HC decomposition*
— *O2 existing*
— *reductant HC $>$ chemical equivalent O_2*

2nd Process
— *atmosphere temp. $>$ reaction temp. of non-burned portion*
— *sufficient O_2*

NOx curtailment methods based on the improvement of the burner structure can broadly be grouped into the three shown in a slide.

6. Low NOx burner
— *slow mixture air & fuel*
— *promotion of unevenness comb.*
— *acceleration of flame heat radiation*

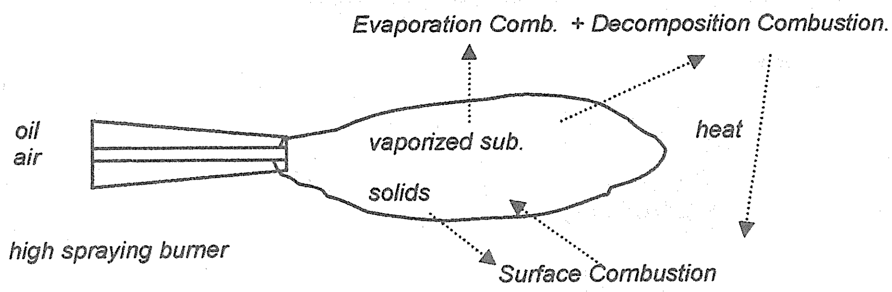
For the detail information, refer to the pages at P.110~112 or E.54~58.

3-2-1 Oil Combustion

Combustion mechanism of fuel oil can be divided into combustion of evaporated substances and combustion of decomposed substances. Fuel oil is a complicated multiple hydrocarbons. The decomposing temperature of hydrocarbons is lower than its ignition or combustion temperature, and then hydrocarbons are decomposed to carbon and flammable gas before its combustion, which combine with oxygen, resulting in combustion. Carbon becomes carbon dioxide gas, as a result of surface combustion, while flammable gas and hydrocarbon oxidized, turning into carbon dioxide gas and water through diffusion combustion. The heat resulting from this combustion further leads to thermal decomposition. Because combustion by decomposition and surface combustion occur alternately or simultaneously, combustion reaction progresses continually.

Combustion reaction is affected by oil jet speed (combustion reaction $\propto$ oil jet speed) and combustion speed (combustion reaction ∝ combustion speed), which are influenced by the contact surface area between fuel and air. The burner with high spraying performance is important to complete combustion.

Oil Combustion Mechanism



Oil properties of JIS C-Heavy Oil as an example are shown in a table. Oil properties effect on exhaust gas composition as shown in a slide. If residual carbon content is much, it is liable to turn into residual carbon-type soot and dust, and carbon is liable to attach to the burner tip, should the combustion condition deteriorate. Fuel oil contains ash content. The ash content includes sodium (Na), potassium (K), iron (Fe), silicon (Si), vanadium (V), aluminum (Al), and nickel (Ni). These are adsorbed by combustion gas, cause melting and chemical change and attach to and accumulate on gas paths, causing the growth of pressure loss, blocking of heat transfer, mechanical wear and chemical corrosion.

Effect of Fuel Oil Properties on Exhaust Gas Composition

Subs.	Con.wt. %	Pollutants	Damages
N	0.01~0.6	NOx	Air pollution
S	0.2~3.0※	$SO_2, SO_3 \rightarrow SO_4$ (SOx)	Air pollution, corrosion clogging
Red. C	4.0~11.5※	Dust	Dust, carbon adhere
Ash (Na, K, V, ----)	< 0.02※	Adherents	Scaling, Vanadium attack, corrosion, mechanical wear, etc.

※: JIS C-Heavy Oil

For the detail information, refer to the pages at P.81, 112~115 or E.58~62.

3-2-2 Oil - NOx Generation

In case of fuel oil combustion, burning is continued due to the evaporation and ignition of oil sprays near a burner. In line with the generation of fuel NOx due to oxidation of nitrogen oxides within fuel oil, high-temperature flames are formed, and the ratio of thermal NOx generation becomes high. However, because the volume of nitrogen compounds in fuel oil is smaller than in coal, the overall NOx emission volume is smaller than that during coal combustion.

NOx Generation and its Control in Oil Combustion

Generation

Thermal NOx (N in Air)
Flame temp.
O2 concentration
Retention time

Fuel NOx (N in Fuel)
O2 concentration
Nitrogen in fuel

Because NOx generation forms are different, based on the kind of fuel, it is necessary to take NOx control measures suitable for individual fuels. In case of oil-firing boilers, NOx control measures such as (1) 2-stage combustion, (2) exhaust gas recycling, (3) the use of low NOx burner and (4) expansion of furnace size (proportion of heat radiation through flames), are adopted.

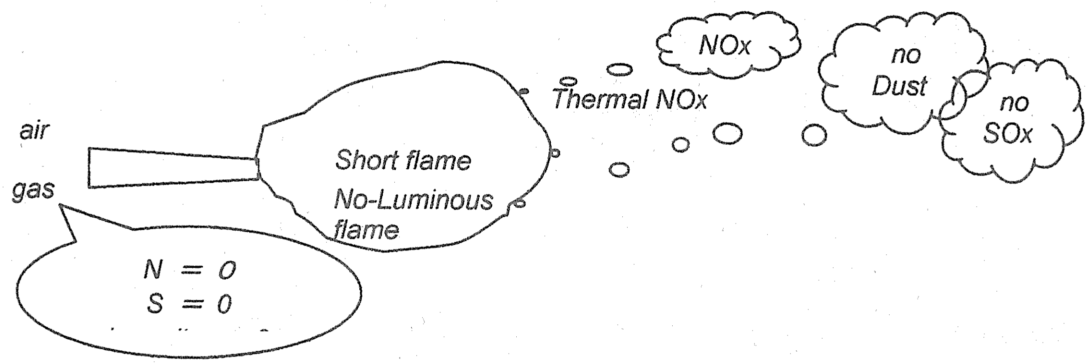
Control Measures

- *2-stage combustion*
- *Exhaust gas recycling*
- *Low NOx burner*
- *Furnace size expansion*

For the detail information, refer to the pages at P.116 or E.62~63.

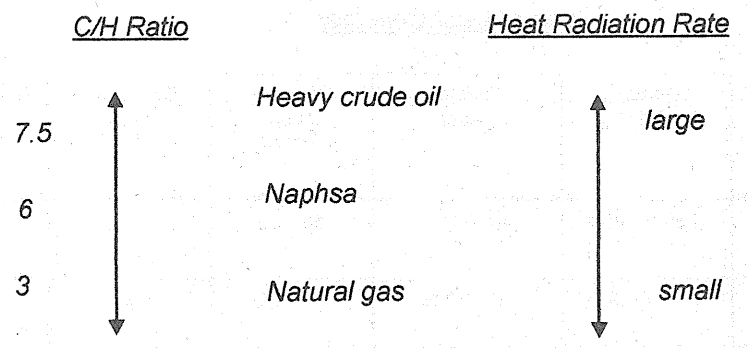
3-3 Gas
Compared with heavy oil combustion, the combustion of natural gas has the following characteristics;

Gas Combustion Mechanism



The combustion is affected through the diffusion (mixing) combustion with air, based on low-pressure fuel jetting. Because there is no spraying/evaporation process seen in heavy oil combustion, flame is short.

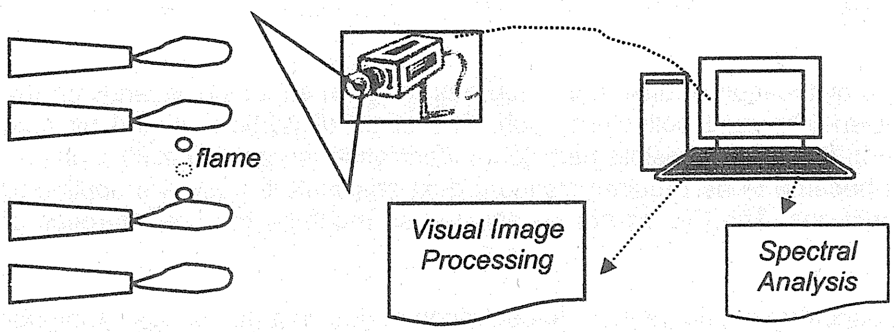
Because C/H of gas is small, no soot is generated in the process of combustion, and generally no-luminous flames are generated in the course of its combustion. Because there is no N content, S content or impurities within the fuel, the staining, wear or corrosion is little, therefore SOx and dust are not discharged.



Although this clean fuel relatively frees from the generation of air pollutants, attention is necessary because if burner design or the handling of fuel is mistaken, oscillation combustion or explosion may occur.

Control of NOx Generation + *Oscillating Combustion Preventive Measures*

It is generally known that the heat radiation ratio of flames decreases as the ratio of the carbon content to the hydrogen content (C/H) within fuel becomes smaller. C/H is 3 for normal gas, 6 for naphtha, and about 7.5 for heavy oil.



During low NOx operation, unburned portions tend to grow, or flames are liable to fill the furnace, affecting the boiler performance. As such, operation control including combustion adjustment is important. Because a thermal power generation-use boiler is equipped with many burners, it is important to adjust the air volume by means of air allocation dampers, etc. to make air ratios of individual burners as even as possible, to curb NOx by preserving the generation of unburned matter and to equalize the length of flames.

For the close combustion adjustment of individual burners, it has become difficult to operate the boiler in an appropriate manner simply through combustion adjustment, based on experience and hunch, as well as on conventional measuring gauges. The individual combustion diagnostic method, based on optoelectronics technology, has recently been developed and put into actual use.

For the detail information, refer to the pages at P.116~118 or E.63~66.

4. Dust Collector
4-1 Types of Dust Collectors
When we select the dust collectors, physical properties of particles and gases as shown in the slide should be taken into consideration;

Type of Dust Collector

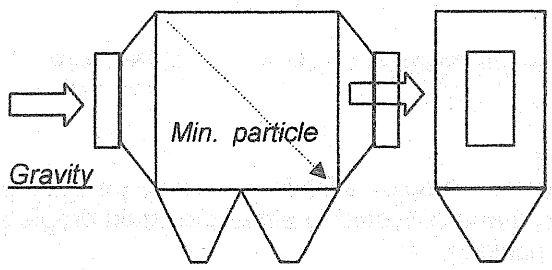
Type	Applic. Particle (μm)	Operating (℃)	Cutback Level	Pressure Drop (mm H_2O)	Equipment Cost	Running Cost
Gravity	≧50	d.p. ~ 400	40~60 %	10~15	S	S
Inertia	≧10	d.p. ~ 400	50~70 %	30~70	S	S
Centrifuge	≧3	d.p. ~ 400	10 mg/m³	50~150	M	M
Scrubbing	~0.1	no-limit	≒ 20 mg/m³	300~800	M	L
Filtration	~0.1	no-limit	5 mg/m³ or less	100~200	M	M
EP	~0.03	d.p. ~ 400	5 mg/m³ or less	10~20	L	S

The sizes and particle distribution of dust in the flue gas have an effect significantly on the particle removal efficiency in dust collectors each. The sizes of particle abated by dust collectors are shown in the table. Invisible particle concentration is said to be 20 mg/Nm³. Filter dust collectors become to be required frequent dust shakings if these are applied to high concentration dust gas. The EP will not be affected so much by the concentration of dust in flue gas.

Regarding the dust concentration, the higher concentration of dust in a gas brings the higher removal efficiency of particle removal for the gravity collector and inertial force dust collector due to the acceleration of collision between large size particles and of coagulation of fine particles. In venturi scrubber and jet scrubber, as the higher concentration of dust causes the wear at the throat part of venturi, these should be applied the gases of dust concentration 10 g/ Nm³ or less.

For the detail information, refer to the pages at P.168~169 or 185, E. 140~143, 172.

4-2 Gravitational, Inertial & Centrifugal Dust Collector
Because of the density difference between solids and gases, in laminar flow their stream lines are different if the direction of flow is changed. This fact is frequently exploited to separate solid particles from a gas stream, usually by suddenly changing the direction of flow of the gas stream.



Gravity

Dust section view

In gravity dust collector, a settling chamber reduces the velocity (normally 1~2 m/second) of the gas stream so that the particles drop out by gravity. It is a large device not often used as a final control mechanism. If it is assumed that Stokes's law applies, then the particle size which will be removed with 100% efficiency is given by the equation.

Stokes' Law

$V=(g/18\mu)(\rho 1-\rho) D^2$ (cm/s)

V: settling velocity (cm/sec)

g: gravitational acceleration (cm/s^2)

μ: gas viscosity (kg/ms)

$\rho 1$: particle density (g/cm^3)

ρ: gas density (g/cm^3)

D: particle diameter (cm)

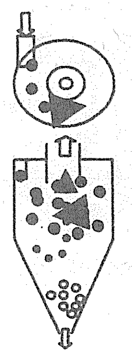
In the centrifugal force collector generally called cyclone dust separator, the centrifugal force exerted on a particle in a cyclone is given by the equation. For a large volume of gas treatment, small cyclones are connected in parallel and used as multi-cyclone. The inlet-gas velocity is set at 10 ~25 m/s.

Centrifugal force (F) = mv^2/R (N)

m: particle mass (kg)

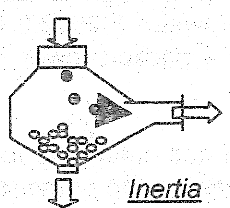
V: particle velocity (m/ s)

R: cyclone radius (m)



Inertia

In an inertial dust collector, the gas stream is forced to collide with an obstacle or the gas flow direction is sharply changed to separate and collect dust particles in gas by using inertial force.



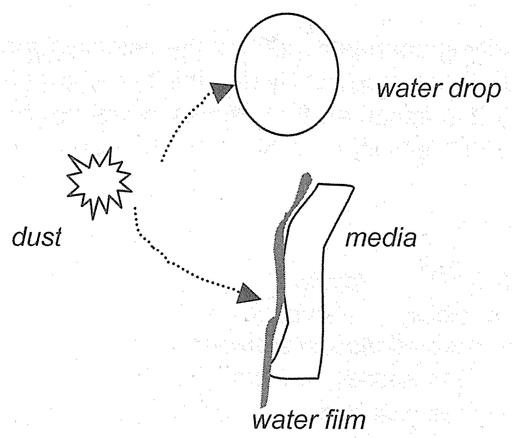
Inertia

For the detail information, refer to the pages at P.170~171 or E.144~146.

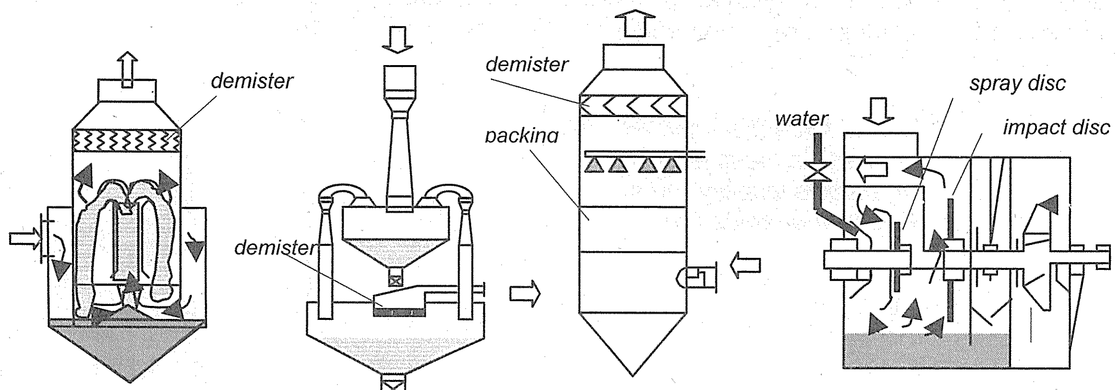
4-3 Scrubbing Dust Collector

Scrubbers, known as wet collectors, employ a liquid to remove particles from a gas stream. In use, the particles are adhered and collected to either the liquid droplets or liquid film that is poured continuously on the packing.

Principle of dust collection;



Various scrubbing dust collector systems have been developed, and can be roughly divided into reservoir type, pressurized water type, packed bed type and rotary type as shown in a slide.



Reservoir type

Pressurized water type

Packed bed type

Rotary type

The use of packing allows a smaller tower to be used but the pressure drop is higher (thereby increasing efficiency). The pressure drop through a spray tower is typically between 0.25~0.5 kPa. For the packed bed it is between 0.25~2.0 kPa. The liquid to gas ratio in a spray tower is typically 1.3~2.7 l/m^3. In a packed tower it is normally between 0.1~0.5 l/m^3.

In the packed bed type, basically, the contaminated gas enters the tower at a low level and rises due to its buoyancy. The scrubbing liquid enters the top of the tower and sprays down on top of the vertically rising dirty gas. At interception the contaminants adsorb to the falling liquid and the purified gas continues to rise and emits from the top the tower. Packing (e.g. random plastic piece) improve the adsorption efficiency. The nozzles on the spray arms atomize the liquid.

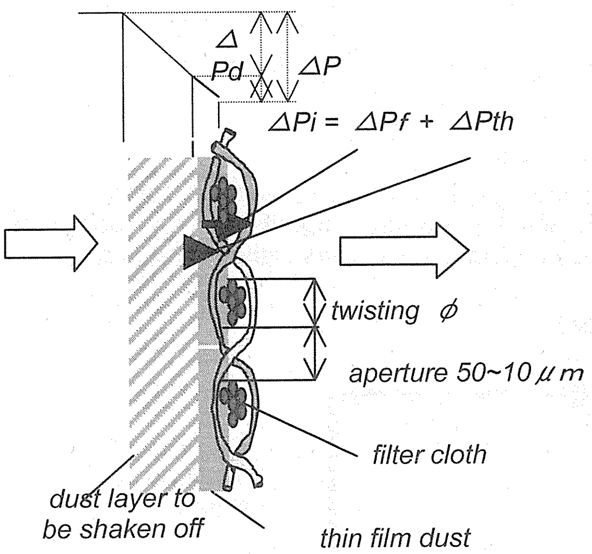
To achieve efficient performance of scrubbing dust collector, it is important to select a gas flow velocity and liquid to gas ratio suitable for the system.

For the detail information, refer to the pages at P.171 or E.147.

4-4 Filter Type Dust Separator

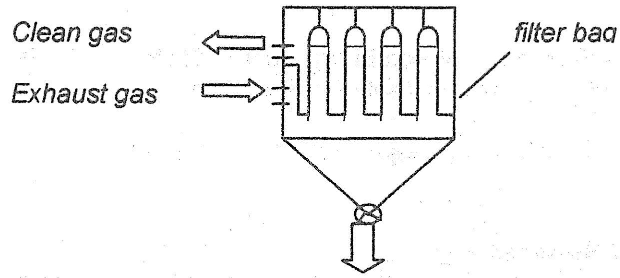
Principal types of filter type dust collectors are (1) the bag filter (2) the cartridge filter. The design of both is quite similar. However the bag filter is the more commonly used.
When gas contained dusts of certain particle sizes is passed through a filter cloth as shown in a slide, they adhere to the filter cloth, and bridges are formed between the strands of cloth. The primary adhesion layer has many fine pores, and these fine pores collect the fine dust particles.

Filtration Mechanism



Various woven fabrics made from natural fiber, synthetic fiber and glass fiber, and non-woven fabrics made from similar materials are used for filter cloth. In the operation of the bag filter type dust collector, prevention of blockage of the filter surface is important. When the pressure loss of the bag filter has reached its regulated value, it is necessary to shake dust off of the bag filter. There are 2 kind pf shake-off methods, the intermittent method and continuous method. In the intermittent method, the dust collecting chamber is partitioned into 3~4 chamber. The dampers installed on both the inlet and outlet of filter is closed and then the dust adhering to the filter cloth is shaken off. In the continuous method, the dust adhering to the filter cloth is constantly shaken off under continuous filtration. Therefore, the pressure loss will remain roughly at a fixed level, making this method suitable for the treatment of gases containing high concentrations of dust and soot and of gases containing adhesive dust and soot.

Typical bag filter unit



The apparent filtration rate (raw gas volume per effective area of filter cloth) should usually fall in the range of 0.3~10 cm /s.

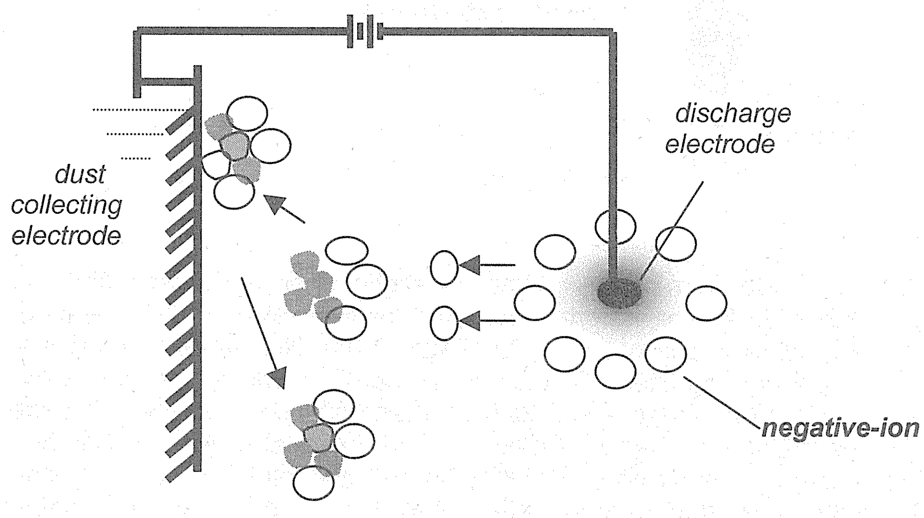
Type:	*Filter cloth:*	*Dust shake-off:*	*Apparent filtration rate:*
(1) bag filter	*(1) woven fabric*	*(1) intermittent*	*0.3~10cm/s*
(2) cartridge filter	*(2) nonwoven fabric*	*(2) continuous*	

For the detail information, refer to the pages at P.171~172 or E.147~148.

4-5-1 Electrostatic Precipitator (EP)

An EP collects dust particles in flue gas by using corona discharge to give them an electrical charge. The EP is not much affected by the properties of gas and dust, can do highly efficient dust collection, and can collect fine particles without pressure loss.

Principle of dust collection



A conductor discharge electrode is used as the negative electrode, and a dust collecting electrode is used as the positive electrode as shown in a slide; high voltage direct current electric power is used for charging. When the strength of the electric field is increased, the gas around the electrode is partially broken down, corona discharge occurs, and a negative corona and many negative ions are generated. Negative ions and free electrons move to the dust collecting electrode, and when the gas containing dust flows past the electrode, the dust particles are momentarily charged. These particles are moved by Coulomb force, and are separated and caught by the dust collecting electrode. Particles collected on the electrode are exfoliated and removed by hammering impact.

Properties of the exhaust gases from boilers are quite different depending on the properties of fuel used and combustion methods. Typical examples of the properties of exhaust gas from heavy oil fired boiler and coal fired boiler are shown in a slide.

Exhaust gas properties;

		Heavy oil	*Coal*
inlet soot & dust	*g/Nm³*	*0.05~0.15*	*10~20*
dust ϕ	*μm*	*1~3*	*20~30*
SiO_2	*Wt %*	*15~20*	*60~75*
C	*Wt %*	*50~60*	*0.4~0.8*
ρ Rate	*Ω·cm*	*10^4~10^6*	*10^{11}~10^{13}*
apparent S.G.	*g/ml*	*0.1~0.2*	*0.6~0.8*

A ρ rate and apparent S.G. are short form of electrical resistance rate and apparent specific gravity respectively. Regarding an influence on dust collection, in case of oil firing boiler, SO_3 mist causes flue, dust collector and chimney corrosion. SO_3 also combine with dust and becomes acid smut, which is discharged from the stack.

As measure to prevent this, NH_3 is injected into the exhaust gas to neutralize SO_3.

Influence on dust collection		*Improving method*
·SO_3 mist	⇒	*·NH_3 injection*

In case of coal firing boiler, composition and physical properties of fly-ash vary depending on coal fields of coal and combustion conditions. An EP' s dust collecting performance varies drastically depending on the electric resistance and particle size of fly-ash. Electric resistance differs according to the (1) exhaust gas temperature, (2) moisture content, (3) SO_3 concentration, (4) properties of coal and composition of dust components.

Influence on dust collection	*Improving method*
·temperature	*·tempering flue gas*
·water	*·electric charge control*
·SO_3 mist	*·dust removal on (+) electrode*
·composition of dust	*·selection of gas temp.*

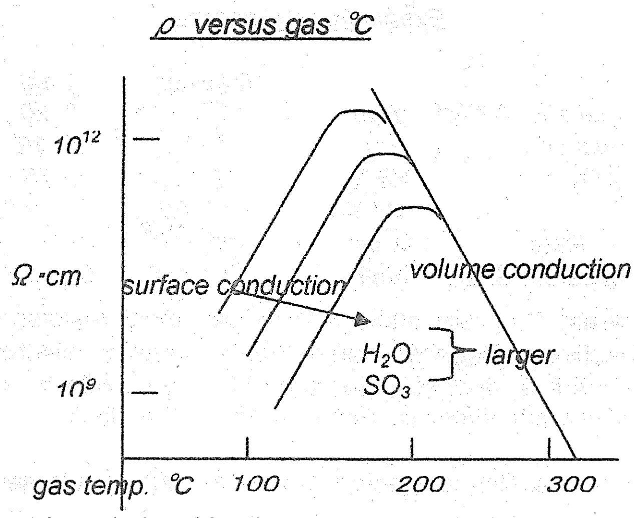
To improve the performance, apparent electrical resistance is controlled at range of between 10^4 and 10^{11} Ω-cm by the methods such as tempering of exhaust gas, electric charge control, etc. However, a manufacturer of EP takes the properties of particles into consideration actually and designs the EP to meet the individual particle peculiarities. Therefore these adjustments are only adopted for emergency measures.

The relationships between the electric resistance of dust and dust collecting performance are shown in a next slide.

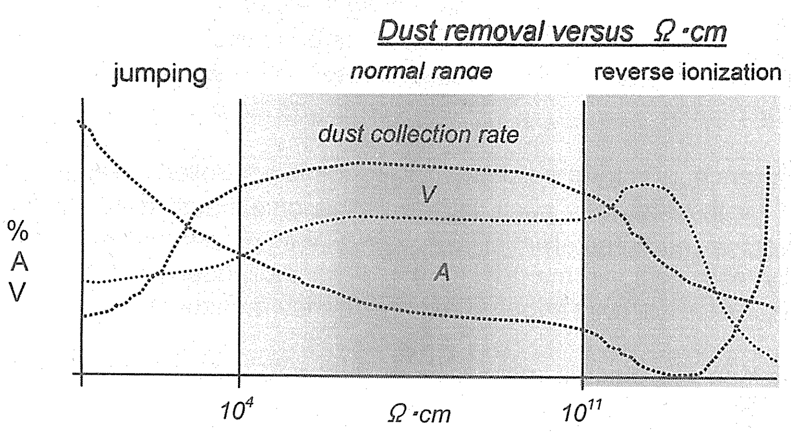
For the detail information, refer to the pages at P.173~179 orE.150~161.

4-5-2 Factors working on Electrostatic Precipitator

The left side figure shows the relationship between the gas temperature and the electric resistance of dust, which generally shows its highest value at the range between 120 and 180℃. This comes from the differences between the way of electric current flows through dust particles in the low temperature range and in the high temperature range. Moisture content and SO_3 in exhaust gas adhere to dust particles in the low temperature range, so electric current can easily flow along the surface of dust particles. On the other hand, in the high temperature range, electric current flow through the inside of dust particles becomes domain. This is affected by the quantity of alkaline metals (Na, K) in the dust.



A right side slide shows the relationships between the electric resistance of dust and dust collecting performance, the characteristics of charged voltage and current in an EP. In the range of 10^4 Ω-cm or less (jumping range), when electrically charged dust adheres to the dust collecting electrode, dust immediately losses its negative electric charge, so dust collecting efficiency decreases. In the range between 10^4 and 10^{11} Ω-cm, ideal dust collection is done. Dust with electric resistance of over 10^{11} Ω-cm (reverse ionization range), electrical neutralization of the negatively-charged dust adhered to the dust collecting electrode becomes slow. Therefore, electric charges accumulate on the surface of the dust, and the strength of electric field inside the dust layer become high, and it causes dielectric breakdown inside the dust layer, and the dust collection efficiency will remarkably decrease.



The disadvantages and disadvantages of an EP are shown in the table.

Advantages and disadvantages of EP

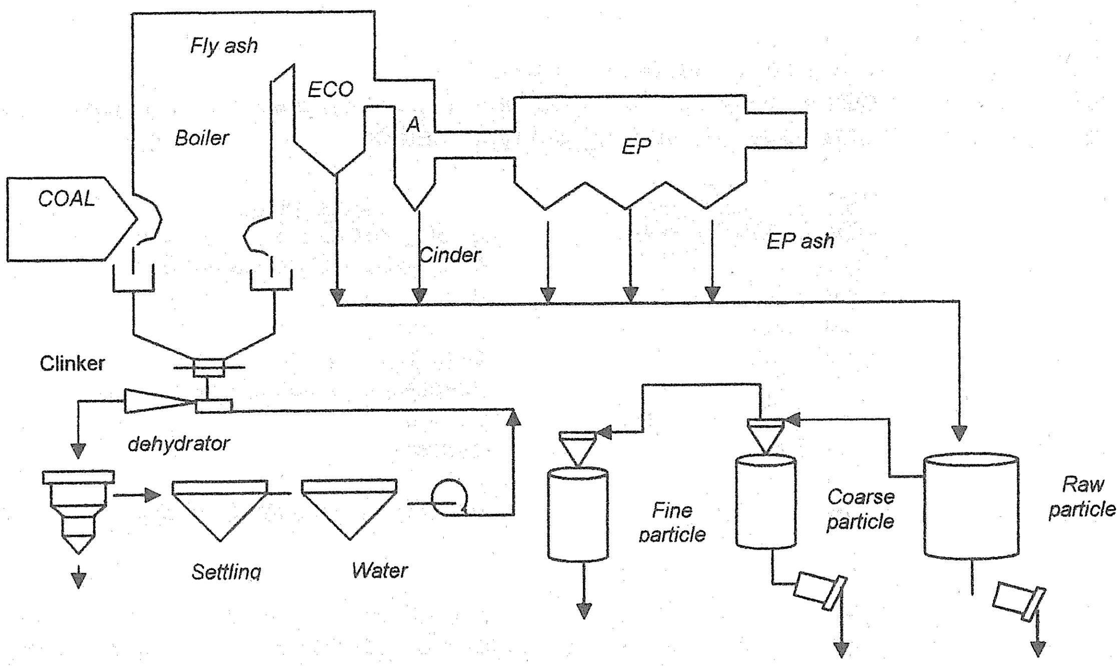
Advantages	Disadvantages
large gas volume	*initial cost – expensive*
fine particles of submicron	*affection of apparent* ρ *(Ω-Cm)*
high temperature gas	*system size- large*
wet type dust collection	*high level accuracy in manufacturing*
suitable operation	
inexpensive maintenance	

For the detail information, refer to the pages at P.176~179 or E.155~161.

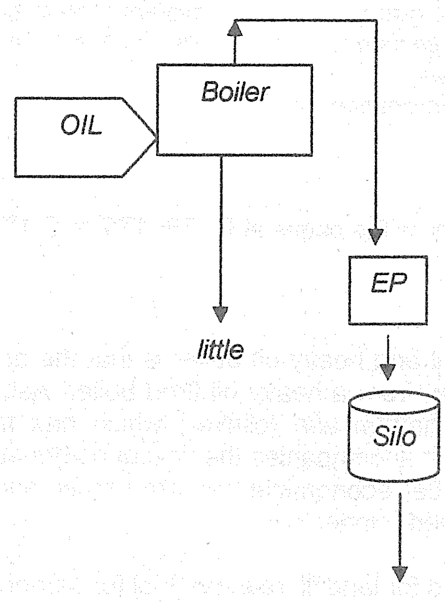
4-6 Ash Treatment

One difference between coal and heavy oil boiler is that the ash volume generated in coal fire boiler is greater than that from a heavy oil fired boiler. Ash discharged from a boiler is roughly classified into the bottom ash (clinker) which has fallen down underneath the furnace, and the fly ash which accompanies the flow of combustion gas, then falls down and collected or stored in the fuel economizer, air pre-heater and EP (ash discharged from former two are generally called "cinder").

Coal ash is effectively utilized for landfill, raw material for cement, fly ash cement, aggregate, civil engineering, architectural material, fishery and agriculture industries , desulphurizing agent, etc.



In case of oil fired boiler, the volume of ash collected and discharged is less than that from a coal fired boiler, and the properties of ash are roughly fixed in accordance with the variety of heavy oil. Also, almost all the ash is collected by the EP. Therefore, the structure of the ash disposal equipment is relatively simple, and ash is transferred from each hopper of EP to the storage silo using the pressure transfer or vacuum transfer method. Ash discharged from oil fired power station contains unburned combustibles and heavy metals, so that almost of this ash is effectively utilized as an alternative fuel for cement manufacturing or as the raw material for the recovery of valuable materials.



For the detail information, refer to the pages at P.179~184 or E.161~170.

5. Flue Gas Desulphurization

5-1 Flue Gas Desulphurization Methods (FGD)

Flue gas desulphurization systems are divided into (1) wet type and (2) dry type; most power generation plants have adopted the wet type method.

Method	Absorbent/ Adsorbent	Byproducts
	$NaOH$ or Na_2SO_3 solution	*Na_2SO_3, $NaNO_3$, SO_2, gypsum*
	NH_3-water	*$(NH_4)_2SO_4$, SO_2, gypsum, S*
	Slaked lime or limestone slurry	*gypsum*
Wet type	*$Mg(OH)_2$-slurry*	*SO_2, gypsum (blended with slaked lime slurry)*
	Basic $Al_2(SO_4)_3$-solution	*gypsum*
	Dilute-H_2SO_4	*gypsum*
Dry type	*Activated carbon*	*$(NH_4)_2SO_4$, gypsum, S, H_2SO_4*

The wet type has become the main stream flue gas desulphurization method. The absorbent for the wet type method, a solution or slurry containing a compound such as a sodium, calcium or magnesium compound which reacts with SO_2 is used. The wet type method is often classified according to the variety of absorbent as shown in a slide. At present, the method called the “lime and gypsum method” , using limestone slurry as the absorbent and recovering gypsum, has been adopted in most power generation plants in Japan because limestone is relatively cheap, the economy of the construction cost and operation cost of the wet type flue gas desulphurization system is good, the stability and safety of system operation are excellent, and gypsum can be sold steadily.

·limestone ⇒ cheap
·initial & operating cost ⇒ economics
·system ⇒ stability & safety
·gypsum ⇒ stable sales

} *reasons of most popularly used*

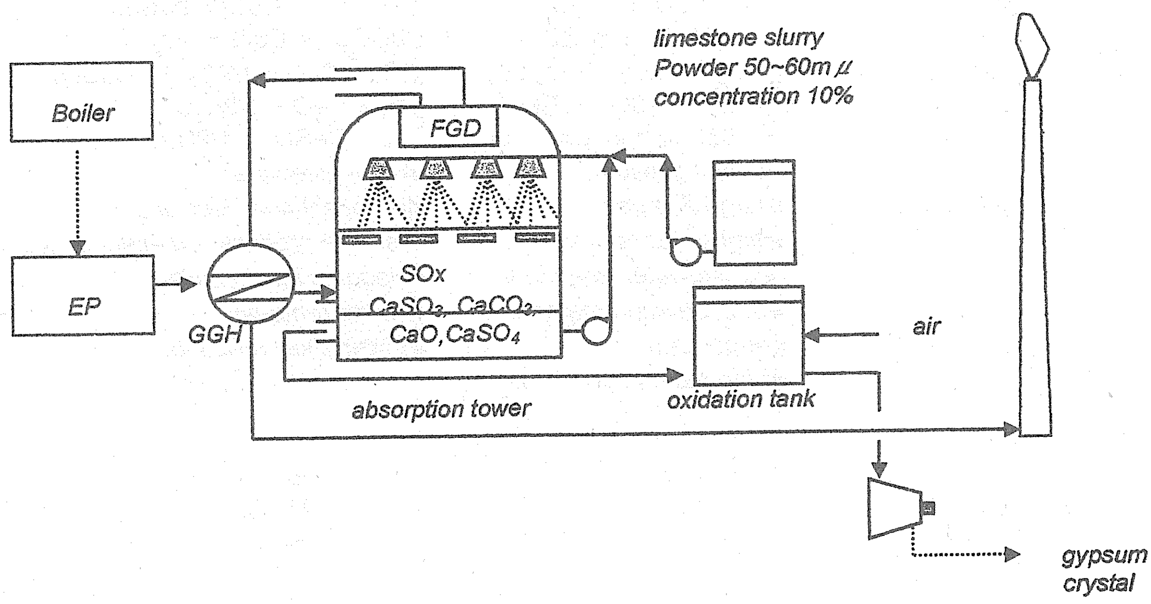
In contrast, the dry type has problems with the safety and deterioration of the absorbent itself, worsening of recycling and recovery rates, generation of effluent, and clogging of equipment accompanying the handling of dry dust, as well as reasons related to the difficulties of maintaining safety, the storage and sales of by-products, and consideration of the safety of long-term continuous operation.

For the detail information, refer to the pages at P.186 or E.175

5-2 Wet Type Lime & Gypsum Method FGD System

Flue gas from the boiler is led to the electrostatic precipitator (EP) to remove soot and dust. Poor performance by the dust collector causes clogging of the gas- gas heater (GGH) and increased leakage of soot and dust, etc. When a large amount of soot and dust collected by the flue gas desulphurization (FGD) system, this causes various mechanical problems and lowers the quality of gypsum, and/or decreases the activity of the absorbent; therefore, it is desirable to install a dust collector which has the highest possible performance.

The GGH is constituted from the recovery side which recovers heat from the gas at the outlet of the dust collector, and the reheating side which increases the gas temperature at the stack inlet by providing the recovered heat.



In the absorption tower, a slurry-like absorption liquid containing limestone powder with particle sizes of around 50~60 microns is circulated in the absorption tower, and when this liquid and flue gas have come into efficient contact, SO_2 in the gas is taken into the liquid and removed. Sulfur dioxide (SO_2) combines with lime (CaO) and changes to calcium sulfite ($CaSO_3$). Part of CaSO3 is naturally oxidized by the oxygen in the flue gas inside the absorption tower, and becomes gypsum ($CaSO_4$), but the rest of the $CaSO_3$ is forcibly oxidized by the air in the oxidation tank.

Reaction Mechanism

$SO_2 + CaO \rightarrow CaSO_3$

$2CaSO_3 + O2 \rightarrow 2CaSO_4$

$CaCO_3 + SO2 \rightarrow CaSO_3 + CO_2$

Gypsum slurry is dehydrated using a dehydrator and taken out as gypsum crystal with a moisture content of 10% or less.

For the detail information, refer to the pages at P.190~192 or E.181~184.

5-3 Simplified FGD System

The wet type lime and gypsum method flue gas desulphurization system consists of three stages of absorption reaction, oxidation reaction, and neutralization reaction as shown in equations from the top in order in a table. This system has the distinctive features previously mentioned, but is expensive to construct. Therefore, the simplified flue gas desulphurization system has been developed and adopted in developing countries.

Comparison of Simplified FGD with Conventional FGD

	Lime & Gypsum Method	Simplified FGD Semi-dry Method Intrafurnace Desulphurization + Water Spray Method
Alkali	$CaCO_3$ powder	$CaCO_3$ powder
Reaction	$SO_2 + H_2O \rightarrow H_2SO_4$ $H_2SO_3 + 1/2O_2 \rightarrow H_2SO_4$ $CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 + 2H_2O + CO_2$	$CaCO_3 \rightarrow CaO + CO_2$ $SO_2 + CaO + 1/2O_2 \rightarrow CaSO_4$ $SO_2 + CaO + 1/2H_2O \rightarrow CaSO_3 + 1/2H_2O$
Advantages	☆useful gypsum ☆large flue gas ☆high-level removal	☆no wastewater ☆compact size, less space ☆simple process, excellent in economics
Disadvantages	★wastewater treatment ★anticorrosion material ★large area ★high maintenance cost	★slagging inside boiler ★lower removal ★lower alkali utilization
Cost		
Equipment	100	20~30
Operation	100	75~80

In simplified FGD, the lime stone powder (CaO) and water are directly injected into the furnace. In a furnace, desulphurization reactions are divided into first FGD of first two equations and 2nd FGD of third equation as shown in a table. The advantages and disadvantages of both methods are summarized in a table by comparison.

The cost reduction of simplified flue gas desulphurization (FGD) system was achieved on the basis of general procedures for curtailing of the construction cost of the system; (1) curtailing of engineering time, (2) making the equipment and machines constituting the system compact, (3)studying the material qualities for equipment and machines, (4) simplification of process, and (5)simplification of equipment, machinery and facility used for the process, by simplification of control method, but care taken by the user's side is also very important.

For the detail information, refer to the pages at P.188~189 or E.178~179.

6. Flue Gas Denitrification

6-1 NOx Abatement Method

The term of NOx implied two major oxides, nitrogen oxide (NO) and nitrogen dioxide (NO_2). In Combustion, NO is the dominant of the two, NO_2 mainly a downstream derivative of NO. There are two main mechanisms of NOx production from combustion process; (1) from the reaction of N_2 in the air with oxygen at the high temperature of the burner chamber, known as thermal NOx, (2) from the nitrogen existing in the fuel with oxygen at high temperature, known as fuel NOx.

Typical efficiencies and the applicability of the various methods of NOx reduction are shown in a table at the top of the slide (quoted from Environmental Engineering, P.777, McGraw-Hill, 1998). Three methods from the top depend on the adoption of innovative design to reduce NOx generation, and latter two are processes selectively used in the industry to remove generated NOx. Recirculation of flue gas acts by reducing the peak flame temperature and the quantity of oxygen present to minimizing NOx formation. In low NOx burner, the burner designed to fire fuel at low excess air. Staged combustion can be used to reduce the peak temperature. Up to three stages can be used, but this requires very tight control over both the fuel and air flow rates to each stage.

Reduction of NOx Generation & Denitrification Methods

Method	*Applicability*	*NOx red. (%)*
Flue gas recirculation	*T-NOx*	*70~80*
Low NOx burner	*F-NOx, T-NOx*	*10~25*
Staged burners	*F-NOx, T-NOx*	*40~70*
SCR	*F-NOx, T-NOx*	*80~90*
SNCR	*F-NOx, T-NOx*	*60~80*

Remarks; T-NOx: Thermal NOx, F-NOx: Fuel NOx

In a lower table, major flue gas denitrification processes are shown. SCR is a simple process for decomposing NOx into N_2 and H_2O, by passing the flue gas with ammonia (NH_3) in the flue gas, through the catalyst layer. This process is suitable for treating large volumes of exhaust gas. SNCR does denitrification without using a catalyst, by injecting ammonia in the high temperature range of about 800~1,000℃. The denitrification rate of this process is low compared to SCR. NSCR does the catalytic reduction of NOx using a noble metal such as platinum (Pt) as the catalyst and CH_4, CO or H_2 as the reducing agent. This process is hard to apply for a large volume of boiler exhaust gas with low concentration of NOx.

Catalytic cracking process, using noble metal at about 450℃, and other processes such as absorption process and adsorption process, has not reached the level of practical use. Wet process are complicated and have a problem of wastewater treatment, so no actual system has been adopted by normal power generation plant.

Denitrification Process

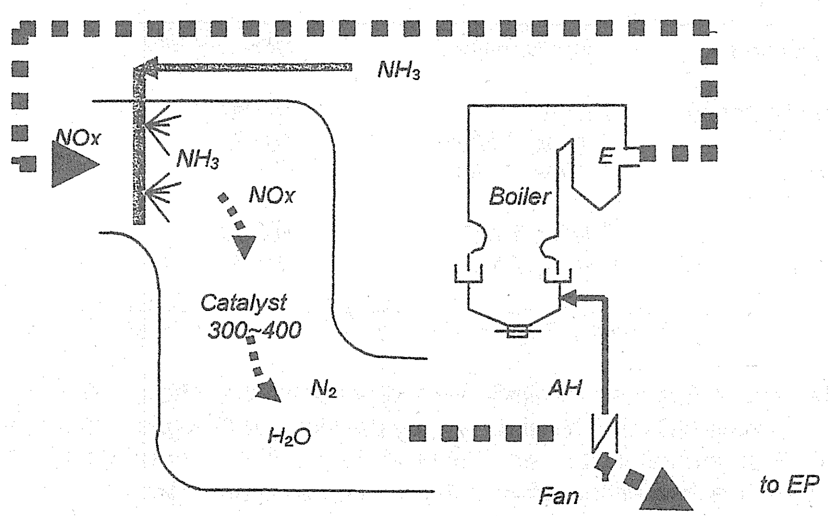
Process	*Method*
Dry Process	
SCR (Selective catalytic reduction)	*NH_3, catalyst*
SNCR (Selective non-catalytic reduction)	*NH_3, Gas temp. 800~ 1,000℃*
NSCR (Non-selective catalytic reduction)	*catalyst (Pt) + CH_4, or CO, or H_2*
Catalytic cracking	*catalyst (Pt, ・・・・)*
Wet Process	*NOx + SOx removal*
	Complicate process
	wastewater treatment

For the detail information, refer to the pages at P.200~201 or E.196~197.

6-2 NH_3 Catalytic Reduction Process

In this process, after ammonia (NH_3) is injected into the flue gas, and this admixture is passed through the catalyst layer, NOx decomposes into N_2 and H_2O as shown in a slide. Ammonia gasified in the carburetor goes through the accumulator and is diluted by some of the air provided by the forced draft fan for boiler, then injected into the exhaust gas from the ammonia injection nozzle. The optimum temperature range for these reactions is 300 ~400℃, equivalent to the gas temperature at the outlet of the boiler economizer (EC). Followings are the features of this process; (1) simple process, easy operation, few troubles and highly reliability, (2) no-wastewater generation and no need of reheating of exhaust gas, (3) high rate of denitrification, (4) no by-product.

SCR Process : Ammonia Catalytic Reduction Process



Reaction

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$2NO_2 + 4NH_3 + O2 \rightarrow 3N_2 + 6H_2O$

Catalyst

support: ceramic (Ti, Al, ・・・)
catalyst: metals
shape: granule, grid-form
honeycomb, plate
control: denirification rate
catalvst bed draft loss

Several kinds of catalysts are in practical use. These mainly use porous ceramic such as titanium or aluminum ceramic as the support, and any of several kinds of metal oxides which are the active components of the catalyst are held by this support in form of granulated, grid-form, honeycomb, or plate. The control of catalyst is done by investigation of changes in the catalyst with elapsed time, record the denitrification rate and operation data including catalyst bed draft loss under the fixed condition.

For the detail information, refer to the pages at P.202~206 or E.199~206.

7. Stack

The objectives for the stack of thermal power generation plant are to lead the exhaust gas generated from the combustion of fuel in the boiler up to the height at which the exhaust gas does not influence the equipment or animals and plants in the surrounding area, and also to diffuse the exhaust gas into the air.

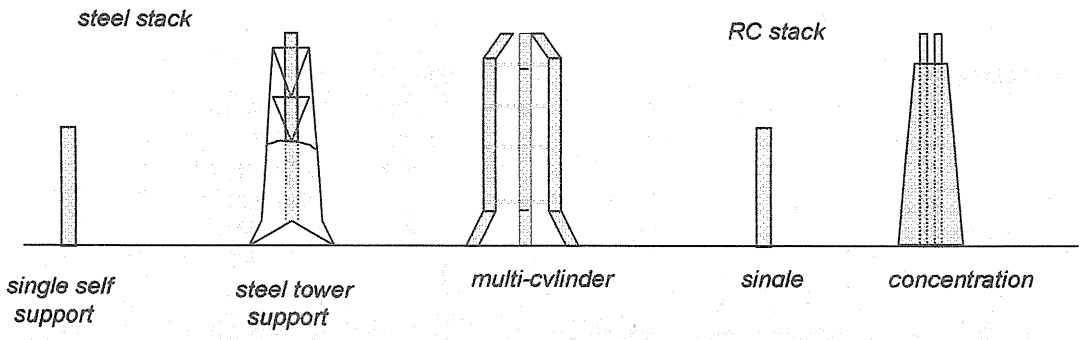
The draft force of a stack can be calculated by subtracting the friction resistance of the flue gas passage section from the sum of the draft forces of the blower and the stack itself. The equation expressed in a slide is generally used for the calculation of relationship between draft force and stack height. Stack height can be determined from this equation. However, it is necessary to increase the stack height in consideration of the flue gas diffusion surface and the height of structures in the surrounding area.

Stack height & Draft force

$$(\gamma a - \gamma g)H_0 + Peb \geqq Vg^2/2g \cdot \gamma g + \Sigma\Delta h > 0$$

$(\gamma a - \gamma g)H_0$: *theoretical draft force* (kg/m^2)
γa: *air specific weight at atmosphere temp.* (kg/m^3)
γg: *exhaust gas* 〃
H_0: *stack height from datum level* (m)
Peb: effective blower pressure (kg/m^2)
Vg: exhaust gas outlet velocity (m/s)
g: gravitational acceleration (m/s^2)
$\Sigma\Delta h$: *total pressure loss in exhaust gas route* = $\alpha \cdot V2/2g \cdot \gamma g$ (kg/m^2)
α: *resistance coefficient*
V: flue gas velocity in route (m/s)

Selection of smokestack type must involve consideration of its structural aspects and harmony of the stack with the surrounding environment in the aspect of scenic view.



The combustion exhaust gas from thermal power plant contains various corrosion products, depending on the fuel used for the boilers. Therefore, the lining must be chosen from physically and chemically stabilized materials, with consideration of the composition, temperature, and flow velocity of exhaust gas, operating conditions of the boiler and the flue gas desulphurization system.

For the detail information, refer to the pages at P.207 or E.208.

8. Environmental Management System

1.In EMS, trend of environmental management: Under worsening of global environmental circumstances, "sustainable development" was agreed on in the United Nations Conference on Environment and Development held in 1992. Based on this, International Organization for Standardization (ISO) has set the international standard of "environmental management / audit (ISO 14000)" in 1996. This is that a company sets a basic policy and a goal for its environmental problems based on the environmental influence caused by its business activities and the legal regulations. The company makes, executes, corrects and audits the system, rules and manuals in order to attain the goal. Such process is repeated so that the system is continuously improved. This cycle is called as PDCA cycle (Plan-Do-Check-Action). The ISO 14000 requires forming the appropriate organization, its duty and controlling system to establish and promote the pollution control.

1. Environmental Management System
- *Trend of environmental management*
- *Organization for environmental management & control*
- *Mission*
- *Pollution control system*

ISO 14000

2. In Cooperation with local government: Cooperation with the local governments is indispensable. This includes such cooperation as installing telemeters for measured data of pollutants and taking preventive measures for emergency. The enterprises must try not only to observe pollution control laws but also to prevent pollution and protect environment positively.

2. Cooperation with Local Government
- *Cooperation in pollution control measures*
- *Handling of complaints*
- *Environmental protection agreement*

3. Data disclosing: The enterprises must report the measurement result of emission concentration and action taken at the accident to the local governments in compliance with the law. On top these, enterprises are required to disclose these results and implementation of pollution measures publicly based on the environmental accountability.

3. Data disclosing

4. Education and Training: The enterprises are required to educate their employees on pollution and environmental problems.

4. Education and Training of Employees

5. Monitoring: The enterprises must observe the emission standard of atmospheric pollutants set by laws. For this purpose, it is necessary to measure, monitor and record regularly the emission concentration of pollutants such as SO_2 in the flue gas.

5. Monitoring

6. Greening of power plant: In Japan, by Factory Location Law, it is obliged to secure 20% or more of the site area for green space in newly constructed power stations.

6. Greening of Power Station

7. Measures against accident and emergency: The director of the power station is required to coordinate with superior, to make manuals and to implement the employees' training always so as to take smooth action immediately to respond to the request from the local government.

7. Measures against Accident and Emergency
- Accident
- Emergency

For the detail information, refer to the pages at P.254~259 or E.281~288.

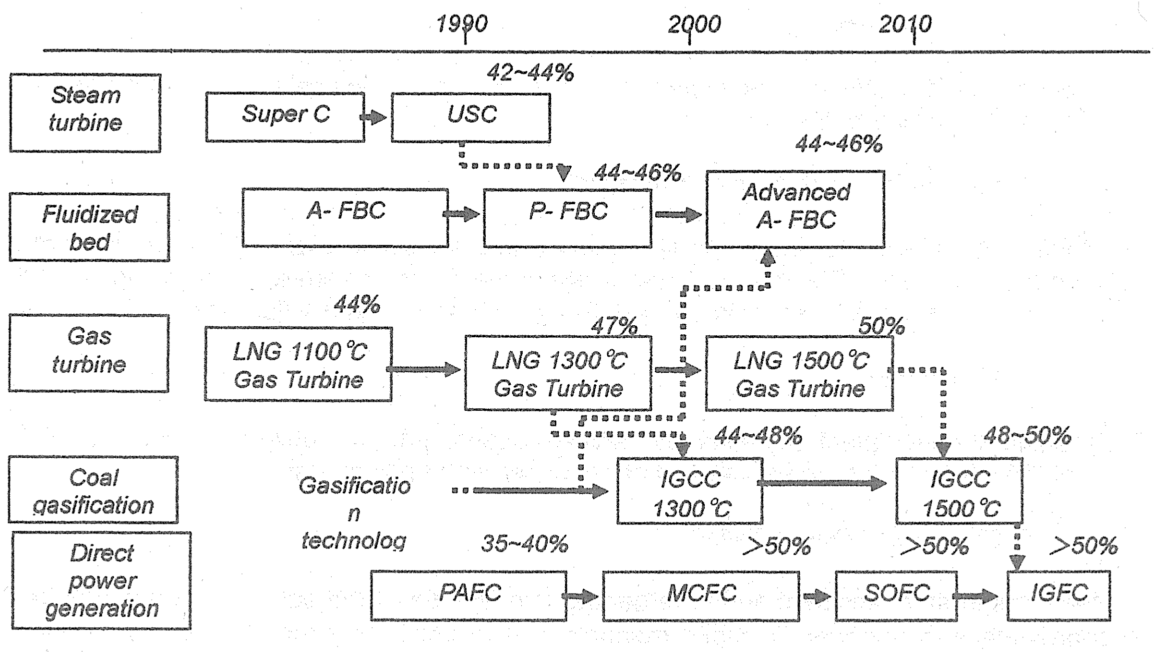
9. Energy Saving

The energy saving in electric power generation is as much as the decreasing of pollution load. It is necessary to promote the development of technology to achieving high efficiency and solve the difficult problems of coal-fired power plants.

Efficiency improvement
= Energy saving
= Pollution decreasing

The high-efficiency power generation technologies and systems over the time series are shown in a slide.

In pulverized coal fired power plants, steam turbine of ultra supercritical 2-stage reheating cycle power generation system (USC) with the efficiency of 42~44%, fluidized bed combustion of atmospheric pressure fluidized bed combustion (A-FBC) and pressurized fluidized bed combustion (P-FBC) have been adopted. In coal gasification, integrated coal gasification combined cycle (IGCC) power generation method become to be adopted with high efficiency of 47%. In gas turbines used for LNG fired boiler, the turbine driven at high temperature of 1,500℃ with high efficiency of 50% is under developing.



In direct power generation, phosphoric acid fuel cell (PAFC) is reaching at the stage of trial applications of 50~500 kW for public facilities, hotels, etc with co-generation system. Melted carbonate fuel cell (MCFC) is under 3rd stage development wit capacity of 300 kw. Solid electrolyte fuel cell (SOFC) and gasification fuel cell (IGFC) are under developing.

For the detail information, refer to the pages at P.147~167 or E.109~139.

Ⅱ.Glass Manufacturing Industry

1. Glass Manufacturing Process and Air Pollutants

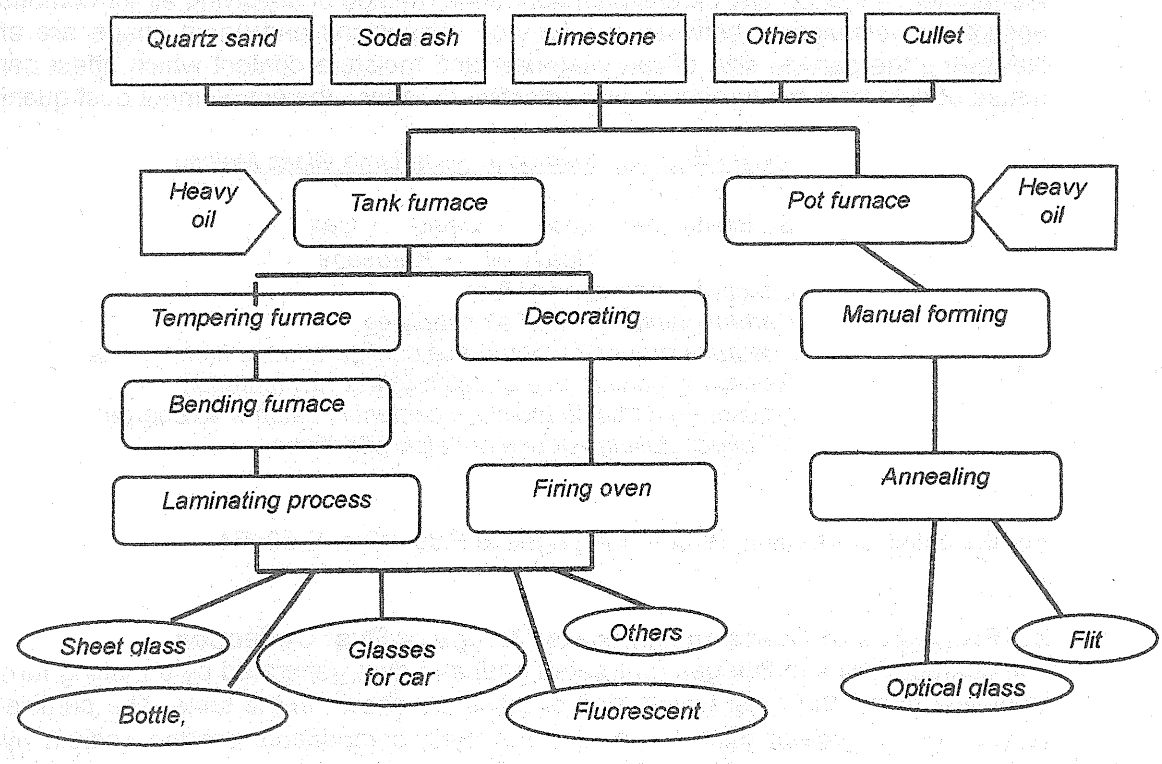
Classifying glass products of according to their composition, the soda-lime glass called "ordinary glass" is the type most generally used. Other than this, special-composition glasses are classified into borosilicate glass (hard glass), lead glass, and alkali-free glass. The main raw materials of glasses are silica (SiO_2), alumina (Al_2O_3), boric acid (B_2O_3)phosphoric acid (P_2O_5), soda (Na_2O), potash (K_2O), lime (CaO), magnesia (MgO), barium oxide (BaO), lead oxide (PbO),zinc oxide (ZnO),etc.

In glass manufacturing process, first raw materials are finely crushed to particle size needed in order to melt glass eventually at high temperature. The crushed materials are melted at very high temperature (melting process) and homogenized (refining process) to remove impurities and bubbles generated in the melted glass.

Glass production methods are classified to 2 combinations of melting and forming;

(1) continuous tank-furnace melting + machine forming, which is suitable for mass production of a few various of product

(2) round pot furnace melting + manual forming, which is suitable for producing small quantities of multiple various of products.



The air pollutants are (1) dust which is generated from crushed materials during the handling, and (2) SOx, NOx and toxic materials which are contained in flue gas from furnace.

For the detail information, refer to the pages at P.3~13 or E.4~18.

2. Soot & Dust Reduction

2-1 Reduction by means of Fuel and Furnace Operation

The dust is generated from combustion of fuel and decomposition of raw materials containing some toxic materials. The particles with 10 ~ 100 μm of large diameter which are scattered from the work processes for storing, mixing, conveying and charging are usually handled separately from the soot and dust in flue gas.

The soot and dust from soda-lime glass melting furnaces consist of (1) the soot generated accompanying the combustion of fuel, (2) ash content, and heavy metals contained in the fuel, (3) scattered substances which are the carry-over from glass materials from the furnace, and (4) fume, which are aggregated evaporated substances.

Causes of Dust

- *Fuel → Dust (soot, ash, heavy metal)*
- *Raw Material → Scattered substances (ash, heavy metal)*
- *Non-uniform mixing fuel and air*

The most easy reduction methods of soot and dust are to change the fuel from solid to gas or from heavy oil to kerosene. Other than these fuels switching, the improvement of furnace operation is practical to deter the generation of dust. For examples, such as (1) effective atomization of fuel (2) pay careful attention to the method of supplying air for combustion (3) ensure the relationship between the furnace dimensions and flame shape are effective. Reviewing the particle size of raw materials and moisture content which affect carry-over nature of dust from the furnace is also effective to reduce the entrainment dust quantities.

Dust Reduction Method in Soda-Lime Glass Melting

- *Switching fuel; Solid → Liquid → Gas*
  Heavy oil → Kerosene
- *Effective atomization of fuel*
- *Careful manipulation of air supplying*
- *Adequate proportion of furnace configuration to flame shape*
- *Reviewing particle size of batch (glass raw material)*
- *Adjustment of batch moisture content in batch wise charge*
- *No direct striking surface of batch with flame*

For the detail information, refer to the pages at P.38~39 or E.53~54.

2-2 Properties of Dust and Applicable Scope of Dust Collection

The characteristics of flue gas (untreated gas) and dust generated by a melting furnace for soda-lime glass, the most typical kind of glass are shown in the table. The particle size is very small, no greater than 1 μm and the main components are the sodium hydrogen sulfate ($NaHSO_4$) and sodium sulfate (Na_2SO_4).

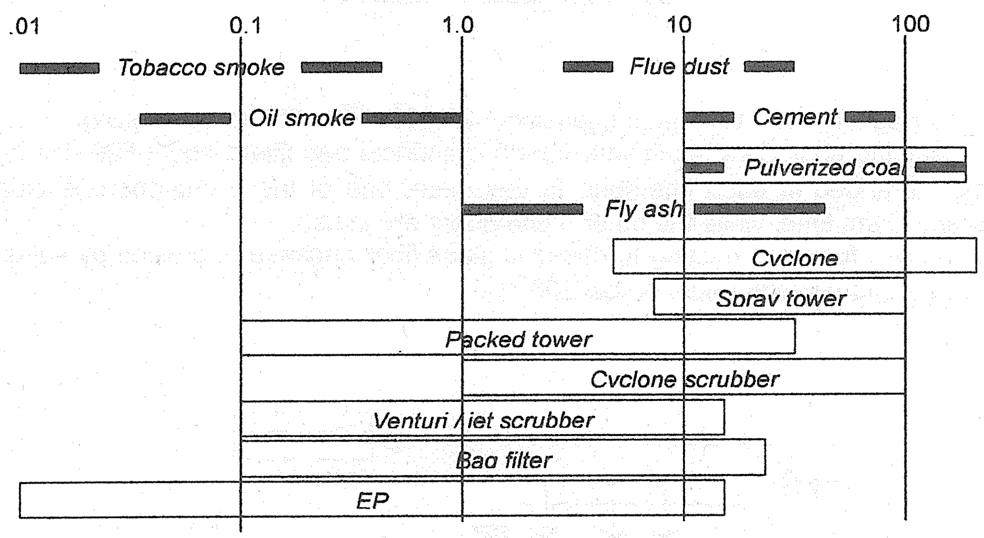
The particle sizes of various dusts and mists, and typical examples of dust collectors applied to them are shown in the figure.

Soda-Lime Glass Melting Furnace Flue Gas

Flue gas (400~600℃)		Dust		
O_2	8~9%	Dust conc.	0.2~0.4 g/Nm3	
CO_2	10%	Particle size	~ 0.5 μm	25%
H_2O	10%		0.5~ 0.3 μm	50%
SOx	500~1,500ppm		0.3~0.1 μm	20%
NOx	400~600ppm		0.1 μm ~	5%

Gravitational dust collectors, inertial dust collectors and centrifugal dust collectors are not suitable for collecting dust with small particle size 1 μm or less, as shown in a figure, and are not used to collect flue gas dust from glass melting furnaces.

Dust Collection



They are most commonly used in glass manufacturing plant to collect raw material particles generated in the processes of storing, mixing and charging of raw materials. Scrubbing dust collectors use large quantity of water and need periodical maintenance; therefore they are not suitable for glass melting furnaces, for which large quantities of flue gas must be continuously treated for long period of time. Therefore, filter dust collectors or electrostatic precipitators are generally used for large tank furnaces.

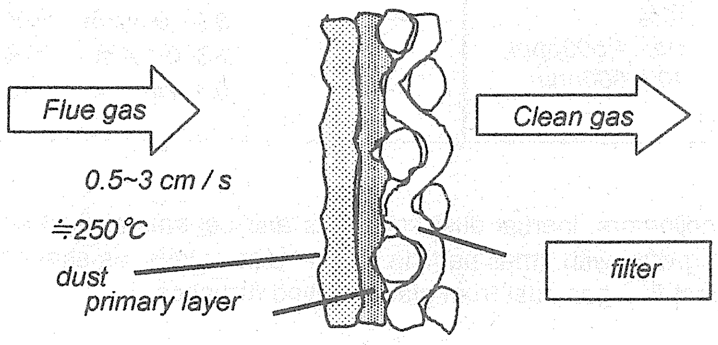
For the detail information, refer to the pages at P.38~41 or E.53~57.

2-3 Filter Dust Collector

Bag filter dust collectors have the widest usage range in all dust collectors. Bag filters can collect fine particles even 0.1 μm in size. When a bag filter is used for the treatment of flue gas from a glass melting furnace, a high dust-collection efficiency rate of 97~99% can be obtained.

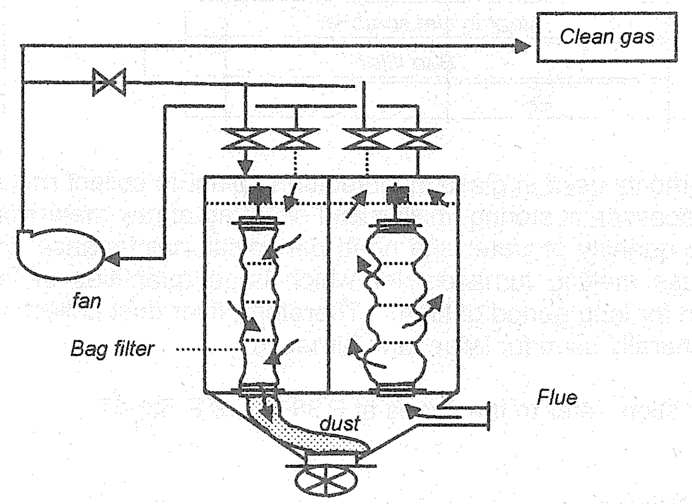
The dust collector mechanism is that the primary layer, which particles have adhered on the surface of the filter cloth, is used as the filtration layer to collect fine particles. The flow rate through the filter is usually around 0.5~3 cm/s. Therefore, when treating a large volume of gas, the dust collector equipment has multiple dust collecting chambers with many bag filters arrangement in parallel.

Filtration Action in Filter Cloth



ΔP≒150 mg Hg → dusting

For example, a bag filter with treatment capacity of 35,000 m^3/h (250℃) for melting furnace has 6 dust collecting chambers, each with 50~60 cylindrical bag filters about 600 cm long and 30 cmϕ, arranged in each chamber. In this case, one of the 6 chambers is being scrubbed at any given time, while the other 5 chambers are in use.
The filter cloth used for glass melting furnaces is glass fiber because of erosion by sulfuric acid due to dew condensation under below 200 ℃.



When the pressure loss has reached about 150 mm Hg after accumulation of dust on the filter, dusting is needed. The dusting method can be either intermittent, most commonly used for glass melting furnaces, or continuous. Dust removal can be done by a method using vibration or a method using reversed air.

Dusting frequency	*Dusting drive*
- intermittent	*- vibration*
- continuous	*- reverse air*

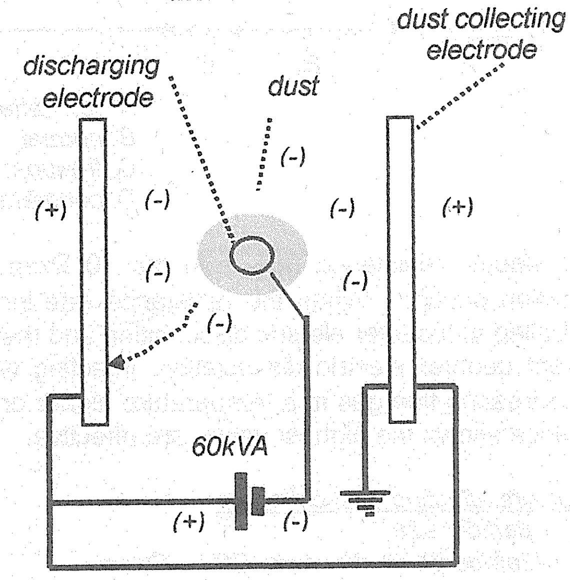
The gas temperature must be kept between 200 and 250 ℃ to avoid over heating for resistance temperature for filter cloth and dew point sulfuric acid.

For the detail information, refer to the pages at P.41~43 or E.57~58.

2-4 Electrostatic Precipitator

The electrostatic precipitator system collects dust by electrifying the dust particles in flue gas by corona discharge. When using an electrostatic precipitator, the influence of properties of flue gas and dust on collection efficiency is less, the collection of fine particles is easy by even when pressure loss is low, and high dust collection efficiency can be obtained. Therefore this system is widely used for the treatment of flue gas from glass melting furnaces.

Principle of EP



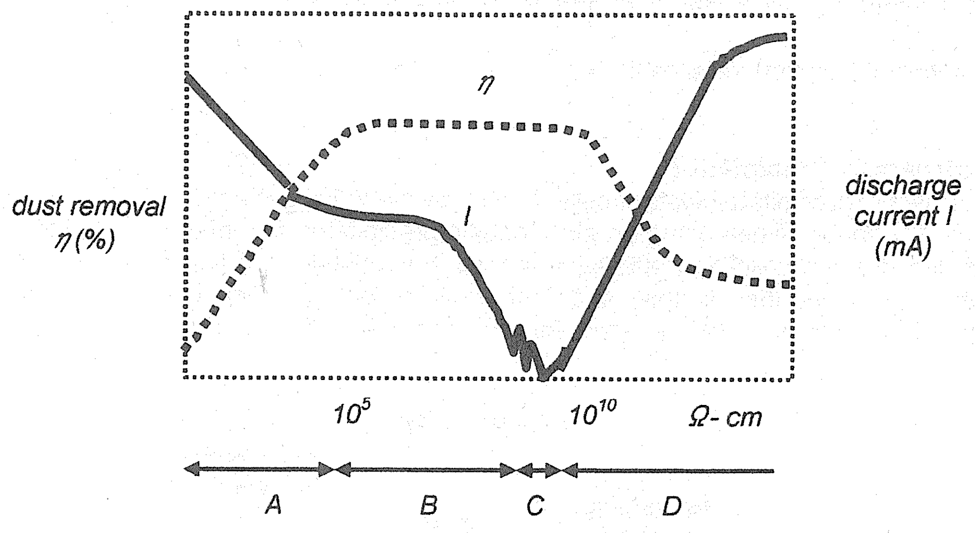
The electrostatic precipitator (EP) is used to remove very small liquid and solid particles from a gas stream. This operates by generating a corona between a high-voltage (60 KVA) electrode, usually a fine wire, and a passive earthed electrode, such as a plate or pipe. Particles passing through such an electric field are ionized by ions migrating from the discharge to collector electrode, with whom they collide. These particles then drift towards the collector electrode to which they are held by electrostatic attraction. The particle are removed from the collector by either a rapping or a water spray periodically.

Feature
- *Less influence of flue gas & dust*
- *Low pressure loss*

Peeling dust from electrode
- *Dry EP : hammering impact*
- *Wet EP: flow down with water film*

As particle size increases, dust collection efficiency is generally higher, although, the apparent electric resistance (Ω-cm) of dust has a great effect on dust collection efficiency. This is affected by gas temperature, moisture and the concentration of SO_3.

Relation between apparent electric resistance and dust removal / discharge current



A: re-scattering
B: normal
C: frequent occurring of sparks
D: counter electric dissociation

When the apparent electric resistance rate is in the 10^5 Ωcm to 10^{11} Ωcm range, ideal electrostatic precipitation occurs. When the resistance rate increases to over 10^{11} Ωcm, the phenomenon is called as counter electric dissociation and then dust collection efficiency decreases. To prevent counter electric dissociation, injecting water or steam, or sulfuric anhydride (SO_3), and treating flue gas at a temperature higher or lower than 150~200℃, at which electric resistance shows the highest value, are effective.

Factors affecting dust collection
- *particle size*
- *temperature, moisture, SO_3→Ω- cm*

For the detail information, refer to the pages at P.43~47 or E.60~66.

3. SOx Reduction Method

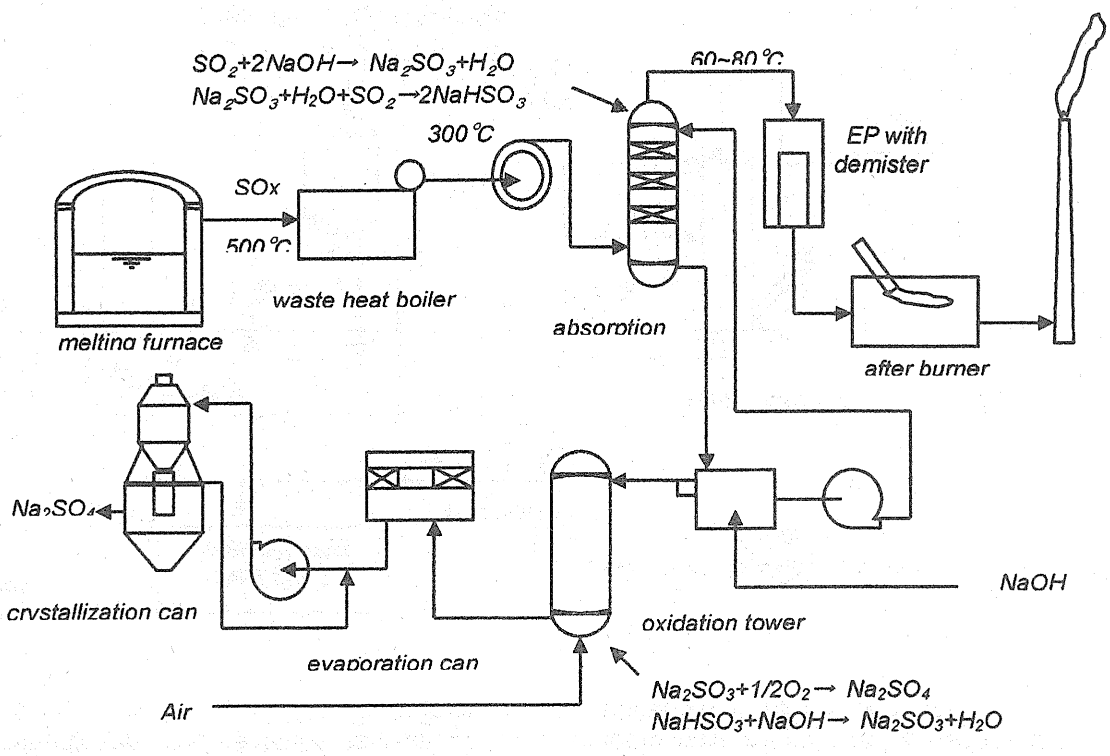
3-1 Desulphurization using Caustic Soda

SOx in flue gas from glass melting furnaces is usually generated by (1) combustion of the sulfur contained in fuel oil, (2) decomposition of sulfates such as sodium sulfate (Na_2SO_4), and gypsum ($CaSO_4$) used in glass raw materials. Flue gas desulphurization systems are generally adopted for glass melting furnaces using high-sulfur heavy oil.

There are many kind of applicable chemical reactions for separating and removing SOx from flue gas. The process of scrubbing using caustic soda and magnesium hydroxide ($Mg(OH)_2$), which is simple from the system view point, is most commonly used for glass melting furnaces.

The typical caustic soda desulphurization process is shown in the figure. Separated SOx is finally recovered as a form of sodium sulfate ($NaSO_4$). This system has achieved a desulphurization rate of over 97% and a dust removal rate of 95% as actual results. After desulphurization and dust removal have been done by this method, it is necessary to raise the temperature of treated gas by doing afterburning using clean gas, in order to eliminate the emission of white smoke containing the steam,: recently, however, concern about energy saving has increased, and since steam does not affect air pollution, there are many cases in which afterburning is not done.

Flow Sheet of Caustic Soda Desulphurization



The wet-type electrostatic precipitator (EP) has become simpler and high efficiency of mist and fumes removal along with dust removal, so wet type electrostatic precipitators with demister has been widely adopted.

For the detail information, refer to the pages at P.48~51 or E.68~72.

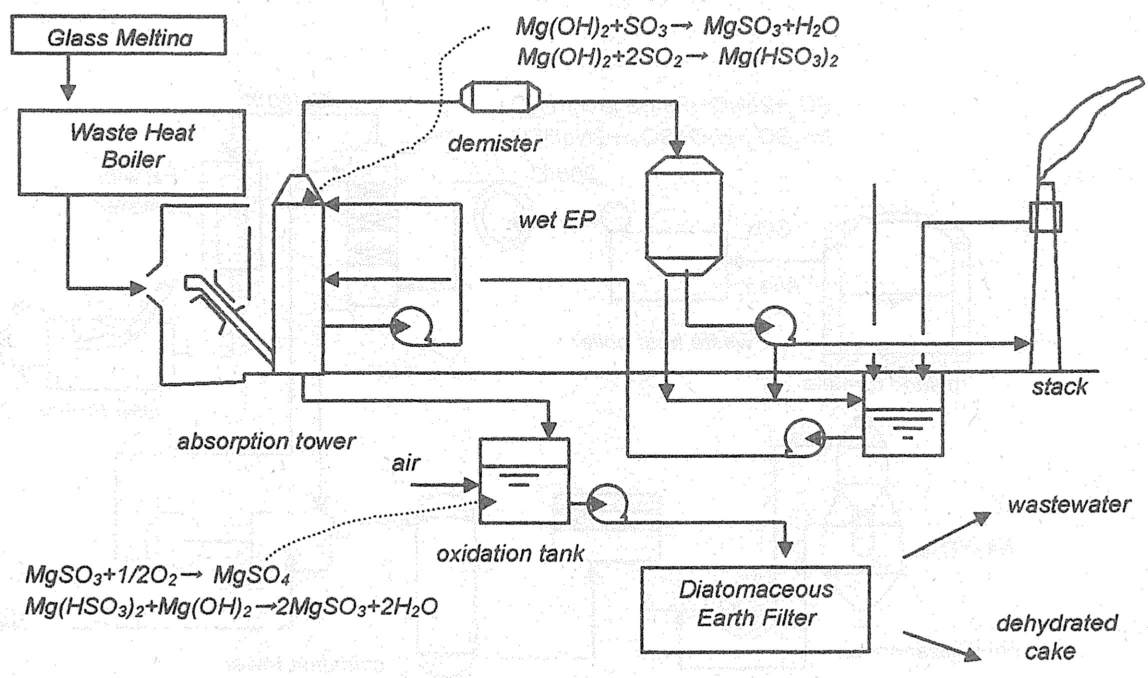
3-2 Desulphurization using Magnesium Hydroxide

When SO_3 is absorbed into magnesium hydroxide ($Mg(OH)_2$) solution, and the solution is oxidized by air, the solution becomes waste liquid containing magnesium sulfate ($MgSO_4$). This method is simple and equipment cost is low; it has been adopted for bottle glass melting furnaces, etc.

Flue gas from the glass melting furnace is cooled to 250 ℃ in a waste heat boiler. Then gas is led to the absorption tower lined with refractory stone and carbon brick. The circulated liquid is sprayed into the gas, adiabatic cooling of the gas occurs, and the flue gas becomes steam saturated gas. The adiabatic cooling action decreases the flue gas temperature to prevent damage to the lining layer of the can body of the tower. Magnesium hydroxide is supplied in the gas scrubber. Flue gas passes through perforated plates, and gradually flows to the upper level. Vigorous gas-liquid contact occurs at this time, and SO_3 is absorbed and removed.

After the greater part of the desulphurized flue gas mist is removed by eliminator, the dust is removed by a wet-type EP, and treated gas is released. Part of the circulating solution which absorbed the gas is drained, aerated and air-oxidized in the oxidation tank, and forms magnesium sulfate($MgSO_4$).

<u>*Flow Sheet of Magnesium Hydroxide Desulphurization*</u>



The drained solution from oxidation tank is filtrated by the pre-coat filter which uses diatomaceous earth as the filter medium. This system has achieved 98% desulphurization rate. The features of this system are (1) simple system, (2) inexpensive initial and operating cost, (3) using no toxicity and no corrosive of chemicals.

For the detail information, refer to the pages at P.51~52 or E.72~73.

3-3 Dry- type Flue Gas Desulphurization

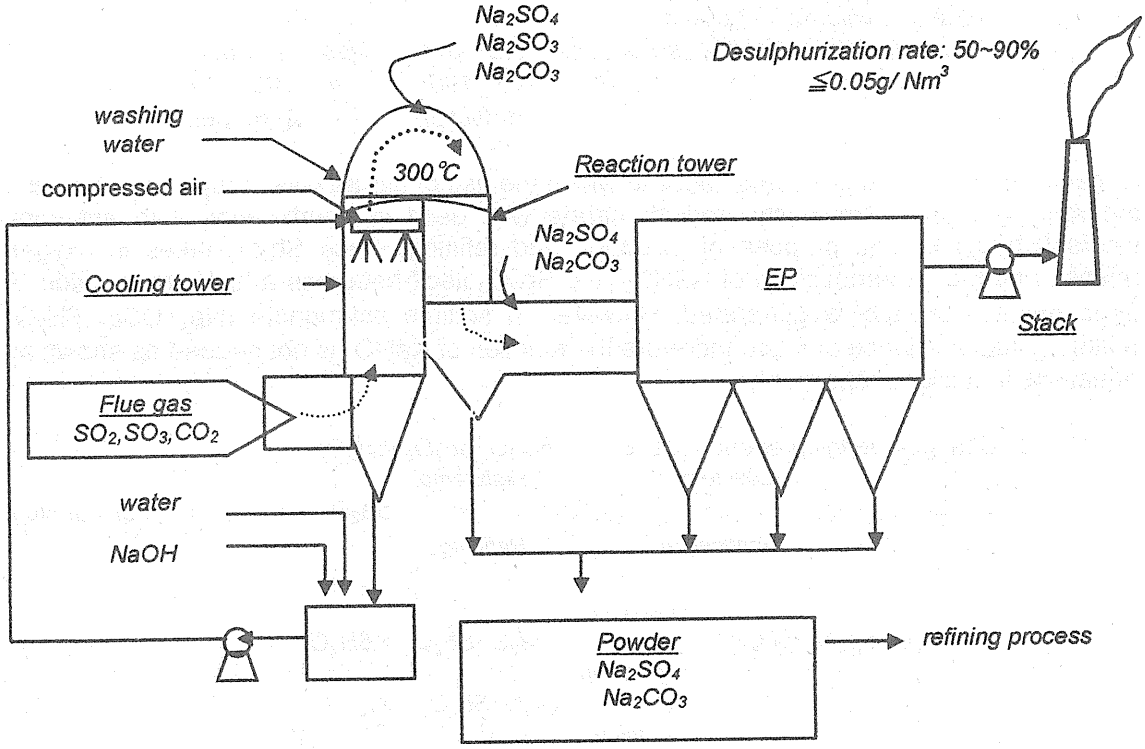
Flue gas led into the cooling tower, where several % of caustic soda solution is sprayed on the flue gas and the temperature is cooled to about 300℃, and at the same time, the SO_2, SO_3, and CO_2 in flue gas are changed to granulated Na_2SO_4, Na_2SO_3, and Na2CO_3.

In the following reaction tower, after Na_2SO_3 has been oxidized to Na_2SO_4, the flue gas is led to the electrostatic precipitator, where Na_2SO_4 and Na_2CO_3 in powder form are removed. The temperature of outlet gas from the electrostatic precipitator is 220~230 ℃, so the flue gas is directly released from the chimney.

This method has achieved desulphurization rate of 50~90% and soot and dust concentration of 0.05 g/Nm^3 or below.

Collected dust at the electrostatic precipitator is dissolved in water to form a solution from which sodium sulfate can be recovered through a refining process. The desulphurization rate of a dry-type desulphurization system is usually lower than that of a wet-type desulphurization system, but the dry-type equipment system is relatively simple and suitable for small and medium-size furnaces.

Flow Sheet of Dry Type Flue Gas Desulphurization



For the detail information, refer to the pages at P.52~53 or E.73~74.

4. NOx Reduction Method

4-1 Reduction of Nitrate in Raw Material

NOx generated from glass melting furnaces by combustion of fuel and also by the decomposition of small quantities of nitrate, used as an oxidizer and refining agent, in the raw materials (nitrates are only used in special furnaces).

NOx generation : $NaNO_3$ *(oxidation, refining agent)*

Reduction of nitrate dosage can be considered as one method for reducing generation of NOx (called material NOx or batch NOx). When nitrate use is stopped or reduced, obviously the quantity of NOx generation is reduced, but the use of nitrate is sometimes indispensable for maintaining glass quality.

There is one example of a lead glass in which glass quality could not be maintained when the use of sodium nitrate was decreased; therefore, changing the flame to make it more oxidative was unavoidable, and as a result, the quantity of NOx could not be reduced. Concerning the use of nitrate, it is necessary to thoroughly consider the variety of glass and flame condition, then make continuing efforts to reduce the use of nitrate.

As an example of the effect when the use of nitrate is reduced, we compared the trial calculation values and actual measured values for the effect when the quantity of sodium nitrate ($NaNO_3$) used was changed, for an end-port furnace, as shown in the slide. Actual measured values were reduced roughly as indicated in theory.

1. Reducing $NaNO_3$ additives
Quantity of pull : 100 t / day
Flue gas volume : 17,000 m^3 / h
Trial calculation: $NaNO_3$: silica sand = 0.5 : 100 NOx 169 ppm
" : " = 0.3 : 100 " 102 "
reduction ▲ 67 ppm

Recently, there have been some cases in which the use of nitrate was stopped by changing the refining agent. Previously, sodium nitrate was used in combination with antimony trioxide(Sb_2O_3) for the purpose of oxidation and refining. Once Sb_2O_3 takes in oxygen released by the decomposition of $NaNO_3$, the Sb_2O_3 itself becomes a high-grade oxide. A large quantity of NOx is generated. However, in sodium antimonate ($Na_2 \cdot OSb_5 \cdot 6H_2O$) antimony has a valence of 5 and therefore the function of $NaNO_3$ is not needed as shown by equations in a slide respectively.

2. Changing refining agent ($Sb_2O_3 \Rightarrow Na_2O \cdot Sb_2O_5 \cdot 6H_2O$)

$$Sb_2O_3 + O_2 \xrightarrow[\text{Vitrification}]{\text{Low temp.}} Sb_2O_5 \xrightarrow[\text{Refining}]{\text{High temp.}} Sb_2O_3 + O_2 \uparrow + \text{thermal NOx} \uparrow$$

$$Na_2O \cdot Sb_2O_5 \cdot 6H_2O \xrightarrow{\text{Low temp.}} Na_2O \cdot Sb_2O_5 + 6H_2O \uparrow$$

$$\xrightarrow[\text{Refining}]{\text{High temp.}} Na_2O \cdot Sb_2O_3 + O_2 \uparrow$$

For the detail information, refer to the pages at P.55~56 or E.77~78.

4-2 NOx Reduction Related to Fuel

Fuel NOx increases as the quantity of nitrogen contained in fuel increases.

N in Fuels

Fuel	Nitrogen (wt %)
Coal	0.7 ~ 2.2
C- heavy oil ※	0.2 ~ 0.4
A- heavy oil ※	0.005 ~ 0.08
Light oil	0.004 ~ 0.006
Kerosene	0.0005 ~ 0.01
LNG	Tr.
LPG	Tr.

※ JIS K2205 kinematic viscosity (cSt, mm2/s) C-heavy oil: 50≦~1,000, A-heavy oil: ≦20

Usually, the quantity of nitrogen in fuel increases in order, from gaseous fuel to light-gravity oil, to heavy-gravity oil. However, because glass-melting furnaces need to be operated at high temperature, 1,500~1,600 ℃, the ratio of thermal NOx in total NOx generated is overwhelmingly greater than the amount of fuel NOx.

Furnace temp. 1,500 ~ 1,600 ℃ ⇒ Thermal NOx ≫ Fuel NOx

In addition, light-gravity oil and gaseous fuel have heating values lower than that of heavy oil, and it is difficult to obtain a bright flame using light-gravity oil and gaseous fuel. Therefore, for a glass furnace which has a heat transfer mechanism almost completely dependent on heat radiation, when the fuel changed from heavy oil to light-gravity oil or gaseous fuel, fuel consumption is certainly to increase. In case of changing to natural gas from the heavy oil, same phenomenon can be seen.

Heating value
Blight flame

Heavy oil > *Light gravity oil*
Gaseous fuel

↓

Fuel increasing

↓

NOx increasing

One reliable and effective measure for glass-melting furnaces would be to switch to electric energy, but we cannot yet say that the technology for total electric glass melting in large tank furnaces has been established. Electric boosting is already widely used. Electric glass melting is mainly internal heating (resistance heating by changing of electricity directly into molten glass), and its thermal efficiency is high.

Electric energy

resistance

For the detail information, refer to the pages at P.56~57 or E.78~79.

4-3 NOx Reduction by Furnace Operation Method

There are several methods to decrease the NOx generation by means of maintaining appropriately the operating conditions of furnace.

(1) Lowering the glass melting temperature is a fundamental measure to reduce NOx, but this has the opposite effect on attempts to improve the various characteristics of glass. To solve this problem; ①the adoption for glass of a chemical composition with melting

at low temperature, ②development of method using the largest possible quantities of cullet (scrap glass).

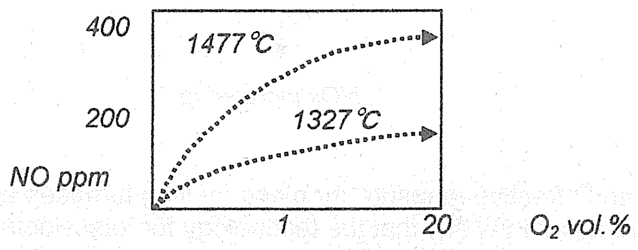
1. Declining Glass Melting Temp.
- chemical composition ----- melting at lower temp.
- using the largest possible quantity of cullet

(2) Lowering the primary air pressure which is used to inject liquid fuel is effective. For example, generation of NOx has been reduced by about 24% by decreasing the pressure from 4 to 3 kg/cm^2. Other than this, mixed gas combustion using fuel gas as the gas for fuel injection, causes no problems in the aspect of maintenance, and is effective for reducing NOx.

2. Lowering Primary Air Pressure
- lowering air pressure for fuel injection
ex. 4 kg /cm2 → 3 kg /cm2 ⇒ NOx ▲24%

(3) When the air ratio (theoretical air ratio: 1) was lowered from 1.2 to 1.1 as shown in the slide, NOx was decreased by 25 %. Therefore, it is desirable to burn fuel using an air ratio as close to the lower limit as permitted.

3. Lowering Secondary Air Volume
- decreasing air ratio ex. 1.2 → 1.1 ⇒ NOx ▲25%



(4) Allotting the fuel distribution to maintain the same average temperature throughout the entire furnace as much as possible is effective to reduce the generation of NOx. Also, combining the direct charging of electricity (electric boosting) with heating by fuel combustion is very effective for decreasing the maximum temperature of the furnace.

4. Lowering Furnace Temp. (Max. Temp.)
- allotting fuel distribution to maintain uniform temp. in furnace
- electric boosting

(5) Work standards for operators are also very important and effective to reduce NOx generation.

5. Combustion Control Work Standards

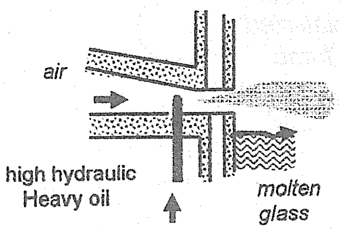
For the detail information, refer to the pages at P.57~58 or E.79~82.

4-4 Using Low NOx Burner

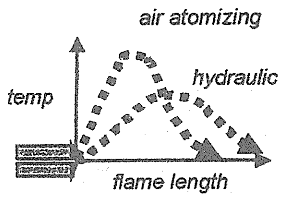
Fuel is usually burned using 10 ~30% excess air (air ratio: 1.1~1.3) in glass melting furnace. While fuel is burned using only the theoretical amount of air, not only it is difficult to maintain furnace temperature due to the formation of soot and unburned substances, but glass quality defects such as coloring of glass can also occur.

1. Hydraulic burner was initially developed for sheet glass melting furnaces for the energy saving and NOx reduction as shown in the table. The method, it uses to atomize heavy oil, is increasing the pressure of heavy oil and injecting it from a spray nozzle, without using air for atomization of the fuel heavy oil.

Hydraulic burner



Burner	Heavy oil use ratio	NOx conc. ratio
Air atomizing	1.00	1.00
Hydraulic	0.88	0.62



2. Supersonic burner is that it utilizes supersonic waves to atomize fuel oil. The amount of atomizing gas (air or steam) needed is said to be about ½ of that for a conventional burner.

- Low O_2 combustion ex. Air 170 → 120 m^3/h ⇒ NOx ▲25~30%

3. Laidlaw Drew burner was developed for bottle glass melting furnaces in England to save the fuel consumption. The amount of primary air required is 30~40% less than for a conventional burner, so it is said that the flame becomes "soft", heat efficiency increases, and fuel consumption decreases, while NOx is also reduced.

- Primary air: 30~40% less than conventional burner ⇒ lower NOx

4. Gas atomizing heavy oil burner uses town gas instead of using primary air and the amount of primary air is decreased. The result of testing done using an end port tank furnace (pull quantity: 100 t/d) for bottle glass were reported that the NOx concentration was decreased by 20~25%, while energy unit requirement is decreased by 3%.

- Town gas is used instead of primary air ⇒ NOx ▲ 20~25%

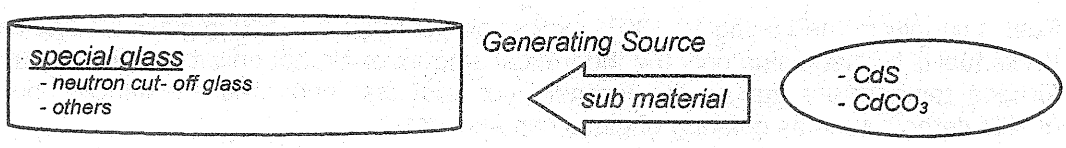
For the detail information, refer to the pages at P.59~63 or E.83~88.

5. Removing Toxic Substances

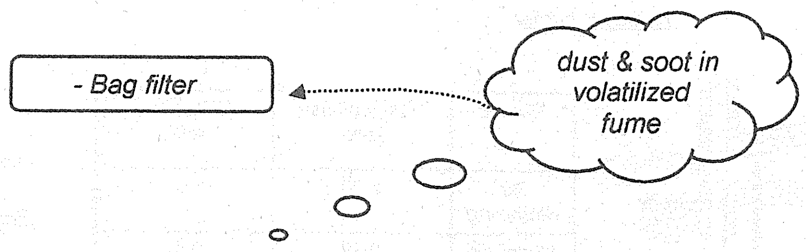
5-1 Cd & its Compounds

Other than SOx and NOx, the toxic substances discharged from glass melting furnaces are cadmium and its compound, lead and its compounds, and fluorine and its compounds.

Cadmium volatizes and diffuses from the cadmium sulfide (CdS) and cadmium carbonate ($CdCO_3$) used as sub materials for manufacturing of special glass such as neutron cut-off glass or other glass products.



Volatilized and diffused cadmium in the fume state is concentrated in flue gas. Cadmium and its compounds are discharged as a form of particles and are therefore removed by the dust collector.

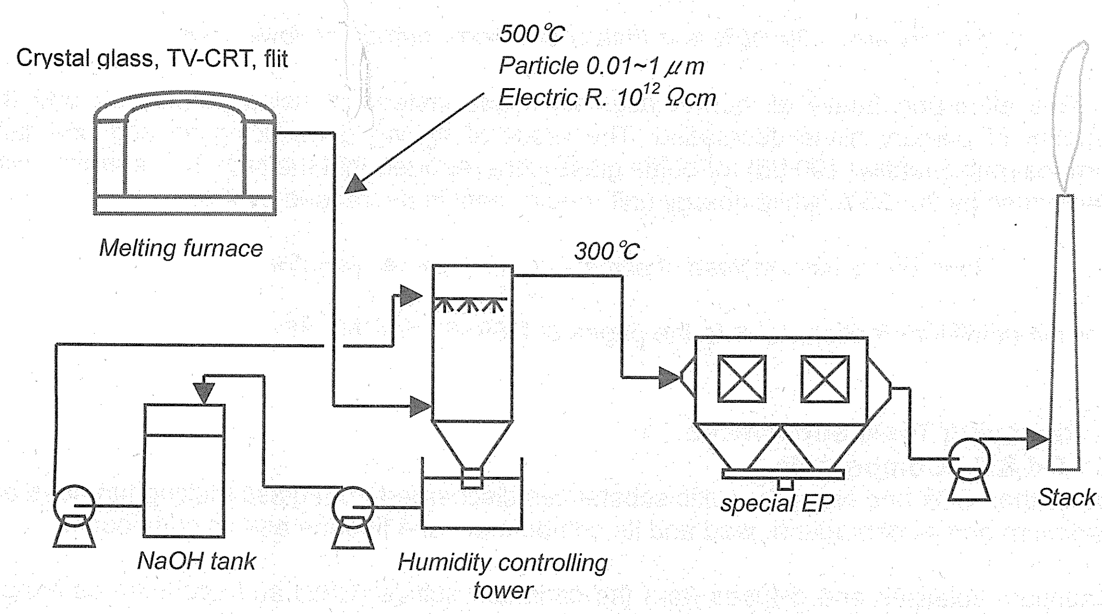


Bag filter and electrostatic precipitator are usually effective.

For the detail information, refer to the pages at P.64 or E.89.

5-2 Pb & its Compounds

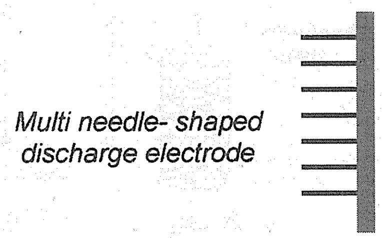
Lead is the main component of crystal glass, and is also used for glass for TV Braun cathode ray tubes (CRT) and frit for glass fusion. The dust in flue gas from the melting furnaces has a lead content of over 50%.



Evaporation of lead becomes vigorous from around 400~500℃, and evaporated lead exists in flue gas as lead fumes. It is necessary to melt raw materials at the lowest temperature possible in order to suppress the evaporation of lead from raw materials. Electric melting is the most desirable, since melting of raw materials can be done while keeping the surface temperature at a low level.

The particle sizes of lead and its compounds are as small as 0.01~ 1 μm, and their electrical resistance can be as much as 10^{12} Ωcm. Therefore when the bag filter used, plugging of the bag filter mesh occurred, and pressure loss increased. Also, when ordinary electric precipitators were used to collect lead and its compounds, stable collection was difficult due to counter electric dissociation. Since about 28 years ago, the stable collection has become possible using specially designed electrostatic precipitator (EP).

special EP



In this system, flue gas is cooled from 500°C to 300°C or below, by the spraying of weak caustic soda solution. This process makes lowering the electric resistance of particles. Also this system designed so that flue gas temperature is kept at around 300°C to prevent the increase of electrical resistance. The flue gas is led into an EP with the distinctive feature that its discharge electrode is not a linear electrode, but a plate with multiple needle-shaped discharge electrodes shown in the slide.

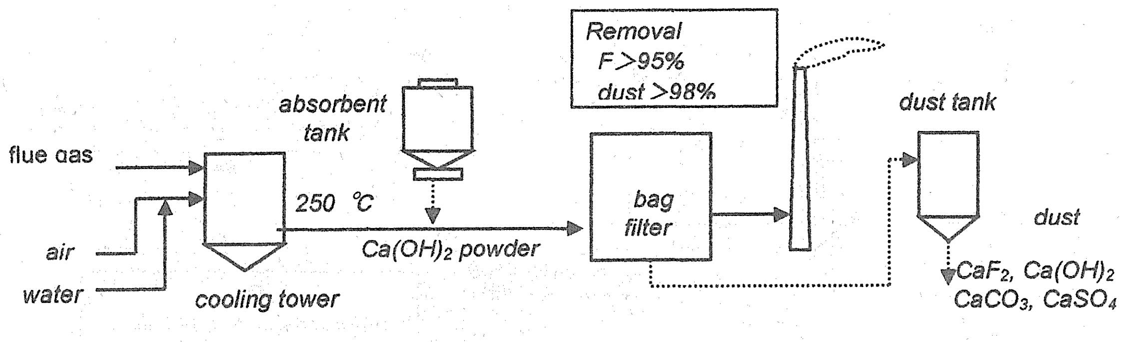
For the detail information, refer to the pages at P. 64~66 or E.89~91.

5-3 F & its Compounds

Fluorine and its compounds are used in many cases as accelerators for melting glass such as electric glass fiber (E-glass-Fiber) and special opaque glass. Fluorite (calcium fluoride) is the fluorine compounds most commonly used in raw materials. Both dry type and wet type methods are used to remove fluorine and its compounds.

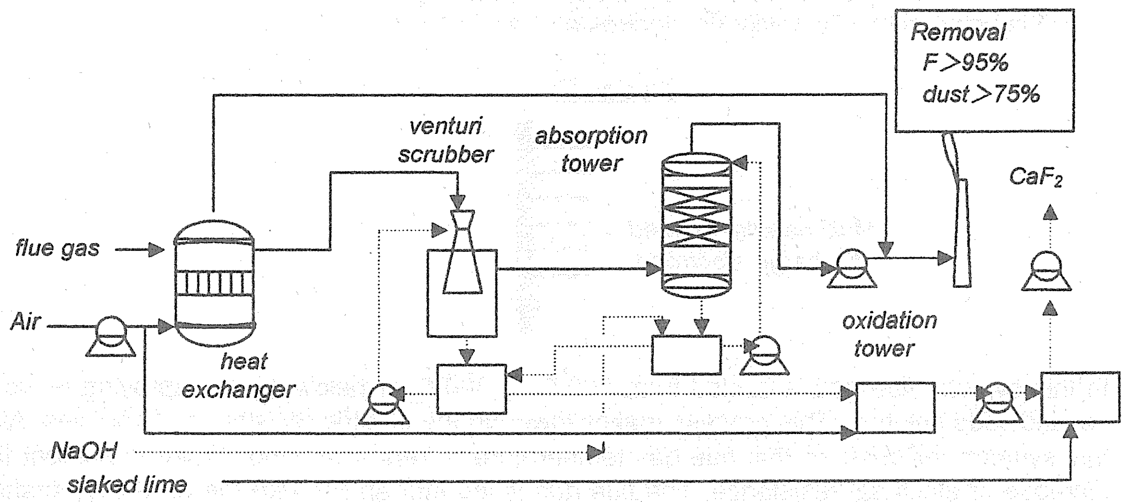
In dry type system, flue gas is cooled to about 250°C by spraying water into the flue gas in the cooling tower. Then, slaked lime powder is supplied to the gas. This operation converts fluorine and its compounds to calcium fluoride (CaF_2), which is collected and removed using a bag filter. $Ca(OH)_2$, $CaCO_3$, $CaSO_4$ coexist in the powder and it is re-used as raw material. This process has achieved fluorine removal rates of over 95% and dust collection rate of over 98%.

Dry type defluorination



The distinctive features of this method are its easy maintenance and low running cost, but its equipment size is fairly large.

Wet type defluorination

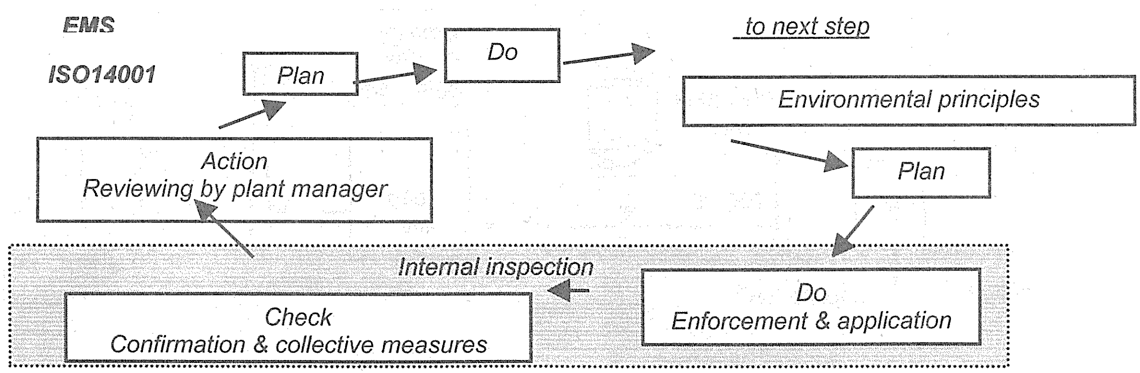


In wet type system, fluorine and its compounds are absorbed by caustic soda solution. This process is constituted of flue gas cooling, flue gas scrubbing, and wastewater treatment. This method removes SOx simultaneously. The fluorine removal rate is over 95%, and the dust removal rate is over 75%. Slaked lime is added to the NaF formed by reaction in the reaction end, to change it to CaF_2, which can be re-used after being separated, concentrated, and dried.

For the detail information, refer to the pages at P.66~67 or E.91~93.

6. Environmental Management System

ISO14001 standards are the basis of the Environmental Management System (EMS). The aims of EMS are to always understand the pollutants discharged by the enterprise itself, to maintain the conditions of a well-managed environment. The ISO 14001 requirements consist of 5 items, ①Environmental principle, ②Plan, ③Enforcement and application, ④Confirmation and collective measures ⑤Reviewing by plant manager.



The items which should be considered at the time of plant construction and operation;

1. Environmental impact assessment is essential to do advance investigation of the natural environmental condition in the area of plant location.

2. To understand the environmental standards and regulations for emission are important.

3. In planning of plant and air pollution control equipment, calculate the allowable value of the pollutants generated by the plant which conform to the emission standards. The most economical treatment methods are determined by selecting from various methods which satisfy the upper limit values for the pollutants emission.

4. Appropriate operation control of entire glass melting furnace system and effective worker training are very important too.
5. The monitor of pollutants emitted from the exhaust ports of glass melting furnaces is important to conform to emission standards.

6. All staff involved with the plant must make their best efforts for its environmental management. The person in charge of the work site where the accident occurred must report the occurrence of accident to related organs, make efforts to minimize damage, and obtain the understandings of local government bodies and local residents.

For the detail information, refer to the pages at P. 14~22 or E. 19~32.

7. Energy Saving Technology

Energy saving as an air pollution control measure is useful for the reduction of production cost, and is effective for reduction of CO_2, which has become a problem; energy saving can support businesses operation for the glass manufacturing industry which consumes large amount of energy.

First, determination of the process how to promote the energy saving including the items of basic policy, recognition for current state, quantitative goal, and measures is useful.

How to promote energy saving
Basic policy→ Understanding current state→ Goal→ Measures

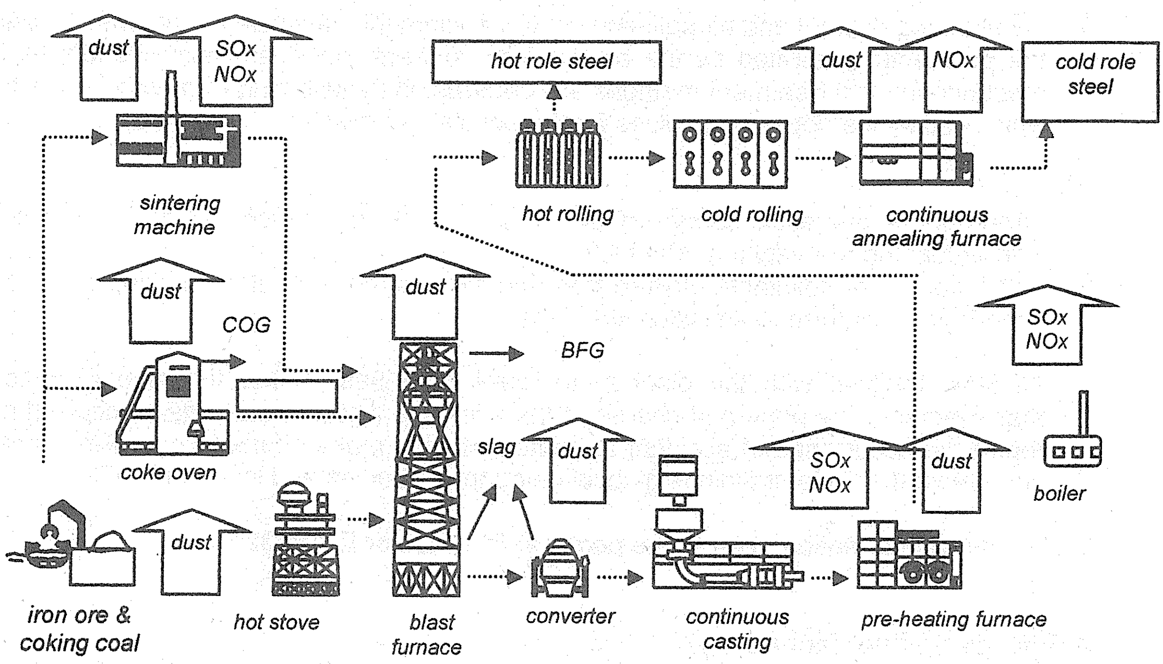
There are various energy saving methods such as ①acceleration of glass melting by increasing cullet use ratio, ②improving combustion condition from the stand points of software and hardware ③minimizing the heat loss ④ waste heat recovery and, ⑤others such as introduction of cogeneration system, etc.

For the detail information, refer to the pages at p.23~37 or E.32~52.

Ⅲ.Steel Industry

1. Iron & Steel Making Process and Air Pollutants

The rough manufacturing process of integrated steel works and air pollutants generated from each process are shown in the slide.



In raw materials treatment process, iron ore and coal are carried in by ships or trains and stored, where the coarse particles are scattered as dust.

In coking process, the dust are generated during the crushing, blending, and charging of coal to coke ovens and pushing out coke from the ovens.

In the sintering process, powdered iron ores are mixed with lime stone and powdered coke to be baked into pellets, where coarse particles are scattered from materials handling process and SOx and NOx are contained in the exhaust gas from baking furnace.

In the blast furnace process, major air pollutant is dust, which is mainly generated at the casting bed. Other than this, dust is generated when raw materials are charged into the upper part of blast furnace.

In the converter steeling process, dust and soot are mainly generated during blowing, and before and after blowing.

In the rolling process, dust, SOx and NOx are generated from a pre-heating furnace and a continuous annealing furnace.

Other than these, boilers in the steel mill emit SOx and NOx too.

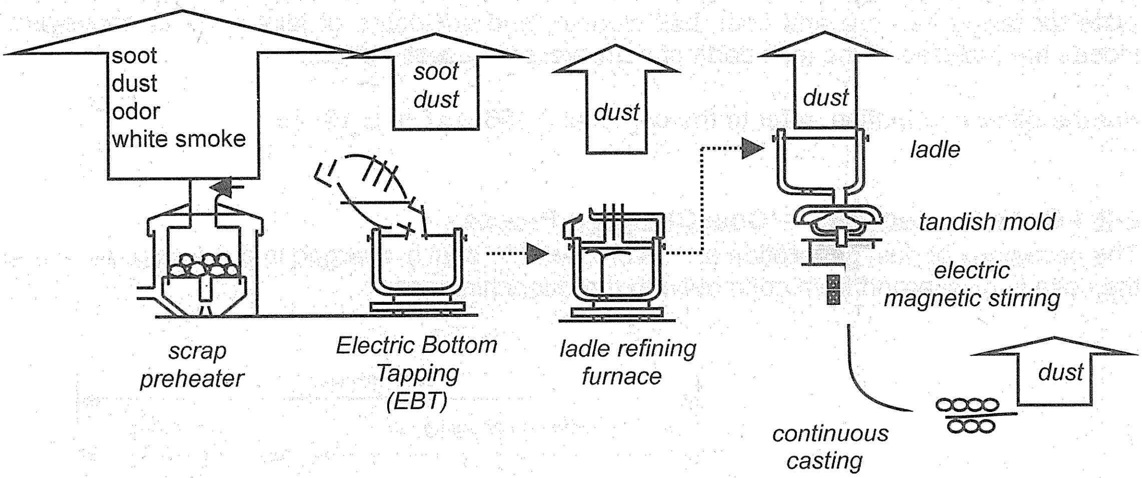
For the detail information, refer to the pages at P.139~151 (Japanese version) or E.1~14 (English version) of "Air Pollution Control Measure Technology in Steel Industry, Kitakyushu International Techno-cooperative Association, March 1997 " under the supervision by Air

Quality Management Division, Environment management Bureau, Ministry of the Environment, Government of Japan

2. Process of Electric Furnace Plant and Air Pollutants

The Steel production process by electric furnace consists of (1) melting process, (2) oxygen blowing process to remove carbon and phosphorus, (3)deoxidized process which makes desulphurization, alloying and temperature adjustment by the reduced slag after removing oxidized slag. Loading and unloading of materials in these processes are operated in discrete runs.

In the slide, typical process which is commonly adopted for the electric furnace steel factory to produce the ordinary steel and low alloy steel is shown.



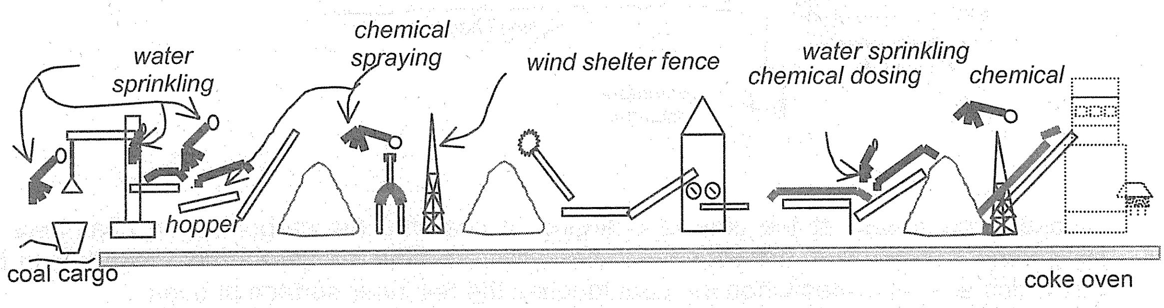
Major portions of exhausted pollutants in the electric furnace steel mill are from electric furnace and ladle refining processes. These gases contain dust, soot, white smoke, and odor.

For the detail information, refer to the pages at P.152~154or E.14~16.

3. Coarse Particle Scattering Prevention

3-1 Coal Handling Process

Outlines of coal handling processes and dust control methods are shown in a slide.



The main stream of dust scattering prevention is a method by water spray. Major portions of water sprinkling in the coal handling process are:

(1) Inside the hatch of ship
(2) unloading bucket
(3) discharging hopper
(4) belt conveyers including joint portions
(5) storage yard

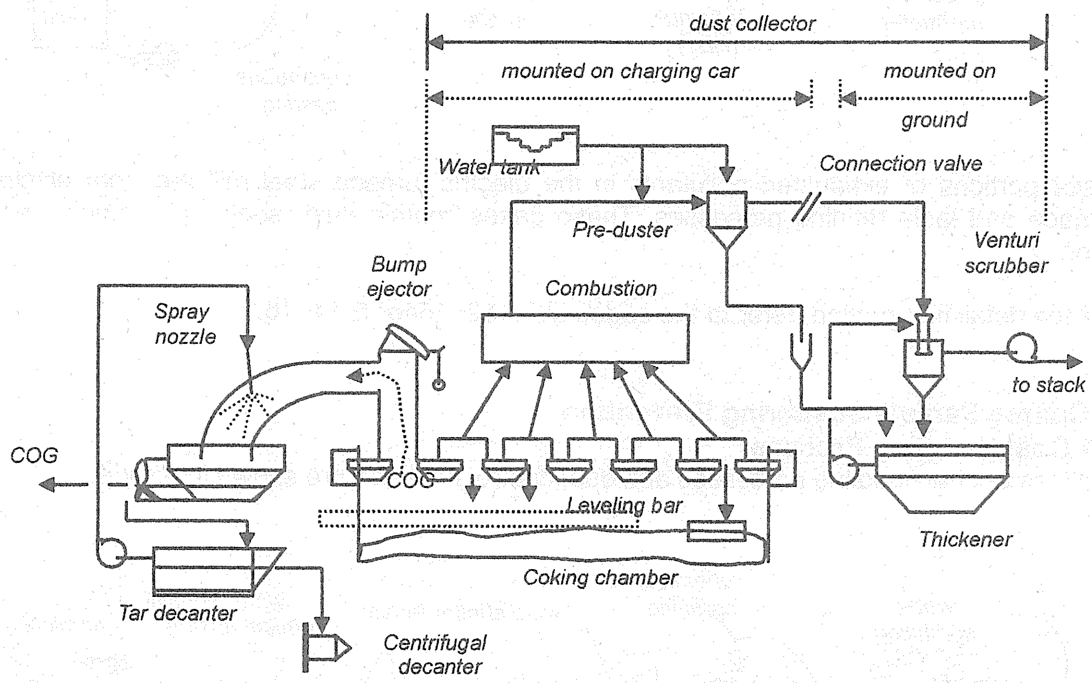
There are cases where the surface of piled raw materials is covered with net or sheet, or sometime be coated by chemicals such as polyvinyl acetate or tar. A wind shelter fence has been installed. A wind shelter fence of 7 m high with 40 % opening area could reportedly reduce the wind velocity by 50% or over.

In belt conveyer transportation, the prevention methods of dust scattering have been controlled by installing belt-conveyer cover, wind shelter plate, water sprinkler, receiving plate for falling iron ore and coal, belt cleaner, and enclosure of joint parts of conveyers. Hoods are installed at the joint parts of conveyers to collect the dust.

For the detail information, refer to the pages at P.156~157 or E.18~19.

3-2-1 Coke Production — Coal Charging Process

The occasions of dust generation are as of when the coal is charged into the coke oven and the coke is discharged from coke oven to the quenching car.

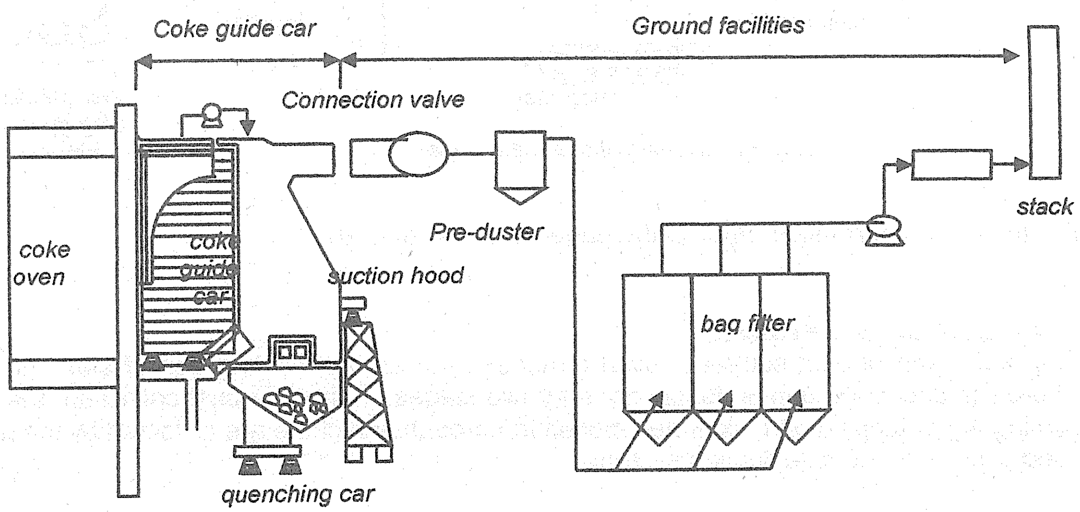


Smoke is generated at the time of charging of coal into the carbonization chambers by replacement of gases in the oven with coal, which contain steam and fine coal dust in the gas which are generated when the coal touches the hot inner surface of oven.

A part of these smokes can be absorbed by bump ejector. However the most smoke is sucked to the dust collector installed on the ground through the combustion chamber mounted on the coal charging car. The sucked gas is first combusted in the combustion chamber, and then washed by water at pre-duster and leads to venturi scrubber, of which water is led to a thickener. The washed and cleaned gas is led to stack and emitted into the air.

For the detail information, refer to the pages at P.156~157 E.19.

3-2-2 Coke Production — Coke Discharging Process
Smoke generation occurs at the time of opening the oven covers of both sides of carbonizing chambers, which discharge remaining gases in the oven along with dust. Also the dust generated when the coke is pushed to the coke-guide girder, when coke falls into the quenching car, and during the transportation of coke by quenching car to quenching tower. The dust generation at the time of coke discharging is huge, so that the dust collection in this operation is very important.



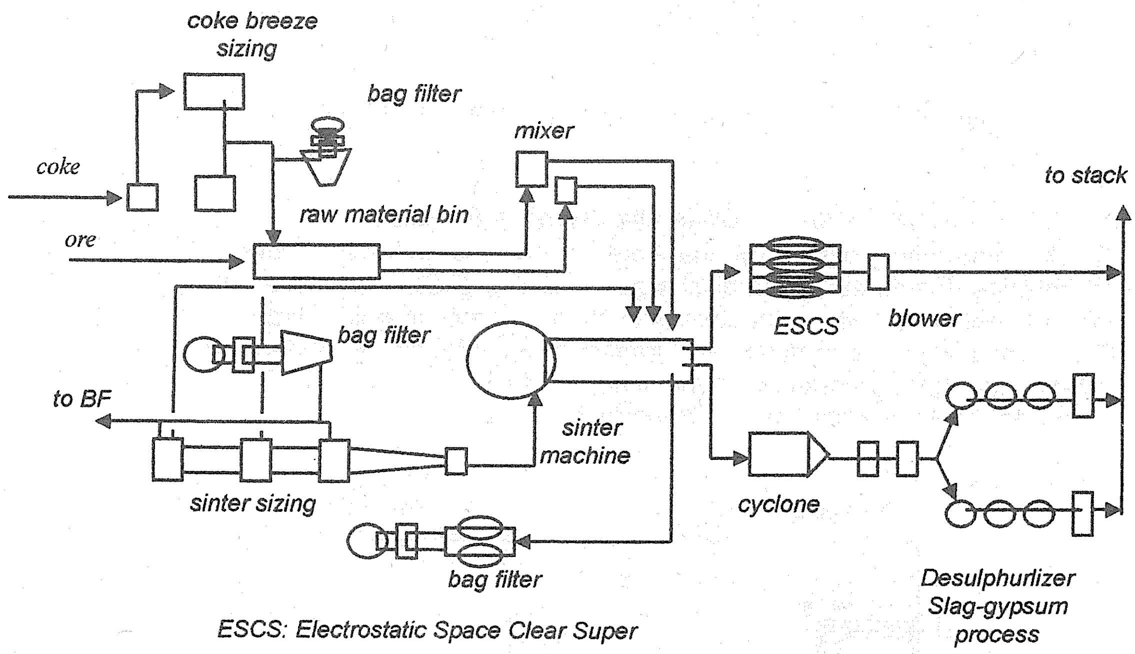
When the red-hot coke falls into the quenching car, the smoke is sucked into the mobile hood, which is moved and stopped at the right side of discharging ovens and just top of quenching car, and is led to bag filters on the ground through connection valve as shown in a slide.

For the detail information, refer to the pages at P.156~157 or E.19.

3-3 Sintering Process
A greater part of dust generation in steel mill comes from the sintering process. The dust generated from sintering process was used to be hard to remove by electrostatic precipitator because of its high apparent electric resistance. However, this problem was solved by the development of ESCS (Electrostatic Space Clear Super).

Other than the dust abatement for sintering process, dust collections for the coke breeze -

sizing process and sinter sizing process are done by bag filters as shown in a slide as well as for the belt conveyer-junctions.

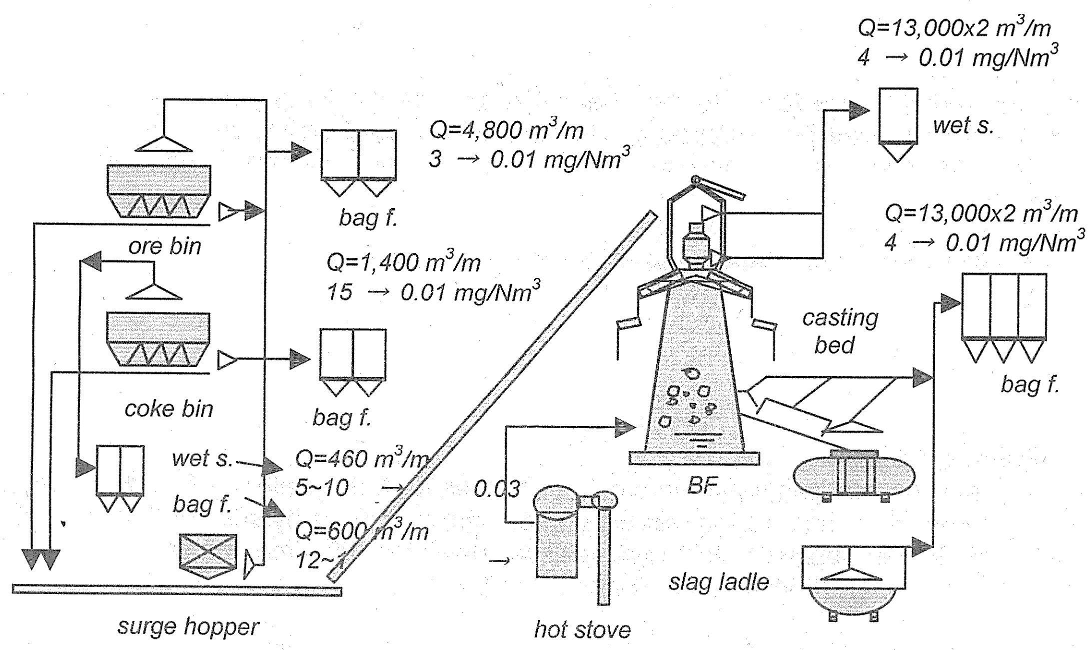


ESCS: Electrostatic Space Clear Super

For the detail information, refer to the pages at P.158 or E.20.

3- 4 Blast Furnace Process

The major part of dust control at blast furnace is the area of casting bed of blast furnace, where the dust collection is doubly done by two stages. In the first dust collection, the dust coming out of tapping part, skimmer, molten iron trough and chute are collected by the upper hood system or the side suction system.



For the dust collection at tapping part of blast furnace, top-hood suction system or side-hood suction system is adopted in consideration of crane manipulation and workability around tapping part.

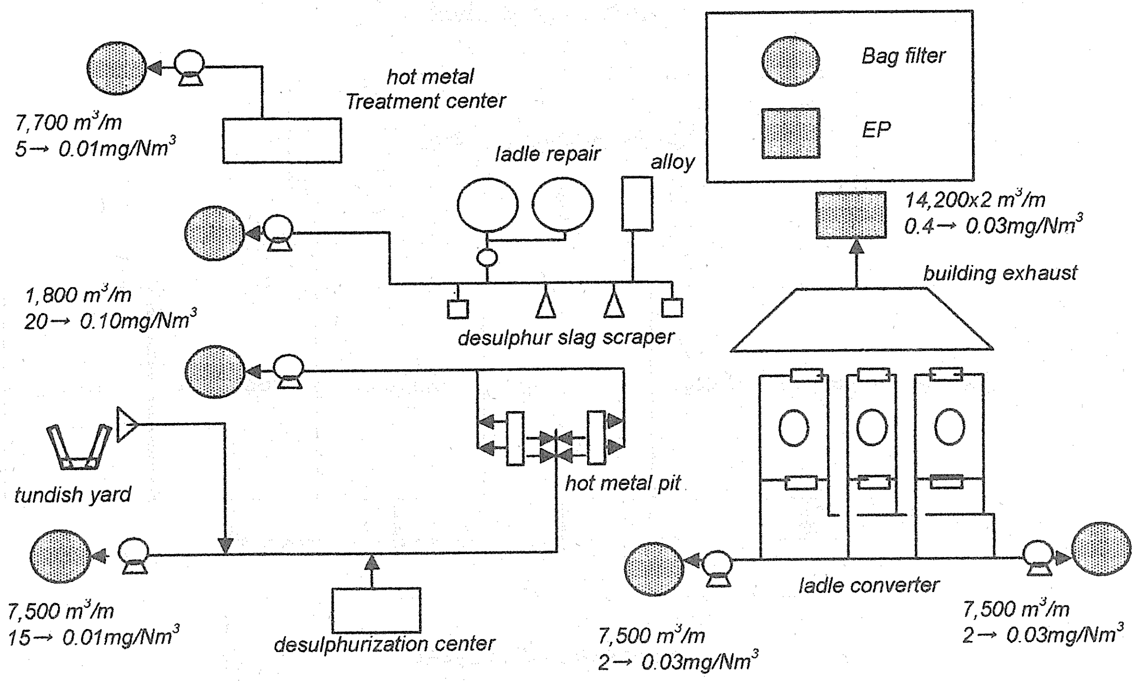
In the second dust collection, the dust which is not captured by the first stage collector system is gathered to small space at upper part of the casting bed as much as possible and collected. The second dust collection system is usually equipped with "storing system" or "curtain system" to cope with dust collecting for large amount of coarse particles generated at early and last stages of tapping, taking the smoking condition and a layout of casting bed into consideration.

In a slide, whole processes involved in blast furnace operation and examples of performance in dust collecting systems are shown.

For the detail information, refer to the pages at P.159 or E.21.

3-5 Steel Manufacturing Process (Converter)

Whole dust collection system in a converter plant is shown in the slide, where the bag filters are mostly used.



Smoke generation in a converter plant occurs before and after the blowing process. Smoke generated during the blowing can be satisfactorily sucked by gas recovery device such as OG device. However, in case of when smoke volume generated at the time of slopping, which is called as bumping phenomenon and emits a red color smoke with high concentration dust, exceeds the treatment capacity of gas recovery device, the leaked smoke is collected to an environmental dust collector, which is called as furnace port dust sucker. The smoke and dust generated at the preparation works for cinder removal and desulphurization, handling of sub-raw materials, and cutting of metal adhered to ladle and lance are sucked through hood and collected by environmental dust collector.

The wet type electrostatic precipitator installed on the rooftop or bag filter installed on the ground are used for dust collection of ladle converter building, though the dust collecting system of the building for converter has not so popular.
To prevent the sloping, stabilization of melting metal compositions is important, however, when such abnormal sloping occurs, necessary measures should be taken to minimize the leakage of dust from the building.

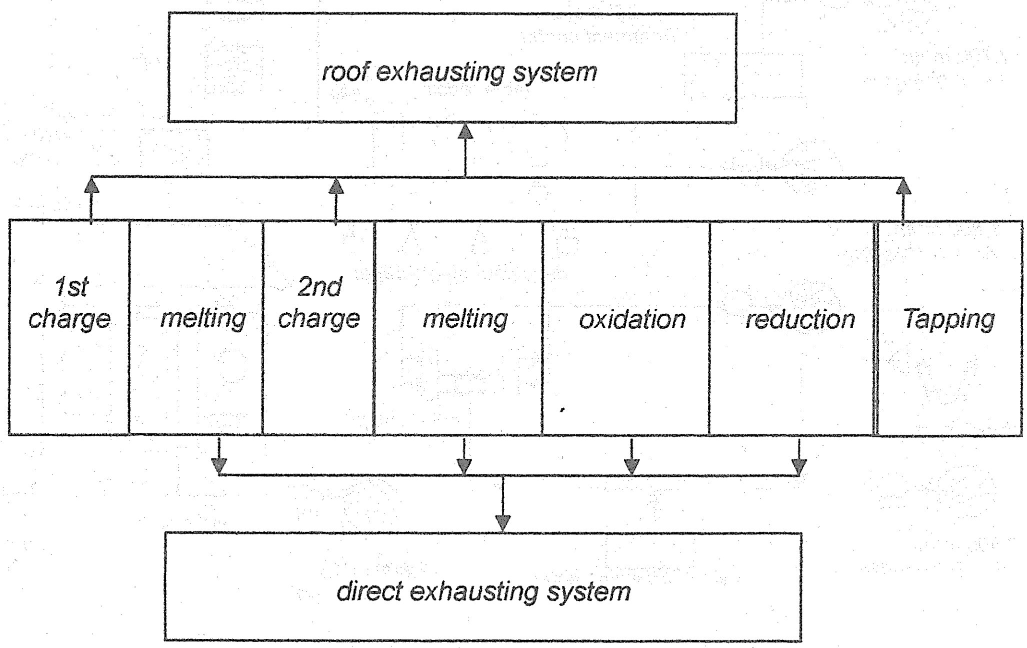
For the detail information, refer to the pages at P.161 or E.24.

3-6 Electric Furnace

The waste gases generated in the steel mill using electric furnace are mainly generated from an electric furnace and ladle at refining process, which contain dust. Further, oils adhered to scrap steel turned to fume with white color and offensive smell during pre-heating of scrap steel.

To abate this fume, there are three dust collecting systems of (1) direct dust collection system, (2) building dust collection system, and (3) doghouse dust collection system. They are effectively and economically well combined and employed.

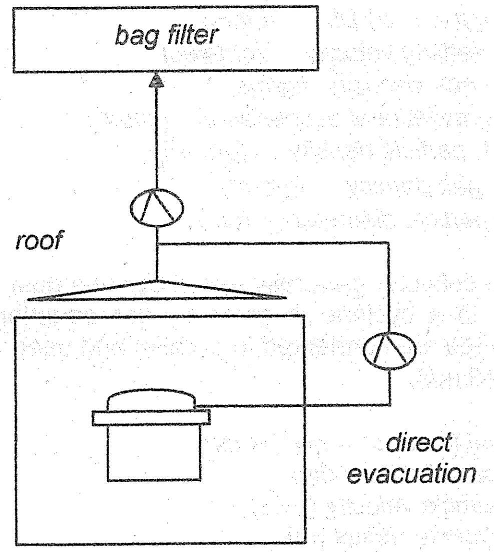
Conventional System



The direct dust collecting system is a method to cool down the high temperature exhaust gas containing dust of high concentration out of electric furnace to the certain level of temperature, and removes the dust.

The building dust collector is to collect the excess exhaust gases which exceed the capacity of direct dust collector at the time when the lid of electric furnace is taken off in order to charge the scrap steel and to discharge the molten steel from the furnace.

Doghouse System



Doghouse System

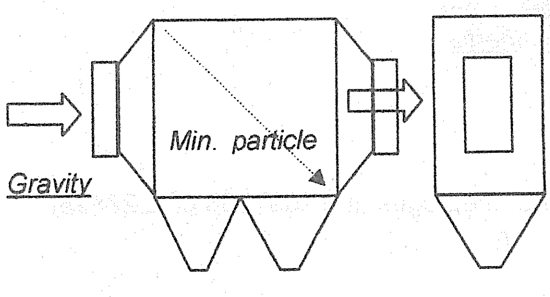
The electric furnace in steel mill plant produces not only a large amount of dust but also noise. For these troublesome, the dog house, which closes the whole electric furnace into the enclosed house, is very effective, and it makes possible to reduce substantially the collecting gas volume by 20~30%.

For the detail information, refer to the pages at P.162~164 or E.24~26.

4. Dust Collection System

4-1 Gravitational, Inertial & Centrifugal Dust Collector

Because of the density difference between solids and gases, in laminar flow their stream lines are different if the direction of flow is changed. This fact is frequently exploited to separate solid particles from a gas stream, usually by suddenly changing the direction of flow of the gas stream.



In gravity dust collector, a settling chamber reduces the velocity (normally 1~2 m/second) of the gas stream so that the particles drop out by gravity. It is a large device not often used as a final control mechanism. If it is assumed that Stokes's law applies, then the particle size which will be removed with 100% efficiency is given by the equation.

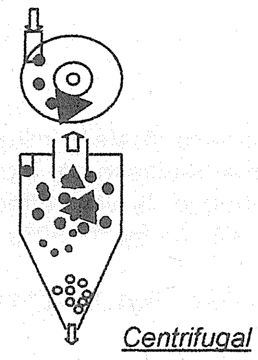
Stokes' Law

$V=(g/18\mu)(\rho 1-\rho)D^2$ (cm/s)

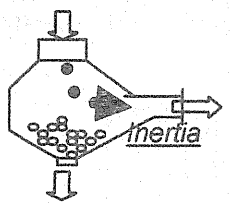
V: settling velocity (cm/sec)
μ: gas viscosity (kg/ms)
g: gravitational acceleration (cm/s²)
ρ1: particle density (g/cm³)
ρ: gas density (g/cm³)
D: particle diameter (cm)

In the centrifugal force collector generally called cyclone dust separator, the centrifugal force exerted on a particle in a cyclone is given by the equation. For a large volume of gas treatment, small cyclones are connected in parallel and used as multi-cyclone. The inlet-gas velocity is set at 10 ~25 m/s.

Centrifugal force (F) = mv^2/R (N)
m: particle mass (kg)
V: particle velocity (m/ s)
R: cyclone radius (m)



In an inertial dust collector, the gas stream is forced to collide with an obstacle or the gas flow direction is sharply changed to separate and collect dust particles in gas by using inertial force.

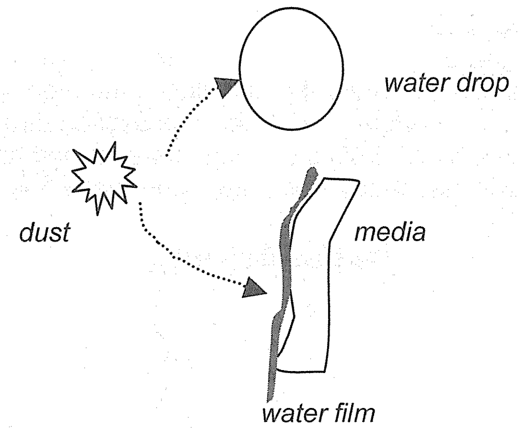


For the detail information, refer to the pages at P.165~166 or E.27~28.

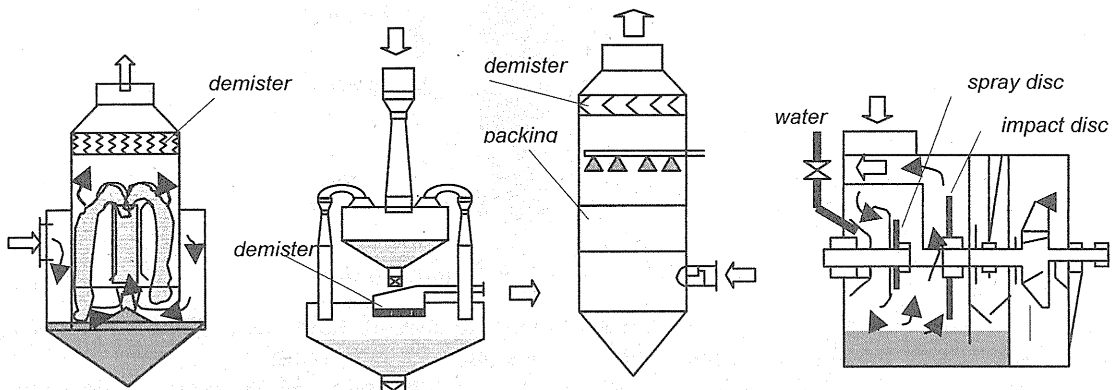
4-2 Scrubbing Dust collector

Scrubbers, known as wet collectors, employ a liquid to remove particles from a gas stream. In use it is either the liquid droplets which collect the particles or liquid that is poured continuously on the porous packing and the particles collected by both the liquid droplets and adhesion to the liquid on the packing.

Principle of dust collection:



Various scrubbing dust collector systems have been developed, and can be roughly divided into reservoir type, pressurized water type, packed bed type and rotary type as shown in a slide.



Reservoir type *Pressurized water type* *Packed bed type* *Rotary type*

The use of packing allows a smaller tower to be used but the pressure drop is higher (thereby increasing efficiency). The pressure drop through a spray tower is typically between 0.25~0.5 kPa. For the packed bed it is between 0.25~2.0 kPa. The liquid to gas ratio in a spray tower is typically 1.3~2.7 l/m^3. In a packed tower it is normally between 0.1~0.5 l/m^3.

In the packing bed type, basically, the contaminated gas enters the tower at a low level and rises due to its buoyancy. The scrubbing liquid enters the top of the tower and sprays down on top of the vertically rising dirty gas. At interception the contaminants adsorb to the falling liquid and the purified gas continues to rise and emits from the top the tower. Packing (e.g. random plastic piece) improve the adsorption efficiency. The nozzles on the spray arms atomize the liquid.

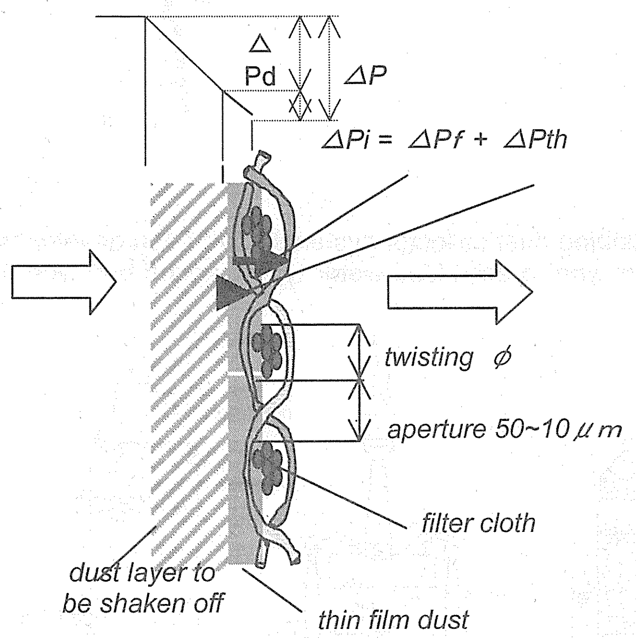
To achieve efficient performance of scrubbing dust collector, it is important to select a gas flow velocity and liquid to gas ratio suitable for the system.

For the detail information, refer to the pages at P.166 or E.28.

4-3 Filter Type Dust Collector

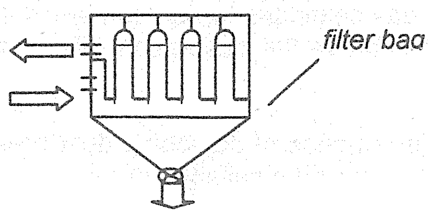
Principal types of filter type dust collectors are (1) the bag filter (2) the cartridge filter. The design of both is quite similar. However the bag filter is the more commonly used.
When gas contained dusts of certain particle sizes is passed through a filter cloth as shown in a slide, they adhere to the filter cloth, and bridges are formed between the strands of cloth. The primary adhesion layer has many fine pores, and these fine pores collect the fine dust particles.

Filtration Mechanism



Various woven fabrics made from natural fiber, synthetic fiber and glass fiber, and non-woven fabrics made from similar materials are used for filter cloth.
In the operation of the bag filter type dust collector, prevention of blockage of the filter surface is important. When the pressure loss of the bag filter has reached its regulated value, it is necessary to shake dust off of the bag filter. There are 2 kind pf shake-off methods, the intermittent method and continuous method. In the intermittent method, the dust collecting chamber is partitioned into 3~4 chamber. The dampers installed on both the inlet and outlet of filter are closed and then the dust adhering to the filter cloth is shaken off. In the continuous method, the dust adhering to the filter cloth is constantly shaken off under continuous filtration. Therefore, the pressure loss will remain roughly at a fixed level, making this method suitable for the treatment of gases containing high concentrations of dust and soot and of gases containing adhesive dust and soot.

Typical bag filter unit



The apparent filtration rate (raw gas volume per effective area of filter cloth) should usually fall in the range of 0.3~10 cm /s.

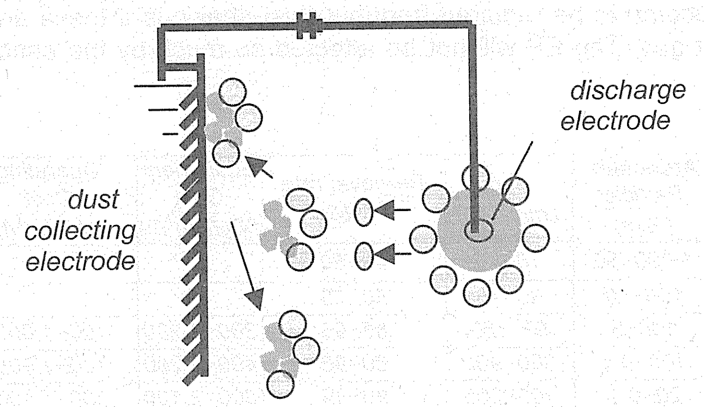
Type:	*Filter cloth:*	*Dust shake-off:*	*Apparent filtration rate:*
(1) bag filter	*(1) woven fabric*	*(1) intermittent*	*0.3~10cm/s*
(2) packed bed filter	*(2) nonwoven fabric*	*(2) continuous*	

For the detail information, refer to the pages at P.167~168 or E.29~30.

4-4 Electrostatic Precipitator

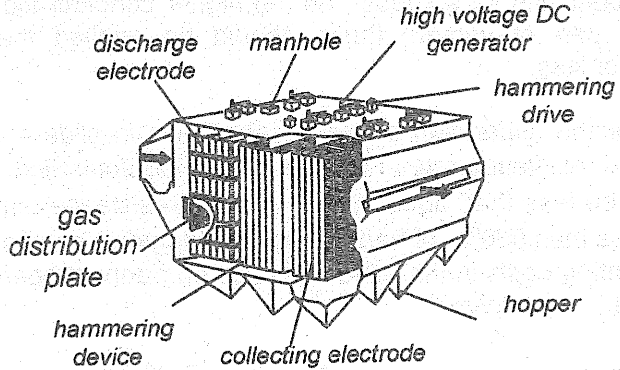
The electrostatic precipitators (EP) are used to remove very small liquid and solid particles from a gas stream. They operate by generating colonna discharge between high-voltage electrodes, usually a fine wire, and a passive earthed electrode, such as a plate or pipe. Particles passing through such an electric field are ionized by ions migrating from the discharge electrode to the collector electrode, with whom they collide. These particles then drift toward to the collector electrode to which they are held by electrostatic attraction.

Principle of dust collection :



The particles are removed from the collector by either a water spray or rapping periodically. The collector can either be flat or tubular units. Usually, a number of discharge electrodes will hang as shown in a slide.

Structure of EP



The EP is not much affected by the properties of gas and dust, can do highly efficient dust collection, and can collect fine particles without pressure loss.

For the detail information, refer to the pages at P.168~169 or E. 30~31.

4-5 Selection of Dust Collector

When we select the dust collectors, physical properties of particle and gases as shown in the slide should be taken into consideration;

Parameter

- *particle distribution*
- *dust concentration*
- *specific gravity*
- *electric resistnace rate*
- *flow rate*
- *due point*
- *gas temp.*

the sizes and particle distribution of dust in the flue gas have an effect significantly on the particle removal efficiency in dust collectors each. The sizes of particle abated by dust collectors are shown in the table. Invisible particle concentration is said to be 20 mg/Nm^3. Filter dust collectors become to be required frequent dust shakings if these are applied to high concentration dust gas. The EP will not be affected so much by the concentration of dust in flue gas.

Collector	Applicable Particle (μm)	Δp (mmH$_2$O)	Removal rate (%)	Equipment Cost (¥/y/Nm^3/h)	Operating Cost (¥/y/Nm^3/h)
Gravity	1,000~50	10~15	40~60		
Inertial	100~10	30~70	50~70		
Centrifugal	100~3	50~150	85~95	300~2,200	100~1,000
Scrubbing	100~0.1	300~900	80~95	400~2,200	100~1,300
Filter	20~0.1	100~200	90~99	300~2,100	300~1,100
EP	20~0.05	10~20	90~99.9	400~4,400	100~1,00

Regarding the dust concentration, the higher concentration of dust in a gas brings the higher removal efficiency of particle removal for the gravity collector and inertial force dust collector due to the acceleration of collision between large size particles and of coagulation of fine particles. In venturi scrubber and jet scrubber, as the higher concentration of dust causes the wear at the throat part of venturi, these should be applied the gases of dust concentration 10 g/ Nm^3 or less.

Specific gravity works for the separation efficiency as shown in slide 4-1. In the EP, the optimum apparent electric resistance rate of particle should be controlled 10^4~$5x10^{10}\Omega$cm. The temperature should be less than about 250℃ of heat resistance temperature of filter cloth for bag filter, and less than 500℃ of heat resistance temperature of steel for the EP. The equipment and operating costs in the table are base on ; annual operating time; 6,100 hours, electric power cost ; ¥14/ kWh.

For the detail information, refer to the pages at P.170~173 or E:32~35.

5. Desulphurization Technology

5-1 Flue Gas Desulphurization in Steel Mill

The SOx emitted from integrated steel mill is mostly generated from a sintering processes, accounting for 57% of total emission in the steel works. A coking process does not emit SOx directly to the atmosphere.

The flue gas desulphurization (FGD) systems are classified as either dry or wet, depending on the phase in which reaction occurs. Either process can remove 90% of SOx in the flue gas. Most FGD systems in use today are wet non-regenerable process. The limestone-gypsum process is the more economical to run and accounts for 40 % of the installed systems.

Method	*Reaction*	*Byproduct*
Activated carbon	$SO_2+H_2O+1/2O_2 \rightarrow H_2SO_4$	H_2SO_4
Caustic soda	$2NaOH+SO_2 \rightarrow Na_2SO_3+H_2O$ $Na_2SO_3+H_2O+SO_2 \rightarrow 2NaHSO_3$	Na_2SO_4
Ammonia	$2NH_4OH+SO_2 \rightarrow (NH_4)_2SO_3+H_2O$ $(NH_4)_2SO_3+SO_3+SO_2+H_2O \rightarrow 2NH_4HSO_3+H_2$	$(NH_4)_2SO_4$
Slaked lime	$CaO+SO_2 \rightarrow CaSO_3$ $CaSO_3 + O_2 \rightarrow 2CaSO_4$	$CaSO_4$

In wet processes, the systems are based around the reaction of sulphur dioxide with lime (CaO), caustic soda (NaOH), ammonia (NH_3), slaked lime ($Ca(OH)_2$), or etc. Slaked lime react to produce calcium sulphite ($CaSO_3$), part of which is converted to calcium sulphate ($CaSO_4$) by both reacting with the excess oxygen in the flue gas and by aeration of the sludge afterwards. The calcium sulphate (known as gypsum) is a stable and the prime ingredient in plasterboard. Other than these, as the lime-gypsum process has economical advantages in installation and operating cost and systems-stability in the process, it has been popularly used in Japan.

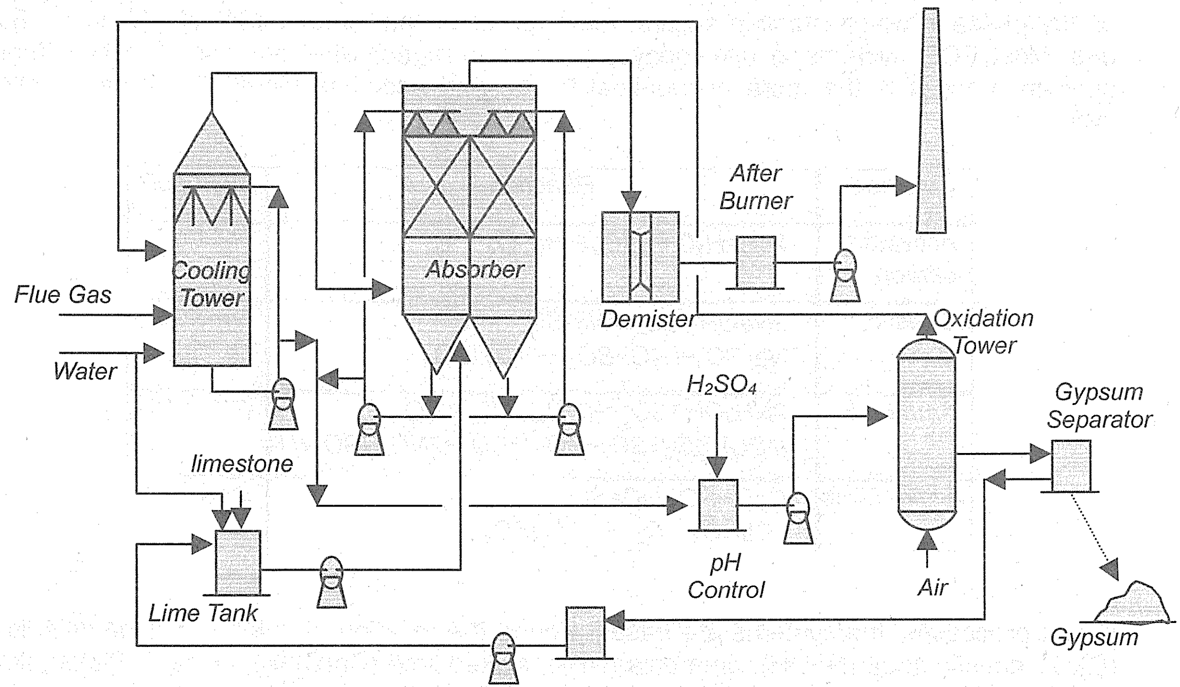
Limestone - Gypsum Process
SOx Rem. >90% ⇨ *most popularly used method In Japan*

- *limestone ⇒ cheap*
- *initial & operating cost ⇒ economical*
- *systems stability ⇒ stable & safe*
- *gypsum ⇒ marketable*

For the detail information, refer to the pages at P.182 or E.44.

5-2 Limestone-Gypsum Process

The flow in a slide is an example of limestone-gypsum process used in steel mill. Flue gas is led to the cooling tower to cool off the temperature of flue gas, and then led to absorber, where a slurry-like absorption liquid (10 to 20 %) containing limestone powder with particle sizes of around 50 – 60 microns is circulated. When this liquid and flue gas have come into efficient contact, SO_2 is taken in the liquid and removed.



In an absorber, lime reacts to produce calcium sulphite ($CaSO_3$), part of which is converted to calcium sulphate ($CaSO_4$) by both reacting with the excess oxygen in the flue gas and by aeration in oxidation tower. Then the flue gas led to the air through demister, after burner and stack.

Reaction

$$SO_2+CaO \rightarrow CaSO_3$$
$$2CaSO_3+O_2 \rightarrow 2CaSO_4$$
$$CaCO_3+SO_2 \rightarrow CaSO_3+CO_2$$

Oxidized absorbent is led to the gypsum separator where the gypsum dehydrated using dehydrator and taken out as gypsum crystal with a moisture content of 10% or less. Supernatant from the dehydrator is returned to lime tank.

The absorbents used in limestone- gypsum process are either limestone powder or slaked lime. Slaked lime, which has strong reactivity, was used when the limestone- gypsum process was first adopted, but is expensive, so the limestone has now become the mainstream absorbent.

For the detail information, refer to the pages at P.183 or E.45.

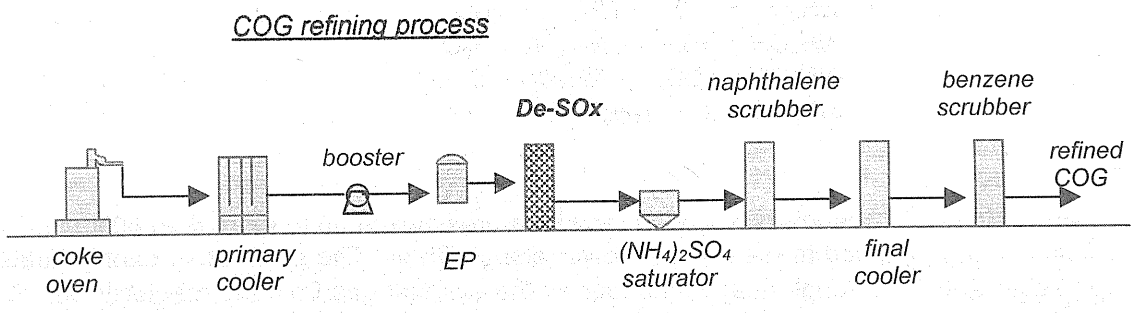
5-3 Coke Oven Gas Desulphurization Process

Coke oven gas (COG) contains 4 to 7 g/ Nm^3 of hydrogen sulphide (H_2S), which is equivalent to the heavy oil which contains 1% of sulphur at the same level of calorie. The desulphurization of COG leads up to the significant SOx reduction measure because the COG is used as a fuel for reheating furnaces. On top of that, desulphurization of COG alleviates the corrosion for inner surface of COG pipe-lines.

The desulphurization of COG is done by ammonia, sodium carbonate, etc as a desulphurizing agent. And the wastewater generated from these processes are treated by the method of oxidation combustion, redox-oxidation, wet oxidation, or others. The Takahax process and Fumax process have now been a mainstream in the COG desulphurization. Several commercially available desulphurization processes for COG are shown in a table including desulphuring agent, catalyst and byproduct.

System	*DeSOx-chemical*	*Catalyst*	*Byproduct*
Takahax-Hirohax	NH_3	*naphtoquinone salfonic acid soda*	$(NH_4)_2SO_4$ + H_2SO_4
Takahax-Reduction Decomposition	Na_2CO_3	*naphtoquinone salfonic acid soda*	*crude S*
Fumax-Hemibau	NH_3	*picric acid*	H_2SO_4
Stred Ford-Combax flue gas De-Sox	Na_2CO_3	*anthoraquinone sulfonic acid soda metavanadate soda T artaric acid soda*	*gypsum*
Diamox-claus	NH_3	*none*	*pure S*
Salfiban-claus	*alkanol amine*	*none*	*pure S*

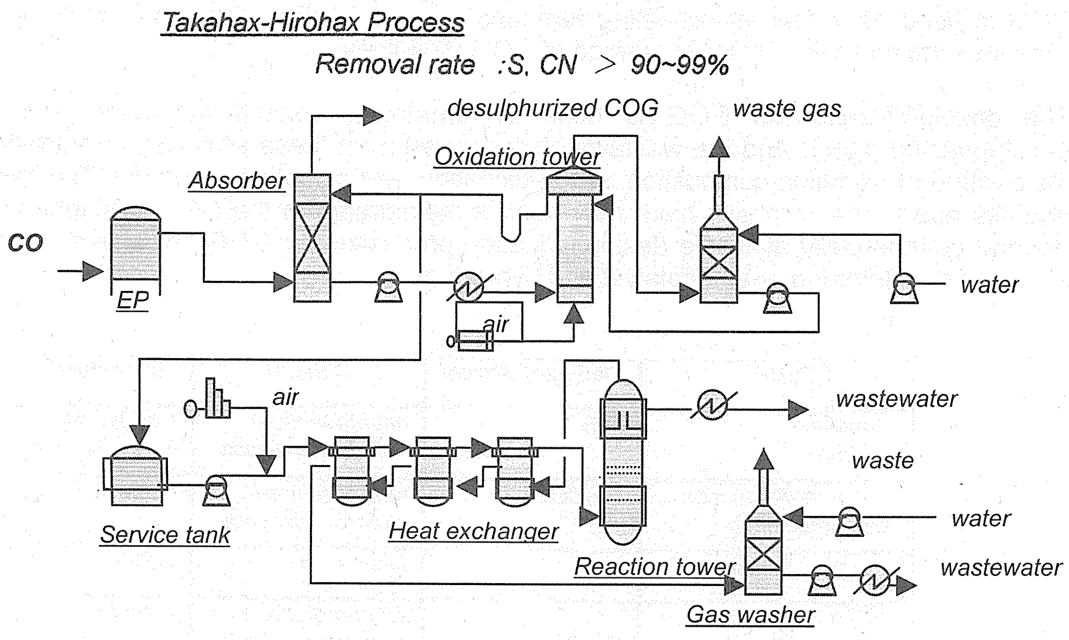
The COG- desulphurization unit is located just at the center of whole COG refining process as shown in a slide.



For the detail information, refer to the pages at P.188~189 or E.50~51.

5-4 Takahax-Hirohax Process

Takahax (desulphurization) and Hirohax (wastewater treatment process) are shown in a slide. COG is led to the EP by boosting blower, and about 99% of tar in the gas is removed. The gas led to an absorber filled with media contacts with liquid containing catalyst (naphtoquinone salfonic acid soda) and then about 30% of ammonia (NH_3) in COG dissolves to the water. This dissolved NH_3 reacts with hydrogen sulphide (H_2S) and hydrogen cyanide (HCN) in COG, which is the process of the desulphurization and decyanization. The removal rates for H_2S and HCN are both 90 to 99%. Then desulphurized COG is led to ammonium sulphate saturator.



The absorbent is led to an oxidation tower to regenerate an ammonium hydroxide (NH_4OH) by aeration under the presence of catalyst and then returned to absorber. During the oxidation, the ammonium cyanate (NH_4CN) is converted to ammonium thiocyanate (NH_4NCS).

Reaction

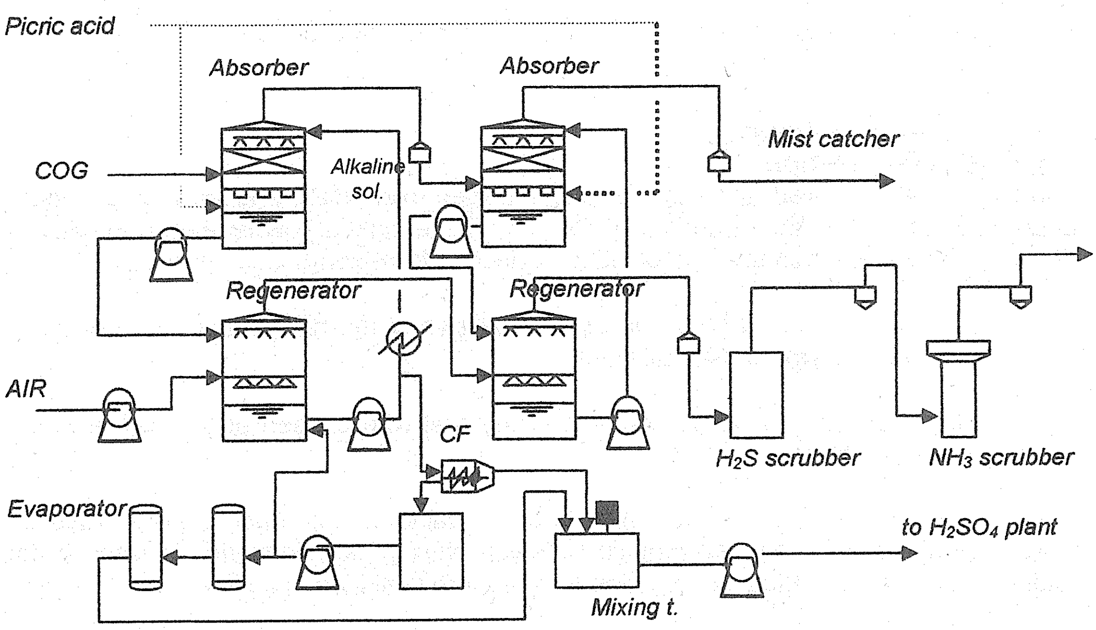
$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH + H_2S \rightarrow NH_4HS + H_2O$$
$$NH_4OH + HCN \rightarrow NH_4CN + H_2O$$
$$NH_4HS + 1/2O_2 \rightarrow NH_4OH + S$$
$$NH_4CN + S \rightarrow NH_4NCS$$

A part of circulated absorbent is sloped, and then pressurized up to more than 60 kg/cm^2 by boosting pump, and led to the reaction tower along with air. The spent absorbent is heated up to over 200 ℃ through heat exchanger by the exhaust gas from the reactor tower. The spent absorbent led to reaction tower is exposed to the wet oxidation condition, and all sulfur compounds are converted to sulphuric acid (H_2SO_4) or ammonium sulphate ($(NH_4)_2SO_4$), and nitrogen compounds are converted to ammonia (NH_3). The wet oxidized liquid is sent to the wastewater treatment plant. The exhaust gas from reaction tower is washed by water and then exhausted. The wastewater from gas washer is led to the wastewater treatment plant.

For the detail information, refer to the pages at P.189~190 or E.51~52.

5-5 Fumax Process

Fumax process is shown in a slide.



COG is given two-stage scrubbings by contacting with ammonium solution and desulphurized. Hydrogen sulphide (H_2S) in COG led to the 1st stage absorber is absorbed to ammonium solution.

Absorption

$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH + H_2S \rightarrow NH_4HS + H_2O$$

Ammonium sulphide (NH_4HS), which is formed by the absorption of H_2S is oxidized by air and regenerated to ammonium hydroxide (NH_4OH) in a regenerator. Regenerated absorbent is repeatedly used in absorber.

Regeneration

$$NH_4HS + 1/2O_2 \rightarrow NH_4OH + S$$

Generated sulphur (S) in a regenerator is separated from spent absorbent by a centrifuge, and then sent to a sulfuric acid plant. The supernatant out of centrifuge is condensed by evaporators and then send to a sulphuric acid plant along with sulphur.

H_2SO4 recovery

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + 1/2O_2 \rightarrow SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

In a sulphric acid plant, the sulfur is oxidized to SO_3, which is absorbed into the water and converted to sulphuric acid.

The exhaust gas from 2nd stage regenerator is scrubbed by a alkaline solution to remove H_2S in a H_2S scrubber and scrubbed by acidic solution to remove NH_3 in a NH_3 scrubber, and emitted to the atmosphere.

For the detail information, refer to the pages at P.190~191 or E.52~53.

6. NOx Control Technology

6-1-1 NOx Generation

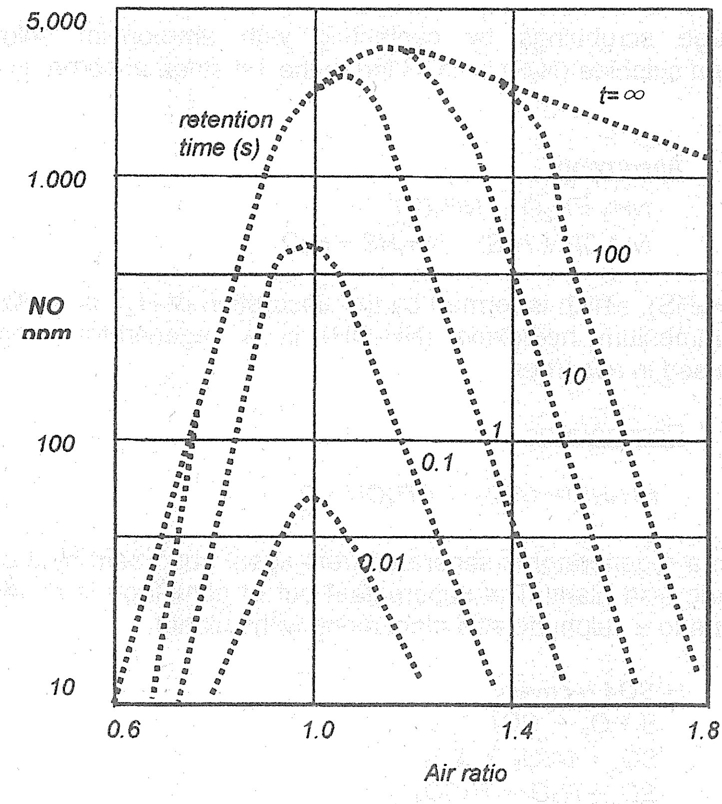
The term of NOx implied two major oxides, nitrogen oxide (NO) and nitrogen dioxide (NO_2). In combustion, NO is the dominant of the two, NO_2 mainly a downstream derivative of NO. There are two main mechanisms of NOx production from combustion process:

(1) from the reaction of N_2 in the air with oxygen at the high temperature of the burner chamber, known as thermal NOx,

(6) from the reaction of nitrogen existing in the fuel with oxygen at the high temperature, known as fuel NOx.

Reduction of NOx by furnace operation is done mainly by decreasing the air ratio and the furnace temperature. The relationship between NOx generation and air ratio at different retention time at theoretical combustion temperature is shown in a slide.

Thermal NOx



When the air ratio is increased to certain level and when the retention time is longer, the NOx concentration is increased proportionally. However, the air ratio exceeds at certain level, NOx concentrations begin to decrease due to the lowering the temperature of combustion, as can be understood from a figure.

Nitrogen and sulfur contents in various fuels are shown In the table shows. The nitrogen in fuels, such as quinoline and pyridine contained in petroleum and coal and hydrogen cyanide (HCN) and ammonia (NH_3) contained in gaseous fuel, is widely known to be more easily converted to NOx than the nitrogen in the air (thermal NOx).

N and S contents in fuels

	Fuel	N	S
Solid wt%	coal	0.7~2.2	0.3~2.6
	coke	0.6~1.4	0.2~1.0
Liquid wt%	crude oil	0.03~0.34	0.1~3.0
	C-oil	0.2~0.4	0.2~0.3
	B-oil	0.08~0.35	0.2~0.3
	A-oil	0.005~0.08	0.2~0.3
	light oil	0.004~0.006	0.03~0.5
	kerosene	0.0005~0.01	0.001~0.2
Gas g/Nm³	COG-crude	0~9	1.5~7
	COG-fine	0.02~0.5	0.05~0.7
	BFG	tr	tr
	LDG	tr	tr
	LPG, LNG	tr	tr

※ JIS K2205 kinematic viscosity (cSt, mm2/s) C-heavy oil: 50≦~1,000, B-heavy oil: 20~50, A-heavy oil: ≦20

The ratio of actual conversion of nitrogen in fuel to NOx over the total nitrogen contained in fuel is called as 'fuel NO conversion ratio'. The ratios are approximately between 12% and 15%.

For the detail information, refer to the pages at P.194~195 or E.56~57.

6-1-2 Factors in NOx Generation & Reduction

The causes influencing NOx generation are:

(1) nitrogen concentration in fuel
(2) air ratio in the combustion
(3) burner flame temperature
(4) retention time of gases in high temperature zone

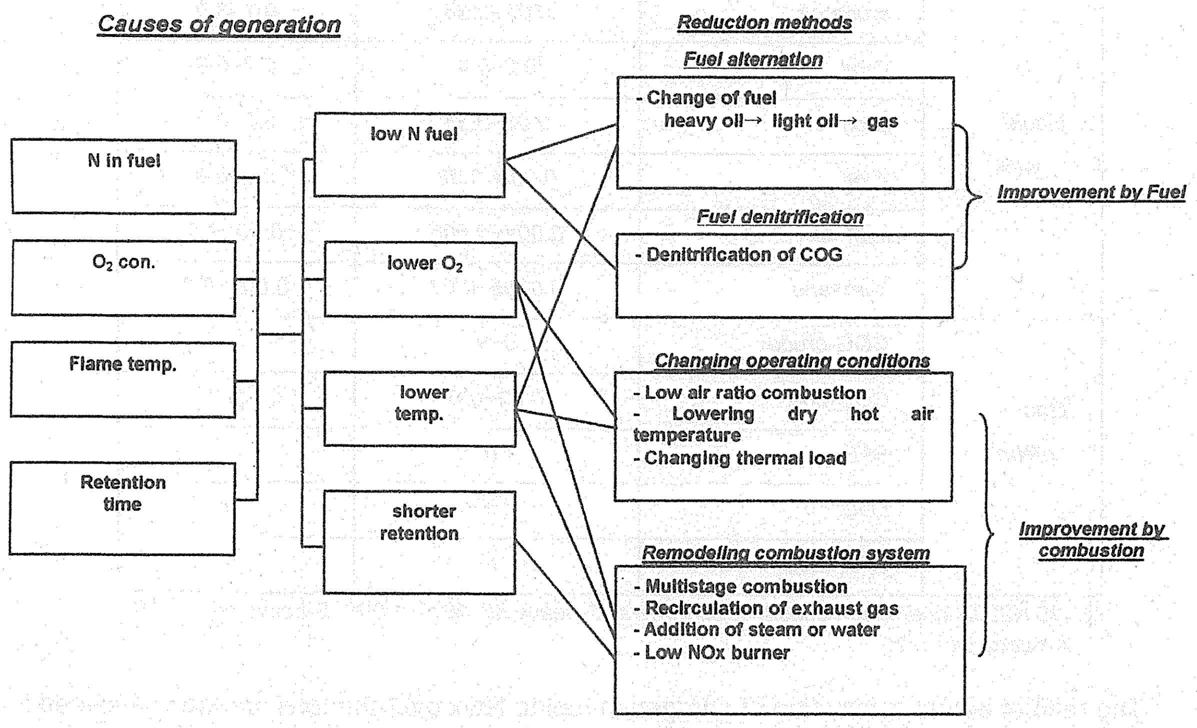
As measures to reduce NOx generation;

Alternation of heavy oil to light oil. or to gas is effective, which is shifting to the lower caloric fuel, and then lets the nitrogen content in fuel and the combustion temperature lower.

COG denitrification gives a direct effect to reduce the NOx emission in steel mill.

Changing operating conditions, such as:

(1) lowering air ratio
(2) lowering dry hot air temperature
(3) lowering the thermal load in combustion chamber are effective



Remodeling combustion systems, if possible, such as:

(1) to adopt multistage combustion
(2) to adopt the recirculation system of exhaust gas
(3) to modify the system to be able to add steam or water into the combustion chamber
(4) to adopt low NOx burner

For the detail information, refer to the pages at P.196 or E.58.

6-2 Fuel Improvement
6-2-1 Fuel Improving
Using a fuel with low nitrogen is effective to reduce NOx generation. The fuel with low

concentration of sulphur has, in general, low concentration of nitrogen proportionally in it. The COG widely used for the fuel of steel mill contains 1~9 g/m^3 of nitrogen. This comes from that the pre-heating time and temperature of fuel gas and air for combustion is in 4 to 6 seconds at high temperature of 800 to 1,000℃, and in addition to these, the air ratio to each oven are hard to control due to the existence of tremendous number of combustion chambers in coke oven.

1. *Use of low N and low S fuel* *S ∝ N*
2. *Denitrification of COG* *N 1~9 g/m^3 800~1,000℃, 4~6 sec.*

For the detail information, refer to the pages at P.196~200 or E.59~62.

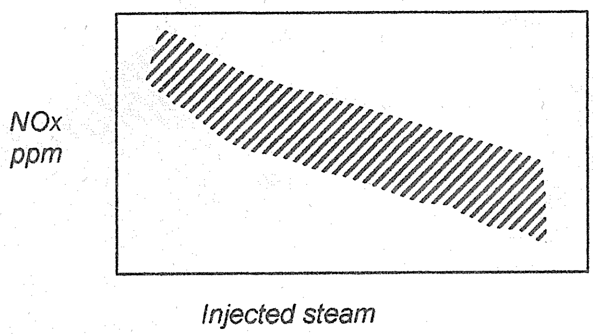
6-2-2 Combustion Improvement

Typically, the air ratio is decreased to the lower, then NOx generation goes down proportionally as explained in previous slide. For example, when oxygen concentration in exhaust gas is reduced by 1%, NOx is decrease by 10%. Multistage combustion is a method in which combustion air is injected by 2-stage or more stages into the combustion port, e.g., 80~90% of theoretical combustion air is fed at 1st stage combustion port and the rest of air is fed at 2nd stage port or latter stage port, e.g., this has reduced NOx by about 20%. The steam or water injection to a combustion chamber is to utilize its latent heat and to increase of heat capacity, therefore the flame temperature is decreased under even same calorific power.

1. *Low air ratio operation* *O_2 1% ↓⇒ NOx 10% ↓*
2. *Multistage combustion* *1st stage air ratio; 80~90%*
   rest air →2nd stage combustion → NOx ≒▲20%

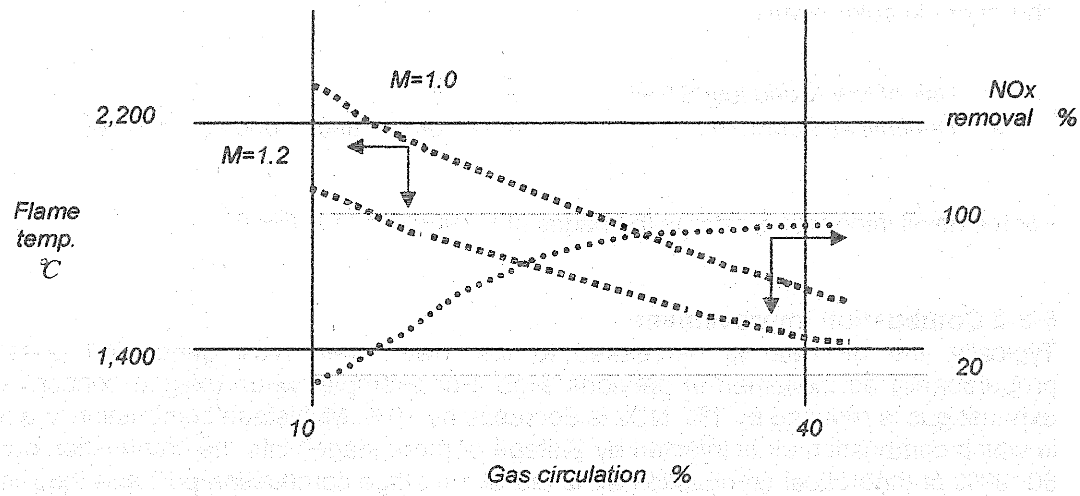
The figure shows the relations between a calories injected by steam and NOx generation.

3. *Steam or Water injection* *flame temp. ↓ ⇒ Knox ↓*
   no-change in generated calorie



In exhaust gas circulation, a part of combustion exhaust gas is mixed into the combustion air. Since the oxygen concentration in combustion air is diluted with exhaust gas and becomes lower than that of normal air, the reaction between oxygen and fuel delays and then the maximum temperature of flame becomes lower. These relations are shown in a figure.

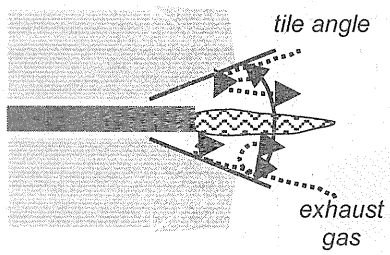
4. Exhaust gas circulation

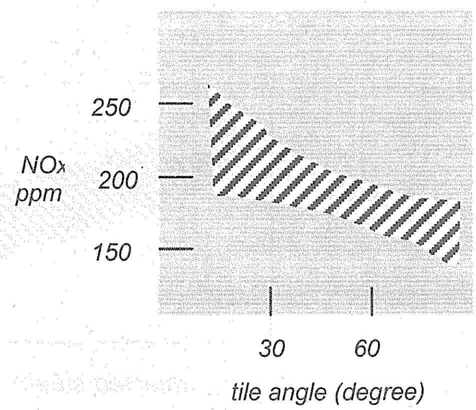


5. Low- NOx burner

The low-NOx burner is a method to reduce NOx in which the burner mechanism is equipped with one or combination of NOx-reducing methods such as lowering of oxygen concentration, lowering of flame temperature, and shortening of gas retention time in high temperature zone.

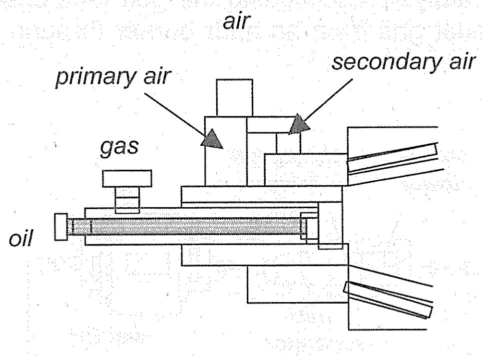
Wide-angle burner tile:
By widening the burner tile angle, the combustion exhaust gas near the tile is sucked within the tile angle by the kinetic energy of flame, by which the oxygen partial pressure of combustion air is decreased and simultaneously the flame temperature is lowered, leading to reduction of NOx generation.

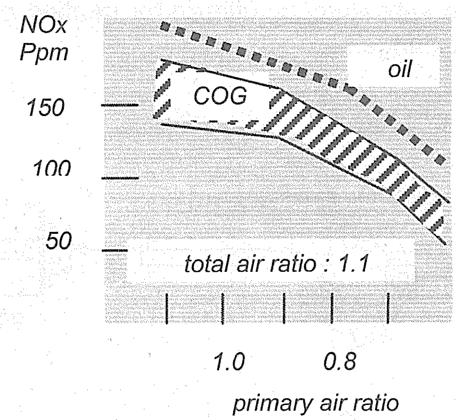




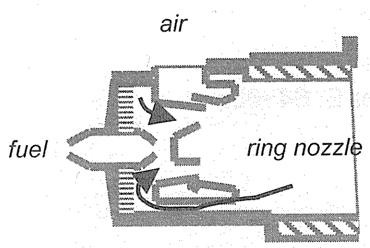
Double-stage combustion burner:
This is a method to provide a double-stage combustion in a burner so as to reduce the

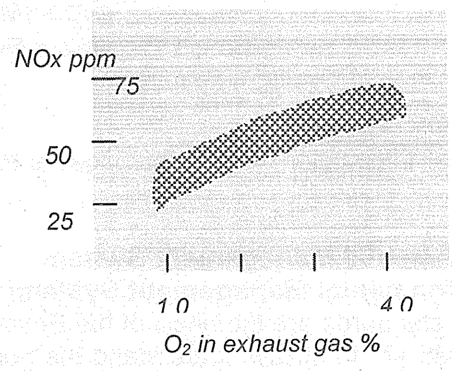
generation of NOx and , by forming a long flame, to lower the maximum temperature of the flame.





Self- circulate combustion burner:
in this burner, the combustion gas is sucked into the flame by the kinetic energy of combustion air so as to lower the flame temperature.





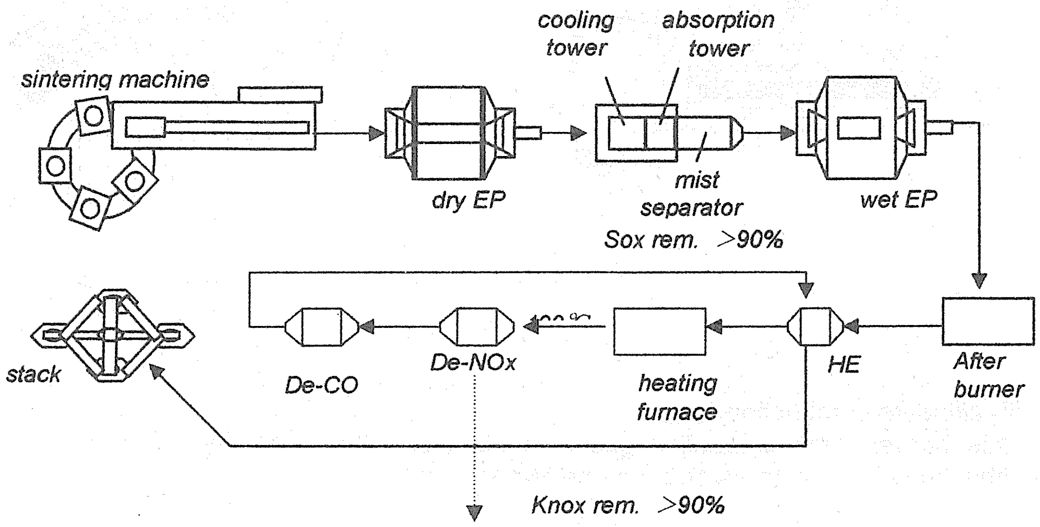
For the detail information, refer to the pages at P.196~202 or E.59~63.

6-3 Denitrification of Exhaust Gas

As the greater part of NOx generated from the combustion of fuel has a low reactivity, the removal of such NOx is technically fairly hard. Among various processes, one method which is regarded as most advanced is a dry type selective contact reduction by use of ammonia (NH_3). This process has already reached the level of commercial use for clean gas (exhaust gas with little dust, soot, and SOx), however, for the dirty gas especially the exhaust gas from sintering furnace, there still remain problems such as deterioration of catalyzer reactivity, plugging of catalyzer media, and etc. if this process is carelessly applied.

The denitrification for sintering process (production capacity: 7,000 ton / day) is shown in a slide. The exhaust gas is led to a dry EP where dust and soot are removed, and then is removed more than 90% of SOx in flue gas desulphurizer using limestone-gypsum process.

At the next process, the gas is treated by wet EP, and then is heated by after burner, heat exchanger, and heating furnace up to 400℃, and then is removed more than 90% of NOx in denitrification system, then follows the carbon monoxide (CO) reduction process, which oxidizes the carbon monoxide in the gas using catalysis and boosts the gas temperature which is subsequently utilized for heating of exhaust gas from an after burner through the heat exchanger.



De-NOx: Dry Type Selective Contact Reduction using NH_3

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

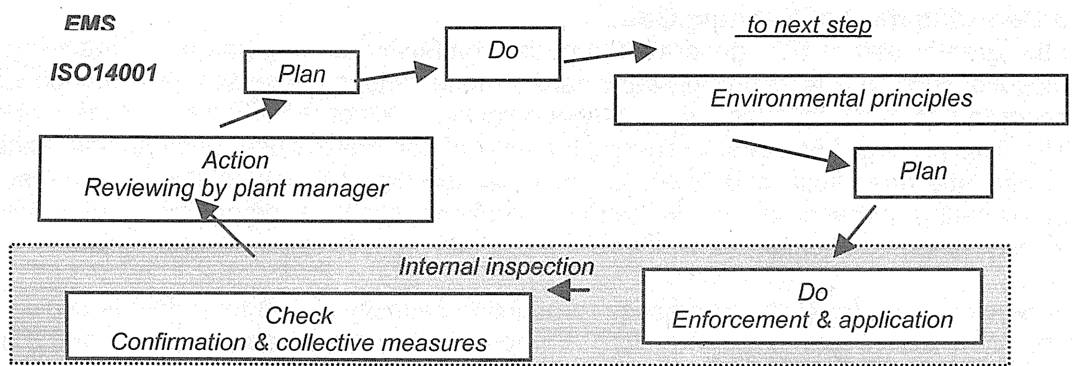
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

For the detail information, refer to the pages at P.202~203 or E. 64~65.

7. Environmental Management System

7-1. Environmental Management System(1/2)

ISO14001 standards are the basis of the Environmental Management System (EMS). The aims of EMS are to always understand the pollutants discharged by the enterprise itself, to maintain the conditions of a well-managed environment. The ISO 14001 requirements consist of 5 items, ①Environmental principle, ②Plan, ③Enforcement and application, ④ Confirmation and collective measures ⑤Reviewing by plant manager.



The items which should be considered at the time of plant construction and operation;

1. Environmental impact assessment is essential to do advance investigation of the natural environmental condition in the area of plant location.

2. To understand the environmental standards and regulations for emission are important.

3. In planning of plant and air pollution control equipment, calculate the allowable value of the pollutants generated by the plant which conform to the emission standards. The most economical treatment methods are determined by selecting from various methods which satisfy the upper limit values for the pollutants emission.

4. Appropriate operation control of entire iron and steel production system and effective worker training are very important too.

5. The monitor of pollutants emitted from the steel mill plant is important to conform to emission standards.

6. All staff involved with the plant must make their best efforts for its environmental management. The person in charge of the work site where the accident occurred must report the occurrence of accident to related organs, make efforts to minimize damage, and obtain the understandings of local government bodies and local residents.

For the detail information, refer to the pages at P. 271~280, E133~141.

7-2. Environmental Management System (2/2)
The businesses must investigate, analyze, and record the emitted gas volume and quality in the plant by themselves (monitoring) in order to justify the situation. Businesses emitting exhaust gases into the air must monitor the exhaust gases quality to understand the situation and check the conformity with the specified quality standards.

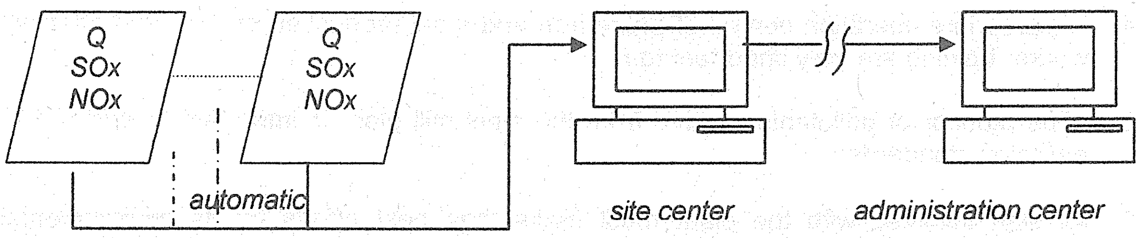
The air pollution quality monitoring in accordance with the Basic Environmental Law and the Air Pollution Control Law is broadly divided into two categories, one is the "monitoring emission quality" done by business, and the other is the "monitoring air pollution" done by local public corporation entities. The items stipulated by the Emission Standard and Environmental Quality Standard (EQS) are listed in a slide.

<u>*Measurement Items*</u>

	Emission Standard	*EQS*
Pollutants	*dust*	*Suspended particle matter*
	sulfur oxide	*SO_2 (sulfur oxide)*
	nitrogen oxide	*NO_2 (nitrogen oxide)*
	Cd, its compounds	
	Cl, HCl	
	F, HF, Si_nF_{2n+2}	*CO*
	Pb, its compounds	*Photochemical oxidant*

The telemeter system is the centralized system mainly composed of automatic measuring instruments for the concentration of exhaust SOx, NOx, exhaust gas volume, and etc. These data is gathered to the control center, where monitors the emitting situations of pollutants under analyzing of total volume of pollutants emitted to the air. The factories located in the area with Areawide Total Pollution Load Control send the data to the environmental monitoring center of prefectural government or municipality.

Telemeter System



For the detail information, refer to the pages at P.253~255, 269~278 or E.115~117, 133~140.

8. Resources Saving

The dust volume collected in integrated steel mill factory where the dust collection systems are well equipped has been 4.9% of pig iron produced. In case of integrated steel mill plant with production capacity of 3 million ton per year, dust volume is estimated as shown in a slide.

Dust Generation & Utilization

Dust Generation at 3 million-ton Crude Steel Production (t / y)

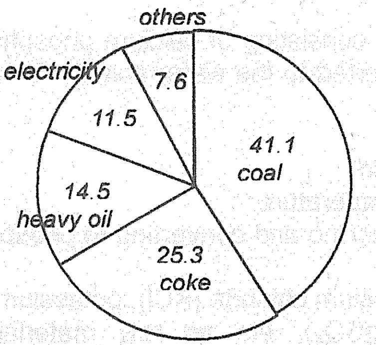
Process	Dry Dust Collector	Wet Dust Collector	Total
Material / Pig Iron	111,000	38,000	149,000 (61%)
Steel	33,000	60,000	93,000 (38%)
Rolling	2,700	300	3,000 (1%)
Total	146,700 (60%)	98,300 (40%)	245,000 (100%)

The dust contains useful ingredient such as iron oxide, carbon, lime, etc., which are recyclable in the steel manufacturing.

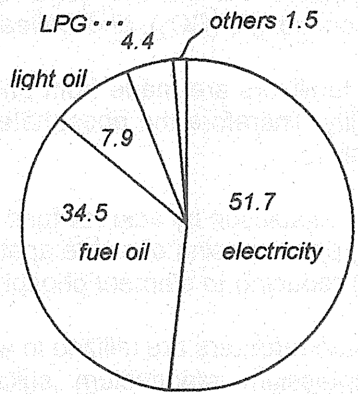
For the detail information, refer to the pages at P.205~206, E.67~68.

9. Energy Saving

The dependency of energy sources varies from integrated steel plant, which has blast furnace, to non-integrated steel plant, which does not have blast furnace. Further, it varies in way of whether the coke, electricity and oxygen are produced in the plant or purchasing from the outside.



Integrated Steel Production



Non-Integrated Steel Production

The energy saving lessens the air pollutants emission into the air. The energy saving methods are ;

(1) to adopt equipment with high efficiency and to make improvement of operating methods

(2) to reduce the number of unit operations as many as possible and to change to continuous process as much as possible

(3) to recover the waste heat as much as possible

Energy saving Method
-high efficient equipment & improving operation
-reducing the number of unit operations
& changing to continuous process
-waste heat recovery

For the detail information, refer to the pages at P.210, 216~220 or E.72, 78~82.

Ⅳ.Fertilizer Manufacturing Industry

1. Air Pollution in Fertilizer Plant

The principal ingredients of fertilizers are three of nitrogen, phosphorus and potassium. For nitrogen fertilizers, sulfuric acid (H_2SO_4), Nitric acid (NO_3), lime stone ($CaCO_3$), ammonia (NH_3), carbon dioxide (CO_2), and Chilean saltpeter are most widely used as raw materials.

Phosphate fertilizers are made from phosphate rock, consisting of calcium phosphate with hard solubility. Therefore the phosphate rock is converted to the water-soluble compounds by either way of:

(1) dissolution by acid (sulfuric acid, nitric acid)
(2) decomposing of stable apatite by high temperature
(3) reducing to element phosphorus (P) by thermo and converting to phosphate

The potassium fertilizers are utilized in a form of potassium chloride (KCl), potassium sulfate (K_2SO_4), potassium magnesium sulfate ($K_2SO_4MgSO_4$), etc as raw materials. The potassium chloride, most widely used potassium fertilizer is made from the ore by floatation method or calssification-crystallization method after grinding it.

Fertilizer	*Raw materials*
Nitrogenous F.	*: ammonia, Chilean saltpeter, limestone + N_2,* ・・・・
Phosphate F.	*: phosphate rock*
Potassium F.	*: ore (ingredient ; KCl + NaCl), KCl,* ・・・・
Coated F.	*: N, P, K + thermo plasticity resin*

Other than these fertilizers, there is a fertilizer in a form of which is wrapped in the thermo plasticity resin in order to control the releasing velocity of nutrients. These are called coated fertilizer and have a fair chance of air pollution.

In fertilizer manufacturing plant, the soot, SOx, NOx, dust, hydrogen fluoride, ammonia, and some solvent are typically given as considerable pollutants which are controlled by the Air Pollution Control Law.

Pollutants	*Origins of Pollutants*
Soot, SOx, NOx	*Boiler, Dryer, Calcining furnace, etc.*
Dust	*Raw material stock yard, Raw material feed equipment, Belt conveyer, Bucket conveyer, Crusher, Mill, Sieve*
HF	*Phosphate fertilizer plant------ Reactor, Calcining furnace, Melting furnace, Phosphoric acid concentration plant*
NH_3	*Pelletizer, Dryer*
Solvent	*Coated fertilizer manufacturing process*

Ammonia is designated as a "Specified Substance" in Air Pollution Control Law, which prescribes the necessary measures in case of malfunctions and damages in synthesis process and decomposition process. When ammonium sulfate, ammonium phosphate and urea are manufactured, the exhaust gas from the drying-pelletizing process of raw materials contains ammonia but it is thin concentration. However, there is no need to provide with an ammonium-oriented abatement device, and for the most case the ammonia is captured together with fertilizer dust generated from drying-pelletizing process. The emission gas after the treatment by this way conforms to the permissible emission level for ammonia.

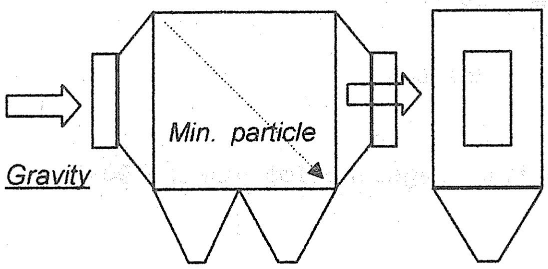
The origins of air pollutants in the processes or unit operations in fertilizer manufacturing plant are summarized in a slide.

For the detail information, refer to the pages at P.1~89.

2. Soot & Dust Collection

2-1 Gravitational, Inertial & Centrifugal Dust Collector

Because of the density difference between solids and gases, in laminar flow their stream lines are different if the direction of flow is changed. This fact is frequently exploited to separate solid particles from a gas stream, usually by suddenly changing the direction of flow of the gas stream.



In gravity dust collector, a settling chamber reduces the velocity (normally 1~2 m/second) of the gas stream so that the particles drop out by gravity. It is a large device not often used as a final control mechanism. If it is assumed that Stokes's law applies, then the particle size which will be removed with 100% efficiency is given by the equation.

Stokes' Law

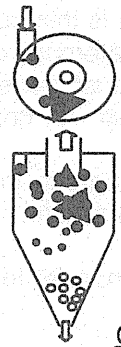
$$V=(g/18\mu)(\rho 1-\rho)D^2 \quad (cm/s)$$

V: settling velocity (cm/sec)
μ: gas viscosity (kg/ms)
g: gravitational acceleration (cm/s^2)
$\rho 1$: particle density (g/cm^3)
ρ: gas density (g/cm^3)
D: particle diameter (cm)

In the centrifugal force collector generally called cyclone dust separator, the centrifugal force exerted on a particle in a cyclone is given by the equation. For a large volume of gas treatment, small cyclones are connected in parallel and used as multi-cyclone. The inlet-gas velocity is set at 10 ~25 m/s.

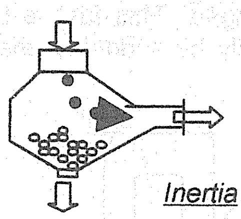
$$\text{Centrifugal force } (F) = mv^2/R \ (N)$$

m: particle mass (kg)
V: particle velocity (m/ s)
R: cyclone radius (m)



Centrifugal

In an inertial dust collector, the gas stream is forced to collide with an obstacle or the gas flow direction is sharply changed to separate and collect dust particles in gas by using inertial force.



Inertia

For the detail information, refer to the pages at P.165~166 or E.90~92.

2-2 Scrubbing Dust Collector

The mechanisms of dust collection working in scrubbing dust collectors are:

(1) Adhesion of dust to water drops and water film
(2) adhesion by diffusion force between dusts
(3) increase of coagulation force of particles by increasing moisture
(4) moisture condensation triggered by dust as a nucleus
(5) particles adhesion by bubbles

The scrubbing dust collectors have been widely used for the abatement of waste gas recently as it can remove not only dust but also the toxic gas containing of fluorine and sulfur oxide at once. The scrubbing dust collectors are generally classified into spray type scrubber, packed type scrubber, jet scrubber, and venturi scrubber.

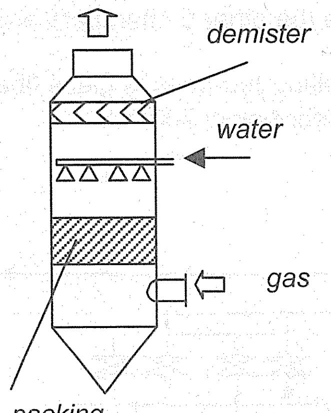
Typical Types of Scrubbers

Type	Velocity m / s	L/G l/m^3	ΔP kPa	Th. Φ μm
Spray	1~2	2~3	0.1~0.5	≧3
Packed	0.5~1	2~3	1~2.5	≧1
Jet	10~20	10~50	0~ -1.5	≧0.2
Venturi	60~90	0.3~1.5	3~8	≧0.1

Th. Φ: Particle size of threshold to allowing 50 % removal

The outline of structure of packed tower scrubber is shown in a figure:

Packed tower



To achieve efficient performance of scrubbing dust collectors, it is important to select a gas flow velocity and liquid to gas ratio suitable for the each system.

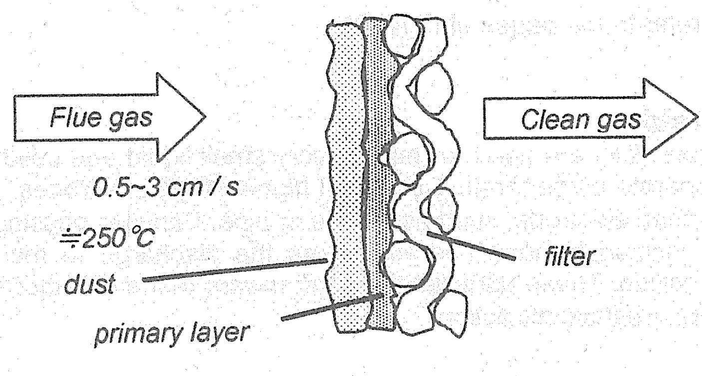
For the detail information, refer to the pages at P.92~94.

2-3 Filter Type Dust Collector

Bag filter dust collectors have the widest usage range of all the filter dust collectors. Bag filters can collect fine particles even 0.1 μm in size. When a bag filter is used for the treatment of flue gas from a glass melting furnace, a high dust-collection efficiency rate of 97~99% can be obtained.

The dust collector mechanism is that the primary layer, to which particles have adhered on the surface of the filter cloth, is used as the filtration layer to collect fine particles. The flow rate through the filter is usually around 0.5~3 cm/s. Therefore, when treating a large volume of gas, the dust collector equipment has multiple dust collecting chambers with many bag filters arrangement in parallel.

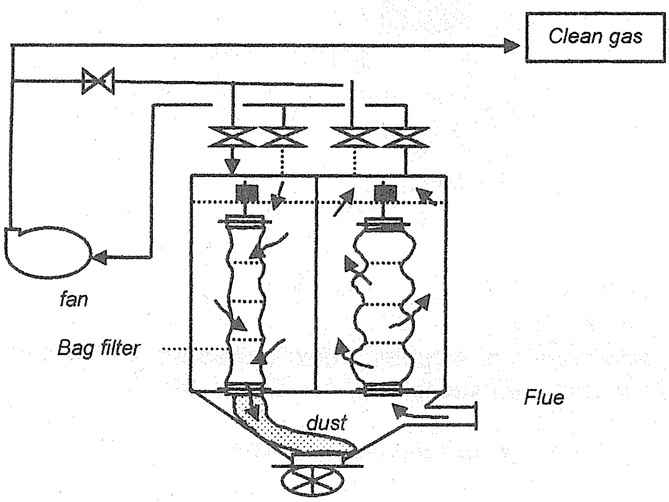
Filtration Action in Filter Cloth



ΔP≒150 mg Hg → dusting

For example, a bag filter with treatment capacity of 35,000 m3/h (250°C) for melting furnace has 6 dust collecting chambers, each with 50~60 cylindrical bag filters about 600 cm long and 30 cmϕ, arranged in each chamber. In this case, one of the 6 chambers is being scrubbed at any given time, while the other 5 chambers are in use.

The filter cloth used for glass melting furnaces is glass fiber because of erosion by sulfuric acid due to dew condensation under below 200 ℃.



When the pressure loss has reached about 150 mm Hg after accumulation of dust on the filter, dusting is needed. The dusting method can be either intermittent, most commonly used for glass melting furnaces, or continuous. Dust removal can be done by a method using vibration or a method using reversed air.

Dusting frequency	*Dusting drive*
- intermittent	*- vibration*
- continuous	*- reverse air*

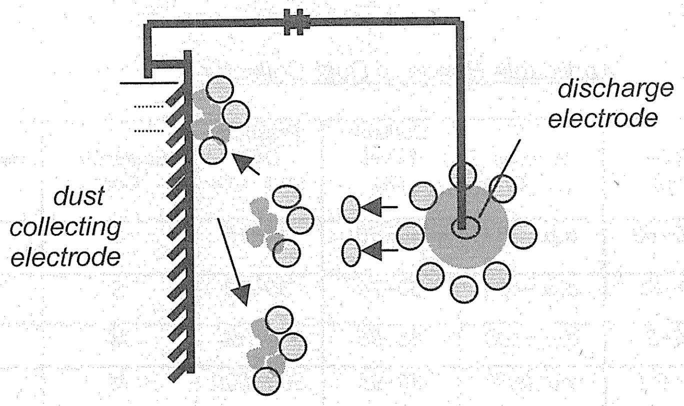
The gas temperature must be kept between 200 and 250 ℃ to avoid over heating for resistance temperature for filter cloth and dew point sulfuric acid.

For the detail information, refer to the pages at P.94~95.

2-4 Electrostatic Precipitator

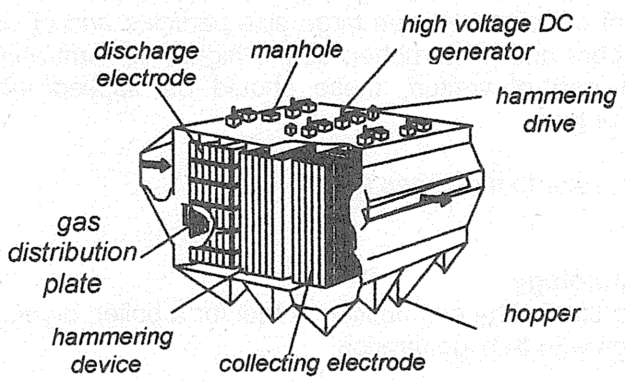
The electrostatic precipitators (EP) are used to remove very small liquid and solid particles from a gas stream. They operate by generating between high-voltage electrodes, usually a fine wire, and a passive earthed electrode, such as a plate or pipe. Particles passing through such an electric field are ionized by ions migrating from the discharge to the collector electrode, with whom they collide. These particles then drift toward to the collector electrode to which they are held by electrostatic attraction.

Principle of dust collection :



The particles are removed from the collector by either a water spray or 'rapping' it periodically. The collector can either be flat or tubular units. Usually, a number of discharge electrodes will hang as shown in a slide.

Structure of EP



The EP is not much affected by the properties of gas and dust, can do highly efficient dust collection, and can collect fine particles without pressure loss.

For the detail information, refer to the pages at 95~96

2-5 Selection of Dust Collector

When we select the dust collectors, physical properties of particle and gases as shown in the slide should be taken into consideration;

Factors affecting Dust Collection:

dust concentration, particle size distribution, temperature of dust,
apparent electric resistance rate, due point, gas temperature,
composition of flue gas, gas volume, etc.

the particle sizes and particle distribution of dust in the flue gas have an effect significantly on the particle removal efficiency in each dust collector. The sizes of particle abated by dust collectors are shown in the table. Invisible particle concentration is said to be 20 mg/Nm^3.

Filter dust collectors become to be required frequent dust shakings if these are applied to high concentration dust gas. The EP will not be affected so much by the concentration of dust in flue gas.

Applicable Range of Dust Collector

Type	*Particle (μm)*	*Working (℃)*	*Cutback Level (%)*	*Pressure Drop (mm H_2O)*	*Equipment Cost*	*Running Cost*
Gravity	*1000~50*	*d.p.~400*	*40~60*	*10~15*	*S*	*S*
Inertia	*100~10*	*d.p.~400*	*50~70*	*30~70*	*S*	*S*
Centrifuge	*100~3*	*d.p.~400*	*85~95*	*50~150*	*M*	*M*
Scrubbing	*100~0.1*	*no- limit*	*80~95*	*300~800*	*M*	*L*
Filtration	*20~0.1*	*no- limit*	*90~99*	*100~200*	*≧M*	*≧M*
EP	*20~0.05*	*d.p.~400*	*90~99.9*	*10~20*	*L*	*S~M*

S: cheap, M: average, L: expensive

Regarding the dust concentration, the higher concentration of dust in a gas brings the higher removal efficiency of particle removal for the gravity collector and inertial force dust collector due to the acceleration of collision between large size particles and of coagulation of fine particles. In venturi scrubber and jet scrubber, as the higher concentration of dust causes the wear at the throat part of venturi, these should be applied the gases of dust concentration 10 g/ Nm^3 or less.

For the detail information, refer to the pages at P.97.

3. SOx Reduction Technology

In fertilizer manufacturing plants, the combustion of fuel for a boiler, dryer, calcining furnace and melting furnace brings with SOx generation.

Sources of SOx: Fuel SOx

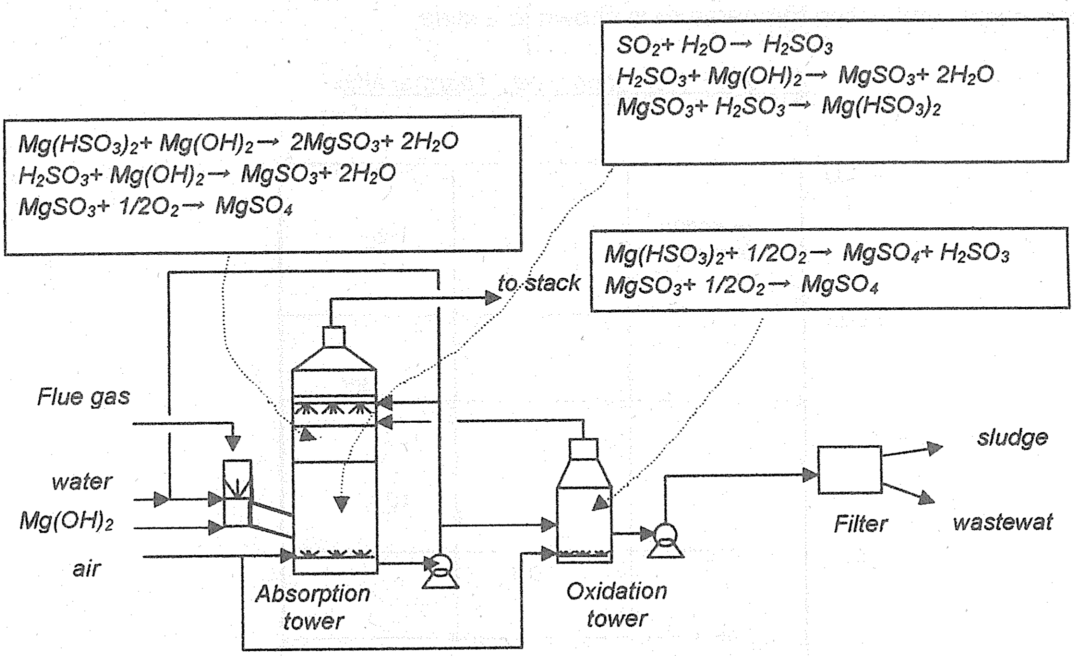
- Boiler - Dryer - Calcining furnace - Melting furnace

However, few fertilizer manufacturing plants have equipped with flue gas desulphurization system in order to fulfill the emission standard in Japan and the prefectural stringent emission standards, but they cope with these to certain extent by using a fuel with low sulfur content.

It is anticipated that the necessity of desulphurization plant will come out when the permissible emission level is strengthened in future,. Flue gas desulphurization systems are classified into wet type, dry type and semi-dry type. About 70% or more of total number of installed desulphurization plants have been wet type method and about 80% or more in gas volume abated.

In wet type method, there are processes such as lime slurry absorption method, magnesium hydroxide slurry absorption method, alkaline solution absorption method, double alkaline method, oxidation absorption method and etc. Among them, magnesium hydroxide absorption process is suitable for the treatment of small-to-medium sized boilers. This process is simple, as shown in a slide, with low construction cost, low raw material cost, less toxicity, less corrosion and safety. The byproduct has a high solubility, so it could avoid clogging problem. The byproduct of magnesium sulfate can be reused as raw material of fertilizer production.

Wet Type Absorption



For the detail information, refer to the pages at P.98~99.

4. NOx Reduction Technology

4-1 NOx Generation in Fertilizer Plant

The term of NOx implied two major oxides, nitrogen oxide (NO) and nitrogen dioxide (NO_2). In Combustion, NO is the dominant of the two, NO_2 mainly a downstream derivative of NO. There are two main mechanisms of NOx production from combustion process:

(1) from the reaction of N2 in the air with oxygen at the high temperature of the burner chamber, known as thermal NOx

(2) from the reaction of nitrogen existing in the fuel with oxygen at the high temperature, known as fuel NOx.

The figure shows relation between air ratio and NOx concentration generated at theoretical combustion temperature, known as fuel NOx. In fertilizer manufacturing plants, the generation of fuel NOx is not so much though C-heavy oil, in which contains nitrogen relatively high, is used. The major NOx generated in the fertilizer plant is considered as thermal NOx.

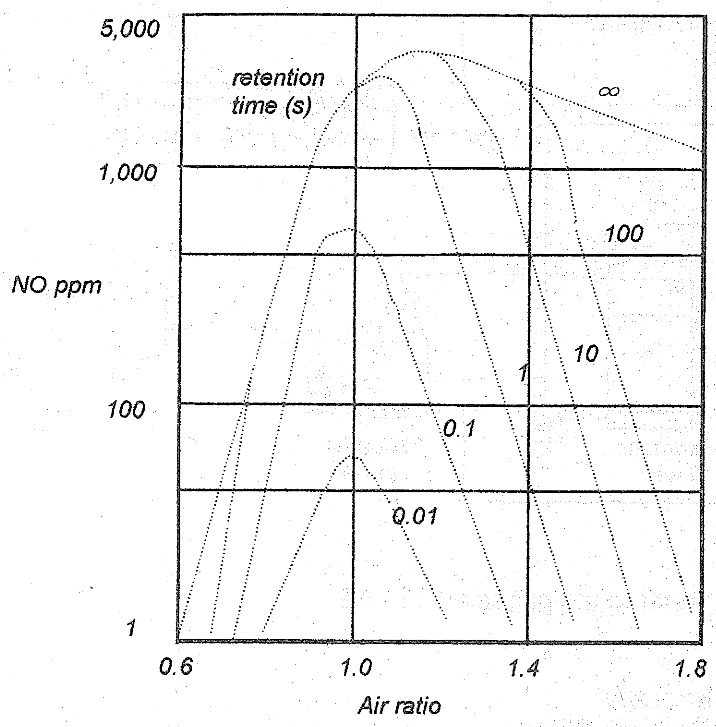
Thermal NOx ≫ Fuel NOx

When the following operating conditions are formed, NOx concentration in the flue gas increases:

(1) combustion at high temperature
(2) high concentration of oxygen in combustion area
(3) longer retention time of combustion gas in high temperature combustion area

The relationship between NOx generation and air ratio at different retention time at theoretical combustion temperature is shown in a slide.

Air ratio ~ Retention time ~Thermal NOx



When the air ratio is increased to certain level and when the retention time is longer, the NOx concentration is increased proportionally. However, the air ratio exceeds at certain level, NOx concentrations begin to decrease due to the lowering the temperature of combustion, as can be understood from a figure.

NOx concentration increases at:
- higher temp. in combustion
- higher O_2 conc.
- longer retention in high temp. zone

For the detail information, refer to the pages at P.99~100.

4-2 NOx Control Methods

Various NOx reduction methods on the basis of previously mentioned theory have been developed and adopted under limited conditions as shown in the table. The marks in the table means;

◎; large effect is expected
○; not so large effect is expected
△; effects vary depending on the equipments
★; affecting on existing equipment is predicted
☆; careful application is required

NOx Reduction Methods	*Decreasing effect* Thermal NOx	*Decreasing effect* Fuel NOx	*Remarks* lowering heat efficiency	*Remarks* lowering heat	*Remarks* enlarging equipment	*Remarks* enlarging
Improving operating						
Lower air ratio combustion	△	◎				☆
Lower heat load	○	○		★	★	
Decreasing pre-heat air temp.	○	○	★	★		☆
Improving equipment configuration						
2-stege combustion	◎	◎				
Rich-lean burner	○	○				☆
Exhaust gas recirculation	◎	○	☆	☆		☆
Steam or water injection		○	☆			
Low NOx burner						
mixing accelerate type	○	○				
flame-divided type	○	◎				
self-circulate type	○	○				
stepwise combustion type	○	◎				☆
Emulsion combustion	○	○	☆			

To summarize: In fertilizer plant, following measures are implemented to reduce the NOx emission;

- low air ratio operation in order to lower the oxygen concentration as much as possible in combustion area
- low heat load operation in order to lower the temperature and heat load in combustion chamber
- adoption of low NOx burner

For the detail information, refer to the pages at P.101.

5. Dust Scattering Prevention

In fertilizer plant, the equipment and facility which are regulated by the air pollution control law are stock yard of raw materials, belt-conveyer and bucket-conveyer, crusher and mill, and screen.

Dust generating equipment & location designated by air pollution control law
- *belt conveyer*
- *bucket conveyer*
- *crusher, mill*
- *sieve*
- *ore stock yard*

Other than these, silo and hopper for raw materials and products, transporting equipment except belt-conveyer and bucket-conveyer, packing machine, etc., are provided with dust collectors to secure the working environment against the risk for the health of workers, although for those of which are not specified by the regulation.

Equipment protected work shop environment from dust scattering
- *silo, hopper for raw material & product*
- *transporting equipment except belt & bucket conveyer*
- *packing machine, etc.*

Raw materials are stored in the house on general principle. However, in the case of outdoor stock of phosphate rock for instance, the surface of raw materials is covered by sheet to prevent the scattering of dust.

- *outdoor stock with sheet cover*

(phosphate rock)

For the dust generating equipment such as belt-conveyer, bucket-conveyer, crusher, mill, sieve, and etc., following dust scattering prevention methods are taken:

(1) to install the equipment and to store materials in the house with the structure to prevent the dust scattering

(2) to install these inside the closed cover structure induced by suction blower to reduce the pressure below atmosphere pressure

(3) to seal off the whole equipment by a cover and to collect dust by suction blower

(4) to hood the dust at generating portion partially by hood covers

- *indoor allocation*
- *closed cover, negative pressure*
- *Sealed dust collecting cover*
- *dust collecting hood*

The dusts captured by these methods are generally led to the cyclone dust collectors and bag filters.

For the detail information, refer to the pages at P.102.

6. NH_3 Removal Technology

Ammonia is regulated by air pollution control law as a specified material, however no legal standard figure for permissible level has been settled. The permissible emission level of ammonia is settled on the basis of the Offensive Smell Control Law both for the boundary of premise and the exhausting points. The former figures is settled by the prefectural governors in the range of between 1 and 5 ppm. The allowable ammonia concentration emitted from a exhaust point are calculated by the equation shown in a slide.

1. *Permissible NH_3 emission:*

   1~ 5 ppm at boundary of premise (set forth by prefecture governors)

   $$Q = 0.108 \times He^2 \times Cm$$

   Q : gas volume (Nm^3 / h)
   He : effective height of exhausting outlet (m)
   Cm : concentration at boundary line of premise (ppm)

The ammonia treatment in the fertilizer plant, as an example, is shown in a slide.

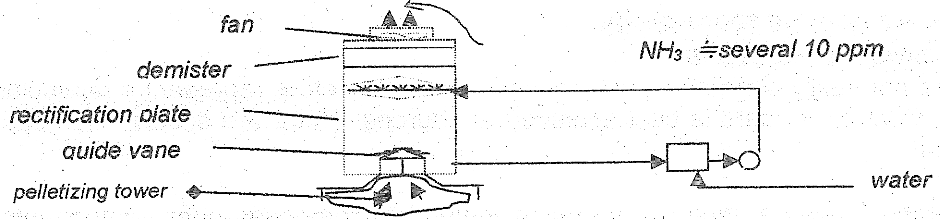
2. *In compound fertilizer plant :*

Process	Origin	Abatement
pelletizer & drying	$(NH_4)_2SO_4$ $(NH_4)_3PO_4$ $CO(NH_2)_2$	reservoir type wet scrubber pressurized water scrubber packed bed water scrubber (NH_4 removal 70~90%, 20~50ppm)

Ammonia is generated from the processes of a pelletizing and a drying, where the raw materials such as ammonium sulfate, ammonium phosphate, urea, etc. are partially decomposed by heat and contacts among raw materials. These exhaust gas is thin in its ammonia concentration and accompanies with powdered fertilizer dust, so that ammonia in the gas is absorbed and recovered by the wet scrubber (as shown in a slide) using water spray or dilute sulfuric acid solution or phosphoric acid solution along with dust. The removal rate of ammonia by these methods is in the range of between 70~90%, and emitted ammonia concentration is 20 to 50 ppm.

At pelletizing tower in an urea manufacturing plant, a particular type of dust collector is used because of that its gas volume is huge and it contains fine urea particles with 1~5 μm in diameter. The structure of dust collector mounted on a pelletizing tower is shown in a slide. The ammonia concentration at the outlet of dust collector is several ten ppm.

3. *In urea plant*



For the detail information, refer to the pages at P.104~106.

7. Fluoride Compounds Removal Technology

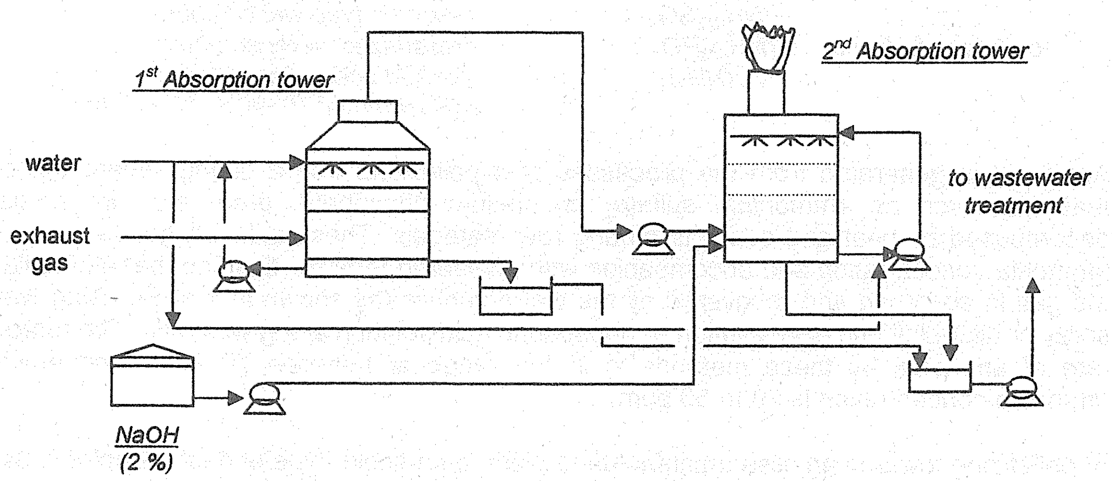
In fertilizer manufacturing plant, fluoride compounds as form of hydrogen fluoride (HF) and tetra fluoride silicon (SiF_4) are generated from the reaction process and concentration process for raw phosphoric acid, calcium superphosphate (P. 41, $Ca(H_2PO_4)_2$), and reaction furnace for fused phosphate, calcined phosphate, etc.

Generation of F
- reaction & condensation process for H_3PO_4 production
- reaction process for $Ca(H_2PO_4)_2$ production
- reaction furnace for fused P and calcined P production

For a treatment method of fluoride compounds, wet process has been adopted as both HF and SiF_4 has a strong affinity with water and relatively large solubility in water.

HF, SiF_4 → with greater hydrophile property

The wet scrubber, packed tower scrubber, jet scrubber, etc are commonly used for the abatement of fluoride compounds. When SiF_4 is absorbed to water, it forms a silicon dioxide (SiO_2) and causes problems of adhesion and clogging, to which should be attentive. Water is generally used for scrubbing liquid, but alkaline such as Na, Ca, etc. is also used for lowering fluorine concentration in exhaust gas furthermore. The abatement system is shown in the slide.



For the detail information, refer to the pages at P.102~104.

8. Odors Abatement technology

8-1 Abatement Processes

Odors are not easily characterized or quantified and therefore represent a particular design problem. Control of odors is best achieved at sources. There are several methods in odor abatement.

In incineration method, direct incineration method decomposes odor components to non smell materials of CO_2 and H_2O for 0.3 to 1.0 second at around 800°C. This method is widely used and has high efficiency in reduction of odors. The regenerative thermal oxidizer is equipped with a regenerator inside the furnace, which is heated up by the combustion of odor components. If the odor components contain the caloric value of equivalent to the toluene of 500 ppm or more, these are burned by themselves without any additional fuel. This system is simple in structure and easy in maintenance, and has high heat exchange efficiency of 95%. The catalytic incineration burns the odor components under the existence of catalyst and converts to non smell substances. The combustion efficiency of odors is 99% or more under the economical combustion temperature of 200 to 350°C.

<u>Incineration method</u>	*decompose to CO_2, H_2O by heat*
direct incineration	*at ≒800℃*
regenerative thermal oxidizer	*regeneration, heat efficiency ＞80%*
catalytic incineration	*using catalysis at 200~ 350 ℃, rem.＞99%*

In scrubbing method, gases with odors are scrubbed in the scrubbing tower by chemical solution or water. This system is cheap and can remove the mist and dust in the gas simultaneously.

<u>Scrubbing method</u>	*scrubbing by chemical solution*
	water, acid, alkaline, oxidant, etc.

In an adsorption method, the activated carbon is used as an adsorbent in a form either recovery type, concentration type or replacement- adsorption type. The regeneration of activated carbon is done by either way of steam regeneration, heated nitrogen gas, oxidation by oxidant, or replacement.

<u>Adsorption method</u>	
recovery type	
fixed bed	*activated carbon, steam regeneration*
fluidized bed	*activated c., heat regeneration by N_2 gas*
concentration type	
honeycomb	*separating odor from low concentration gas*
replacement type	*replacing saturated adsorbent or oxidant*

In biological method, odor components are decomposed by microorganisms in soil bed or in the bio-film media.

<u>Biological method</u>	*biodegradation by microorganisms*
soil bed	*using soil bacteria*
packed tower	*using bio-film on the media*

Deodorizer or masking agent converts chemically the offending compounds into harmless inoffensive compounds.

<u>Deodorizer, masking agent</u>	*deodorize or easing offending gas*

For the detail information, refer to the pages at P.106.

8-2 Troubles in Abatement Processes (examples)

Examples of troubles in deodorizing methods are shown in a slide.

In combustion method, as the direct incineration is operated at high temperature, it generates higher concentration of NOx, exceeding the permissible emission level. In regenerative thermal oxidizer and catalytic incineration, when the solvent with chlorine compounds are mixed in the gas, hydrochloric acid is generated. When paints are mixed in the gas, clogging problem and catalyst deterioration would occur.

Combustion method

Deodorizing Method	*Trigger*	*Trouble*
direct incineration	*NOx ↑*	*permission level ↑*
regenerative thermal ox.	*mixture of Cl_2, paint, etc.*	*HCl ↑, clogging*
catalytic incineration	*mixture of Cl_2, paint, S, etc.*	*catalyst deterioration*

In adsorption method, the mixture of solvents such as ketone, cycohexane, etc. causes firing of activated carbon, raising temperature of exhaust gas, and deterioration of activated carbon, etc.

Adsorption method

Deodorizing Method	*Trigger*	*Trouble*
recovery type		
fixed bed	*mixture of ketone, high B.P. substance*	*firing, deterioration of activated carbon*
fluidized bed	*high temp. of exhaust gas*	*A.C. deterioration*
concentration type		
honeycomb	*mixture of cyclohexane*	*firing*
replacement type	*conc.> several ppm*	*short term A.C. replacement*

In biological methods, if the soil bed is become dry, the decomposing function is getting weak and finally gets out of order. In the case of packed tower, it takes a relatively long period to grow the microorganisms on the surface of media.

Biological method

Deodorizing Method	*Trigger*	*Trouble*
soil bed	*drying of soil*	*malfunction*
packed tower	*slow acclimatization*	*slow starter*

In scrubbing method, less sprinkling water volume leads to the deterioration of performance. When the gas contains a lot of dust, it would cause a clogging problem at the inner part of scrubbing tower.

Scrubbing

	less sprinkling water	*malfunction*
	dust in gas	*clogging internals*

For the detail information, refer to the pages at P.110~111.

9. Solvent Recovery & Abatement technology

The occasion which needs a recovery of organic solvent is only for the production process of thermo plasticity resin based coated fertilizer. The coated materials concentration in the solution is generally estimated at around 10%.

1. Sources of Generation
coated fertilizer (thermoplasticity resin)

The recovery of solvent from the exhaust gas process exerts a great influence on the economics of product cost. Therefore, the recovery of solvent has become the inevitable conclusion for cost control before the measures for pollution control. Then, the residual solvent that is left over due to economical reason is abated by air pollution control device.

2. Abatement
recovery of solvent brings profit ⇒ production cost reduction
residual solvent value ≪ recovery cost ⇒ pollution control

Previously mentioned abatement methods are applied to control the air pollution. In cooling condensation method, the solvent vapor is cooled down to the lower temperature against the vapor pressure for liquid. This method is not so practical because of remaining of solvent equivalent to its partial pressure.

3. Abatement Process
- cooling condensation method
cool down flue gas below vapor pressure

In absorption-diffusion method, when the absorbent with high solubility against targeted solvent and extremely low vapor pressure can be obtained, this method could be applied.

- absorption & dispersion method
absorbing of solvent to absorbent with lower vapor pressure

In adsorption-diffusion method, these methods can be applied to the solvent containing exhaust gas with low vapor pressure and non-existence of antagonist ingredients. These systems are simple in mechanism and inexpensive in operating cost. There are three types of adsorber; fixed bed, moving bed and fluidized bed. The typically used adsorbents are an activated carbon (granular type, powder type), silica gel, molecular sieve, aluminum gel, etc. The regeneration (diffusion) of adsorbents are generally done by the method using heated gas, steam, heat transfer, extraction under decompression, etc.

- adsorption & dispersion method
- ☆ *applicable to compositions with low vapor pressure and non-existence of antagonist. Adsorbed at under pressure or lower temp..*
- ☆ *adsorber: fixed bed, moving bed, fluidized bed*
- ☆ *adsorbent: A.C., silica gel, molecular sieve, aluminum gel*
- ☆ *regeneration method: heated gas, steam, heat transfer, extraction under decompression*

For the detail information, refer to the pages at P.112~114.

10. Environmental Management System

1. In EMS, trend of environmental management: Under worsening of global environmental circumstances, "sustainable development" was agreed on in the United Nations Conference

on Environment and Development held in 1992. Based on this, International Organization for Standardization (ISO) has set the international standard of "environmental management / audit (ISO 14000) in 1996. This is that a company sets a basic policy and a goal for its environmental problems based on the environmental influence caused by its business activities and the legal regulations. The company makes, executes, corrects and audits the system, rules and manuals in order to attain the goal. Such process is repeated so that the system is continuously improved. This cycle is called as PDCA cycle (Plan-Do-Check-Action). The ISO 14000 requires forming the appropriate organization, its duty and controlling system to establish and promote the pollution control.

1. Environmental Management System
- *Organization for Environmental Control*
- *ISO 14000 series----- PDCA cycle*
- *Responsible for environmental protection*

ISO 14000

2. The pollution control is managed based on manuals which settle the operating method of pollution control equipment, inspection of pollution control equipment, education and training, emergency measures at the malfunction of system, and etc.

2. Environmental Control Manual
- *Operation Standard Manual*

3. In education and training of employees, the person in charge of pollution control, the pollution control chief manager, and etc are required to possess the qualifications necessary for the environment control. Therefore, well organized education and training program and the maintenance of environmental control manual are important.

3. Education & Training
- *legally qualified expert of environment control*
- *training program and preparation of manual*

4. As a lot of inorganic powders are handled in a fertilizer manufacturing plant, the dust control is important to protect the health of workers and to minimize the loss.

4. Environmental Control at Work Shop

5. Environment monitoring: The enterprises must observe the emission standard of atmospheric pollutants set by laws. For this purpose, it is necessary to measure, monitor and record regularly the emission concentration of pollutants. The emission of SOx, NOx, and dust are regulated by air pollution control law for fertilizer manufacturing plant.

5. Environment Monitoring
- *maintaining monitoring system*
- *monitoring of air pollution state*
- *legal emission permissible level*

For the detail information, refer to the pages at P.147~160, 118~131.

Instructions for Power Point of Air pollution Control Technology

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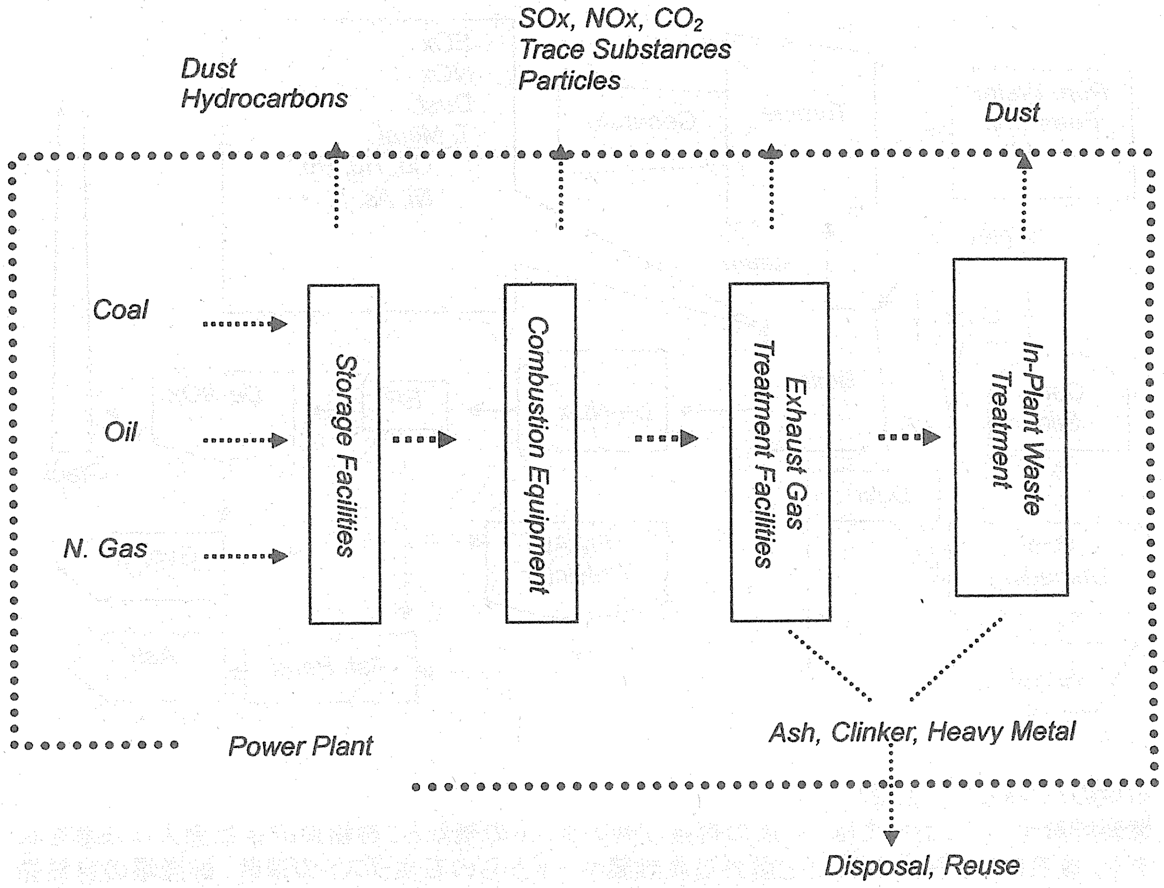
Ⅰ.電力業

1. 火力発電所の大気汚染

1-1 汚染物質の排出

火力発電所ではタービン発電機を動かすために、通常は石炭、油、天然ガス(N Gas) が燃料として使われる。スライドに示すように、火力発電の工程においては、SOx、 NOx、 CO_2、ダスト、炭化水素、それに微量物質が大気汚染物質として排出され、処理工程副産物は再利用されるか、あるいは廃棄処分される。



これらの汚染物質の個々の具体的な除去方法については、2ページ以降に記載する。ただし炭酸ガスに付いては今回触れていない。

当然、地球環境問題の中で、近年世界中で議論の高まっている「地球温暖化」と「酸性雨」の問題は、火力発電と深い係わり合いをもっている。

議論されている地球温暖化については、温室効果ガスとして、二酸化炭素(CO_2)、メタン (CH_4)、酸化窒素(N_2O)、などがあり、化石燃料の燃焼によって排出される CO_2 がこの問題に大きな影響を与えていると考えられる。この地球温暖化の問題はまだ解明されておらず、われわれの経済活動を維持し続けるために、その因果関係と対策の科学的解明に至っていない。地球温暖化は国家が扱う問題であり、京都議定書に基づき温室効果ガスの排出量を低下、あるいは、封じ込め

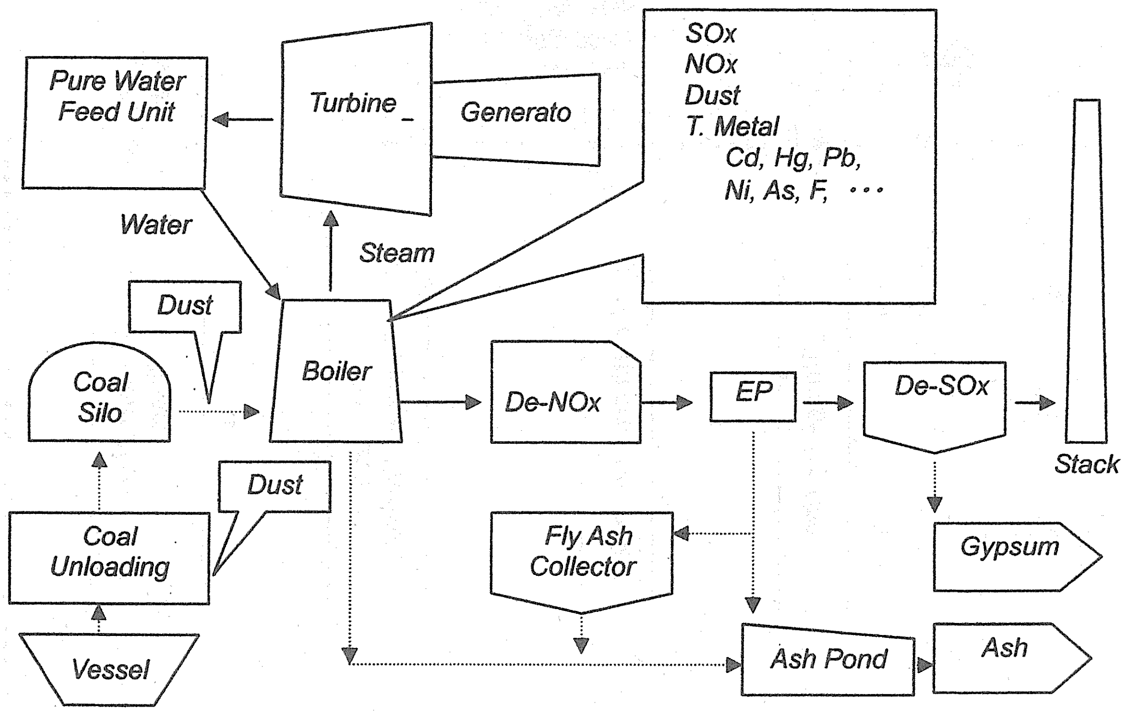
を行っていくべきである。

酸性雨対策については、後述の SOxの低減対策に関するスライドでいくつかの防止方法を説明する。

詳細情報については、P.71~76 を参照

1-2 石炭火力発電所における汚染物質と汚染防止

石炭火力発電所では、主に(1) ボイラーから汚染物質が排出され、その他には(2)乾燥石炭の荷揚げサイトからも発生する。石炭火力発電所における大気汚染物質の発生についてはスライドに示す通りである。



石炭のハンドリング工程:

燃料貯蔵ヤードでおいては、石炭の荷揚げ時のダストの飛散と、微粉炭の自然発火に注意を要する。後者には、石炭ホイストと屋外石炭貯蔵ヤードからの石炭ダストの飛散、貯炭場の自然発火、それに屋内貯炭場における石炭粉塵爆発がある。

また、大気汚染は貯炭ハウスからボイラーに移送する工程や、粉砕工程でも起こる。

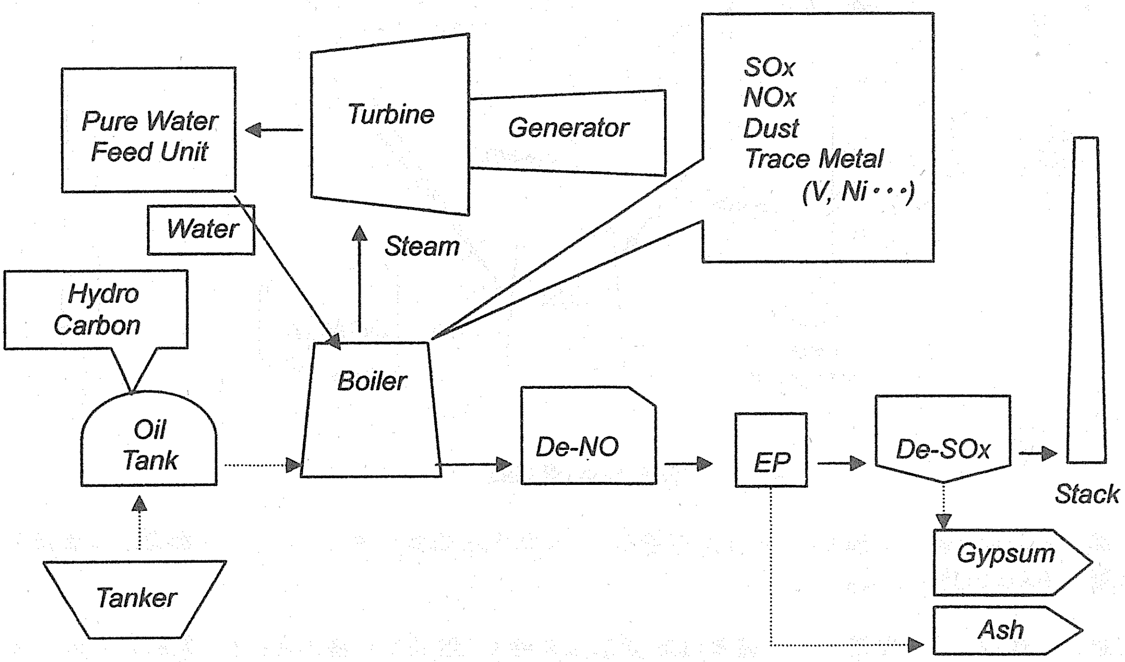
燃料燃焼行程:

燃料燃焼行程からは、SOx、 NOx、 ダスト、 微量金属、例えば、カドミウム(Cd)、 水銀(Hg)、鉛(Pb)、 ニッケル (Ni)、 砒素(As)、 フッ素(F)、 などが生成される。石炭炊ボイラーの排ガスは、脱硝装置、電気集塵機、脱硫装置へと導かれ、その後、煙突に入る。汚染物質は灰と石膏の形で回収される。

詳細情報については、P.73~76 を参照

1-3 石油火力発電所における大気汚染物質と大気汚染防止

石油火力発電所において、汚染物質が、(1)主にボイラーと、わずかではあるが(2)燃料油貯槽から発生する。石油火力発電所における大気汚染物質の発生箇所をスライドに示す。



燃料油貯槽では、炭化水素ベーパーが発生する。燃料油を取り扱う工程では、石炭と異なり大気汚染物質は発生しない。石油を燃焼する際、SOx、NOx、ダスト、バナジウム(V),ニッケル(Ni),などの微量金属が発生する。

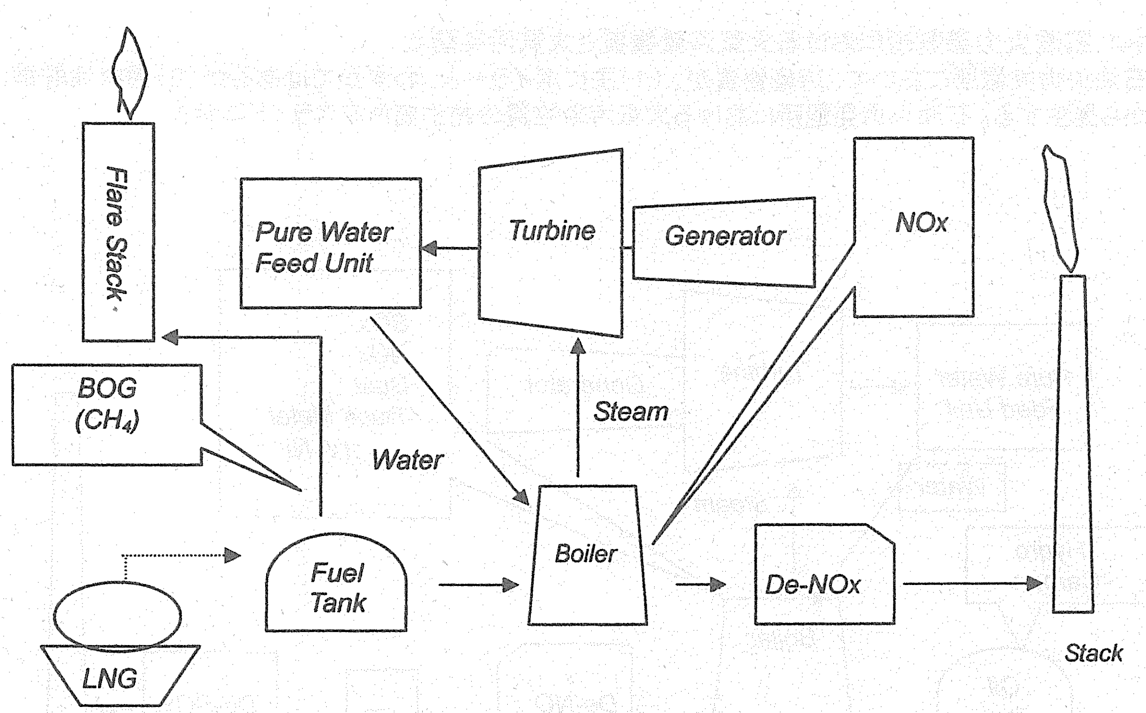
石油炊ボイラーの排ガスは脱硝装置、電気集塵機、脱硫装置を経て煙突から排出される。除去された汚染物質は灰と石膏の形で回収される。

詳細については P.73~75 を参照。

1-4 ガス火力発電所における大気汚染物質と大気汚染防止

ガス火力発電所において、汚染物質は、(1)主にボイラーと、(2)わずかではあるが燃料貯槽から発生する。天然ガス火力発電所から発生する大気汚染物質は、石油火力発電所、あるいは石炭火力発電所と異なり、スライドに示されるように非常に単純である。

燃料タンクヤードでは、メタンなどのボイルオフガスが発生する。



BOG: Boil-off Gas

天然ガスの取り扱い工程では、石炭とは異なり、大気汚染物質は発生しない。天然ガスの燃焼では唯一 NOxが発生する。

天然ガス炊ボイラーの排ガスは通常は脱硝装置を経て、煙突から排出される。天然ガス火力発電所では、大気汚染防止工程からの廃棄物の発生はない。

詳細については P.73~76 を参照。

2. 燃料に対する対策

2-1 石炭火力発電所

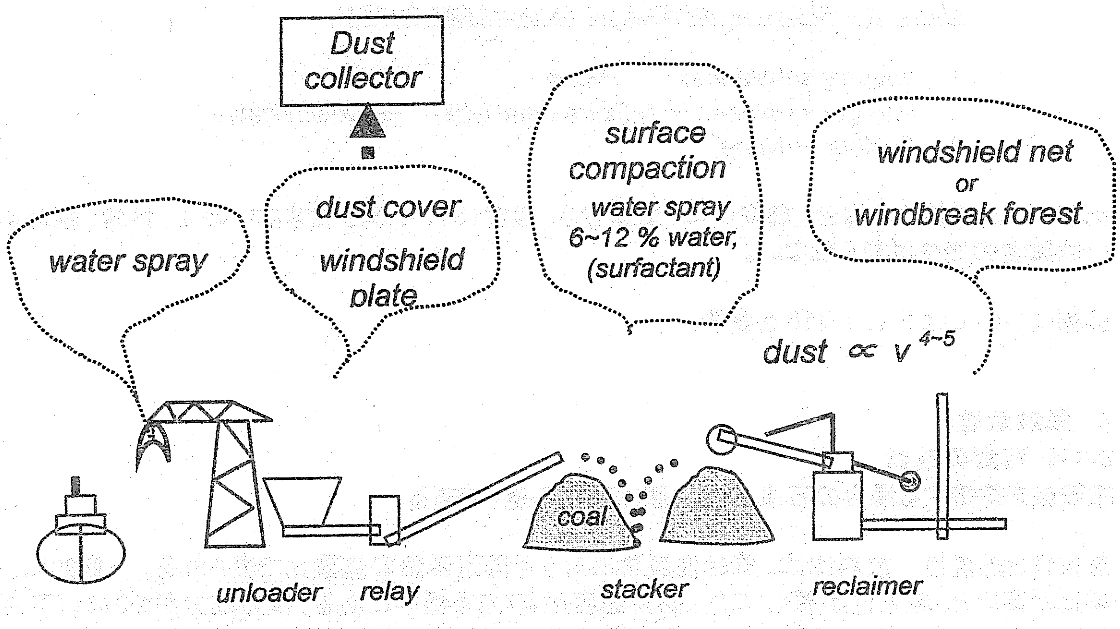
屋外貯炭を伴う石炭火力発電所を建設するに際しては、発電所の周辺に飛散する石炭粉塵量を試算し予測する。貯炭場周辺の防風フェンスの高さ、配置、石炭の含水率が適切に行われ、石炭煤塵による周辺環境への影響は排除される。

散水により、石炭中の水分の増加が図られ、石炭粉塵の飛散防止には効果がある。石炭の種類によっては非常に撥水性が高く、粉塵防止には僅かしか効果がないことがある。この場合は、炭塵防止剤を添加する。

防風フェンス、防風ネット、防風林が炭塵飛散防止に使われるが、それは、炭塵飛散量が風速(V)の4～5乗に比例して増加すると言われていることによる。

密封形コンベヤ、風防付コンベヤ、集塵機、貯炭場石炭の表面固めも同様に効果がある。近年、連続荷揚装置が作業効率改善と環境対策の両面から広く採用されている。屋内貯炭の場合には、屋外貯炭の場合のように炭塵飛散に神経を使う必要はないが、集塵と排気を行う際の粉塵爆発に配慮が必要である。

操炭工程と、大気汚染物質発生源、大気汚染物質、大気汚染防止法の概要をスライドに示す。



詳細については P.92~97 を参照。

2-2　石油およびガス火力発電所

石油燃料の場合、環境問題を引き起こす排ガスの成分は、窒素酸化物（NOx）、硫黄酸化物（SOx）、粉塵、煤塵とボイラー腐食性物質である。残留炭素の内容は、空気の供給を遮断した状態で形成されるコークス状の炭素残分と同じである。残留炭素は煤塵と粉塵になりやすい性質を持っている。

Effect of fuel oil properties on exhaust gas quality

1. *Residual Carbon → Soot, Dust → Dust collection*
2. *Nitrogen → NOx → Denitrification*
3. *Sulphur → SOx → Desulphurization*
4. *Ash → Pressure drop, Heat transfer broke, Mechanical Wear, Corrosion → Maintenance*

重油に含まれる窒素含有量は概略0．01～0．6%であり、燃焼により、その一部が NOxとして排出される。

燃料油は硫黄を硫黄化合物などの形で含んでいる。これらが燃焼すると、二酸化硫黄(SO_2)と,その一部がさらに酸化されて無水硫酸(SO_3)になる。排気ガスの温度が露点以下になれば、SO_3 は排ガス中の水分と結合して、硫酸(H_2SO_4)となり、部材の鋼材に腐食をもたらす。.

僅かではあるが、燃料油には灰分が含まれる。灰分はナトリウム、カリウム、鉄、珪素、バナジウム、ニッケルを含んでいる。燃焼に際し、これらの金属は、ガス配管に付着蓄積して、圧力損失の増大、熱伝導の低下、機械的磨耗、化学腐食を誘引する。

Effect of fuel gas properties on exhaust gas quality

1. *Impurity substances・・・・・None*
2. *Nitrogen・・・None → NOx (thermal type) → Denitrification*
3. *Sulphur・・・None*

天然ガスを燃焼する場合、燃料中に、窒素(N)、硫黄(S)、不純を含まないので、付着、磨耗あるいは腐食の発生は見られない。

詳細については P.113~118 を参照。

3. 燃焼監理

3-1-1 石炭の性状

微粉炭を燃焼する場合の石炭の特性値は以下の通りである。

着火性と燃焼性: 燃料比は、揮発性炭素に対する固定炭素の重量比で表される。一般的に、燃料比が高いと、着火性が悪く、また、燃焼速度が遅くなる傾向にある。揮発成分が20%以下であれば、着火安定対策が必要である。着火性の指標は石炭の着火性を示しており、35以下であれば着火性の改善策が必要となる。ボタン指数は粉炭のバーナーノズルなどに対する付着傾向を示す。ボタン指数が6~7以上の場合は、問題回避のために対策が必要である。

Effect of Coal Properties on Pulverized Coal Combustion

Ignitability & Combustibility	*optimum range*	*effects in case of off-spec.*
Fixed-C / volatile content	*<2.5~3.0*	*increase of non-burn loss*
Volatile content	*>20%*	*unstable ignition*
Ignitability Index	*>35*	*hard ignition*
Button Index (viscosity)	*<6~7*	*clogging, adhesion*
Grindability		
Proper size	*50~100 μm*	*increase of non-burn loss*
Dryness	*H_2O < 20 %*	*lowering mill performance*
Slagging		
Ash Melting Temp.	*>1,300℃*	*slagging*
Ash Alkaline Ratio	*<0.5*	*slagging*
Fe_2O_3/CaO	*<0.3~3<*	*slagging*
S/coal	*<2 %*	*slagging*
Fouling	*basic content; Na_2O, K_2O, Cl, CaO, S*	*fouling on inner furnace, radiation heating surface*
Wear-out Nature	*quart, Fe_2O_3, S*	*wear of mill, coal tube, heat transfer surface*

粉砕性: 微粉炭の燃焼は、石炭を50から100μmの粒径に粉砕し、それを乾燥した状態で燃焼させることに特長がある。燃焼過程で重要な点は、燃焼室で完全燃焼をさせることである。規格外の場合、未燃ロスが増加する。水分が20%以上含まれると、破砕機の能力の低下に結びつく。

スラッギング性: 石炭燃焼時に起こる、スラッギングは、ボイラーの燃焼室で石炭中の灰分が溶解してできるスラグが冷やされると、火炉内の放熱伝熱面に付着し、硬化し、蓄積する現象である。

灰分の溶融温度は、伝熱面付近のガス温度より高いか低いかを基準に判定される。アルカリ度の高い灰分は、低融点酸化物と複合塩が形成されやすく、スラッギング性があると考えられる。もし、灰分中の Fe_2O_3/CaO の比が0．3～3の間であれば、低融点物質を形成する傾向がある。硫黄は低融点化合物を形成し、ハウリングを助長する。

ハウリングは、溶融した灰分が Na_2O などを含んでいるために、燃焼室の内面に凝結する現象である。

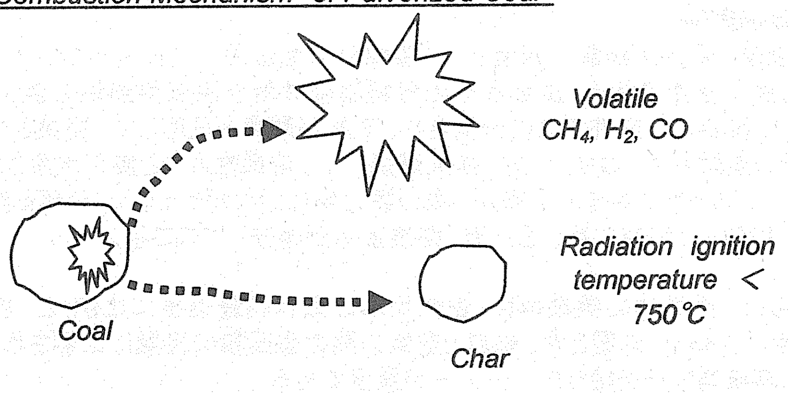
破砕機、管路、伝熱面などに磨耗を起こす度合いは、石英などの含有量の分析値から判断できる。

詳細については P.107~110 を参照。

3-1-2 石炭の燃焼

石炭を微粉にして浮遊させて燃焼すると着火時間と燃焼時間が非常に短縮され、あたかも燃料油やガス燃料に近い形でバーナーを使って燃焼することが可能となる。微粉炭の燃焼では、一次燃焼域では、CH_4, H_2 や CO の揮発性物質の燃焼が主体となって進む。二次燃焼域では、原則的にチャーの燃焼域である。このチャーの燃焼速度は、揮発性物質の燃焼と比べて極めて遅い。その結果、チャーの燃焼時間は全燃焼時間の80から90％を占める。通常の微粉炭炊ボイラーでは、放射着火温度が 750℃以下であれば、燃焼に伴う問題が起こらないことが経験的に知られている。

Combustion Mechanism of Pulverized Coal



燃料を完全燃焼させるためには、理論空気量より多い空気（揮発成分を多く含む瀝青炭の場合の空気比は1．2～1．25）が必要である。したがって、NOxの発生量を低減させるために、スライドに示す種々の方法が用いられている。スライド中の1～4の項目は、操炉の変更で対応ができる。

1. *Reduction of surplus air ratio (high volatile coal; 1.2～1.25)*
2. *Lowering combustion air temp. (normally 250～350 ℃)*
3. *Two stage combustion (1st burner + 2nd burner)*
4. *Recycling exhaust gas (<20~30%)*

炉内脱硝法は、同じ炉内で発生する NO に炭化水素により炉内で還元し低減する方法である。この方法は、2段に分けて行われる。このプロセスを有効にするためには、先ず、(1)雰囲気温度を炭化水素の分解温度より高く保ち、(2)酸素が存在し、(3)混合物(燃料)として使用される還元用炭化水素量は、存在酸素より化学等量的に多くなければならない。第2段の反応では、未燃物の

完全燃焼が必要である。このためには、(1)雰囲気温度は、未燃物の反応温度より高く、(2)未燃物の完全燃焼を図るために十分な酸素が供給されなければならない。

2. *Inner-furnace denitrification*

1st Process

— furnace ＞900℃ HC decomposition

— O2 existing

— reductant HC ＞ chemical equivalent O_2

2nd Process

— atmosphere temp. ＞ reaction temp. of non-burned portion

— sufficient O_2

バーナーの構造を改良してNOxの発生量を低減する方法はスライドに示す3つの方法に大きく分類できる。

6. Low NOx burner

— slow mixture air & fuel

— promotion of unevenness comb.

— acceleration of flame heat radiation

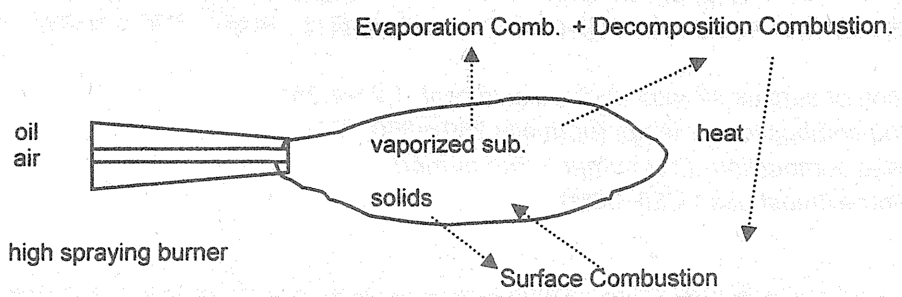
詳細についてはP.110~112を参照。

3-2-1 石油燃焼

油の燃焼は、揮発性物質の燃焼と、分解成分の燃焼の二つに分けられる。燃料油は多くの成分からなる炭化水素である。炭化水素の分解温度は着火温度や燃焼温度より低く、そのため燃焼する前に、炭素と可燃性ガスに分解され、それが酸素と反応して、燃焼となる。炭素はその表面燃焼により炭酸ガスとなり、一方、拡散燃焼により可燃性ガスと炭化水素は酸化され、炭酸ガスと水になる。このときに発生する熱が、次の熱分解につながっていく。分解と表面燃焼による燃焼が交互に、あるいは同時に起こるため、燃焼反応が連続して起こる。

燃焼反応は、燃料油の噴霧速度(燃焼反応は燃料噴霧速度に比例)と、燃焼速度(燃焼反応は燃焼速度に比例)に影響され、燃料と空気の間の表面積の接触に影響される。完全燃焼を図るためには、高噴霧性能を持ったバーナーが重要である。

Oil Combustion Mechanism



JIS規格に示されるC重油の性状をスライドに示す。スライドに示すように、油の性状が排出ガスの性状に影響を与える。若し、残留炭素の含有量が多いと、残留炭素起因の煤塵となりやすく、

バーナーチップに付着して、燃焼を劣化させる。燃料油は灰分を含んでいる。灰分にはナトリウム(Na)，カリウム(K)，鉄(Fe)，珪素(Si)，バナジウム(V)，アルミ(Al)，とニッケル(Ni)が含まれる。これらの金属は燃焼ガスに取り込まれ、溶解し、化学変化を起こし、排ガスラインに付着・蓄積し、圧力損失の増加、伝熱を妨げ、機械的磨耗と化学的腐食を起こす。

Effect of Fuel Oil Properties on Exhaust Gas Composition

Subs.	*Con.wt. %*	*Pollutants*	*Damages*
N	*0.01~0.6*	*NOx*	*Air pollution*
S	*0.2~3.0※*	$SO_2, SO_3 \rightarrow SO_4$ *(SOx)*	*Air pollution, corrosion clogging*
Red. C	*4.0~11.5※*	*Dust*	*Dust, carbon adhere*
Ash (Na, K, V, ----)	*＜ 0.02※*	*Adherents*	*Scaling, Vanadium attack, corrosion, mechanical wear, etc.*

※: JIS C-Heavy Oil

詳細についてはP.110~115を参照。

3-2-2 燃料油 と NOx発生

燃料油を燃焼するときは、バーナー付近で噴霧された油の揮発と燃焼により燃焼が継続する。燃料油に含まれる窒素酸化物の酸化によるフューエルNOxの生成に続き、高温の火炎が形成され、サーマルNOxの比率が高くなる。しかし、燃料油に含まれる窒素は石炭と比べて低いため、石炭燃焼に比べて、NOxの排出量は少ない。

NOx Generation and its Control in Oil Combustion

Generation

Thermal NOx (N in Air)
- *Flame temp.*
- *O2 concentration*
- *Retention time*

Fuel NOx (N in Fuel)
- *O2 concentration*
- *Nitrogen in fuel*

NOx の生成は燃料によって異なるので、個々の燃料に適した低減対策が必要である。油炊ボイ

ラーの場合は、(1)二段燃焼、(2)燃焼ガス循環、(3)低NOxバーナーの使用(4)炉の寸法の拡大(火炎の熱放射の促進)が採用される。

Control Measures

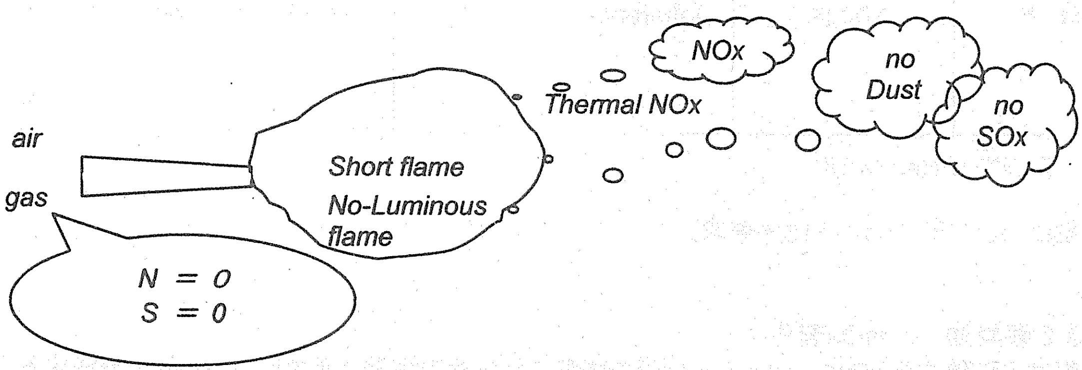
- *2-stage combustion*
- *Exhaust gas recycling*
- *Low NOx burner*
- *Furnace size expansion*

詳細についてはP.116を参照。

3-3 ガス

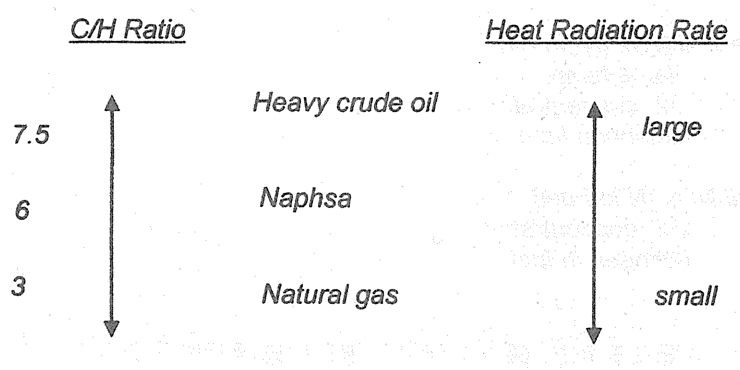
重油の燃焼と比べて、天然ガスの燃焼は次の特徴をもっている:

Gas Combustion Mechanism



天然ガスの燃焼は、低圧燃料噴霧で行われるために空気との拡散(混合)燃焼を通して行われる。重油の燃焼の場合と異なり、噴霧蒸発過程がないために、短炎である。

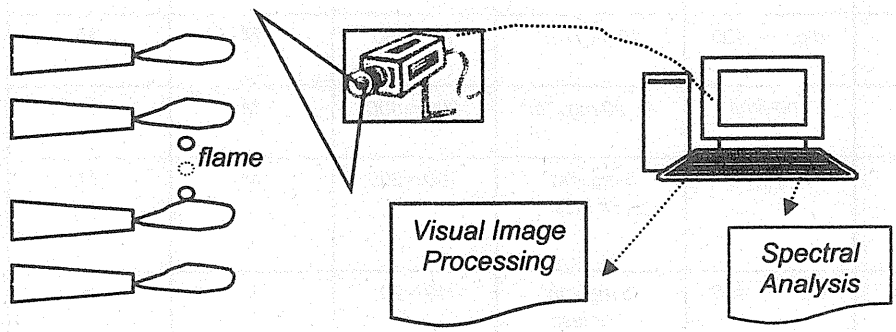
燃料の C/H 比が小さいので、燃焼過程で煤が発生しないし、一般的に不揮炎となる。燃料中にN, S, 不純物を含まないので、付着、磨耗、腐食はなく、SOxやダストの発生を伴わない。



クリーンな燃料は大気汚染物質の生成が比較的少ないが、バーナーの設計や燃料の取り扱いを間違えると、振動燃焼や爆発が起こる可能性があるので、注意が必要である。

Control of NOx Generation ＋ *Oscillating Combustion Preventive Measures*

燃料中の水素に対する炭素の比率（C/H）が小さくなるにしたがって、熱放射率は小さくなる。通常のガスのC/Hは3で、ナフサが6、重油が約7．5である。



低NOx運転を行う場合、不完全燃焼部が増え、火炎が炉内に広がる傾向があって、ボイラーの性能に影響を及ぼす。この場合、燃焼調節を含む、運転管理が重要である。火力発電用のボイラーは多くのバーナーを備えているので、未燃物の発生を抑えながら、同じ火炎長さに保つように個々のバーナーの空気比をできるだけ均等に調整して、NOxの発生を制御していくことが重要である。

個々のバーナーの微妙な燃焼調整を、経験や勘、それに従来の計測計に基づく単なる燃焼調整でボイラーを運転することが困難になってきている。近年では、オプトエロクトロニクス技術を使った個別燃焼診断法が開発され、実用かされている。

詳細については P.116～118を参照。

4．集塵装置

4-1　重力集塵装置、慣勢力集塵装置、遠心力集塵装置

集塵装置を選択する場合、表に示す粒子とガスの物性を考慮する必要がある。

排ガス中の粉塵の粒径と粒径分布がそれぞれの集塵機の粒子除去効率に大きく影響している。集塵機で捕捉される粒子径を表に示す。目視できない粒子濃度は 20 mg/Nm^3 と言われている。ろ過集塵装置を高濃度粒子排ガス処理に適用すると、頻繁なダスト払い落しが必要になる。電気集塵機は、排ガス中のダスト濃度の影響を余り受けない。

重力集塵装置と慣勢力集塵装置の場合の粉塵濃度に関しては、ガス中の粉塵濃度が高いほど、大口径粒子間の衝突と、微細粒子間の凝集が加速されるので、高い集塵除去率を得ることできる。ベンチュリースクラバーとジエットスクラバーは、高濃度の粉塵に対して、スロート部に磨耗を生じるので、10 g/ Nm^3 の排ガス処理に適用すべきである。

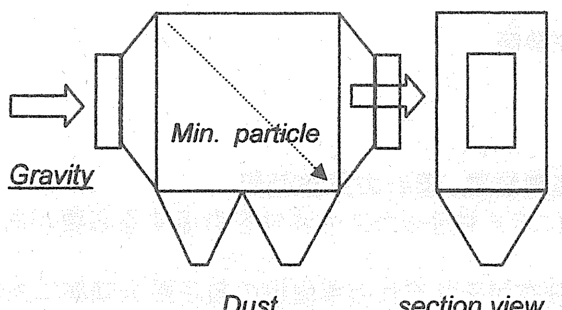
Type of Dust Collector

Type	Applic. Particle (μm)	Operating (℃)	Cutback Level	Pressure Drop (mm H_2O)	Equipment Cost	Running Cost
Gravity	≧50	d.p. ～ 400	40～60 %	10～15	S	S
Inertia	≧10	d.p. ～ 400	50～70 %	30～70	S	S
Centrifuge	≧3	d.p. ～ 400	10 mg／m^3	50～150	M	M
Scrubbing	~0.1	no-limit	≒ 20 mg／m^3	300～800	M	L
Filtration	~0.1	no-limit	5 mg／m^3 or less	100～200	M	M
EP	~0.03	d.p. ～ 400	5 mg／m^3 or less	10～20	L	S

詳細についてはP.168～169を参照。

4-2 重力集塵装置、慣性力集塵装置、遠心力集塵装置

粒子とガスの密度が異なるため、層流状態のガス流の方向を変えれば、それぞれの流れ方向が変わる。これを利用して、しばしばガスの中の固形粒子を分離する方法が行われており、通常はガスの流れ方向を急変させて方法がとられる。



重力集塵装置では、沈降室で流速を低下(通常1～2m/秒)させ、それによって重力で沈降させる。重力集塵装置は装置が大きく、最終集塵処理に用いられることがほとんどない。ストークスの法則が適用できると考えられ、100%除去される場合の粒径サイズは次式で表される。

Stokes' Law

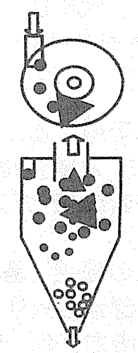
$$V=(g/18\mu)(\rho 1-\rho)D^2 \quad (cm/s)$$

V: settling velocity (cm/sec)

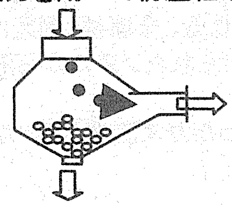
g: gravitational acceleration (cm/s²)
μ: gas viscosity (kg/ms)
ρ1: particle density (g/cm³)
ρ: gas density (g/cm³)
D: particle diameter (cm)

一般的にサイクロンと呼ばれる遠心力集塵装置は、サイクロンの中の粒子に遠心力が作用し、次式で示される。大容量のガスを処理する場合、小さなサイクロンが並列するマルチサイクロンが用いられる。流入部のガス流速は10～25m/秒で設計される。

Centrifugal force (F) = mv^2/R (N)
m: particle mass (kg)
V: particle velocity (m/ s)
R: cyclone radius (m)



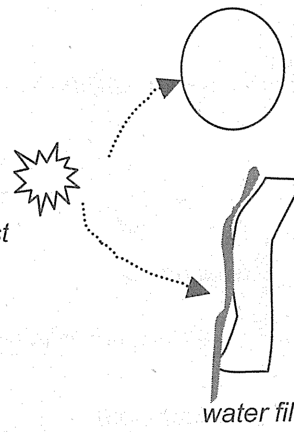
慣性力集塵装置では、ガスの流れを邪魔板に衝突させるか、あるいは急激に流れ方向を変えて慣性力を用いて粉塵粒子を除去・捕集する。



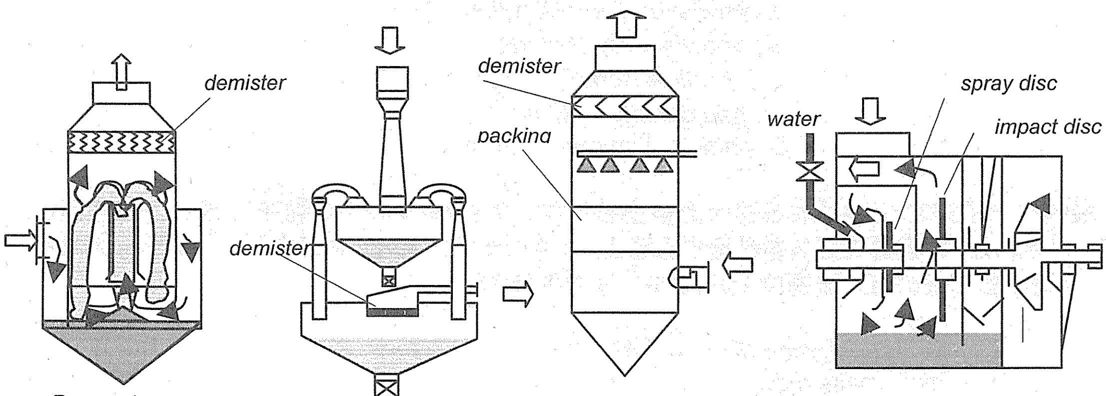
詳細についてはP.170～171を参照。

4-3 洗浄集塵装置
湿式集塵装置で知られるスクラバーは、ガス中の粒子を除去するのに液体を用いる。この方法では、粒子は液滴か、連続的に充填材の表面を流れる液膜に付着して捕捉される。

Principle of dust collection;



種々のスクラバーが使われており、スライドに示すように、溜水式、加圧水式、充填層式、回転式に大きく分けられる。



Reservoir type　Pressurized water type　Packed bed type　Rotary type

充填材を用いると、塔を小さくできるが、圧力損失が高くなる(効率は高くなる)。スプレー塔の一般的な圧力損失は0．25～0．5kPaである。充填式の場合は、0．25～2kPaである。スプレー塔の場合の液･ガス比は1．3～2．7l/m³であり、充填式の場合は0．1～0．5l/m³である。

充填式の場合、基本的には、排ガスは塔の下部から入り、上昇流で上部へ移動する。洗浄水は塔の上部から入り、上昇移動してきた汚染ガスの先頭部にスプレーされる。汚染物質は落下流体に接触吸収され、清浄化されたガスは上部から排出される。充填材(例えば、不規則なプラスチック片)は吸収効率の改善につながる。散水管に取り付けられたノズルから液体が噴霧される。

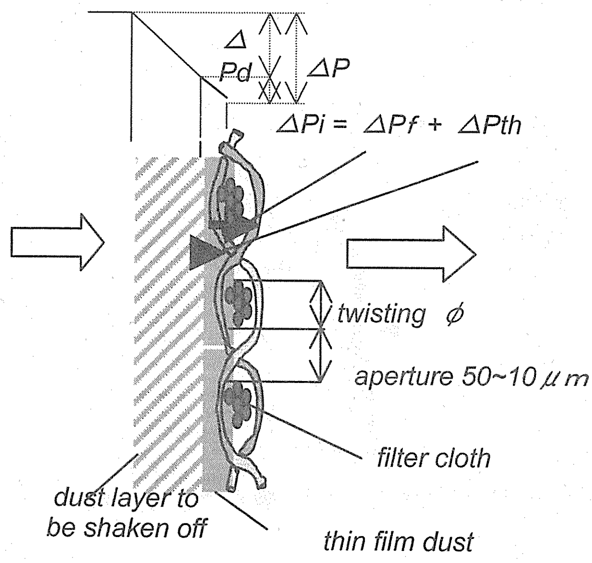
洗浄集塵装置の効率を保つには、その装置特性に合ったガス流速と液･ガス比を選定することが大切である。

詳細についてはP.171を参照。

4-4 ろ過形集塵装置

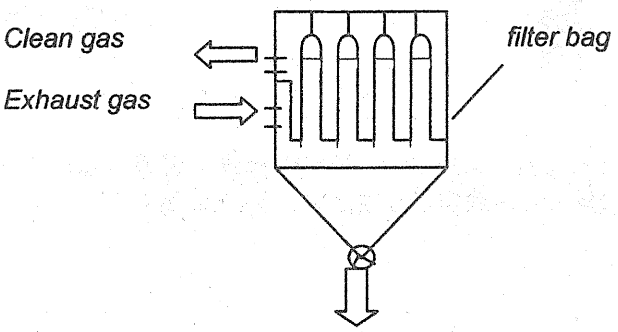
ろ過形集塵装置には、大きく分けて(1)バグフイルターと(2)カートリッジフイルターがある。しかし、バグフイルターが最も一般的に用いられている。

Filtration Mechanism



ある粒径を盛った粉塵を含むガスが、スライドで示すフイルターを通過するとき、ダストはろ布に付着し、布織糸の間にブリッジを形成する。その初期付着層は多くの細孔を有し、この細孔が微細粒子を捕捉する。ろ布には、天然繊維、合成繊維、ガラス繊維などを用いた種々の織布や、同様な素材を用いた不織布が使われる。バグフイルター集塵装置の運転では、ろ布表面の閉塞を防ぐことが重要である。バグフイルターの圧力損失が規定値に達すると、ろ布に蓄積したダストを払い落とす必要がある。その方法には二通りあって、間歇式と連続式がある。間歇式では、集塵室が3～4室に区切られている。ろ過装置の入り口と出口の両方に取り付けられたダンパーを閉じて、ろ布に付着したダストを払い落す。連続式の場合には、ろ過を止めることなく、ろ布に付着したダストを絶えず払い落す。そのため、圧力損失はほぼ一定値を保ち、高濃度の煤塵・粉塵を含むガスや、付着性の煤塵・粉塵を含むガスの処理に適している。

Typical bag filter unit



見掛上のろ過速度（有効ろ過面積当りの原ガス量）は通常0．3～10cm/秒である。

Type:	*Filter cloth:*	*Dust shake-off:*	*Apparent filtration rate:*
(1) bag filter	*(1) woven fabric*	*(1) intermittent*	*0.3~10cm/s*
(2) cartridge filter	*(2) nonwoven fabric*	*(2) continuous*	

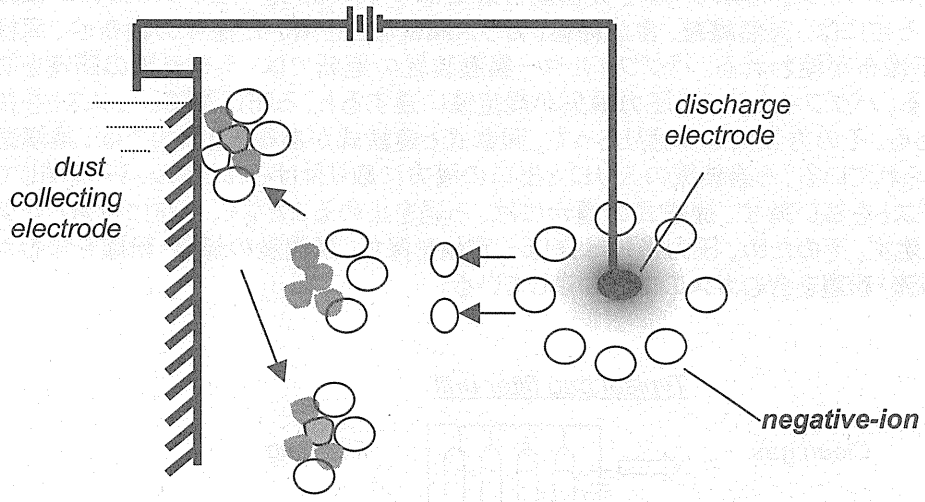
詳細についてはP.171～172を参照。

4-5-1 電気集塵装置(EP)

電気集塵機はコロナ放電により粒子に電荷を与えて集塵する方法である。電気集塵機はガスや粉塵の性状の影響を大きく受けずに、微細な粒子を圧力損失のない状態で集塵することができる。

スライドに示すように、心線の放電電極が負極として用いられ、集塵電極は正極としてつかわれる。高圧直流電力が放電に使われる。電界が強くなると、放電極の周辺のガスは局部破壊し、コロナ放電が生じ、マイナス電荷を持ったコロナと多くのマイナスイオンが発生する。マイナスイオンと自由電子は集塵電極に向かって移動をし、ダストを含むガスが電極を通過すると、粉塵粒子は瞬間的に荷電される。荷電された粒子は、クーロン力で移動をして集塵電極に捕捉される。集塵電極に捕捉された粉塵は槌打衝撃により剥離される。

Principle of dust collection



ボイラーの排ガスに含まれる粒子の性状は、燃料の種類や燃焼方法によって異なる。重油炊ボイラーと石炭炊ボイラーの排ガスの典型的な性状をスライドに示す。

Exhaust gas properties;

		Heavy oil	Coal
inlet soot & dust	g/Nm^3	0.05~0.15	10~20
dust ϕ	μm	1~3	20~30
SiO_2	Wt %	15~20	60~75
C	Wt %	50~60	0.4~0.8
ρ Rate	$\Omega \cdot cm$	10^4~10^6	10^{11}~10^{13}
apparent S.G.	g/ml	0.1~0.2	0.6~0.8

ρ は電気抵抗率を示し、apparent S.G.は見掛比重を示す。集塵への影響に関しては、油炊ボイラーの場合、SO_3 ミストは煙道、集塵装置、煙突を腐食させる。さらに、SO_3 ミストは粉塵に付着して、酸性煤煙となり、煙突から排出される。

これを防ぐためには、排ガス中に NH_3 を注入して、SO_3.の中和を行う。

Influence on dust collection		*Improving method*
・SO_3 mist	⇒	・NH_3 injection

石炭炊ボイラーの場合、フライアッシュの成分と物性は産炭地と燃焼法によって異なる。電気集塵装置の性能は、フライアッシュの電気抵抗値と粒径サイズによって大きく変化する。電気抵抗値は(1)排ガス温度、(2)水分、(3)SO_3 濃度、(4)石炭の性状と粉塵組成によって変わる。

Influence on dust collection	*Improving method*
・*temperature*	・*tempering flue gas*
・*water*	・*electric charge control*
・*SO_3 mist*	・*dust removal on (+) electrode*
・*composition of dust*	・*selection of gas temp.*

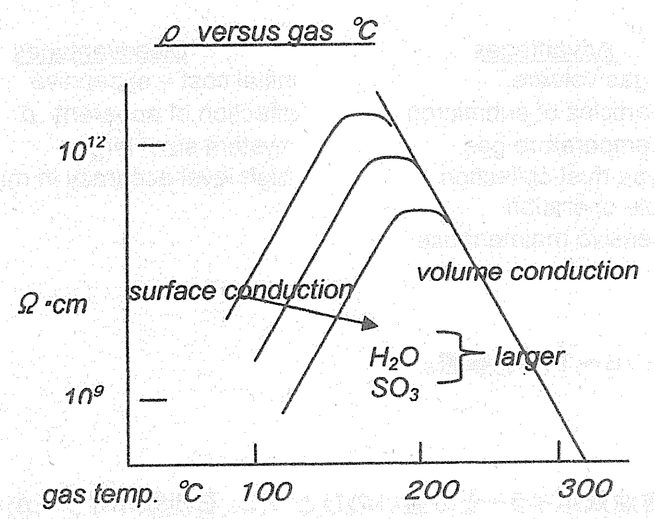
性能を改善するためには、排ガス温度、荷電調節などを行って、電気抵抗率を 10^{11} Ω-cm に調整する。実際には、電気集塵装置メーカーは粒子の特性を考慮に入れて、EPの性能が発揮されるように設計している。したがってこれらの調整は緊急時にのみ用いられる。

粉塵電気抵抗と粉塵除去性能の関係を次のスライドに示す。

詳細についてはP.173～179を参照。

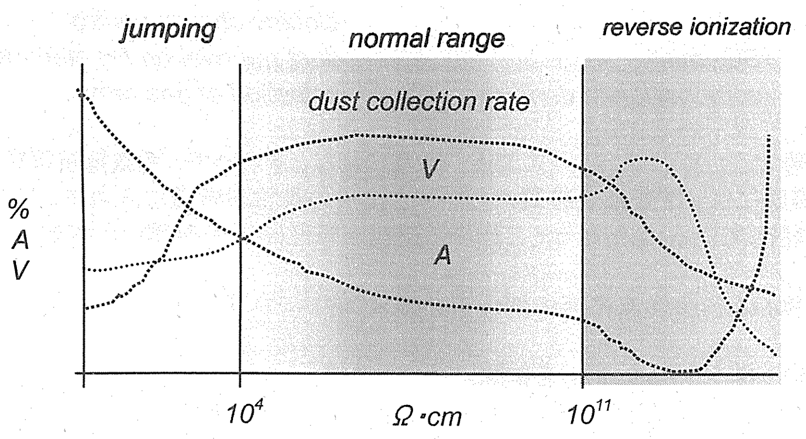
4-5-2 電気集塵装置の働く要因

左側の図は、ガス温度と電気抵抗率の関係を示す。一般的に、電気抵抗率は120から180℃の範囲で最高値を示す。これは、粒子中を流れる電流が高温域と低温域では異なることによる。排ガス中の水分と SO_3 が、低温域では容易に粉塵粒子に付着して、粉塵表面に沿って電気が流れやすくなるためである。一方、高温域においては、電流の流れは粒子内が主流となる。これは、粒子中のアルカリ金属量に左右される。



右側の図は、粒子の電気抵抗率とEPの除去性能、荷電電圧、電流の関係を示す。10^4 Ω-cm 以下(ジャンピング領域)では、荷電された粒子は集塵電極に付着し、直ちにマイナス電荷を失うために、集塵効果が低下する。10^4 ～10^{11} Ω-cm 範囲は理想的集塵領域である。電気抵抗率が 10^{11} Ω-cm （逆電離範囲）以上になると、集塵電極に付着したマイナス荷電された粉塵の電気的中和が遅くなる。そのために、粉塵の表面に電気が貯まり、粉塵表面内の電界強度が高くなり、粉塵内層で絶縁破壊が起こり、集塵率が著しく低下する。

Dust removal versus Ω·cm



電気集塵装置の利点・欠点を表に示す。

Advantages and disadvantages of EP

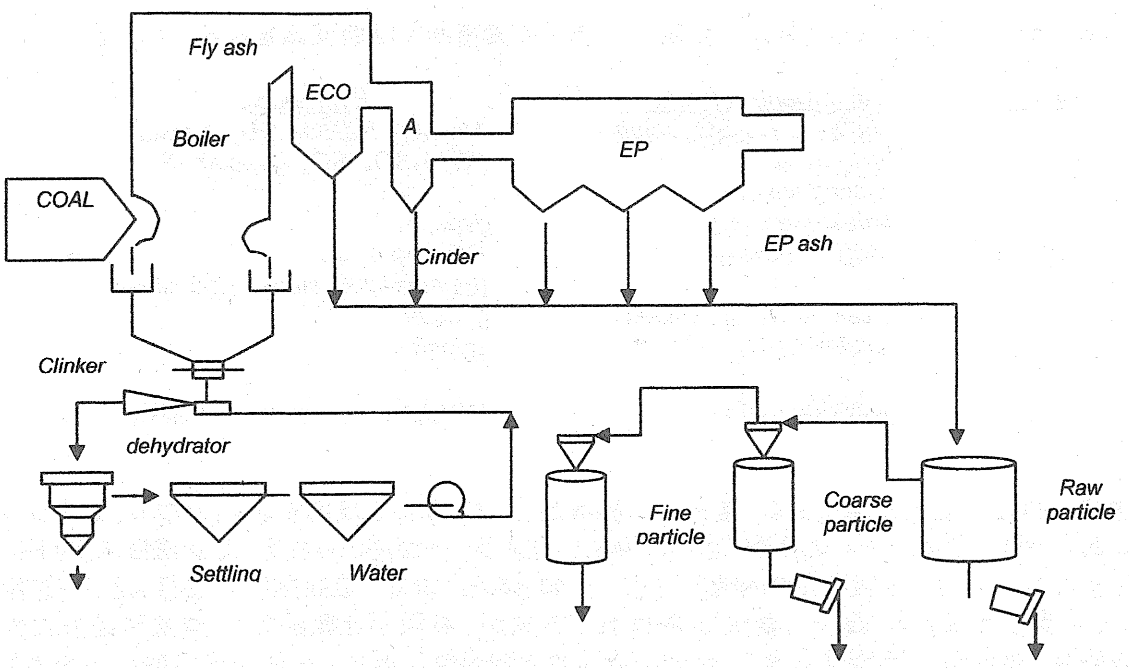
Advantages	Disadvantages
large gas volume	initial cost – expensive
fine particles of submicron	affection of apparent ρ (Ω-cm)
high temperature gas	system size- large
wet type dust collection	high level accuracy in manufacturing
suitable operation	
inexpensive maintenance	

詳細については P.176～179を参照。

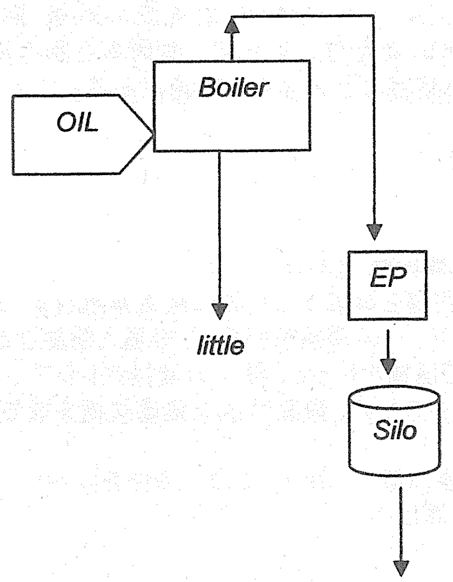
4-6 灰の処理

石炭炊ボイラーと重油炊ボイラーとの違いのひとつに、石炭炊ボイラーから発生する灰の量が、重油炊ボイラーより多いことにある。ボイラーで発生する灰は、炉底から排出されるボトムアッシュ（クリンカ）と、燃焼ガスに流されて、節炭機、空気予熱器、EP で落下し集められるフライアッシュに大別できる。(先の二つ一般的にはシンダーと呼ぶ)

石炭灰は、埋立、セメント原料、フライアッシュセメント、凝集剤、土木、農水産業、脱硫剤などに利用される。



重油炊ボイラーに場合、ボイラーで発生する灰の量は石炭炊に比べて少なく、灰の性状は、重油の種類に応じてほぼ一定している。また、ほとんど灰が EP で捕集される。したがって、灰処理装置は比較的簡単で、EP のそれぞれのホッパーに集められた灰は、圧力送風か減圧送風で送られる。重油炊発電所から排出される灰は未燃物と重金属を含むため、セメント工場の代替燃料や、有価金属回収の原料に用いられる。



詳細については P.179～184を参照。

5. 排煙脱硫

5-1 排煙脱硫方法 (FGD)

脱硫方式は（1）乾式と（2）湿式に分類でき、多くの発電所では湿式法を採用している。

Method	Absorbent/ Adsorbent	Byproducts
	NaOH or Na_2SO_3 solution	Na_2SO_3, $NaNO_3$, SO_2, gypsum
	NH_3-water	$(NH_4)_2SO_4$, SO_2, gypsum, S
	Slaked lime or limestone slurry	gypsum
Wet type	$Mg(OH)_2$-slurry	SO_2, gypsum (blended with slaked lime slurry)
	Basic $Al_2(SO_4)_3$-solution	gypsum
	Dilute-H_2SO_4	gypsum
Dry type	Activated carbon	$(NH_4)_2SO_4$, gypsum, S, H_2SO_4

湿式が排煙脱硫の主流である。湿式法の吸収剤として、SO_2 と反応するナトリウム、カルシウムあるいはマグネシウム化合物の溶液、あるいはスラリーが用いられる。湿式法はスライドに示すように、しばしば吸収剤の種類によって分類される。現在、吸収剤に石灰石スラリーを用い、石膏を回収する"石灰石膏法"と呼ばれる方法が、石灰が比較的安く、湿式脱硫方式の建設費、運転費の経済性が高く、運転の安全性と安定性に優れ、石膏が安定的に販売できるので、日本の発電所では多く採用されている。

- ·limestone ⇒ cheap
- ·initial & operating cost ⇒ economics
- ·system ⇒ stability & safety
- ·gypsum ⇒ stable sales

} reasons of most popularly used

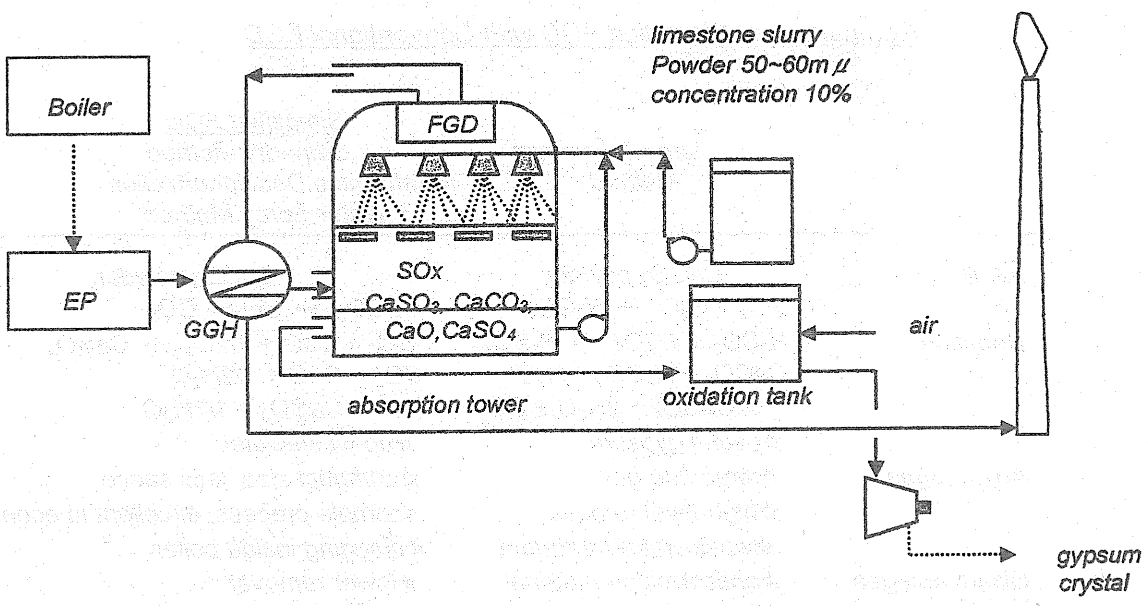
それとは対照的に、乾式法には、安全性確保、副産物の貯蔵・販売、長期安定運転に対する配慮の難しさの他に、吸収剤の安全性と劣化性、循環率と回収率の悪化、廃液の発生、ドライダストのハンドリングに伴う閉塞などの多くの問題がある。

詳細については P.186を参照。

5-2 湿式石灰石膏法排煙脱硫装置 FGD システム

ボイラーの煙道ガスは煤塵と粉塵を除去するために電気集塵装置（EP）に入る。集塵装置が機能しないとガスーガスヒーター（GGH）の閉塞を引起し、煤塵と粉塵などの流出が増大する。多量の煤塵と粉塵が排煙脱硫装置で捕集されると、種々の機械的トラブルと石膏の質の低下と、または、吸収剤の活性低下を起こす。そのため、最高性能の集塵装置を設置することが望ましい。

GGH は熱回収側からは、集塵装置から出てくるガスの熱を回収し、再加熱側では、回収した熱を煙突に入るガス温度の上昇に渡している。



吸収塔では、粒径50～60ミクロンの石灰粉末を含む吸収液が循環していて、この液とガスがうまく接触して、ガス中のSO_2が液側に取込まれ、除去される。二酸化硫黄((SO_2)は石灰(CaO)と結びつき亜硫酸カルシウム($CaSO_3$)に変わる。$CaSO_3$ の一部は、吸収塔に置いて、排ガス中に含まれる酸素によって自然酸化され、石膏($CaSO_4$)になるが、残りの $CaSO_3$ は酸化槽で空気酸化される。

Reaction Mechanism

$$SO_2 + CaO \rightarrow CaSO_3$$
$$2CaSO_3 + O2 \rightarrow 2CaSO_4$$
$$CaCO_3 + SO2 \rightarrow CaSO_3 + CO_2$$

石膏スラリーは脱水機で脱水され、水分10%以下の石膏として回収される。

詳細についてはP.190～192を参照。

5-3 簡易排煙脱硫装置

湿式の石灰石膏法による脱硫装置は、表に示されるように、上から吸収反応、酸化反応、中和反応の3段階の化学反応式で構成される。この装置は先に述べたように優れた特長を持っているが、建設費が高い。そのために、簡易排煙脱硫装置が開発され、開発途上国で使われている。

簡易排煙脱硫装置では、石灰粉末(CaO)と水が、直接炉に注入される。炉内では、脱硫反応は表に示すように、第一段階の脱硫と第二段階の脱硫に分けておこなわれる。両者の長所と短所の比較を表に示す。

簡易排煙脱硫装置の原価低減は、装置価格低減の常套手段である、(1)エンジニアリング時間の削減、(2)装置を構成する機器のコンパクト化、(3)機器の材質の検討、(4)プロセスの簡易化、(5)ユーザー側に経って重要なことに配慮をしながら、制御方法のシンプル化によるプロセス機器、装置の簡易化によって行った。

Comparison of Simplified FGD with Conventional FGD

	Lime & Gypsum Method	Simplified FGD Semi-dry Method Intrafurnace Desulphurization + Water Spray Method
Alkali	$CaCO_3$ powder	$CaCO_3$ powder
Reaction	$SO_2 + H_2O \rightarrow H_2SO_4$ $H_2SO_3 + 1/2O_2 \rightarrow H_2SO_4$ $CaCO_3 + H_2SO_4 + H_2O$ $\rightarrow CaSO_4 + 2H_2O + CO_2$	$CaCO_3 \rightarrow CaO + CO_2$ $SO_2 + CaO + 1/2O_2 \rightarrow CaSO_4$ $SO_2 + CaO + 1/2H_2O$ $\rightarrow CaSO_3 + 1/2H_2O$
Advantages	☆useful gypsum ☆large flue gas ☆high-level removal	☆no wastewater ☆compact size, less space ☆simple process, excellent in economics
Disadvantages	★wastewater treatment ★anticorrosion material ★large area ★high maintenance cost	★slagging inside boiler ★lower removal ★lower alkali utilization
Cost		
Equipment	100	20~30
Operation	100	75~80

詳細については P.188～189を参照。

6. 排煙脱硝

6-1 NOx 除去方法

NOxとは、主に酸化窒素(NO)と二酸化窒素(NO_2)のことである。燃焼において、NO が二つの中では支配的であって、NO_2 は主に NO から生成される。燃焼過程における NOxの生成の主なメカニズムは、(1)バーナー室の高温雰囲気で空気中の N_2 が酸素と反応して生じる、いわゆるサーマル NOxと、(2)燃料中に存在する窒素が高温雰囲気中で酸素と反応してできるフューエル NOx の二通りがある。

種々の脱硝方式の代表的な効率と適用性を、スライドの上側の表に示す(出展：Environmental Engineering,P.777, McGraw-Hill, 1998)。

Reduction of NOx Generation & Denitrification Methods

Method	Applicability	NOx red. (%)
Flue gas recirculation	T-NOx	70~80
Low NOx burner	F-NOx, T-NOx	10~25
Staged burners	F-NOx, T-NOx	40~70
SCR	F-NOx, T-NOx	80~90
SNCR	F-NOx, T-NOx	60~80

Remarks; T-NOx: Thermal NOx, F-NOx: Fuel NOx

上から3つの方法は、NOx 発生の抑制を刷新的な設計で行うもので、後の2つは、発生した NOx を低減するために産業界で選択的に使われているプロセスである。排煙ガスを循環する方法は、

火炎の最高温度と酸素量を低減して NOxの生成を抑えるものである。低 NOx バーナーは、最小の過剰空気で燃料を燃やせるように設計されている。多段燃焼は最高温度を低減することができる。3段燃焼まで使えるが、格段のバーナーの燃料と空気の比率に非常に緻密な制御を必要とする。

下の表に、主な排煙脱硝プロセスを示す。SCR は排煙の中にアンモニア(NH_3)を注入して、触媒層を通し、NOx を N_2 と H_2O に分解する簡易なプロセスである。この方式は大容量のガス処理に適している。SNCR は、約800～1,000℃の高温域にアンモニアを注入し、触媒を使わずに脱硝することができる。この方式の脱硝率は、SCR と比べると低い。NSCR は白金(Pb)などの貴金属の触媒を使い、さらに、CH_4, CO あるいは H_2 を還元剤として使って脱硝を行う。この方式を、低濃度 NOxの、大容量ボイラー排ガスに適用することは難しい。450℃位いで貴金属触媒を用いる触媒分解方式、吸収法、吸着法などの方法は、実用段階に至っていない。湿式法式は複雑であり、廃液が出るため、通常の発電所では使われていない。

Denitrification Process

Process	*Method*
Dry Process	
SCR (Selective catalytic reduction)	*NH_3, catalyst*
SNCR (Selective non-catalytic reduction)	*NH_3, Gas temp. 800~ 1,000℃*
NSCR (Non-selective catalytic reduction)	*catalyst (Pt) + CH_4, or CO, or H_2*
Catalytic cracking	*catalyst (Pt, ・・・・)*
Wet Process	*NOx + SOx removal* *Complicate process* *wastewater treatment*

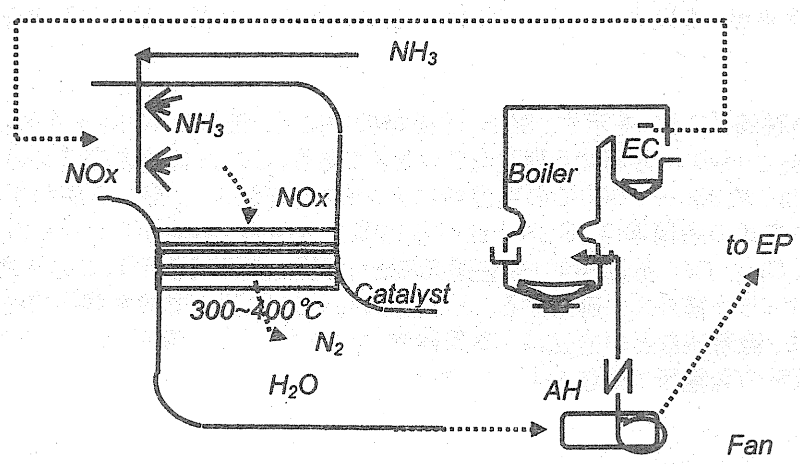
詳細については P.200～201を参照。

6-2 NH_3 触媒脱硝法

この方式は、煙道ガスにアンモニア(NH_3)を注入した後、この混合ガスを触媒層を通過させ、スライドに示すようにNOxを N_2 と H_2O に分解する。アンモニアは気化器でガス化して、アキュムレーターを経て、ボイラー用の送風機の空気で希釈をして、アンモニア注入ノズルから排煙ガス中に注入する。この反応の最適な温度範囲はボイラーのエコノマイザー(EC)の出口と同じ温度の300～400℃である。この方式の特長は(1)簡単なプロセス、運転が容易、故障が無く信頼性が高く、(2)廃水の発生をともなわず、排ガスの再加熱が不要で、(3)脱硝率が高く、(4)副生物が無いことである。

何種類かの触媒が実際に使われている。これらは主に、チタニウムまたはアルミニウムなどの多孔質セラミックと、補助材として、触媒活性物質よして金属酸化物の何種類かが用いられ、これらは補助材に粒状や、格子状、ハニカム状、あるいは板状で保持されている。触媒の管理は、触媒における、経過時間、脱硝率と触媒層の圧力損失を含む運転データの記録における変化を精査することによって行われる。

SCR Process : *Ammonia Catalytic Reduction Process*



Reaction

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$2NO_2 + 4NH_3 + O2 \rightarrow 3N_2 + 6H_2O$

Catalyst

support: ceramic (Ti, Al, ・・・)
catalyst: metals
shape: granule, grid-form
honeycomb, plate
control: denirification rate
catalyst bed draft loss

詳細についてはP.202～206を参照。

7. 煙突

火力発電所の煙突の目的は、ボイラーの燃料の燃焼に伴って発生する排ガスが周辺の機器や動植物に影響を与えない高所で排気を行い、大気中に拡散させるために建てられる。

Stack height & Draft force

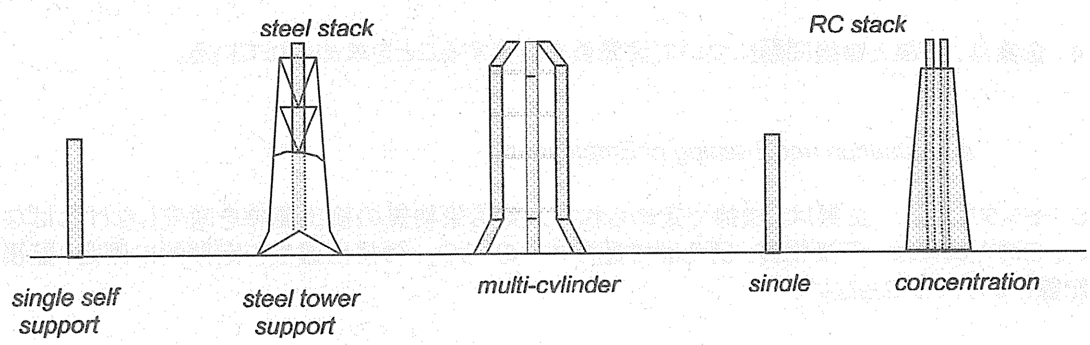
$$(\gamma a - \gamma g)H_0 + Peb \geqq Vg^2/2g \cdot \gamma g + \Sigma\Delta h > 0$$

$(\gamma a - \gamma g)H_0$: theoretical draft force (kg/m^2)
γa: air specific weight at atmosphere temp. (kg/m^3)
γg: exhaust gas 〃
H_0: stack height from datum level (m)
Peb: effective blower pressure (kg/m^2)
Vg: exhaust gas outlet velocity (m/s)
g: gravitational acceleration (m/s^2)
$\Sigma\Delta h$: total pressure loss in exhaust gas route = $\alpha \cdot V2/2g \cdot \gamma g$ (kg/m^2)
α: resistance coefficient
V: flue gas velocity in route (m/s)

煙突の吸引力は、送風機の送圧と煙突自身が持つ吸引力の和から、煙道における圧力損失を差し引いた値である。スライドに示す式は、吸引力と煙突高さの関係を表すのに一般的に用いられ

る。煙突の高さは本式から求めることができる。しかし、ガス拡散表面と周辺構造物を考慮に入れて、煙突の高さを決定しなければならない。

煙突の形の選定に当っては、構造面と周辺環境との調和に配慮が必要である。



火力発電所の排ガスはボイラーに使う燃料の種類によって異なるが、種々の腐食性物質を含んでいる。そのため、ガス成分、温度、排ガスの流速、ボイラーと脱硫装置の運転状態を考慮に入れて、物理的、化学的に安定なライニング材を選ぶ必要がある。

詳細についてはP.207～208を参照。

8. 環境管理システム

1. EMS: 環境管理システム(EMS)の傾向は、悪化の一途をたどる地球環境の状況下にあって、1992 年に開かれた環境と開発に関する国連会議で"持続可能な開発"が合意された。この決議に基づき、国際標準化機構(ISO)は 1996 年に"環境マネージメント・監査"を設定した。これにより、企業は企業活動が与える環境への影響と法規制に基づき、企業が持っている環境問題に対して、基本方針と目標を設定する。企業は、これを実行に移し、目標を達成するために、システムを修正し、監査していく。この作業は繰り返し行われ、仕組みは改善されていく。このサイクルはPDCA サイクル(Plan-Do-Check-Action)と呼ばれる。ISO 14000 は、環境管理を確立し推進していくために、適切な組織、義務、管理システムを作ることを要求している。

1. Environmental Management System
- Trend of environmental management
- Organization for environmental management & control
- Mission
- Pollution control system

ISO 14000

2. 地方自治体との協調: 地方自治体との強調は不可欠である。この協調には、汚染物質測定データー用テレメーターの設置と緊急事態に対する防データーなどが含まれる。企業は、汚染防止法を守るに留まらず、汚染を防ぎ、環境を積極的に守らなければならない。

2. Cooperation with Local Government
- Cooperation in pollution control measures
- Handling of complaints
- Environmental protection agreement

3. データの開示: 企業は排出濃度の測定結果の報告と、法律に従って事故時の処置に付いて

自治体に報告しなければならない。これらの他に、企業は環境説明責任に基づき、これらの結果と汚染防止に対して実施した内容を公表することを求められている。

3. Data disclosing

４．企業は、汚染と環境問題について従業員を教育することを求められている。

4. Education and Training of Employees

５．モニタリング： 企業は、法律で定められた大気汚染物質の排出基準を順守しなければならない。このためには、汚染物質、例えば排煙ガス中の SO_2、の排出濃度を定期的に測定、監視して記録しなければならない。

5. Monitoring

６．発電所の緑化： 日本では、工場立地方により、新設工場の敷地の２０％以上を緑化することが義務付けられている。

6. Greening of Power Station

７．事故、緊急事態への対応： 発電所の所長は、自治体からの要求に対して、スムーズに即応できるように、マニュアルを整備し、従業員の教育を常に実施するように、上位期間と調整を図ることを求められている。

7. Measures against Accident and Emergency
- Accident
- Emergency

詳細については P.254～259を参照。

9. 省エネルギー

発電所における省エネルギーは汚染物質負荷の低減と同じことを意味する。高効率化を図る技術開発の推進と石炭炊発電所の難しい問題の解決を図ることが必要である。

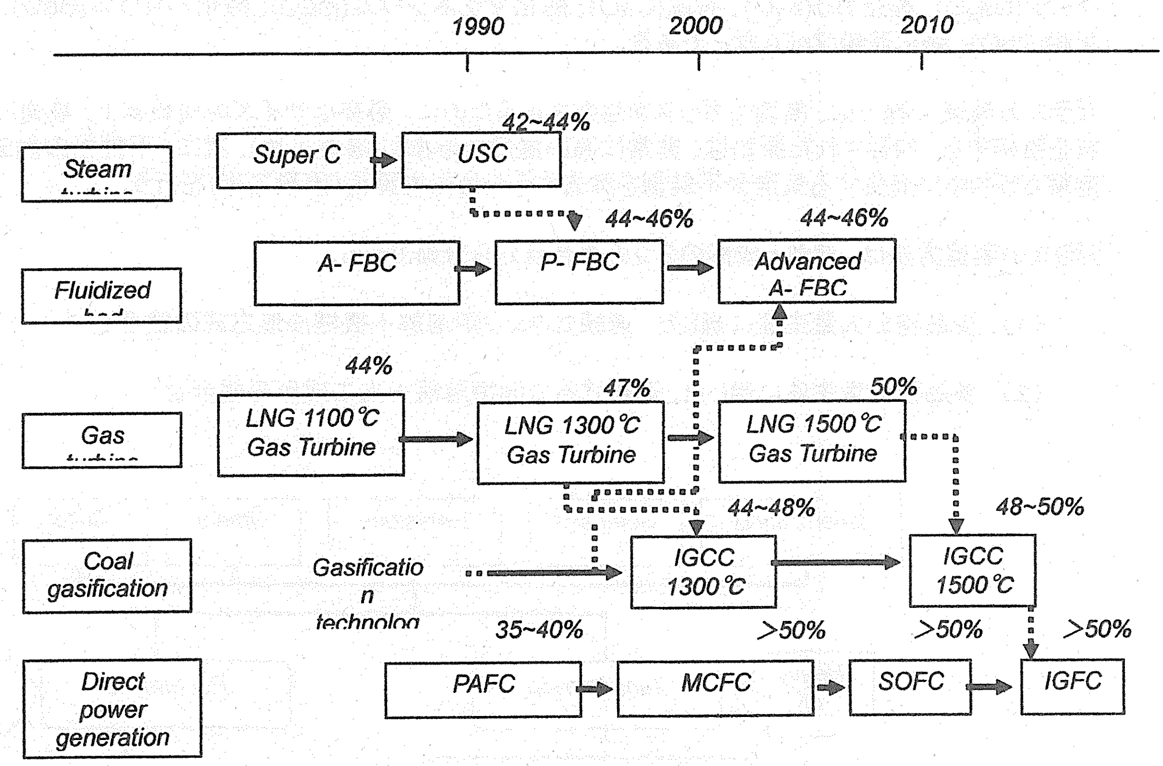
Efficiency improvement
= Energy saving
= Pollution decreasing

高効率発電技術とシステムと時系列の関係をスライドに示す。

微粉炭炊発電所では、効率４２～４４％の超臨界 2 段再熱発電方式（USC）、常圧流動床動焼（A-FBC）と加圧流動床燃焼（P-FBC）のスチームタービンが使われている。石炭ガス化では、４７％の高い効率を持つ、石炭ガス化複合発電（IGCC）発電装置が使われるようになってきている。

LNG 炊ボイラーを用いるガスタービンでは、1，500℃の高温で運転され、効率50%を有するタービンが開発途上にある。

直接発電では、50～500kW の燐酸燃料電池(PAFC)が、公共施設、ホテルなどでコジェネレーションと組み合わされて、試験的に使われている。溶融炭酸燃料電池(MCFM)は300kW 容量の第 3 期の開発に入っている。固体電解質燃料電池(SOFC)とガス化燃料電池(IGFC)は開発中である。



詳細についてはP.147～167を参照。

Ⅱ.ガラス製造業

1. ガラス製造業と大気汚染

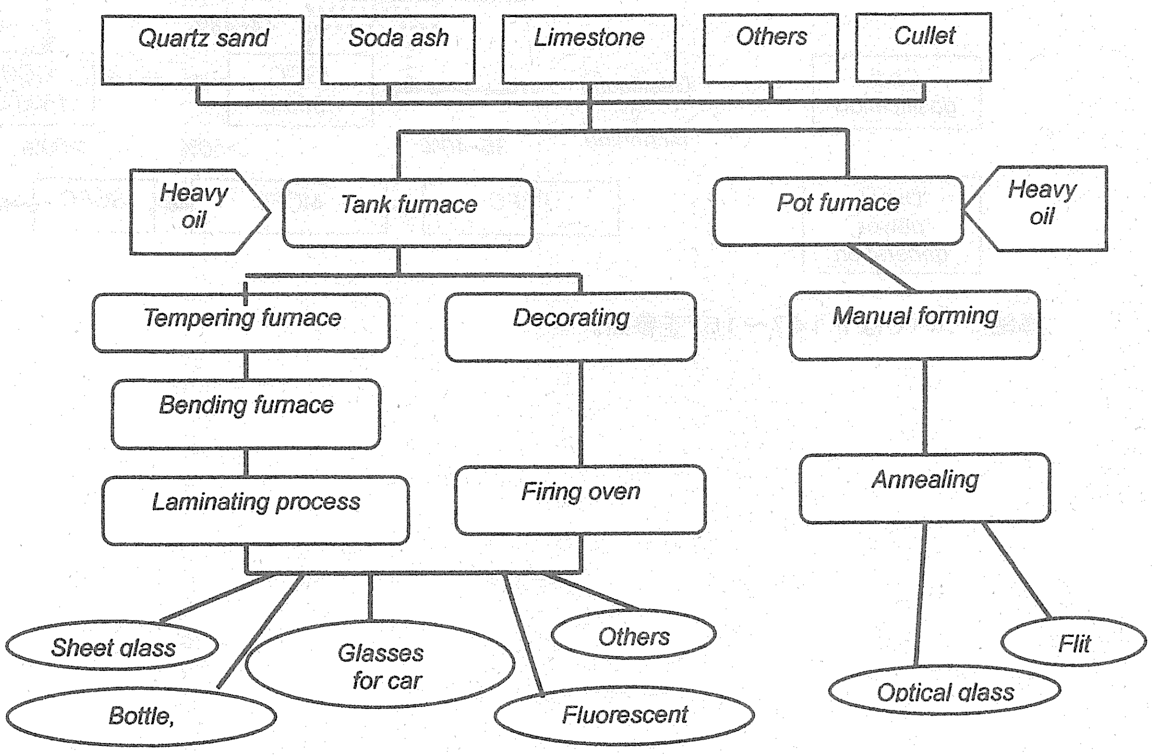
ガラス製品を成分から分類すると、"普通ガラス"と呼ばれるソーダ石灰ガラスが最も広く使われている。このほかに、特殊成分ガラスがあって、ホウケイ酸ガラス(硬質ガラス)、鉛ガラスと無アルカリガラスがある。ガラスの主な原料は、珪酸(SiO_2)、アルミナ(Al_2O_3)、ホウ酸(B_2O_3)、燐酸(P_2O_5)、ソーダ(Na_2O)、酸化カリ(K_2O)、石灰(CaO)、酸化マグネシウム(MgO)、酸化バリウム(BaO)、酸化鉛(PbO)、酸化亜鉛(ZnO),などである。

ガラスの製造工程では、高温でガラスを溶解させるために、必要なサイズの粒径まで、最初に原料を粉砕する。粉砕された原料は、非常に高い温度で溶解し(溶解工程)、次に、不純物の除去と溶解ガラス中に発生する気泡や不純物を除去するために均質化(清澄工程)を行う。

ガラスの製造方法は、溶解と成形の2つの組合せから分類できる。

（1） 少品種の大量生産に適した、連続式タンク炉溶解＋機械成形方式の組合せ

（2） 多品種少量生産に適した、連帯式るつぼ炉溶解＋人工成形の組合せ



大気汚染物質は、(1)粉砕した原料の取扱い中に発生するダストと(2)炉の排煙ガスに含まれるSOx、NOxと有害物質がある。

詳細についてはP.3～13を参照。

2. 煤塵と粉塵の除去

2-1 燃料と操炉による低減

ダストは、燃料の燃焼と原料の分解から発生し、有害物質をいくらか含んでいる。貯蔵作業、混合作業、移送中に飛散する10～100μm の粒径のダストは、通常、排煙の粉塵、煤塵とは別に扱われる。

ソーダ石灰ガラスの溶解炉から発生する煤塵と粉塵は、(1)燃料の燃焼に伴い生成される煤塵、(2)燃料に含まれる灰分と重金属、(3)炉からの排ガスに随伴して飛散する物質と、(4)蒸発物質が凝縮したヒュームがある。

Causes of Dust

- *Fuel → Dust (soot, ash, heavy metal)*
- *Raw Material → Scattered substances (ash, heavy metal)*
- *Non-uniform mixing fuel and air*

煤塵と粉塵を減らす最も簡単な方法は、固体燃料をガスに、あるいは、重油を経由に燃料転換することである。これらの燃料転換以外の方法としては、操炉面の改善を行うことが、ダストの低減に現実的方法である。例えば、(1)効率的な燃料噴霧、(2)燃焼空気の供給方法に対する細心の配慮、(3)炉の寸法と火炎形状の関係の適正化が有効である。炉からのキャリーオーバーに影響を与える原料の粒径と水分の見直しも、同伴ダスト量の低減に効果的である。

Dust Reduction Method in Soda-Lime Glass Melting

- *Switching fuel; Solid → Liquid → Gas*
  Heavy oil → Kerosene
- *Effective atomization of fuel*
- *Careful manipulation of air supplying*
- *Adequate proportion of furnace configuration to flame shape*
- *Reviewing particle size of batch (glass raw material)*
- *Adjustment of batch moisture content in batch wise charge*
- *No direct striking surface of batch with flame*

詳細についてはP.38～39を参照。

2-2 ダストの性状と集塵装置の適用範囲

最も一般的に用いられるソーダ石灰ガラス溶解炉の排煙ガス(未処理)と溶解炉で生成するダストの性状を表に示す。

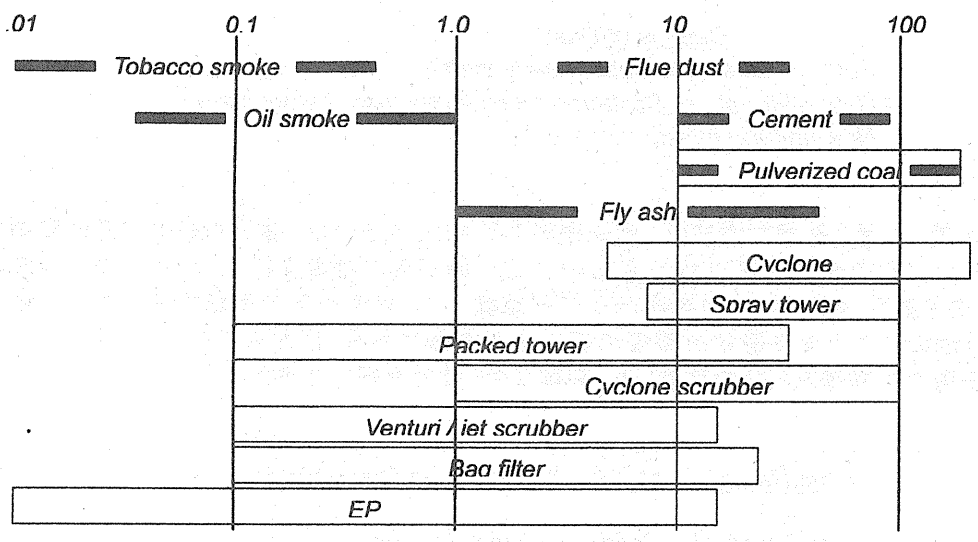
Soda-Lime Glass Melting Furnace Flue Gas

Flue gas (400~600℃)		Dust		
O_2	8~9%	Dust conc.	0.2~0.4 g/Nm3	
CO_2	10%	Particle size	~ 0.5 μm	25%
H_2O	10%		0.5~ 0.3 μm	50%
SOx	500~1,500ppm		0.3~0.1 μm	20%
NOx	400~600ppm		0.1 μm ~	5%

粒径は非常に小さく、1μm 以下であり、主成分は硫酸水素ナトリウム $NaHSO_4$)と硫酸ソーダ(Na_2SO_4)である。

種々のダストとミストの粒径と、適用できる集塵装置の代表的な例を図に示す。図に示されるように、重力集塵装置、慣性力集塵装置、遠心力集塵装置は1μm 以下の粒径のダストの集塵には適していないので、ガラス溶解炉で使われることはない。

Dust Collection



これらは、ガラス製造工場における原料の貯蔵、混合、投入で発生する原料粒子の集塵に使われる。洗浄集塵装置は大量の水を使い、定期的なメンテナンスを必要とする。そのため、大容量の排煙ガスを長期間にわたって連続処理をしなければならないガラス溶解炉には適していない。そのため、大型のタンク炉にはろ過集塵装置か電気塵装置が一般的に使われる。

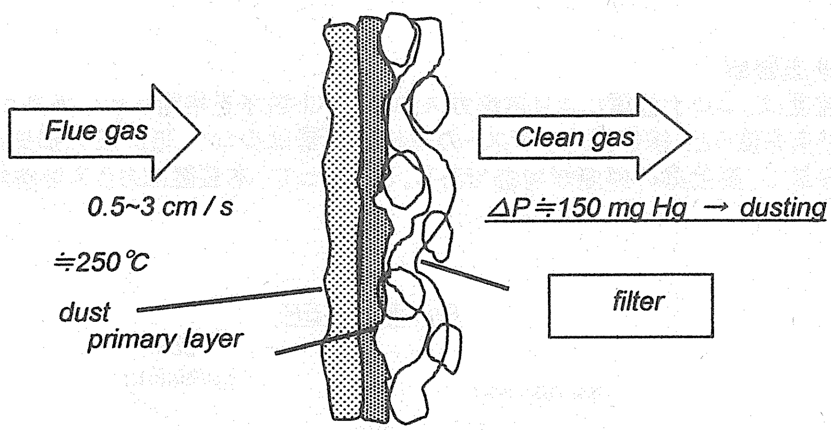
詳細については P.38～41を参照。

2-3 ろ過集塵装置

バグフイルター集塵装置は全ての集塵装置の中で最も広範囲に使用されている。バグフイルターは0. 1μm 粒径の粒子でも捕集できる。バグフイルターをガラス溶解炉の排煙ガス処理に使った場合、97～99%の集塵率を得ることができる。

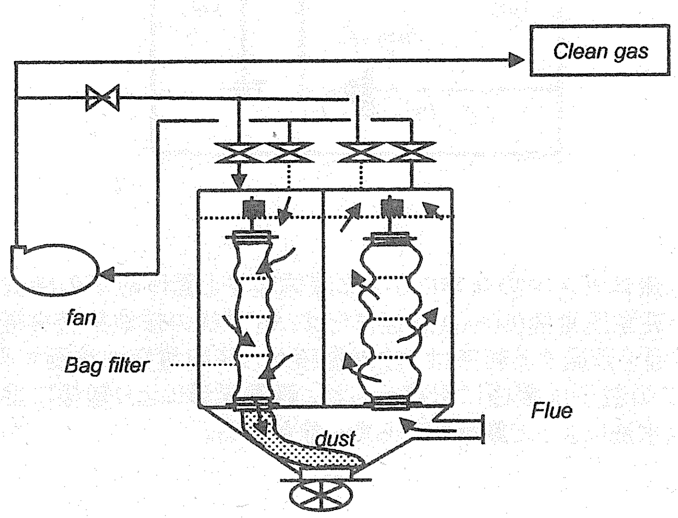
集塵機構は、ろ布の表面に最初に付着した粒子層(初層)がろ過層として微粒子を捕集する。ろ過層の排煙ガスの通過速度は、おおよそ0. 5～3cm/cm である。したがって、大容量のガスを処理する場合は、多くのバグフイルターを並列して用いる多室集塵装置が用いられる。

Filtration Action in Filter Cloth



例えば、溶解炉の排ガス35，000m³/h （250℃）処理のバグフイルターは、6集塵室をもち、各室には直径30cm、長さ約600cm の円筒形フイルターが50～60本配置されている。この場合、6室の内の1室は、ある一定時間ダストの払落しがおこなわれ、残りの室が除塵をおこなう。

ガラス溶解炉に使われるろ布は、200 ℃以下で結露による硫酸腐食が起こるので、ガラスファイバーが用いられる。



ろ布上にダストが蓄積して圧力損失が 150 mm Hg に達すると、ダストの払落しが必要である。ダストの払落しは、ガラス溶解炉の場合、最も一般的に使われている間歇式と、連続式がある。ダストの剥離除去は振動法か、逆気流法でおこなわれる。

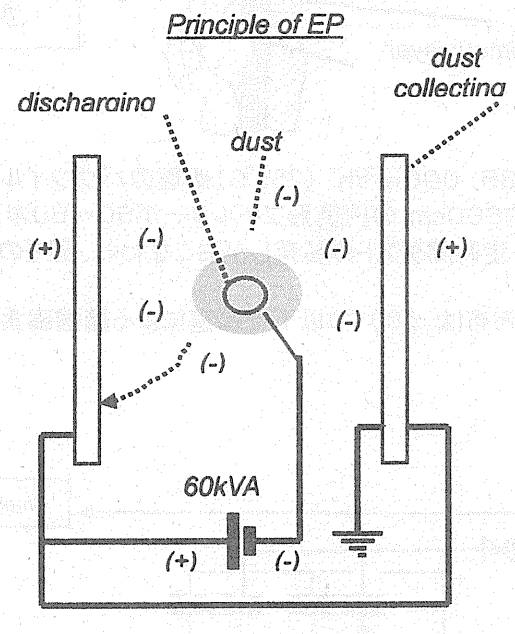
Dusting frequency	*Dusting drive*
- intermittent	- vibration
- continuous	- reverse air

温度は、ろ布の耐熱温度を超えないように、また、硫酸の露点を避けるために200から250℃の間に保たれる。

詳細についてはP.41～43を参照。

2-4 電気集塵装置

電気集塵装置は、コロナ放電により排煙ガス中のダスト粒子を帯電させて捕集するものである。電気集塵装置を使うと、排煙ガスやダストの性状の影響は少なく、低い圧力損失の下に、微粒子の集塵が容易で、高効率の集塵が可能である。したがって、本装置はガラス溶解炉の排煙ガス処理に広く使われる。



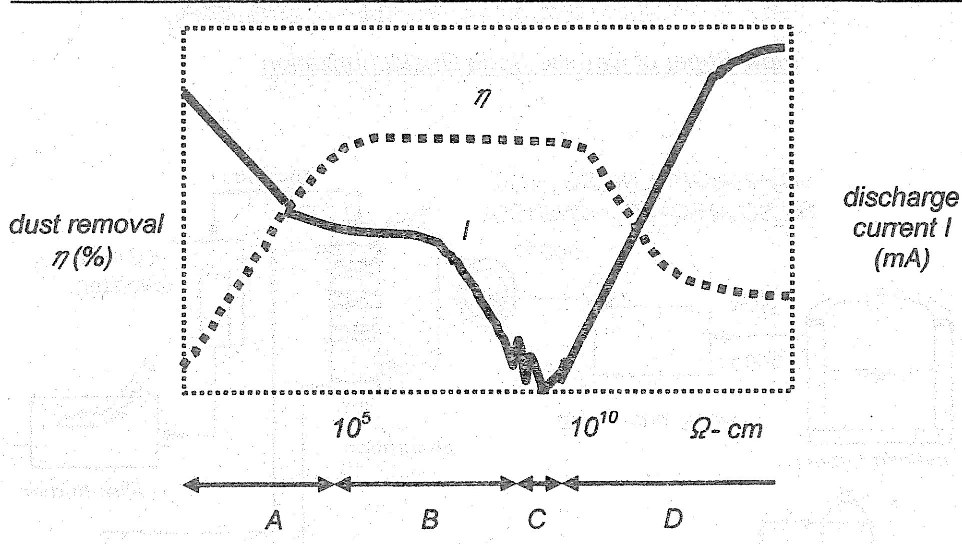
電気集塵装置（EP）は流体ガス中の非常に小さな液体粒子と固体粒子の除去に使われる。この装置は、通常、心線の高電圧電極(60kvA)と板またはパイプ状の接地集塵電極との間にコロナ放電を形成する。この電場を通過する粒子は、放電電極から集塵電極に移動するイオンと衝突しながらイオン化される。この粒子は電極に引寄せられ、静電誘導により電極に捉えられる。付着粒子は、槌打衝撃または水洗によって集塵板から取り除かれる。

Feature
- *Less influence of flue gas & dust*
- *Low pressure loss*

Peeling dust from electrode
- *Dry EP : hammering impact*
- *Wet EP: flow down with water film*

ダストの見掛電気抵抗（Ω-cm）が集塵効率に大きな影響を持っているが、粒子の大きさが大きくなるほど、集塵効率は一般的に高くなる。この見掛電気抵抗率は、ガス温度、水分、の影響を受ける。

Relation between apparent electric resistance and dust removal / discharge current



A: re-scattering
B: normal
C: frequent occurring of sparks
D: counter electric dissociation

見掛電気抵抗率が10^5Ωcm から10^{11}Ωcm の範囲にあると理想的な電気集塵がおこなえる。見掛電気抵抗率が10^{11}Ωcm より大きくなると、逆電離と呼ばれる現象が起こり、集塵効率が低下する。逆電離を防ぐ方法として、水、水蒸気、または亜硫酸（(SO_3)の注入と、排煙ガス温度を電気抵抗値が最大値を示す150～200℃より高温側にするか、低温側にして処理をすると効果的である。

Factors affecting dust collection
- particle size
- temperature, moisture, SO_3→Ω- cm

詳細についてはP.43～47を参照。

3. SOx 除去方法

3-1 苛性ソーダを用いる脱硫方法

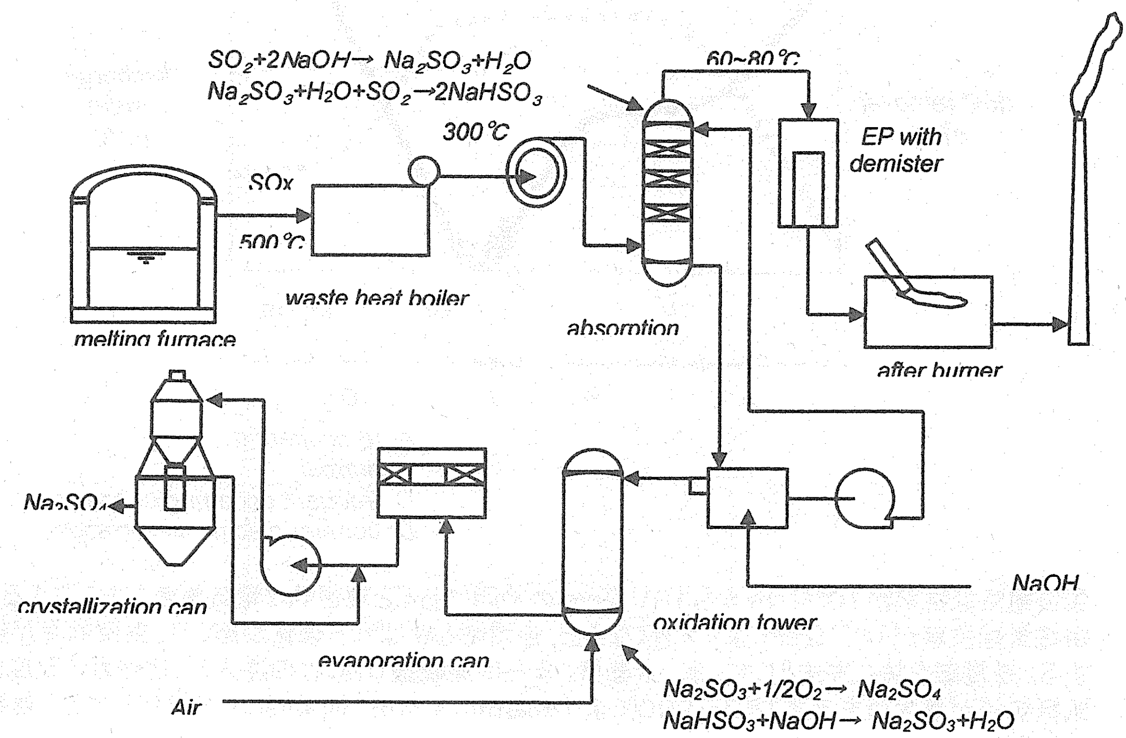
ガラス溶解炉から発生するSOxは、通常、(1)燃料中の硫黄成分の燃焼、(2)ガラス原料に使われている硫酸ソーダ(Na_2SO_4)や硫酸カルシウム($CaSO_4$)などの硫酸塩の分解による。排煙脱硫装置は、通常、硫黄含有量の高い重油を使用するガラス溶解炉に用いられている。

排煙中のSOxを分離・除去するのに、種々の薬品が使われている。苛性ソーダと水酸化マグネシウム($Mg(OH)_2$)を用いる、水洗法は、装置が簡単であるため、ガラス溶解炉には最も広く用いられている。

代表的な苛性ソーダ脱硫法を図に示す。分離された SOxは最終的には硫酸ソーダ($NaSO_4$)の形で回収される。この装置は、実績として脱硫率97％以上、除塵率95％を達成している。この方法で脱硫と除塵をおこなったガスに、再加熱した清浄な空気を混入して温度を上昇させ、水蒸気を含む白煙の排出を防止している。しかし、近年、省エネルギーに対する関心の高まりから、水蒸

気は大気汚染に影響を与えないので、再加熱を行っていなケースが多くある。

<u>*Flow Sheet of Caustic Soda Desulphurization*</u>



湿式集塵機(EP)はダストの除去と共に、ミストとヒュームを高効率に除去できるようになり、デミスター付きの湿式集塵装置が広く採用されるようになっている。

詳細については P.48～51を参照。

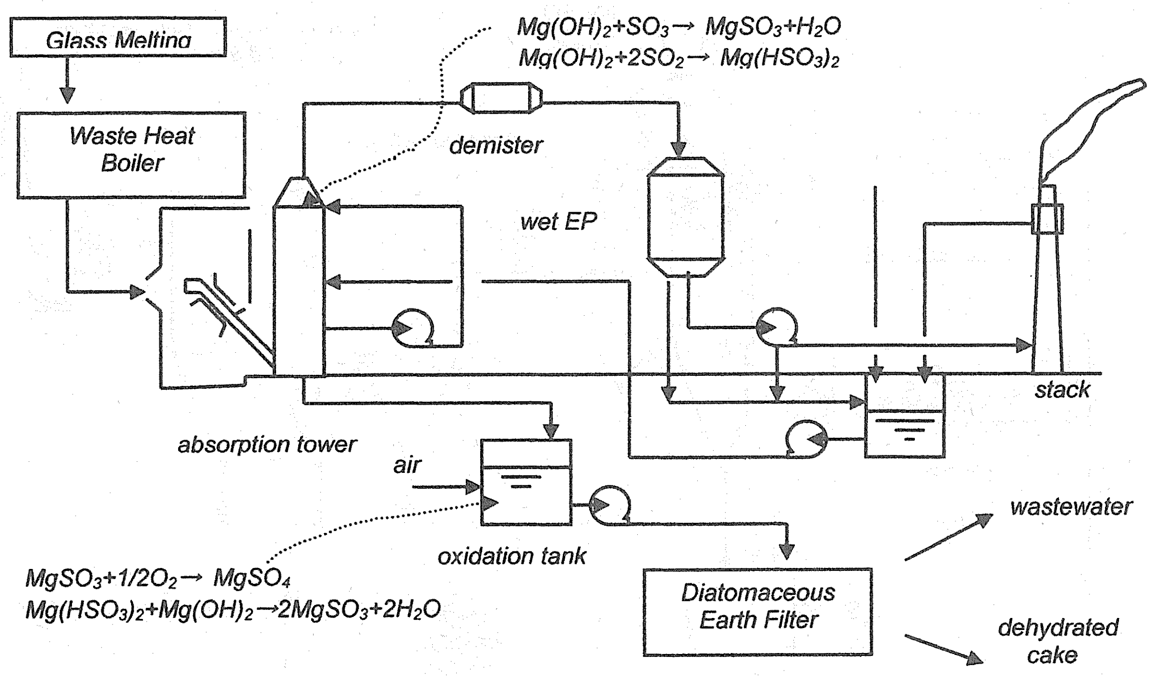
3-2 水酸化マグネシウムを用いる脱硫方法

水酸化マグネシウム($Mg(OH)_2$)溶液に SO_3 が吸収され、溶液が空気で酸化されると、その溶液は硫酸マグネシウム($MgSO_4$)を含む廃液となる。この方法は簡単であって、装置コストも安いので、ビンガラス製造溶解炉などに採用されている。

ガラス溶解炉から排出される排煙ガスは、廃熱回収ボイラーで 250 ℃に冷却される。その後、ガスは抗火石とカーボン煉瓦でライニングされた吸収塔に入る。循環液がガスに噴霧され、ガスの断熱冷却が起こり、排煙ガスは水蒸気飽和ガスとなる。断熱冷却は排煙ガスの温度を低下させ、塔缶体のライニング層の損傷を防ぐ。水酸化マグネシウムがガススクラバーに供給される。排煙ガスが目皿板の間を通過しながら、ゆっくりと上層部に移動をする。この間に、ガスと液が激しく接触し、SO_3 は吸収されて除去される。

排煙ガス中の大部分のミストがエリミネーターで除去された後、粉塵は湿式EPで処理されて放出される。ガスを吸収した循環液の一部は引抜かれ、酸化槽でばっ気され、空気酸化されて、硫酸マグネシウム($MgSO_4$)を形成する。

Flow Sheet of Magnesium Hydroxide Desulphurization



酸化槽から引抜かれた液は、ろ材として珪藻土を用いるプレコートフイルターでろ過される。このシステムの脱硫率は98%に達する。このシステムの特長は(1)システムが簡単、(2)建設費、運転費が低廉、(3)有害な化学品や腐食性のある薬品を使用しない点である。

詳細についてはP.51～52を参照。

3-3 乾式脱硫方法

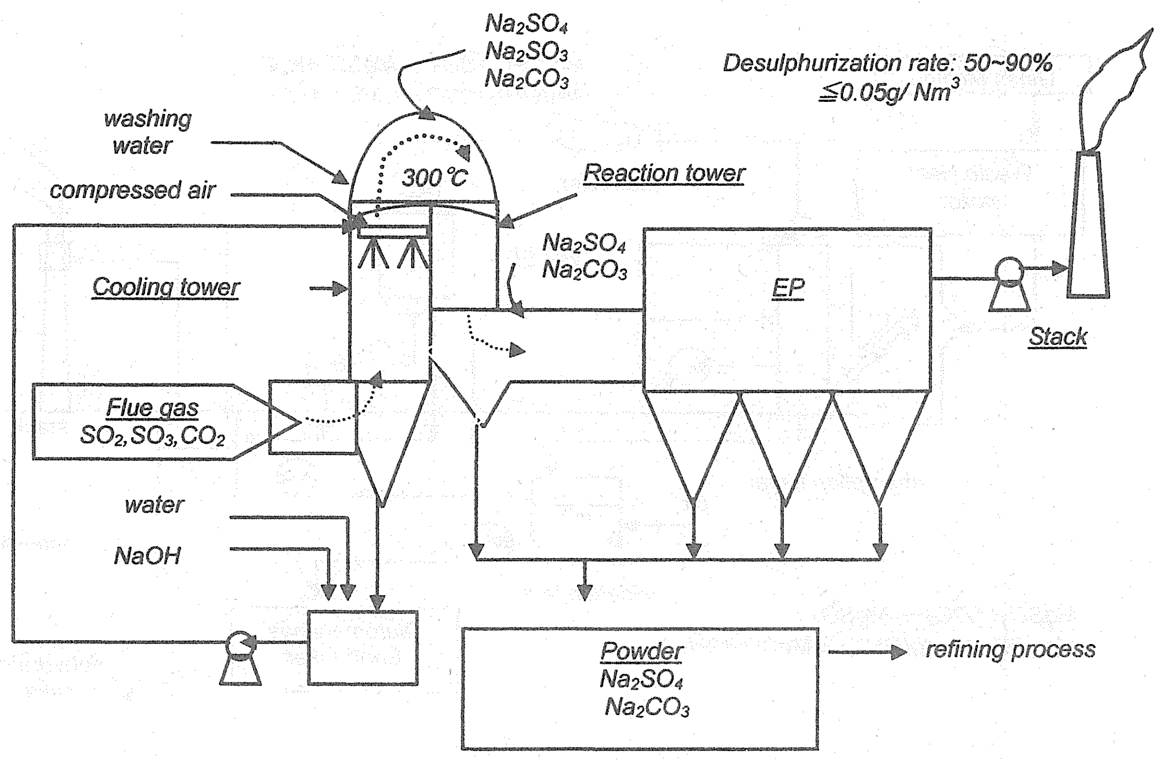
冷却塔に導かれた排煙ガスは、そこで数パーセント濃度の苛性ソーダ溶液と接触して、ガス温度が300℃位に低下し、ガス中の SO_2、SO_3、CO_2 が粒状の Na_2SO_4、Na_2SO_4、Na_2SO_4 に変わる。

次の反応塔で、Na_2SO_3 が Na_2SO_4 に酸化された後、排煙ガスは電気集塵装置に入り、そこで粉体状態の Na_2SO_4 と Na_2CO_3 は除去される。電気集塵装置の出口のガス温度は、220~230 ℃であるので、排煙ガスは煙突から直接排出できる。

この方法で、脱硫率50～90%、煤塵・粉塵 0.05 g/Nm^3 以下を得られる。

電気集塵装置で捕集されたダストは水に溶解され、精製工程を経て硫酸ソーダとして回収される。乾式脱硫装置の脱硫率は、湿式脱硫装置の除去率に比べて通常は低いが、乾式集塵装置は比較的簡単であり、小規模から中規模の炉に適している。

Flow Sheet of Dry Type Flue Gas Desulphurization



詳細についてはP.52～53を参照。

4. NOx 除去方法

4-1 原料に含まれる硝酸塩の削減

ガラス溶解炉から発生するNOxは、燃料の燃焼に伴うものと、原料の中に、酸化清澄剤として加えられる少量の硝酸塩の分解に伴うものがある。(特殊な炉のみが硝酸塩を使用する)

NOx generation :　NaNO3 (oxidation, refining agent)

硝酸塩の削減は、NOx（原料NOxあるいはバッチNOxと呼ばれる）の発生削減のひとつとして考えられる。硝酸塩の使用を止めるか、あるいは削減することは確かにNOx発生量の低減になるが、時には、ガラスの品質維持のために硝酸塩の使用が不可欠なこともある。

ひとつの例として、鉛ガラスの場合には硝酸ソーダの使用量を減らすとガラスの品質が保てなくなる。それを実現しようとすれば、フレームをより酸化性に変えなければならないが、その結果としては、NOx量を削減することができなかった例もある。硝酸塩の使用に関しては、ガラスの種類と火炎状態をよく考慮に入れなければならないし、硝酸塩の使用量を削減する努力を怠ってはならない。

硝酸塩の使用量を削減した時のその効果の例として、エンドポートの炉で使用する硝酸ソーダ

($NaNO_3$)の削減効果の試算結果と、実測値の比較結果をスライドに示す。

1. Reducing $NaNO_3$ additives
Quantity of pull : 100 t / day
Flue gas volume : 17,000 m^3 / h
Trial calculation: $NaNO_3$: silica sand = 0.5 : 100　　NOx　169 ppm
〃　:　〃　= 0.3 : 100　　〃　102　〃
reduction　　▲ 67 ppm

近年、清澄剤を変更して硝酸塩の使用を中止した幾つかの例がある。これまでは、硝酸塩は、酸化清澄のために三酸化アンチモン(Sb_2O_3)と一緒に使われていた。Sb_2O_3は$NaNO_3$が分解されて放出する酸素を取り込み、Sb_2O_3自体が高酸化物となる。多量のNOxが生成される。しかし、アンチモン酸ソーダ($Na_2 \cdot OSb_5 \cdot 6H_2O$)のアンチモンの原子価は5であり、スライドの反応式で示すように$NaNO_3$の必要性がない。

2. Changing refining agent　(Sb_2O_3 ⇒ $Na_2O \cdot Sb_2O_5 \cdot 6H_2O$)

$$Sb_2O_3 + O_2 \uparrow \xrightarrow[\text{Vitrification}]{\text{Low temp.}} Sb_2O_5 \xrightarrow[\text{Refining}]{\text{High temp.}} Sb_2O_3 + O_2 \uparrow + \text{thermal NOx}$$

$$Na_2O \cdot Sb_2O_5 \cdot 6H_2O \xrightarrow{\text{Low temp.}} Na_2O \cdot Sb_2O_5 + 6H_2O \uparrow$$

$$\xrightarrow[\text{Refining}]{\text{High temp.}} Na_2O \cdot Sb_2O_3 + O_2 \uparrow$$

詳細についてはP.55～56を参照。

4-2 燃料面からのNOxの削減

フューエルNOxは燃料に含まれる窒素が増えると増加する。

N in Fuels

Fuel	Nitrogen (wt %)
Coal	0.7 ~ 2.2
C- heavy oil ※	0.2 ~ 0.4
A- heavy oil ※	0.005 ~ 0.08
Light oil	0.004 ~ 0.006
Kerosene	0.0005 ~ 0.01
LNG	Tr.
LPG	Tr.

※ *JIS K2205 kinematic viscosity (cSt, mm2/s) C-heavy oil: 50≦~1,000, A-heavy oil: ≦20*

通常、燃料中の窒素量は気体燃料、軽質油、重質油の順に増加する。しかし、ガラス溶解炉は1，500～1，600℃の高温を必要とするため、全NOx発生量に占めるサーマルNOxの割合は、フューエルNOxより圧倒的に多い。

Furnace temp. 1,500 ~ 1,600 ℃ ⇒ Thermal NOx ≫ Fuel NOx

そのうえ、軽質油と気体燃料は、重油よりも発熱量が低く、軽油と気体燃料を用いて、輝炎を得ることが困難である。そのため、ほとんど全てを熱放射に依存する伝熱構造を持つガラス炉では、重油を軽質油あるいは気体燃料に変更すると、燃料消費量が間違いなく増加する。重油から、天然ガスに変更した場合にも、同じ現象が見られる筈である。

Heating value
Blight flame

Heavy oil > *Light gravity oil*, *Gaseous fuel*

↓

Fuel increasing

↓

NOx increasing

確実で効果的な対策のひとつに、電気エネルギーに変える方法があるが、大型タンク炉の全てを電気ガラス溶解炉にする技術はまだ確立されていない。電気ブースティングはすでに広く使われている。電気ガラス炉には内部加熱（電気を直接溶融ガラスに通電する電気抵抗加熱）が使われており、熱効率は高い。

Electric energy

resistance

詳細についてはP.56～57を参照。

4-3 操炉面からのNOxの削減

炉の状態を適正に保ち、操炉を行うことにより、NOxの生成を削減できる幾つかの方法がある。

（1）ガラスの溶融温度を低下させることが、NOxを低減する基本であるが、ガラスの種々の特性を改善しようとする場合には逆効果となる。この問題の解決には、①低い温度で溶融する化学組成のガラスの採用、②できるだけ多くのカレット（ガラス屑）を用いる方法の開発がある。

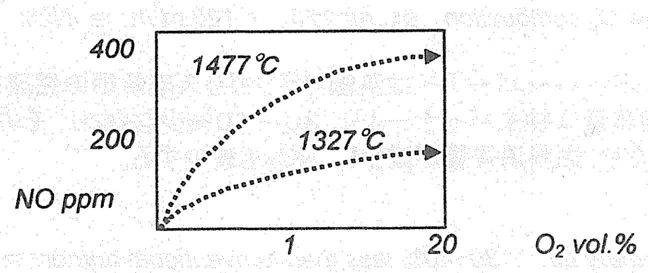
1. *Declining Glass Melting Temp.*
- *chemical composition ----- melting at lower temp.*
- *using the largest possible quantity of cullet*

(2)液体燃料を噴霧するために用いられる一次空気圧を低くすることは効果的である。例えば、圧力を4から3kg/cm^2 に低減することにより、NOxの生成量が約24%削減された実績がある。このほかに、燃料ガスを燃料噴霧に用いるガス混合燃焼は、保守管理面の問題もなく、NOxを有効に低減できる方法である。

2. *Lowering Primary Air Pressure*
- *lowering air pressure for fuel injection*
  ex. 4 kg /cm2 → 3 kg /cm2 ⇒ NOx ▲24%

(3)空気比(理論空気比: 1)を1．2から1．1に下げると、スライドに示すように NOxは25%削減できた。したがって、燃料の燃焼を空気比の許容下限値に近いところで燃焼させることが好ましい。

3. *Lowering Secondary Air Volume*
- *decreasing air ratio ex. 1.2 → 1.1 ⇒ NOx ▲25%*



(4)炉内全体をできる限り同じ温度分布に保てる燃料分配が、NOxの生成削減に効果がある。また、燃料燃焼加熱に、直接通電による加熱法の併用(電気ブースティング)を併用する方法は、炉内最高温度を下げる効果が非常にある。

4. *Lowering Furnace Temp. (Max. Temp.)*
- *allotting fuel distribution to maintain uniform temp. in furnace*
- *electric boosting*

(5)作業標準は非常に重要であり、NOx削減に大きな効果がある。

5. *Combustion Control Work Standards*

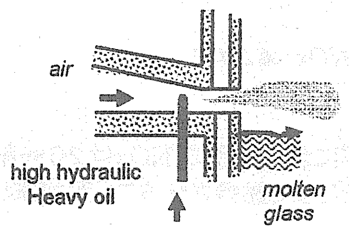
詳細についてはP.57～58を参照。

4-4 低 NOxバーナーの使用

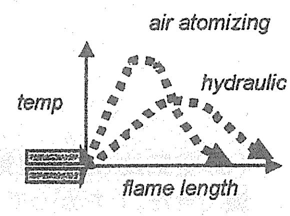
ガラス溶解炉では、燃料は10～30%の過剰空気(空気比1．1～1．3)を使って燃焼される。一方、理論空気量の空気で燃焼すれば、煤と未燃物の生成のために、炉内温度の維持が困難なだけでなく、ガラスへの着色などが起こり、品質上の欠陥をもたらすことがある。

1．油圧バーナーは本来、表に示されるように板ガラス溶解炉の省エネルギーと NOx削減のために開発されたものである。燃料重油の霧化のために噴霧用の空気を用いずに、重油の圧力を高めることにより、噴霧ノズルから重油を噴霧することができる。

Hydraulic burner



Burner	Heavy oil use ratio	NOx conc. ratio
Air atomizing	1.00	1.00
Hydraulic	0.88	0.62



2．超音波バーナーは燃料油の噴霧に超音波を利用している。必要な噴霧用ガス量(空気または蒸気)は、従来法のバーナーの必要量のおおよそ半分である。

- Low O_2 combustion　ex. Air 170 → 120 m^3/h ⇒ NOx ▲25~30%

3．レイドロー・ドリュー・バーナーは英国でビンガラス溶解炉の燃費を抑えるために開発された。必要な一次空気量は従来バーナーより、30～40%少なくなり、その結果、火炎は"ソフト"になり、熱効率が良くなり、燃料消費量が減少し、NOxも減少する。

- Primary air:　30~40% less than conventional burner ⇒ lower NOx

4．ガス噴霧型重油バーナーは一次空気の変わりに都市ガスを用いるので、一次空気量が減少する。ビンガラスのエンドポート式溶解炉(引出量100t/d)を使った実験では、NOxの濃度が20～25%低下しエネルギー原単位が3%減少したことが報告されている。

- Town gas is used instead of primary air ⇒ NOx ▲ 20~25%

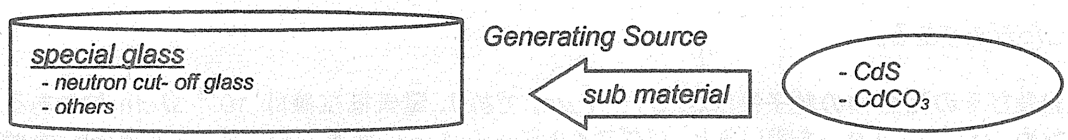
詳細についてはP.59～63を参照。

5. 有毒物質の除去

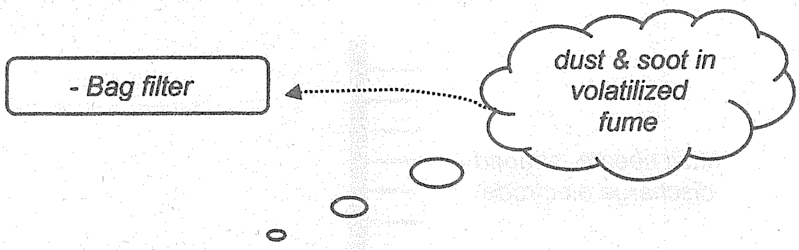
5-1 カドミウムとその化合物

ガラス溶解炉からは、SOxや NOxのほかに、カドミウム、カドミウム化合物、鉛、鉛化合物、フッ素、その化合物が有害物質として排出される。

カドミウムは、中性子遮断ガラスやそのほかの特殊ガラスを製造する時に、副原料として用いられる硫化カドミウムと炭酸カドミウムから蒸発し、飛散する。



蒸発拡散したヒューム状になったカドミウムは煙道ガス中で濃縮される。カドミウムとその化合物は粒子状態で排出されるので、集塵装置で捕集される。

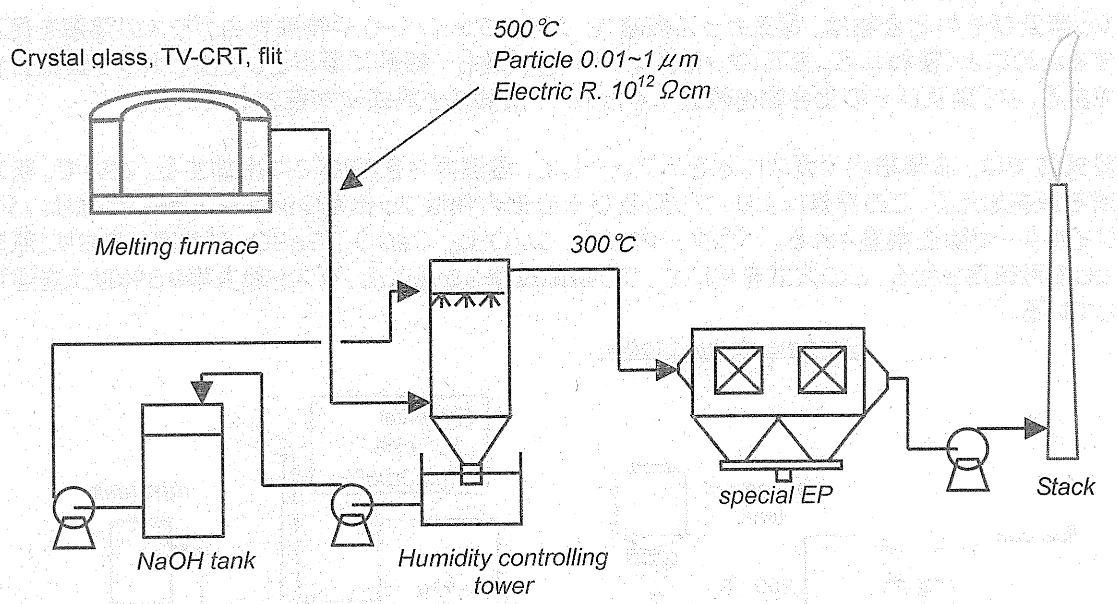


通常、バグフイルターと電気集塵装置が有効である。

詳細については P.64を参照。

5-2 鉛とその化合物

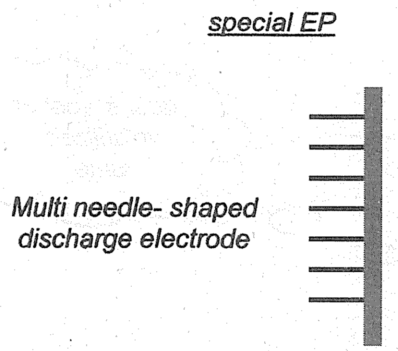
鉛はクリスタルガラスの主要成分であり、テレビのブラウン管(CRT)やガラス釉薬のフリットに使われる。溶解炉の排ガス中のダストの50%以上が鉛で占められる。



鉛の蒸発は、400～500℃付近で活発になり、蒸発した鉛は、煙道ガス中に鉛ヒュームとして存在する。原料から蒸発する鉛の量を抑制するためには、原料を可能な限りの低温で溶融する必要がある。電気溶解は、表面温度を低いレベルに保ったまま、原料の溶解ができるので、最も適

した方法である。

鉛及びその化合物の粒子径は0．01～1 μm であり、電気抵抗値は 10^{12} Ωcm 位である。そのため、バグフイルターを用いると、バグフイルターメッシュに閉塞が起こり、圧力損失が増加する。また、通常の電気集塵装置を鉛及びその化合物の集塵に用いると、逆電離が生じるために安定的な集塵が困難となる。28 年前に、特別に設計された電気集塵装置（EP）が使われるようになり、安定的な集塵が可能となった。



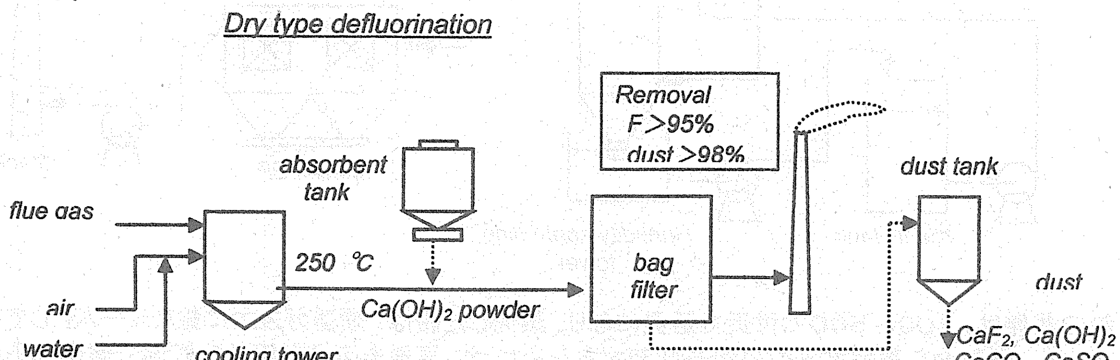
この装置は、煙道ガスに苛性ソーダの希薄溶液をスプレーし、ガス温度を500℃から300℃に低下させる。この方法により、粒子の電気抵抗値を下げることができる。また、この装置は、電気抵抗値の上昇を防ぐために、温度を300℃に保てるようになっている。煙道ガスは、スライドに示されるような、放電極が線状ではなく、針状の放電極を板の上に沢山つけた特殊な EP に導かれる。

詳細についてはP.64～66を参照。

5-3 フッ素及びその化合物

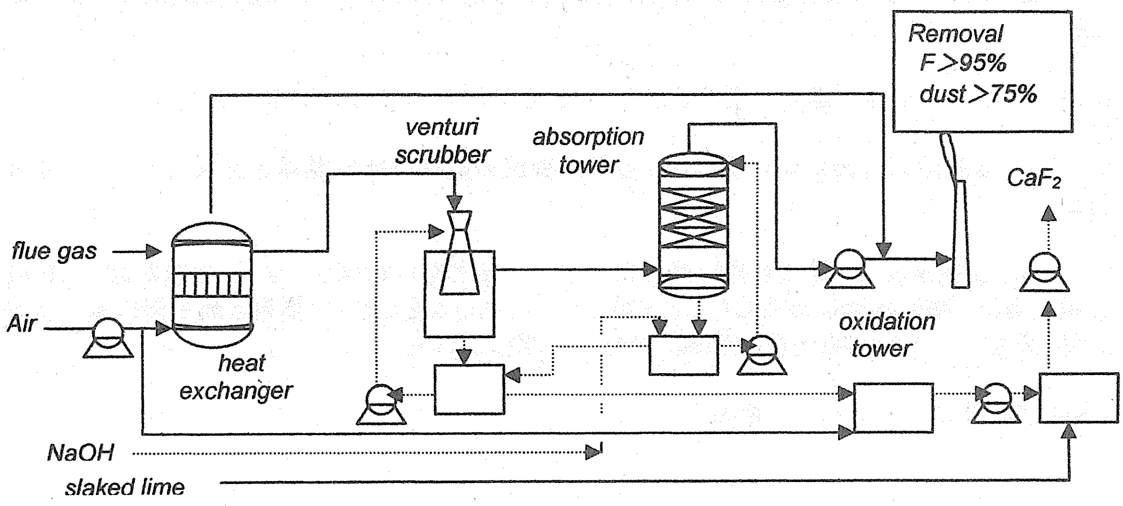
フッ素及びその化合物は、電気ガラス繊維（E ガラスファイバー）や特殊乳白ガラスの溶解を促進するためによく使われる。蛍石(フッ化カルシウム)が最も一般的に原料として使われフッ素化合物である。フッ素及びその化合物を除去するために、湿式法と乾式法が使われている。

乾式法では、冷却塔内でガスに水をスプレーして、煙道ガスを250℃に冷却する。次いで、粉末消石灰を加える。この操作により、フッ素及びその化合物はフッ化カルシウム（CaF_2）になり、バグフイルターで除去集塵される。パウダー内には、$Ca(OH)_2$, $CaCO_3$, $CaSO_4$ が共存しており、原料として再使用される。この方式を用いて、フッ素除去率95%以上、ダスト除去率98%以上を達成している。



この方法の特長は、管理が容易で、運転費が安い点であるが、装置がやや大きくなる。

Wet type defluorination

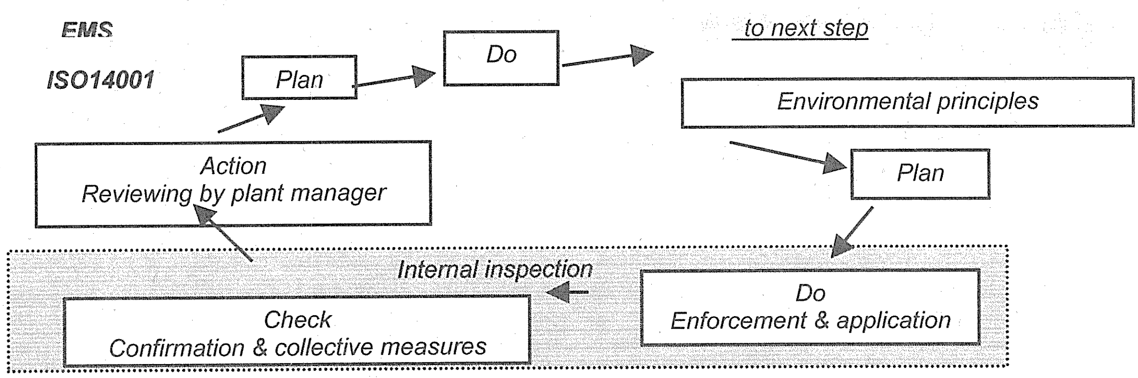


湿式法では、フッ素及びその化合物は苛性ソーダ溶液に吸収される。この方式は、煙道ガス冷却装置、ガススクラバー、廃水処理からなっている。この方式を用いると、SOxも同時に除去できる。フッ素除去率は95%以上、ダスト除去率は75%以上である。最終反応物のNaFに、消石灰を加え、NaFをCaF_2に変え、分離、濃縮、乾燥して再使用される。

詳細についてはP.66～67を参照。

6. 環境管理システム

ISO14001標が環境管理システム(EMS)の基本となっている。EMSの狙いは、企業自身が排出する汚染物質を常に把握し、良好に管理された環境条件を保つことにある。ISO 14001は、①環境方針の決定、②計画、③実施と運用、④点検と是正、⑤経営層による見直しを要求している。



工場建設および操業時に考慮しなければならないことは:

1. 環境影響評価は、工場周辺の自然環境状態の事前調査を行うことを絶対に必要としている。

2. 排出に対する環境基準と規制を理解することが重要である。

3. 工場と大気汚染防止装置を計画するとき、排出基準に適合する、許容汚染物量を計算すること。工場で発生する汚染物質排出上限値を満足する種々の方法から、最も経済的な方法を選ぶこと。

4. ガラス溶解炉全体の適正な運転管理と、作業者のトレーニングが重要である。

5. ガラス溶解炉の排出口から排出される汚染物質の監視は排出基準を達成するために重要である。

6. 工場の全従業員は、環境管理に最大限の努力を払わなければならない。事故が起こった現場の担当者は、関係機関に発生したことを報告しなければならないし、損害を最小限に食い止めるように努力をし、自治体と住民の理解を得なければならない。

詳細についてはP.14～22を参照。

7. 省エネルギー技術

大気汚染防止対策として、省エネルギー化を図ることは、問題となっている CO_2 を削減するのに効果的である。また、省エネルギーは多量のエネルギーを消費するガラス産業の経営を支えることになる。

最初に、基本方針、現状認識、定量的な目標、対策の項目を含む、省エネルギー推進方法を策定することが有効である。

<u>How to promote energy saving</u>
Basic policy→ Understanding current state→ Goal→ Measures

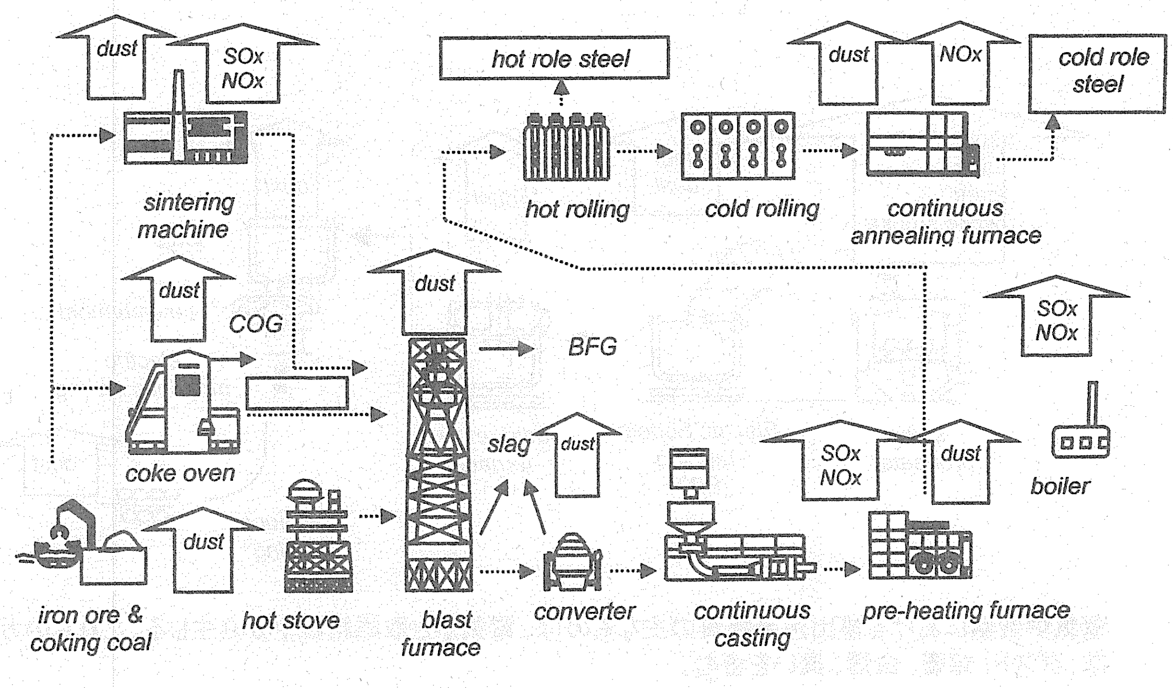
省エネルギーの方法としては、①カレットの使用比率の向上によるガラス溶解の促進、②操炉方法および装置面からの燃焼条件の改善、③熱損失の最小化、④廃熱回収、⑤コジェネレーションの導入など色々とある。

詳細についてはP.23～37を参照。

Ⅲ.鉄鋼産業

1. 製鉄工程と大気汚染物質

一環製鉄所の概略製造工程と各工程で発生する大気汚染物質をスライドに示す。



原料処理工程では、鉄鉱石と石炭が船または列車から荷降ろしされ、貯蔵されるが、そこから大きな粒子がダストとして飛散する。

コーク製造工程では、石炭の破砕、混合、石炭のコークス炉への挿入と炉からの出炭時にダストが発生する。

焼結工程では、粉砕された鉄鉱石、石灰石、微粉コークスを混ぜてペレットに焼結されるが、その原料処理工程から、粒子の大きなダストが飛散する。焼結炉から排出される排ガスには SOv、NOxが含まれる。

高炉工程では、主な汚染物質はダストであり、主に鋳床で発生する。そのほかに、原料が炉頂から投入されるときにダストが発生する。

転炉工程では、主にダストと煤煙が吹錬時とその前後に発生する。

圧延工程では、余熱炉と連続鋳造炉から、ダスト、SOx、NOxが発生する。

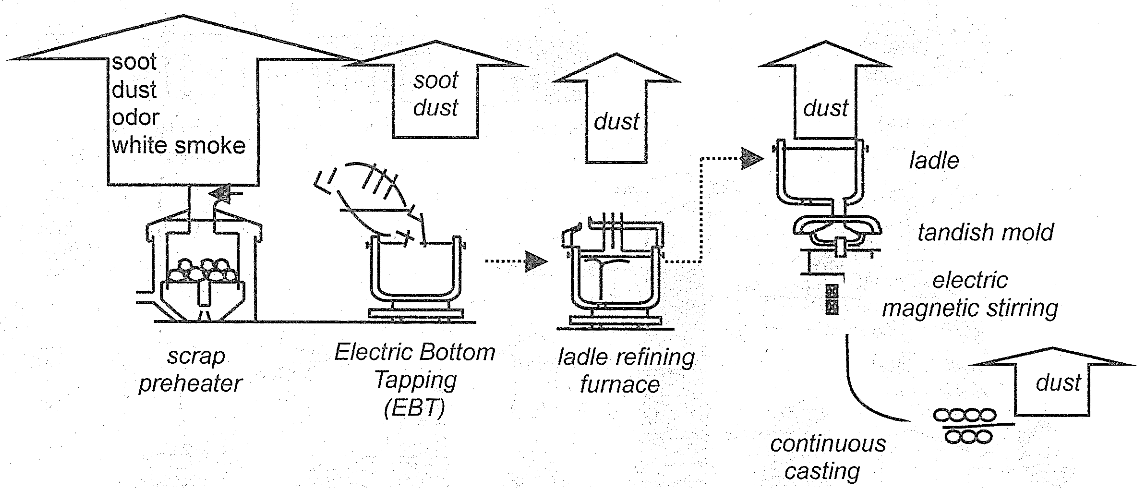
そのほかに、製鉄所にあるボイラーから SOx、NOxが発生する。

詳細については P.139～151を参照。

2. 電気炉製造工程と大気汚染物質

電気炉による製鉄は、(1)溶解工程、(2)脱炭脱燐のための酸化精錬工程、(3)酸化スラグ除滓後の還元スラグによる脱硫、合金、温度調整を行う還元工程からなる。これらの工程で行われる原料の投入、取出しは不連続作業である。

スライドには、電気炉製鉄所で一般的に行われている普通鋼と合金製造の代表的な工程を示す。



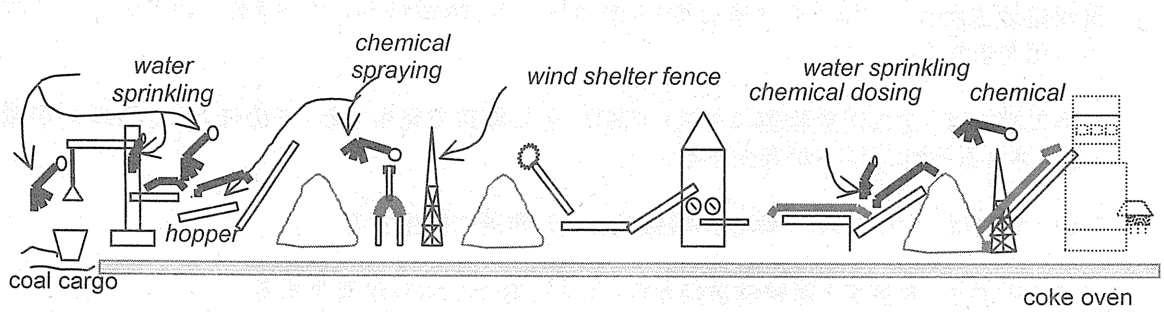
電気炉製鋼における排出汚染物質の主なものは、電気炉と取鍋精錬炉から生じる。これらのガスは、ダスト、煤塵、白煙、臭いを含む。

詳細については P.152～154を参照。

3. 粉塵の飛散防止

3-1 石炭処理工程

概略の石炭処理工程とダスト防止方法をスライドに示す。



ダスト飛散防止技術の主流は、散水法である。石炭処理工程における主な散水箇所は:

(1)貨物船のハッチ内
(2)荷降バケット
(3)払出ホッパー

(4)ベルトコンベアー、同接続箇所
(5)貯炭場

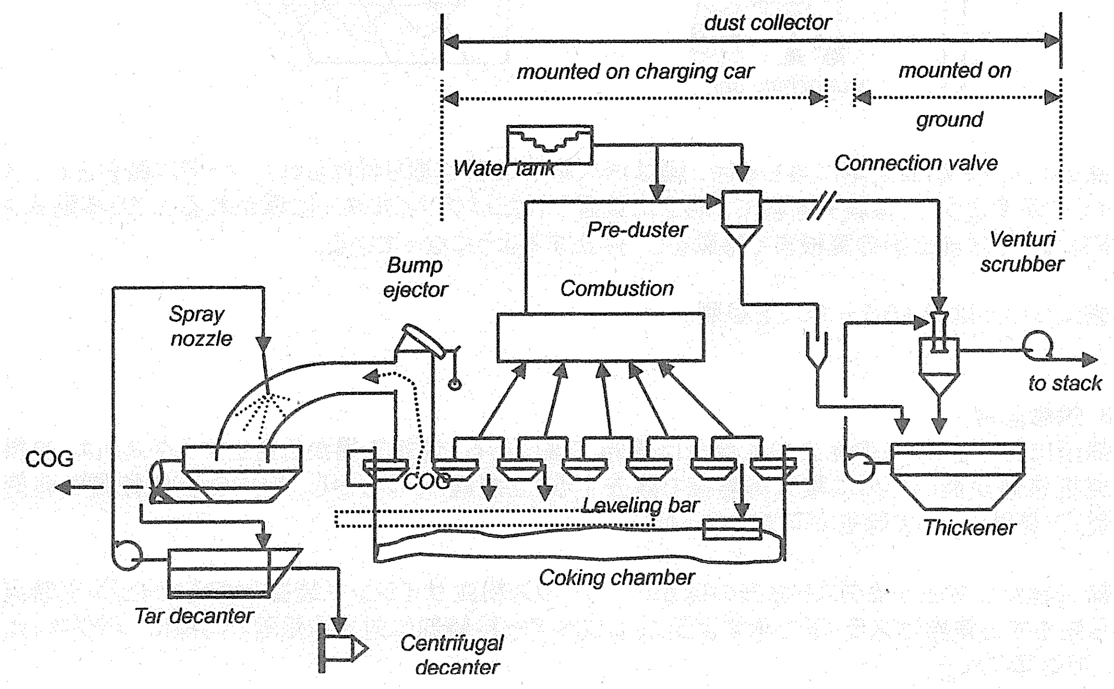
積上げられた原料の表面をネットまたはシートで、時には、ポリビニールアセテートあるいはタールのような化学剤で覆うことがある。防風フェンスが設置されることもある。開口面積40%を持つ、高さ7mの防風フェンスで、風速を50%以上低下させることができるという報告がある。

ベルトコンベアー輸送では、ダスト飛散防止のために、ベルトコンベアーカバー設置、防風板の取付け、散水機取り付、落下鉄鉱石・石炭の受皿取付、ベルトクリーナー取付、コンベアー接続部の密閉化が行われている。ダストの集塵を行うために、コンベアーの接合部にはフードが設けられる。

詳細については P.156～157を参照。

3-2-1 コークス製造— 石炭挿入工程

ダストは、石炭をコークス炉に挿入した時と、コークスをコークス炉から消火車に排出したときに発生する。



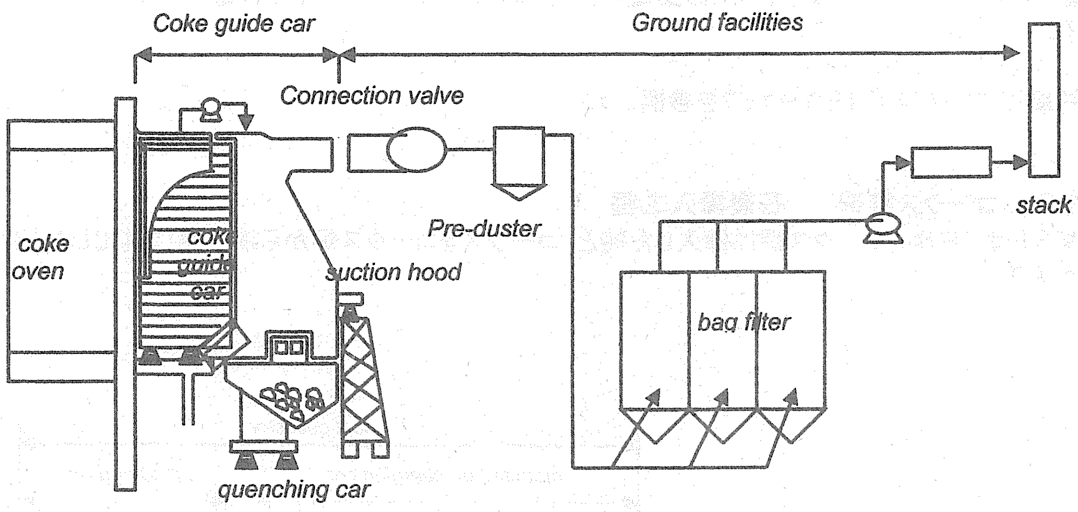
石炭を炭化室に挿入したときに、炉内ガスと石炭の置換により、煙が発生するが、その煙は、石炭が高温の炉内表面に接触したときに発生する水蒸気と微細石炭粉塵を含む。

これらの煙の一部は、上昇管エジェクターに吸い込まれる。しかし、大半の煙は、石炭挿入車に搭載されている燃焼室を経て、地上に設置されている集塵機に吸い込まれる。吸引されたガスは燃焼室で最初に燃焼され、次いで、予備集塵装置で水洗され、さらにベンチュリースクラバーを経て煙突から大気中に排出される。ベンチュリースクラバーの水はシックナーに送られる。

詳細についてはP.156～157を参照。

3-2-2 コークスの製造 ― コークス排出工程

炭化室の両側の炉扉を開ける時に、残留ガスがダストと共に煙となって出る。また、コークスがコークスガイド格子に押出される時と、消火車に落ちる時にも、また、それを消火車で消火塔に搬送する際にもダストが発生する。コークスを押出すときには多量のダストが発生するので、この操作中の集塵は非常に大切である。



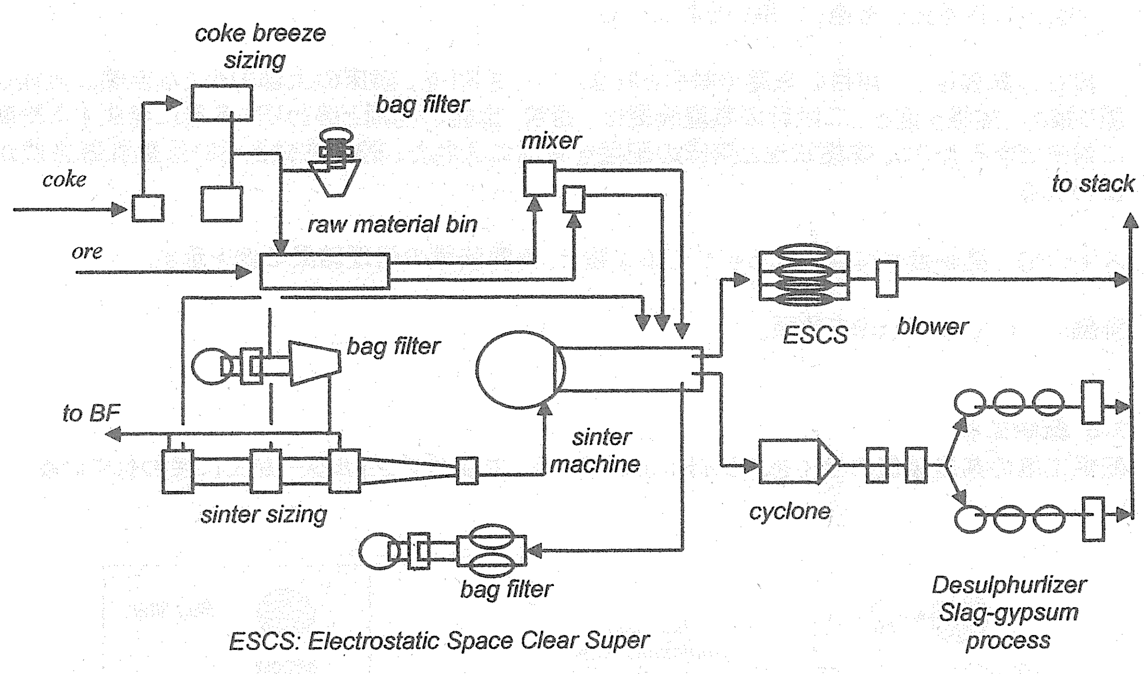
赤熱のコークスが消火車に落ちる時、煙は消火車の上部に取り付けられたフードに吸引され、スライドに示すように、接続弁を経て、地上に設置されたバグフイルターに導かれる。この移動式フードはコークス排出炉の真横まで移動をし、停止するようになっている。

詳細についてはP.156～157を参照。

3-3 焼結工程

製鉄所におけるダストの発生の大部分は焼結工場にある。焼結工場から発生するダストは、見掛電気抵抗値が高いために電気集塵機で除去することが難しい。しかし、ESCS(高性能電気集塵装置)の登場によって除去が可能となった。

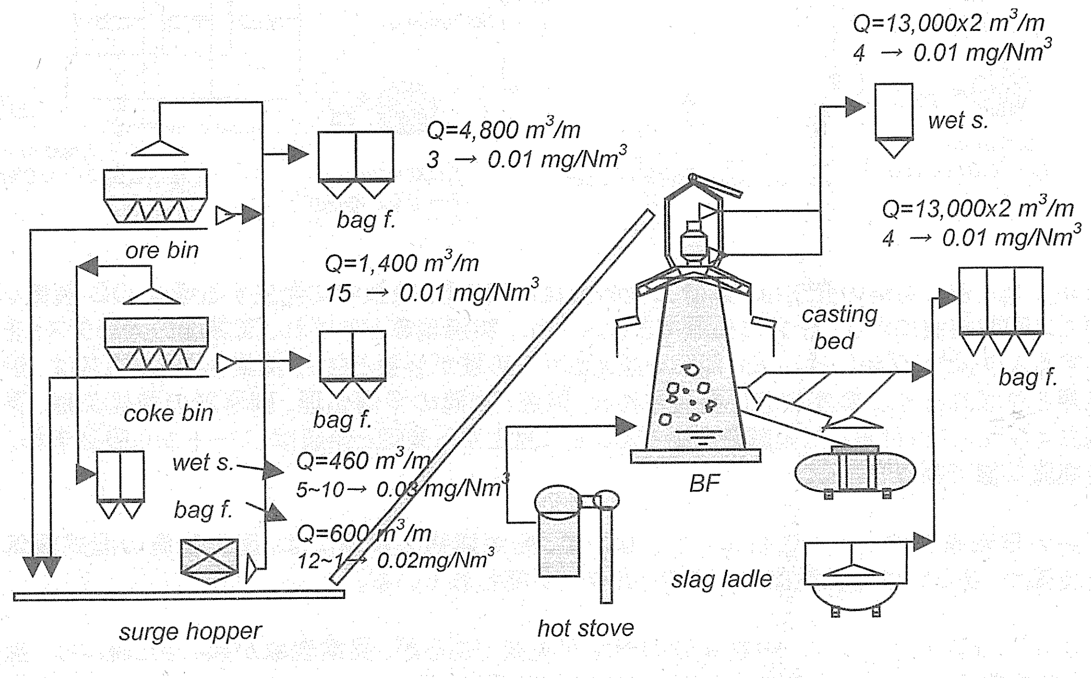
焼結工程から発生するダスト除去のほかに、コークス粉炭サイジング装置と焼結サイジング装置から発生する集塵はスライドで示すように、コンベアー接続部に対する処理と同様に、バグフィルターで処理される。



詳細については P.158を参照。

3-4 高炉工程

高炉におけるダスト管理の主なところは、高炉の鋳床の辺りであり、そこでは2段処理が使われている。最初の集塵では、出銑口、スキマー、熔銑桶および落口から排出されるダストは、上部フードまたは、サイド吸引装置によって吸収される。



高炉の出銑口の集塵に対して上部フード吸引方式あるいは、サイド吸引方式が、出銑口部のクレ

ーン操作の作業性を考慮して用いられている。

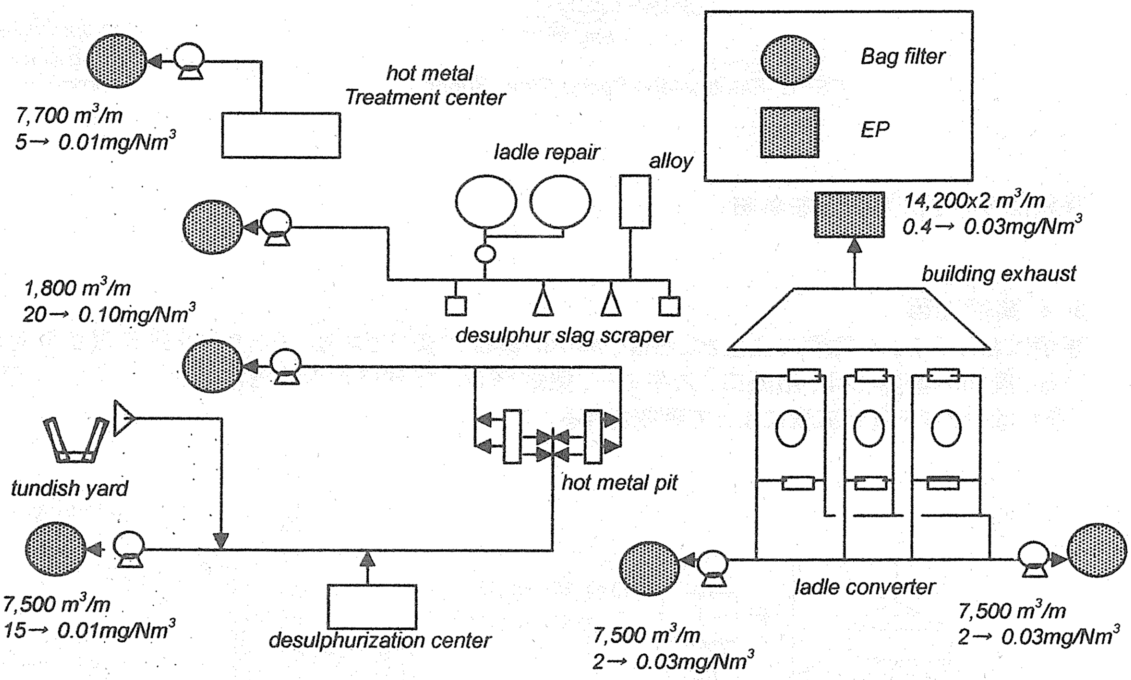
二段目の集塵は、一段目の集塵で吸引されなかったダストを、鋳床の上部の小さな空間に可能な限り集め、捕集を図る。二段目の集塵装置は、通常、出銑の初期と終わりに多量に発生する粉塵に対処できるように、排煙状況と鋳床の配置を考慮に入れた、貯留方式あるいは垂れ幕方式が使われる。

スライドに、高炉操作に含まれるすべての工程と、集塵装置の処理結果の例を示す。

詳細については P.159を参照。

3-5 転炉工程

転炉工場の集塵装置の全てをスライドにしめす。そこではバグフイルターが主に使われている。



転炉工場における煙の発生は、吹錬工程の前後に起こる。吹錬中に発生する煙は OG 装置などのガス回収装置によって十分に処理できる。しかし、突沸現象と呼ばれ、高濃度の赤いダストを排出するスロッピング時には、OG 能力を超えるガス処理が必要となり、捕集されないガスは、炉口集塵と呼ばれる環境集塵装置に集煙される。除滓、脱硫の予備処理、副原料の取扱工程、要綱鍋およびランスに付着した金属を切断するときに発生する発煙と発塵は、フードから吸込まれ、環境集塵装置で集塵される。

転炉の建物集塵はそれほど普及していないが、転炉建物の集塵には、屋上設置の湿式電気集塵装置か、あるいは地上設置のバグフイルターが使われている。

スロッピング防止のために、熔銑成分の安定が重要であるが、異常現象が起こった時には、建物からの粉塵の漏洩を最小限にする必要な対策が必要である。

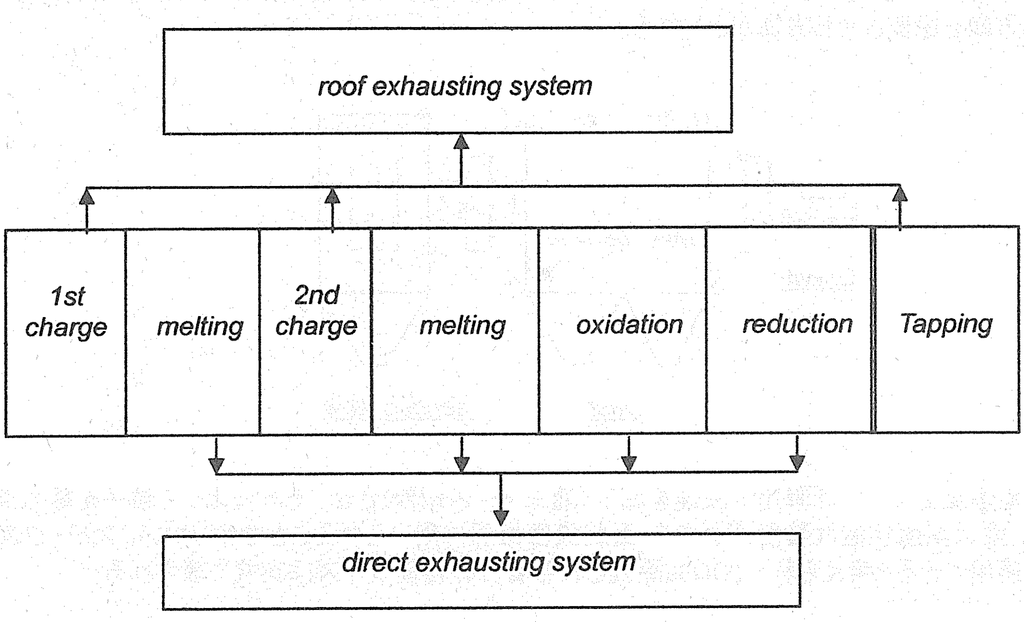
詳細については P.161 を参照。

3-6 電気炉

電気炉を使っている製鉄所で発生する排ガスは、主に電気炉と取鍋精錬から発生し、粉塵を含む。さらに、スクラップ鉄に付着した油分が、スクラップ鉄の余熱時に白煙と不快臭を持つヒュームを変わる。

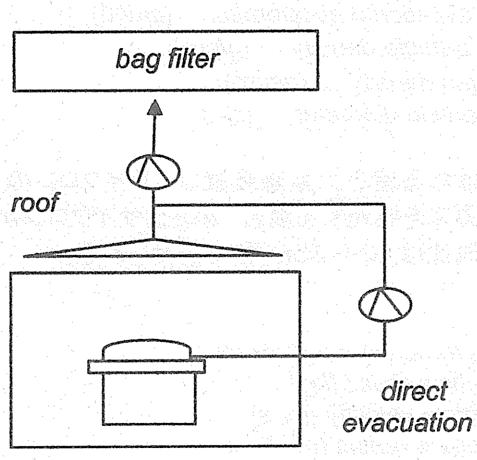
このヒュームを除去するために、(1)直引集塵装置、(2)建屋集塵装置、(3)ドッグハウス集塵装置が用いられる。

Conventional System



直引集塵装置は、電気炉から排出される高濃度の粉塵を含む高温ガスを一定の温度まで下げて、ダストを除去する方法が取られる。

Doghouse System



建屋集塵装置は、スクラップ鉄を挿入したり、溶解鉄を炉から排出するために、電気炉の炉蓋を

開けたときに、直引集塵装置の処理能力を超えて漏れた排ガスを捕集するためのものである。

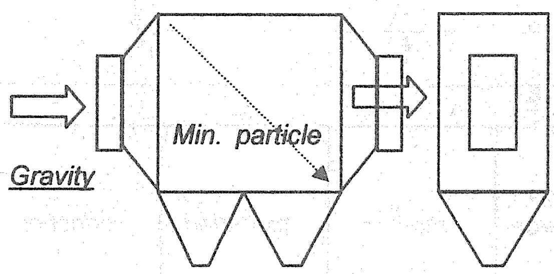
製鉄所の電気炉は、多量の粉塵とともに、騒音を発生する。これらの問題に対して、炉全体を密閉にするドッグハウスは効果的であり、排ガス量を20～30%減らすことも可能である。

詳細についてはP.162～164を参照。

4. 集塵装置

4-1 Gravitational, Inertial & Centrifugal Dust Collector

粒子とガスの密度が異なるため、層流状態のガスの流れ方向を変えれば、それぞれの流れ方向が変わる。これを利用して、しばしばガスの中の固形粒子の分離が行われており、通常はガスの流れ方向を急変させる方法がとられる。



重力集塵装置では、沈降室で流速を低下(通常1～2m/秒)させ、それによって粒子を重力沈降させる。重力集塵装置は装置が大きく、最終集塵処理に用いられることは余りない。ストークスの法則が適用できると考えられ、100%除去される場合の粒径サイズは次式で表される。

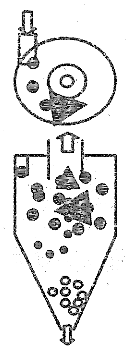
Stokes' Law

$$V=(g/18\mu)(\rho 1-\rho)D^2 \quad (cm/s)$$

V: settling velocity (cm/sec)
μ: gas viscosity (kg/ms)
g: gravitational acceleration (cm/s^2)
ρ1: particle density (g/cm^3)
ρ: gas density (g/cm^3)
D: particle diameter (cm)

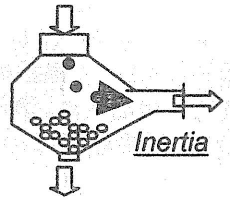
一般的にサイクロンと呼ばれる遠心力集塵装置は、サイクロンの中の粒子に遠心力が作用し、次式で示される。大容量のガスを処理する場合、小さなサイクロンが並列するマルチサイクロンが用いられる。流入部のガス流速は10～25m/秒で設定される。

Centrifugal force (F) = mv^2/R (N)
m: particle mass (kg)
V: particle velocity (m/ s)
R: cyclone radius (m)



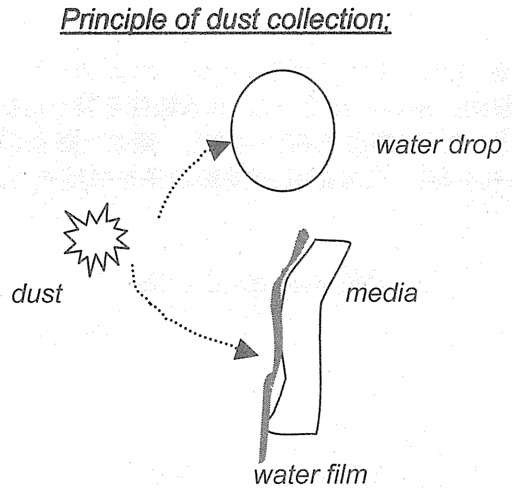
慣性力集塵装置では、ガスの流れを邪魔板に衝突させるか、あるいは急激に方向を変えて慣性力を用いて粉塵粒子を除去・捕集する。

詳細についてはP.165～166を参照。

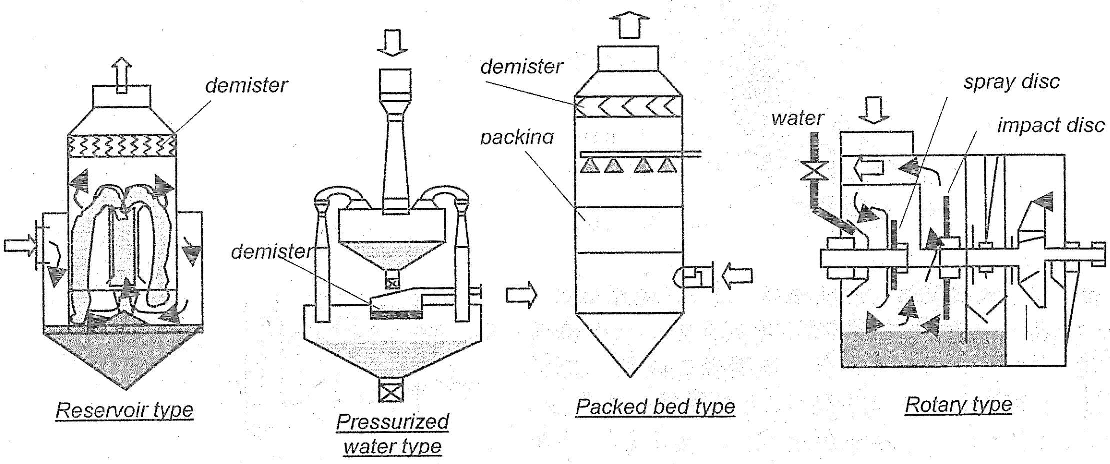


4-2 洗浄集塵装置

湿式集塵装置で知られる、スクラバーはガス中の粒子を除去するのに液体を用いる。湿式集塵装置では、粒子が液滴か、連続的に充填材の表面を流れる液膜に付着して捕捉される。



いろいろな種類のスクラバーが使われており、スライドに示すように、溜水式、加圧水式、充填層式、回転式に大きく分けられる。



充填材を用いると、塔を小さくできるが、圧力損失が高くなる(それによって効率は高くなる)。スプレー塔の一般的な圧力損失は0．25～0．5kPaである。充填式の場合は、0．25～2kPaである。スプレー塔の場合、液・ガス比は1．3～2．7l/m^{3}であり、充填式の場合は0．1～0．5l/m^3 である。

充填式の場合、基本的には、排ガスは塔の下部から入り、上昇流で上部へ移動する。洗浄水は塔の上部から入り、上昇移動してきた汚染ガスの先頭部にスプレーされる。接触により汚染物質は落下流体に吸収され、清浄化されたガスは上部から排出される。充填材（例えば、不規則なプラスチック片）は吸収効率の改善につながる。散水管に取り付けられたノズルから液体が噴霧される。

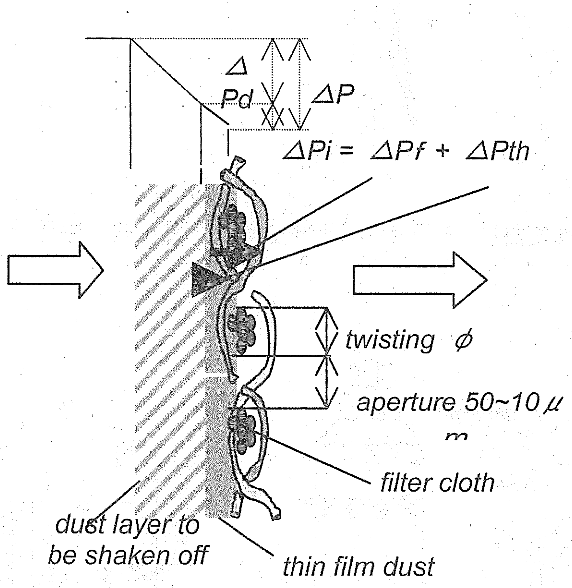
洗浄集塵装置の効率を保つには、その装置特性に合ったガス流速と液・ガス比を選定することが大切である。

詳細についてはＰ.166を参照。

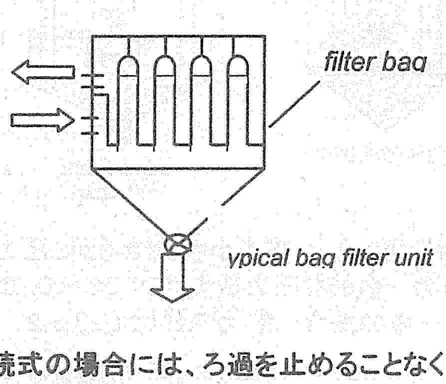
4-3 ろ過集塵装置

ろ過形集塵装置には、大きく分けて（1）バグフイルターと（2）カートリッジフイルターがある。しかし、バグフイルターが最も一般的に用いられている。ある粒径を持った粉塵を含むガスが、スライドで示すフイルターを通過するとき、粉塵はろ布に付着し、織糸と織糸の間にブリッジを形成する。その初期付着層は多くの細孔を有し、この細孔が微細粒子を捕捉する。

Filtration Mechanism



ろ布には、天然繊維、合成繊維、ガラス繊維などを用いた種々の織布や、同様な素材を用いた不織布が使われる。バグフイルター集塵機の運転においては、ろ布表面の閉塞を防ぐことが重要である。バグフイルターの圧力損失が規定値に達すると、ろ布に蓄積したダストを払い落とす必要がある。その方法には二通りあって、間歇式と連続式がある。間歇式では、集塵室が3～4室に区切られている。ろ過装置の入り口と出口の両方に取り付けられたダンパーを閉じて、ろ布に付着したダストを払い落す。連続式の場合には、ろ過を止めることなく、ろ布に付着したダストを絶えず払い落す。そのため、圧力損失はほぼ一定値を保ち、高濃度の煤塵・



粉塵を含むガスや、付着性の煤塵・粉塵を含むガスの処理に適している。

見掛上のろ過速度（有効ろ過面積当りの原ガス量）は通常0．3～10cm/秒である。

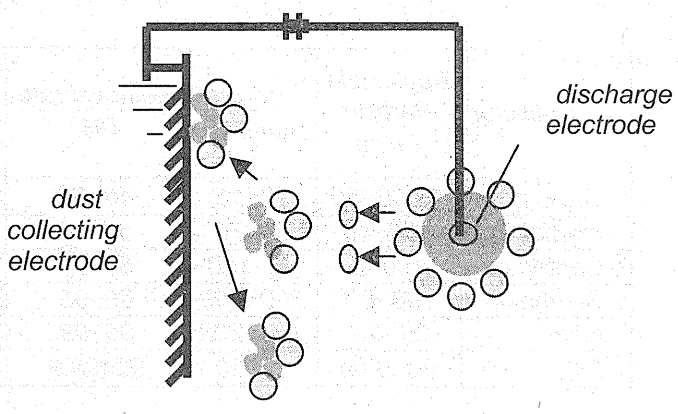
Type:	*Filter cloth:*	*Dust shake-off:*	*Apparent filtration rate:*
(1) bag filter	*(1) woven fabric*	*(1) intermittent*	*0.3~10cm/s*
(2) packed bed filter	*(2) nonwoven fabric*	*(2) continuous*	

詳細については P.167～168を参照。

4-4 電気集塵装置

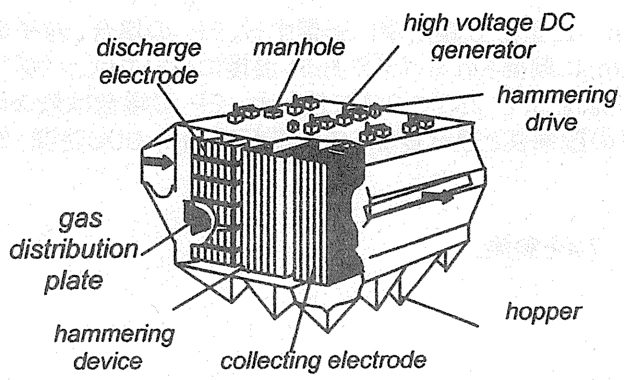
電気集塵装置（EP）は排ガス中の非常に小さな液体や固体粒子を除去するのに用いられる。装置は通常は心線の高電圧電極と、板または管の接地陽電極の間にコロナ放電を発生させる。この電場を衝突しながら通過する粒子は、放電極から集塵電極に移動するイオンによってイオン化される。そしてこれらの粒子は集塵電極に引き寄せられ、集塵電極に静電力で保持される。

Principle of dust collection ;



粒子は、槌打衝撃法または水洗によって定期的に取り除かれる。集塵装置は平板か管のどちらかを使うことができる。通常は、スライドに示すように多くの数の電極が付いている。

Structure of EP



EP はガスと粒子の性状にあまり左右されることは無く、高効率集塵が可能であり、圧力損失を伴わずに集塵できる。

詳細については P.168～169を参照。

4-5 集塵装置の選定

集塵装置の選定を行う場合、スライドに示す粒子とガスの物性を考慮しなければならない。

Parameter

—particle distribution
—dust concentration
—specific gravity
—electric resistnace rate

—flow rate
—due point
—gas temp.

排煙ガス中のダストの大きさと粒径分布は、それぞれの集塵装置の粒子除去効率に大きな影響を及ぼす。それぞれの集塵装置で除去される粒子径を表に示す。見えない粒子濃度は 20 mg/Nm^3 といわれている。もし、高濃度煤塵ガスにろ布集塵装置を適用すれば、ダスト振い落しを頻繁に行わなければならない。EP は排煙ガスの濃度の影響をそれほど受けない。

Collector	Applicable Particle (μm)	Δp (mmH$_2$O)	Removal rate (%)	Equipment Cost (¥/y /Nm^3/h)	Operating Cost (¥/y/Nm^3/h)
Gravity	1,000~50	10~15	40~60		
Inertial	100~10	30~70	50~70		
Centrifugal	100~3	50~150	85~95	300~2,200	100~1,000
Scrubbing	100~0.1	300~900	80~95	400~2,200	100~1,300
Filter	20~0.1	100~200	90~99	300~2,100	300~1,100
EP	20~0.05	10~20	90~99.9	400~4,400	100~1,00

粉塵濃度に関しては、重力集塵装置と慣性力集塵装置の場合、大きな粒子と小さな粒子の凝集が促進されるので、粉塵ガス濃度が高くなるにしたがって、高い除去率が得られる。ベンチュリースクラバーとジエットスクラバーの場合、煤塵を高濃度に含むガスに適用すると、ベンチュリーのスロート部が摩滅するので、ダスト濃度 10 g/ Nm^3 以下のガスに適用すべきである。

スライド4－1に示したように、比重が分離効率に影響する。EP の場合、粒子の最適な見掛電気抵抗率は 10^4~5×10^{10} Ωcm に制御されるべきである。温度に付いては、バグフイルターの場合、ろ布の耐熱温度の限界からおおよそ 250℃以下で使われ、EP の場合は鉄の耐熱温度限界から 500℃以下で使われる。表の設備費と運転費は、年間運転時間6，000時間、電力代￥14/ kWh を基準に求めている。

詳細についてはP.170～173を参照。

5. 脱硫技術

5-1 製鉄所における排煙脱硫

一貫製鉄所から排出されるSOxは主に焼結工場で発生しており、工場全体の57%を占めている。コークス製造工程から、直接 SOX が大気中に排出されることはない。

排煙脱硫装置（FGD）は反応過程により乾式と湿式に分類される。どちらの方式も排煙中の SOx を90%除去することができる。今日広く用いられているFGDは、湿式非再生方式である。石灰石

膏法は、運転費が経済的に優れているため、納入装置の40%を占めている。

Method	Reaction	Byproduct
Activated carbon	$SO_2+H_2O+1/2O_2 \rightarrow H_2SO_4$	H_2SO_4
Caustic soda	$2NaOH+SO_2 \rightarrow Na_2SO_3+H_2O$ $Na_2SO_3+H_2O+SO_2 \rightarrow 2NaHSO_3$	Na_2SO_4
Ammonia	$2NH_4OH+SO_2 \rightarrow (NH_4)_2SO_3+H_2O$ $(NH_4)_2SO_3+SO_3+SO_2+H_2O \rightarrow 2NH_4HSO_3+H_2$	$(NH_4)_2SO_4$
Slaked lime	$CaO+SO_2 \rightarrow CaSO_3$ $CaSO_3 + O_2 \rightarrow 2CaSO_4$	$CaSO_4$

湿式方式において、二酸化硫黄は、石灰(CaO)、苛性ソーダ(NaOH)、アンモニア((NH_3)、消石灰($Ca(OH)_2$)などと反応する。消石灰は亜硫酸カルシウム($CaSO_3$)を生成し、その一部は煙道ガス中の酸素との反応と、後段のスラッジのばっ気により硫酸カルシウム($CaSO_4$)に変換される。硫酸カルシウム(石膏)は安定物質であり、石膏板の主成分である。そのほかに、石灰石膏法は設備費と運転費が経済的に優れており、装置の安定性が高いために、日本では広く使われている。

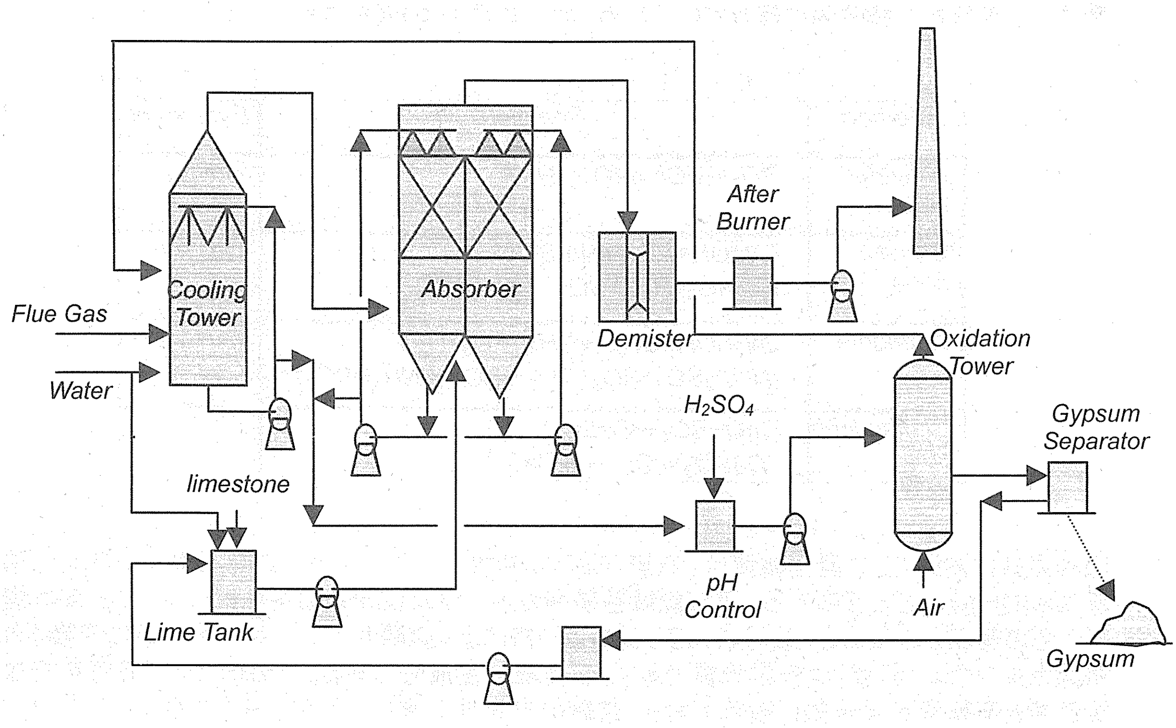
Limestone - Gypsum Process
SOx Rem. >90% ⇨ *most popularly used method In Japan*

- *limestone ⇒ cheap*
- *initial & operating cost ⇒ economical*
- *systems stability ⇒ stable & safe*
- *gypsum ⇒ marketable*

詳細についてはP.182を参照。

5-2 石灰石膏法

スライドに示すフローは製鉄所で使われている石灰石膏法の例である。煙道ガスは温度を下げるために、冷却塔に導かれ、次いで吸収塔に入り、そこで粒径50～60ミクロンの石灰粉を含むスラリー状の循環吸収液(10～20%)と効率よく接触し、SO_2は液に吸収され除去される。



吸収塔で、石灰は亜硫酸カルシウム（$CaSO_3$）を生成し、その一部は煙道ガス中の酸素との反応と、酸化塔のばっ気により硫酸カルシウム（$CaSO_4$）に変換される。その後、煙道ガスは、デミスター、アフターバーナー、煙突を通り大気中に放出される。

Reaction

$$SO_2+CaO \rightarrow CaSO_3$$
$$2CaSO_3+O_2 \rightarrow 2CaSO_4$$
$$CaCO_3+SO_2 \rightarrow CaSO_3+CO_2$$

された吸収液は石膏分離機に運ばれ、そこで脱水機によって、水分10%以下の結晶石膏として取出される。脱水機の上澄み液は石灰タンクに返送される。

石灰石膏法に使われる吸収液は石膏粉末もしくは消石灰である。強い反応性を有する消石灰は、当初用いられたが、値段が高いために現在では石灰法が主流となっている。

詳細についてはP.183を参照。

5-3 コークス炉ガスの脱硫法

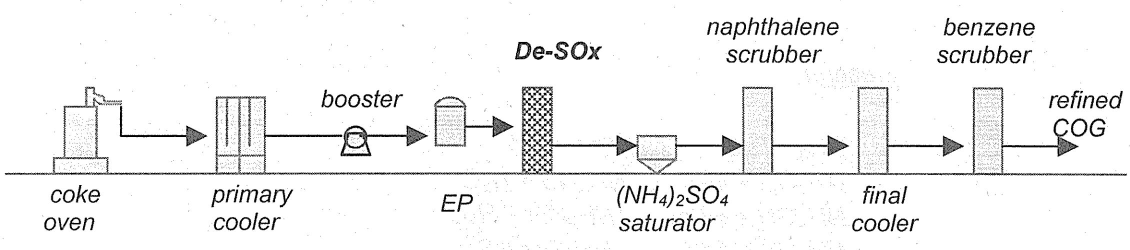
コークス炉ガス（COG）は4～7g/ Nm^3 の硫化水素（H_2S）を含み、同じカロリーを持つ、1%の硫黄を含む重油に匹敵する。COG は再加熱炉の燃料に使われるので、COG の脱硫は SOx低減対策としては大きな効果をもたらす。その上、脱硫は COG 配管内部の腐食を緩和する。

COG の脱硫は脱硫剤にアンモニア、炭酸ソーダなどを使って行われる。これらの工程で発生する廃液は、酸化燃焼法、還元酸化、湿式酸化などの方法で処理される。現在では、タカハックスプロセスとフマックスプロセスが COG 脱硫の主流となっている。商業的に利用できる幾つかの COG

脱硫方式と、それらの脱硫剤、触媒と副産物を表に示す。

System	DeSOx-chemical	Catalyst	Byproduct
Takahax- Hirohax	NH_3	naphtoquinone salfonic acid soda	$(NH_4)_2SO_4$ + H_2SO_4
Takahax-Reduction Decomposition	Na_2CO_3	naphtoquinone salfonic acid soda	crude S
Fumax-Hemibau	NH_3	picric acid	H_2SO_4
Stred Ford- Combax flue gas De-Sox	Na_2CO_3	anthoraquinone sulfonic acid soda metavanadate soda T artaric acid soda	gypsum
Diamox-claus	NH_3	none	pure S
Salfiban-claus	alkanol amine	none	pure S

COG の脱硫装置はスライドに示すように、COG 精製工程のちょうど中間で行われる。



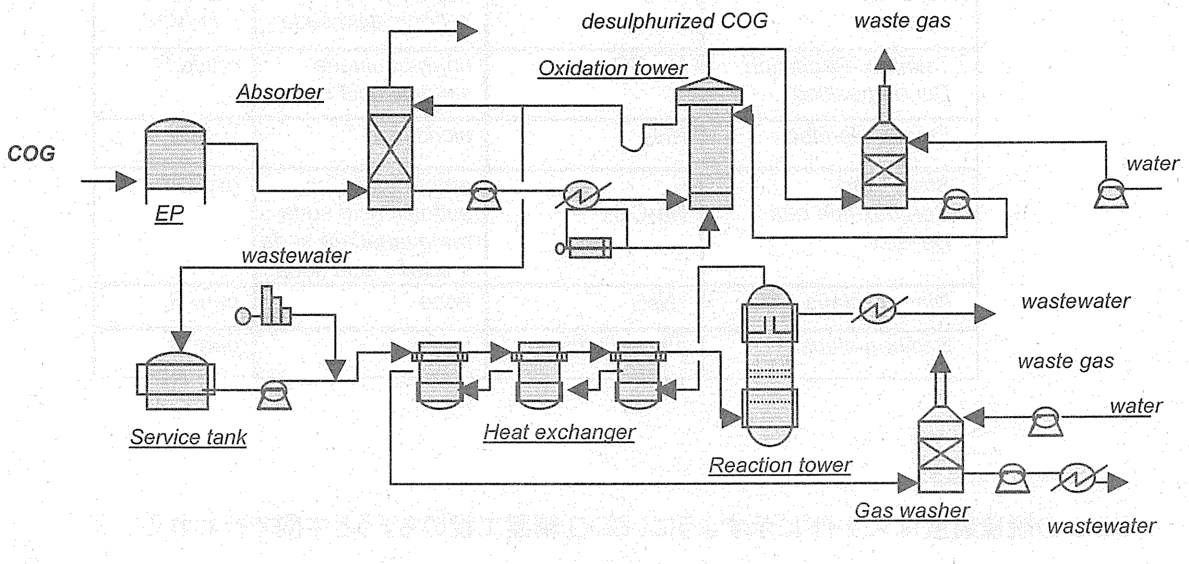
詳細についてはP.188～189を参照。

5-4 タカハックス・ヒロハックス法

タカハックス(脱硫)とヒロハックス(廃液処理)のプロセスをスライドに示す。COG は昇圧送風機で昇圧され、EP に入り、ガス中のタールはおおよそ99%除去される。次に、ガスは充填接触材の入った吸収塔で触媒(1, 4－ナフトキノンスルホン酸ナトリウム)を含む液と接触し、COG 中の約30%のアンモニア(NH_3)が水に溶ける。この溶解した NH_3 は、COG 中の硫化水素(H_2S)とシアン化水素(HCN)と反応し、いわゆる脱硫と脱シアンが行われる。H_2S と HCN の除去率は共に90～99%である。その後、脱硫された COG はアンモニア飽和器に入る。

Takahax-Hirohax Process

Removal rate :S, CN ＞ 90~99%



吸収液は酸化塔に入り、触媒下で空気酸化によって水酸化アンモニウム（NH_4OH）に再生される。この酸化の間に、シアン化アンモニウム（NH_4CN）はチオシアンアンモニウム（NH_4NCS）に変換される。

Reaction

$NH_3 + H_2O \rightarrow NH_4OH$

$NH_4OH + H_2S \rightarrow NH_4HS + H_2O$

$NH_4OH + HCN \rightarrow NH_4CN + H_2O$

$NH_4HS + 1/2O_2 \rightarrow NH_4OH + S$

$NH_4CN + S \rightarrow NH_4NCS$

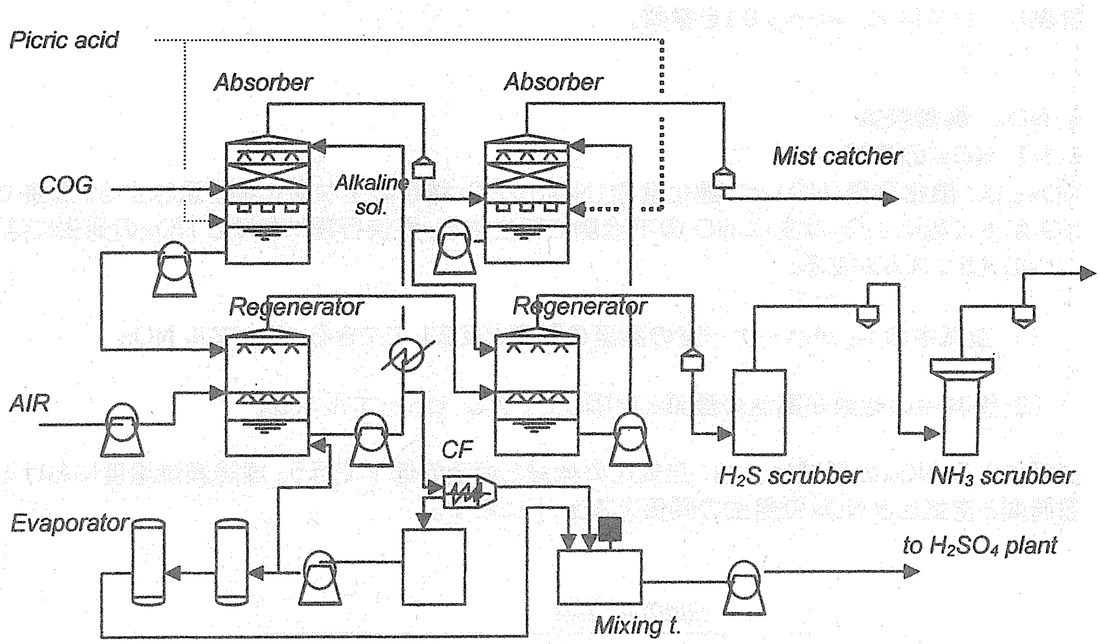
循環吸収液の一部は抜取られ、60 kg/cm^{2}まで昇圧ポンプで加圧され、空気と一緒に反応塔に入る。廃吸収液は熱交換器で反応塔の排ガスで 200 ℃以上に加熱される。反応塔に入った廃吸収液は湿式酸化状態におかれ、すべての硫黄酸化物は硫酸（(H_2SO_4）あるいは硫酸アンモニウム（$(NH_4)_2SO_4$）に、また、窒素化合物はアンモニア（NH_3）に変換される。湿式酸化液は廃液処理装置に送られる。反応塔からの排ガスは水洗され、大気中に排出される。ガス洗浄塔の廃液も廃水処理設備に送られる。

詳細についてはP.189～190を参照。

5-5 フマックス法

フマックス法をスライドに示す。

Fumax Process



COG は 2 段スクラバーでアンモニア溶液と接触し、脱硫される。一段目の吸収塔で COG 中の硫化水素(H_2S)はアンモニア溶液に吸収される。

Absorption

$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH + H_2S \rightarrow NH_4HS + H_2O$$

H_2S の吸収によって形成された硫化アンモニウム(NH_4HS)は、空気で酸化され、再生塔で水酸化アンモニウム(NH_4OH)に再生される。再生された吸収液は吸収塔で繰返し使用される。

Regeneration

$$NH_4HS + 1/2O_2 \rightarrow NH_4OH + S$$

再生塔でできる硫黄(S)は遠心分離機により、廃吸収液から分離され、硫酸製造工場へ送られる。遠心分離機の分離液は蒸発器で濃縮され、硫黄と一緒に硫酸工場に送られる。

H_2SO4 recovery

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + 1/2O_2 \rightarrow SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

硫酸工場では、硫黄は SO_3 に酸化され、水に吸収して、硫酸に変換する。

二段目の再生塔の排ガスは、H_2S スクラバーでアルカリ溶液洗浄されて H_2S が除去され、NH_3 スクラバーで酸溶液洗浄による NH_3 除去後、大気中に排出される。

詳細についてはP.190～191を参照。

6. NOx　制御技術

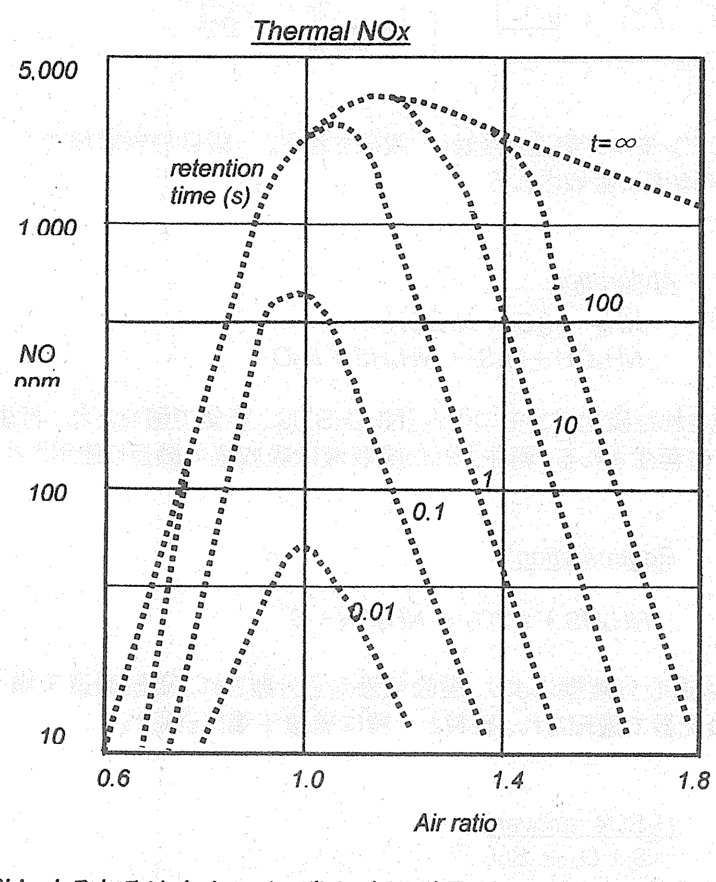
6-1-1　NOxの生成

NOxとは、酸化窒素（NO）と二酸化窒素（NO_2）の 2 種類の主な酸化物を意味する。燃焼では、NO が主であり、NO_2 は主に NO の下流側で派生する。燃焼行程における NOxの発生には主に二つのメカニズムがある。

（1）空気中の N_2 がバーナー室の高温の酸素と反応してできる、サーマル NOx

（2）燃料中の窒素が高温の酸素と反応してできる、ヒューエル NOx

操炉による NOxの低減は、主に空気比の低減と炉温の低下で行う。理論燃焼温度における、滞留時間と空気比と NOxの発生の関係をスライドに示す。



空気比が増加するある地点までは、滞留時間が長くなるほど、NOx濃度は比例的に増加する。しかし、図から判るように、空気比が一定値を越えると、燃焼温度の低下に伴い、NOx濃度は減少し始める。

種々の燃料中の窒素と硫黄の含有量を表に示す。燃料中に含まれる窒素で、石油や石炭に入っているキノリンやピリジン、また、気体燃料に含まれるシアン化水素（HCN）やアンモニア（NH_3）は、空気中の窒素（サーマル NOx）より容易に NOxに変わることが知られている。

N and S contents in fuels

	Fuel	N	S
Solid wt%	coal	0.7~2.2	0.3~2.6
	coke	0.6~1.4	0.2~1.0
Liquid wt%	crude oil	0.03~0.34	0.1~3.0
	C-oil	0.2~0.4	0.2~0.3
	B-oil	0.08~0.35	0.2~0.3
	A-oil	0.005~0.08	0.2~0.3
	light oil	0.004~0.006	0.03~0.5
	kerosene	0.0005~0.01	0.001~0.2
Gas g/Nm^3	COG-crude	0~9	1.5~7
	COG-fine	0.02~0.5	0.05~0.7
	BFG	tr	tr
	LDG	tr	tr
	LPG, LNG	tr	tr

※ JIS K2205 kinematic viscosity (cSt, mm2/s) C-heavy oil: 50≦~1,000, B-heavy oil: 20~50, A-heavy oil: ≦20

燃料中の全窒素に対して、燃料中の窒素の NOxに実際変わる比率を"燃料 NO 変換率"と言う。その比率はおおよそ12～15%の範囲である。

詳細については P.194～195を参照。

6-1-2 NOx 生成と低減の要因

NOx生成に関係する要因は:

(1)燃料中の窒素濃度
(2)燃焼時の空気比
(3)バーナー火炎温度
(4)高温域におけるガスの滞留時間

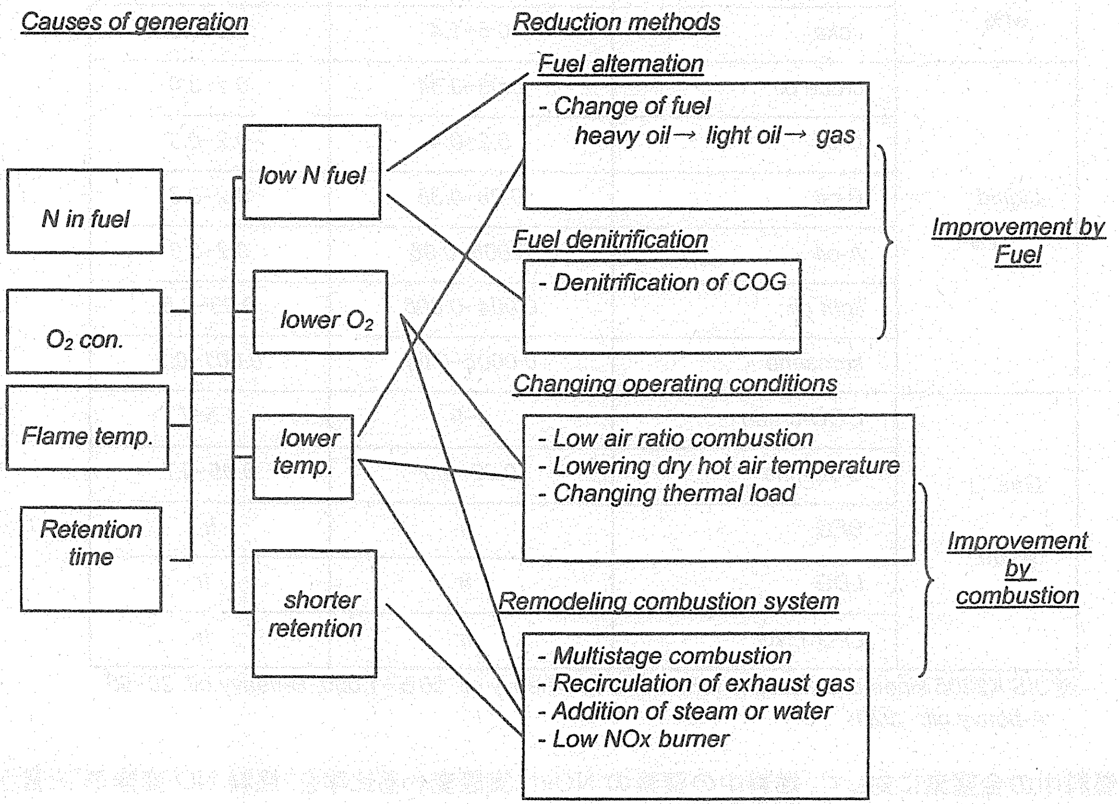
NOxの発生を低減する対策として:

重油から、軽油またはガスへの燃料転換は有効であり、低カロリー燃料に変えていくことになり、燃料中の窒素が低下し、燃焼温度が低下する。

製鉄所では、COG の脱窒は NOx排出の低減に直接効果がある。

操業条件のつぎのような変更は効果的である:

(1)空気比低減
(2)乾燥高温空気温度を下げる
(3)燃焼室への熱負荷の低減



若し可能であれば、燃焼装置を次のように変更する:

(1)多段燃焼の採用
(2)排ガス循環方式の採用
(3)燃焼室に水蒸気または水を注入できる構造に変更
(4)低 NOxバーナーの採用

詳細については P.196を参照。

6-2 燃料の改善

6-2-1 燃料改善

Nox 低減のためには低窒素含有燃料の使用が有効である。一般的に、硫黄含有量の低い燃料は、窒素の含有率も低い。製鉄所で広く使われる COG は 1~9 g/m^3 の窒素を含んでいる。これは、燃料ガスと燃焼用空気の予熱時間と温度が、800～1,000℃で、滞留時間が4～6秒である上に、コークス炉には膨大な数の燃焼室があるため、各炉の空気比を制御することが困難なことによる。

1. *Use of low N and low S fuel* $S \propto N$
2. *Denitrification of COG* *N 1~9 g/m³ 800~1,000℃, 4~6 sec.*

詳細についてはP.196～200を参照。

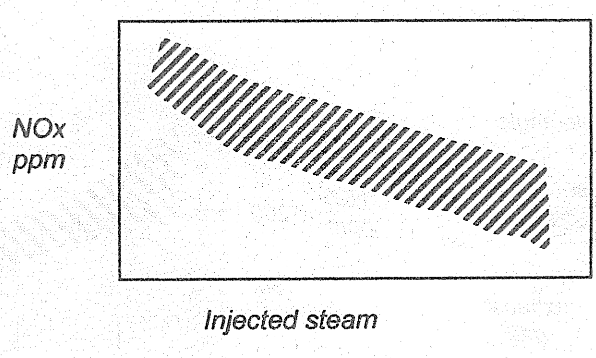
6-2-2 燃焼方法の改善

前のスライドで説明したように、空気比を低下させると、確実に NOxの生成量は少なくなる。例えば、排ガス中の酸素濃度が1%低くなれば、NOxは10%低下する。多段燃焼法は、燃焼用空気を 2 段もしくは多段に分けて燃焼ポートに送るが、例えば、一段目に理論空気量の80～90%を送風し、残りの空気を二段目、あるいはそれ以降のポートに送風して燃焼すると、NOxは20%低下した実績がある。水蒸気または水を燃焼室に注入することは、潜熱を利用することにより、熱容量を高めることになるので、同じ熱量であっても火炎温度を低くし、NOxが抑制される。

1. *Low air ratio operation* O_2 *1% ↓ ⇒ NOx 10% ↓*
2. *Multistage combustion* *1st stage air ratio; 80~90%*
   rest air →2nd stage combustion → NOx ≒▲20%

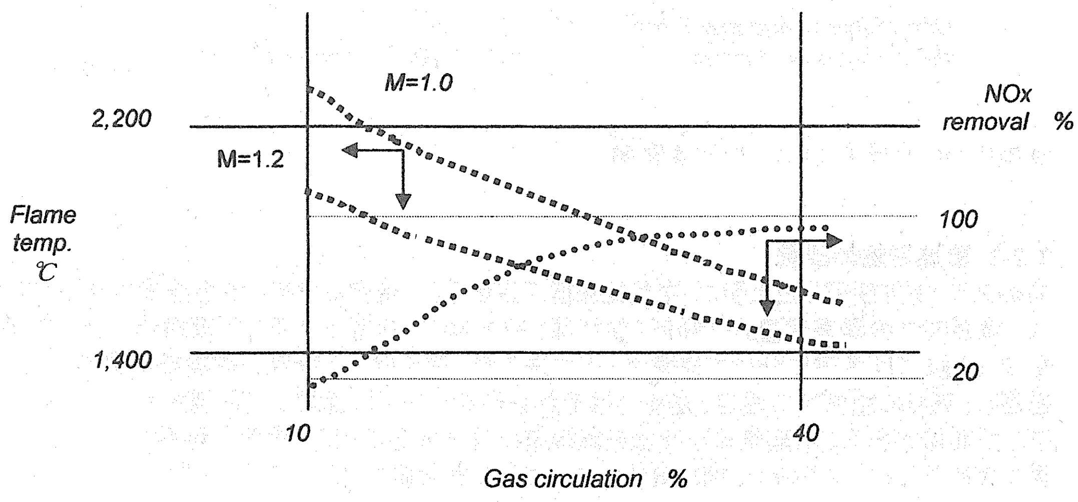
図には、水蒸気で注入される熱量とNOx発生濃度の関係を示す:

3. *Steam or Water injection* *flame temp. ↓ ⇒ Knox ↓*
   no-change in generated calorie



排ガス循環では、燃焼排ガスの一部が燃焼空気に混合される。燃焼空気の酸素濃度が排ガスによって希釈され、通常空気より低くなり、酸素と燃料の反応が遅くなり、その結果、火炎の最高温度が低くなる。これらの関係を図に示す。

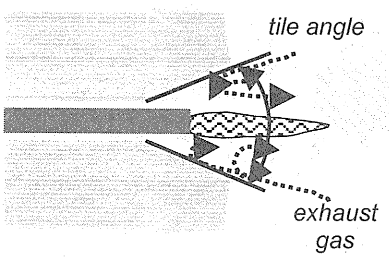
4. Exhaust gas circulation

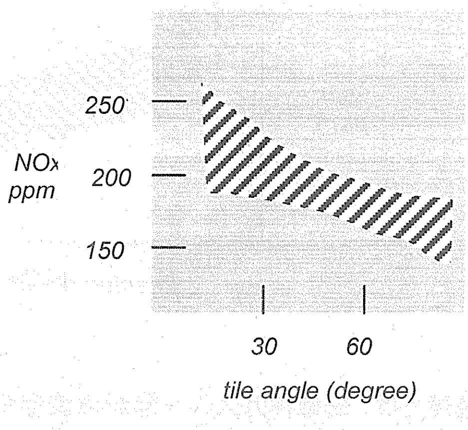


5. Low- NOx burner

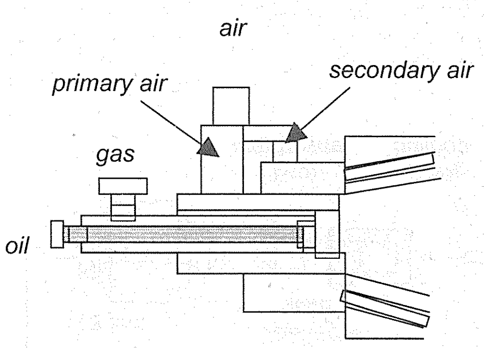
低 NOxバーナーは NOxを低減する方法のひとつであり、酸素濃度の低下、火炎温度の低下、高温温度域におけるガス滞留時間の短縮などの何れかの方法を採用するか、これらの方法を組合せた構造を有している。

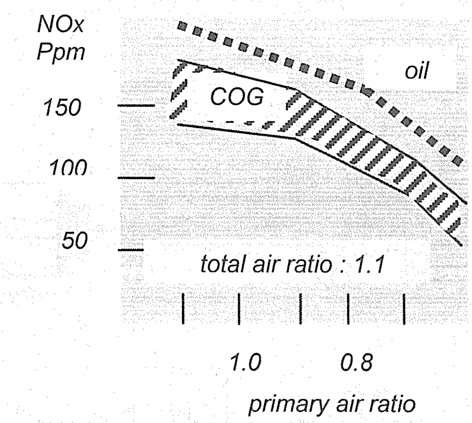
広角バーナータイル:
バーナータイル角を広くすると、タイル近くの燃焼排ガスは、火炎の運動エネルギーによってタイル角内に吸込まれ、燃焼空気の酸素分圧が低くなり、同時に、火炎温度が低下し、NOx生成の低減につながる。



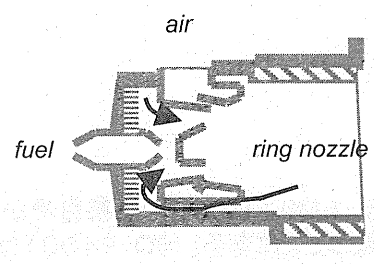


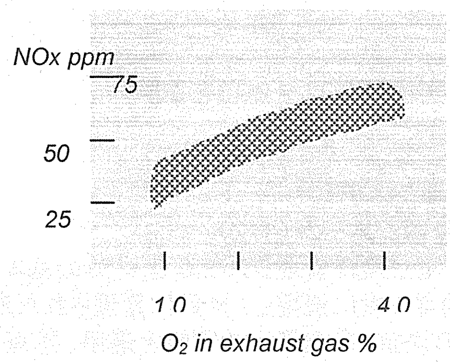
二段燃焼バーナー:
この方法はバーナーを二段燃焼にすることにより、長い火炎を形成し、火炎の最高温度を下げ、NOxの生成を低減する。





自己再循環バーナー:
このバーナーは、燃焼空気の運動エネルギーによって、燃焼ガスがフレームの中に吸込まれ、その結果、火炎温度が低くなる。





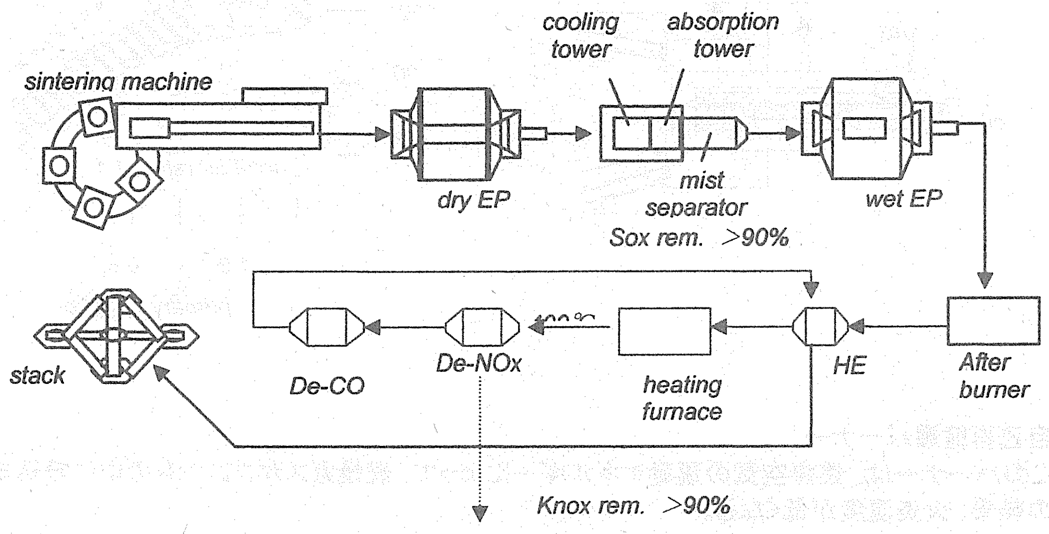
詳細については P.196～202を参照。

6-3 排ガスの脱硝

燃料の燃焼で発生する NOxの大部分は、反応性が低いので、このような NOxを除去することは技術的に困難である。種々あるプロセスの中で、最も革新的な方法に、アンモニア(NH_3)を用いる乾式の選択接触還元法がある。この方式は、クリーンなガス(煤塵、煤煙、SOxを含まない排ガス)処理に対して商業的に適用でき状態まで達しているが、特に焼結工程などの汚染ガスに不用意に適用すると、触媒活性の低下、触媒層の閉塞などの問題がまだ残っている。

焼結工場(生産能力7,000t/d)における脱硝の例をスライドに示す。排ガスは、乾式EPに入り、そこで煤塵と煤煙が除去され、石灰石膏法による排煙脱硫装置により90%以上の SOxが除去される。次工程で、ガスは EP で処理され、アフターバーナー、熱交換器、加熱炉により 400℃に昇温され、脱硝装置で90%以上の NOx が除去され、一酸化炭素(CO)除去装置に入り、触媒を用い

て一酸化炭素を酸化し、ガス温度を上昇させ、その後、熱交換器を介してアフターバーナーから出てくる排ガスの加熱に利用される。



De-NOx: Dry Type Selective Contact Reduction using NH_3

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

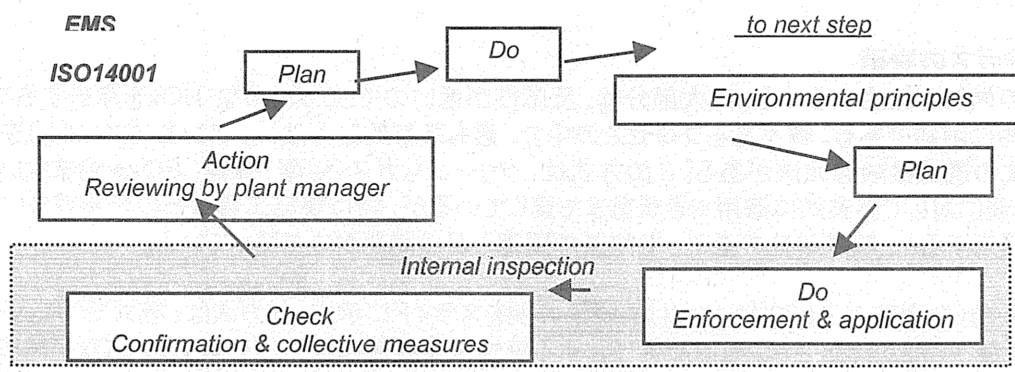
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

詳細についてはP.202～203を参照。

7. 環境管理システム

7-1 環境管理システム(1/2)

ISO14001 標が環境管理システム(EMS)の基本となっている。EMS の狙いは、企業自身が排出する汚染物質を常に把握し、良好に管理された環境条件を保つことにある。ISO 14001は、①環境方針の決定、②計画、③実施と運用、④点検と是正、⑤経営層による見直しを要求している。



工場建設および操業時に考慮しなければならないことは:

1. 環境影響評価は、工場周辺の自然環境状態の事前調査を行うことを絶対に必要としている。

2. 排出に対する環境基準と規制を理解することが重要である。

3. 工場と大気汚染防止装置を計画するとき、排出基準に適合する、許容汚染物量を計算すること。工場で発生する汚染物質排出上限値を満足する種々の方法から、最も経済的な方法を選ぶこと。

4. 全製鉄所の適正な運転管理と、作業者のトレーニングが重要である。

5. 製鉄所から排出される汚染物質の監視は排出基準を達成するために重要である。

6. 工場の全従業員は、環境管理に最大限の努力を払わなければならない。事故が起こった現場の担当者は、関係機関に発生したことを報告しなければならないし、損害を最小限に食い止めるように努力をし、自治体と住民の理解を得なければならない。

詳細についてはP.271～280を参照。

7-2 環境管理システム(2/2)

企業は状況に適合するために、工場から排出されるガス量と性状に付いて自らが調査、分析、記録をしなければならない(モニタリング)。大気中に排ガスを排出する企業は、排気ガスの性状が定められた排出基準にたいする適合状態を把握し、点検するために監視しなければならない。

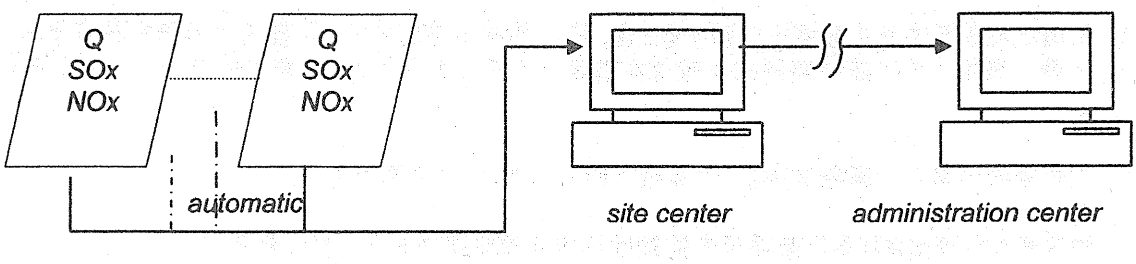
環境基本法と大気汚染防止法に基づく大気汚染物質のモニタリングは、企業が行う"排出性状の監視"と、自治体が行う "大気汚染監視"に大別される。排気ガス基準と環境基準(EQS)で規定されている項目をスライドに示す。

Measurement Items

	Emission Standard	*EQS*
Pollutants	*dust* *sulfur oxide* *nitrogen oxide* *Cd, its compounds* *Cl, HCl* *F, HF, Si_nF_{2n+2}* *Pb, its compounds*	*Suspended particle matter* *SO_2 (sulfur oxide)* *NO_2 (nitrogen oxide)* *CO* *Photochemical oxidant*

テレメーターシステムは、主に、排ガス中の SOx、NOx濃度、排ガス量などを自動的に計測する機器で構成されている。それらのデーターは、コントロールセンターに集められ、そこで大気中に排出される全汚染物質量を分析し、汚染物質の排出状況を監視する。総量規制を受けている工場は、各地方自治体の監視センターにデータを送る。

Telemeter System



詳細については P.253～255を参照。

8. 省資源

粉塵の収集設備の行き届いた一貫製鉄所で集められるダスト量は銑鉄生産量の4．9%である。生産能力 3 百万トンの一貫製鉄所の場合の、ダスト発生推定量をスライドに示す。

Dust Generation & Utilization

Dust Generation at 3 million-ton Crude Steel Production (t / y)

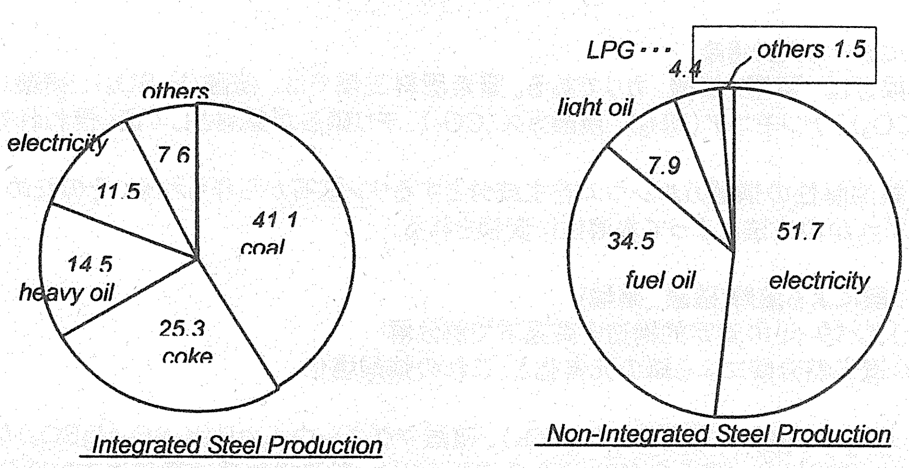
Process	Dry Dust Collector	Wet Dust Collector	Total
Material / Pig Iron	111,000	38,000	149,000 (61%)
Steel	33,000	60,000	93,000 (38%)
Rolling	2,700	300	3,000 (1%)
Total	146,700 (60%)	98,300 (40%)	245,000 (100%)

ダストは、酸化鉄、炭素、石膏などの有用な成分を含み、製鉄所内で再使用される。

詳細については P.205～206を参照。

9. 省エネルギー

エネルギー源は製鉄所が高炉を有するか、あるいは高炉を持たない非一貫製鉄所により大きく異なる。さらに、コークス、電気、酸素が工場内で作られるか、外部から購入するかによっても異なる。



省エネルギーは大気汚染物質を削減することにつながる。省エネルギーの方法としては:

(1)高効率機器の採用と、操業方法の改善

(2)単位操作の数を可能なだけ削減し、可能な限りの連続運転方式に変える

(3)廃熱の可能な限りの回収

Energy saving Method

-high efficient equipment & improving operation

-reducing the number of unit operations
& changing to continuous process

-waste heat recovery

詳細についてはP.210, 216~220を参照。

Ⅳ. 肥料製造業

1. 肥料工場における大気汚染

肥料の主な成分は、窒素、燐酸、カリである。窒素肥料工場では、硫酸(H_2SO_4)、硝酸(NO_3)、石灰石($CaCO_3$)、アンモニア(NH_3)、炭酸ガス(CO_2)、チリ硝石が原料として広く使われている。

燐酸肥料は難溶解性の燐酸カルシウムを主成分とするリン鉱石から作られる。そのため、リン鉱石は次のいずれかの方法によって水溶性に変換される:

(1)酸による溶解(硫酸、硝酸)
(2)アパタイトの安定的構造を高温下で熱分解
(3)還元熱分解による燐の元素化と、これの燐酸塩化

カリ肥料は、塩化カリ(KCl)、硫酸カリ(K_2SO_4)、硫酸マグネシウムカリ($K_2SO_4MgSO_4$)などを原料に用いる。カリ肥料として最も広く用いられる塩化カリは、粉砕後に浮遊選鉱法または分別結晶法により作られる。

Fertilizer	*Raw materials*
Nitrogenous F.	*: ammonia, Chilean saltpeter, limestone + N_2, ・・・・*
Phosphate F.	*: phosphate rock*
Potassium F.	*: ore (ingredient ; KCl + NaCl), KCl, ・・・・*
Coated F.	*: N, P, K ＋ thermo plasticity resin*

これらの肥料以外に、栄養分の溶出速度を制御するために、熱可塑性樹脂で包まれた肥料がある。これらは被覆肥料と呼ばれ、大気汚染をかなり起こす可能性がある。

肥料製造工場では、煤煙、SOx、NOx、ダスト、フッ化水素、アンモニア、溶媒が、大気汚染防止法で代表的な物質として規定されている。

Pollutants	*Origins of Pollutants*
Soot, SOx, NOx	*Boiler, Dryer, Calcining furnace, etc.*
Dust	*Raw material stock yard, Raw material feed equipment, Belt conveyer, Bucket conveyer, Crusher, Mill, Sieve*
HF	*Phosphate fertilizer plant------ Reactor, Calcining furnace, Melting furnace, Phosphoric acid concentration plant*
NH_3	*Pelletizer, Dryer*
Solvent	*Coated fertilizer manufacturing process*

アンモニアは大気汚染防止法の"特定物質"に指定されていて、合成工程と分解工程で故障・破損が起こった時の必要な対策が規制されている。硫酸アンモニウム、燐酸アンモニウム、尿素を製造する場合、原料の乾燥造粒工程の排ガスはアンモニアを含んでいるが、希薄である。しかし、アンモニア専用除去装置を設置する必要はないが、大抵の場合は、乾燥造粒工程で発生する肥料ダストの除去と一緒に除去している。この方法で処理された排ガス中のアンモニア濃度は排出許容値を満足する。

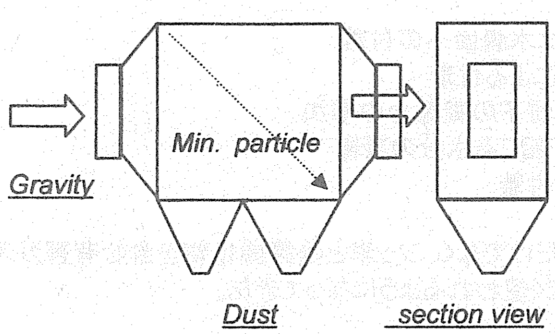
肥料製造工場の処理工程と単位操作における大気汚染物質の発生源をスライドにまとめている。

詳細については P.1～89を参照。

2. 煤煙と煤塵の除去

2-1 重力集塵装置、慣性力集塵装置、遠心力集塵装置

粒子とガスの密度が異なるため、層流状態のガスの流れ方向を変えれば、それぞれの流れ方向が変わる。しばしば、この方法によるガスの中の固形粒子の分離がが行われており、通常はガスの流れ方向を急変させて方法がとられる。



重力集塵装置では、沈降室で流速を低下（通常1～2m/秒）させ、それによって重力で沈降させる。重力集塵装置は装置が大きく、最終集塵処理に使用されることはほとんどない。ストークスの法則が適用できると考えられ、100%除去される場合の粒径サイズは次式で表される。

Stokes' Law

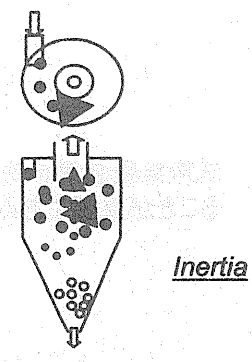
$$V=(g/18\mu)(\rho 1-\rho)D^2 \quad (cm/s)$$

V: settling velocity (cm/sec)
g: gravitational acceleration (cm/s^2)
μ: gas viscosity (kg/ms)
ρ1: particle density (g/cm^3)
ρ: gas density (g/cm^3)
D: particle diameter (cm)

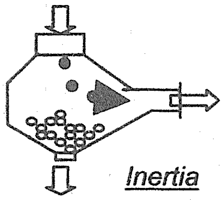
一般的にサイクロンと呼ばれる遠心力集塵装置は、サイクロンの中の粒子に遠心力が作用し、次式で示される。大容量のガスを処理する場合、小さなサイクロンが並列するマルチサイクロンが用いられる。流入部のガス流速は10～25m/秒で設定される。

$$\text{Centrifugal force } (F) = mv^2/R \quad (N)$$

m: particle mass (kg)
V: particle velocity (m/s)
R: cyclone radius (m)



慣性力集塵装置では、ガスの流れを邪魔板に衝突させるか、あるいは急激に方向を変えて慣性力を用いて粉塵粒子を除去・捕集する。



Inertia

詳細についてはP.165～166を参照。

2-2 洗浄集塵装置

洗浄集塵装置の集塵に働くメカニズムは:

(1)ダストの水滴または水膜面への付着
(2)ダスト間の拡散力による付着
(3)水分の増加に伴う粒子の凝集力の増加
(4)ダストが核となって起こる水分の凝縮
(5)気泡による粒子の付着

洗浄集塵装置は、近年、ダストだけでなく、フッ素と硫黄酸化物を含む有害ガスの除去が同時にできるので、近年、ガス処理に広く使われるようになってきた。

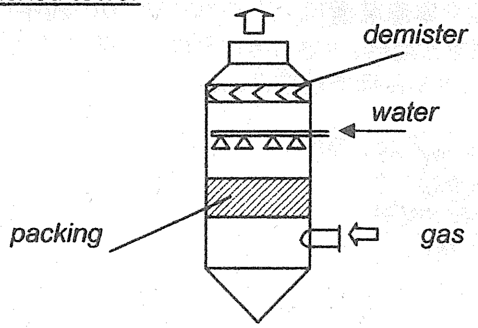
Typical Types of Scrubbers

Type	Velocity m / s	L/G l/m^3	ΔP kPa	Th. Φ μm
Spray	1~2	2~3	0.1~0.5	≧3
Packed	0.5~1	2~3	1~2.5	≧1
Jet	10~20	10~50	0~ -1.5	≧0.2
Venturi	60~90	0.3~1.5	3~8	≧0.1

Th. Φ: Particle size of threshold to allowing 50 % removal

充填式洗浄集塵装置の構造の概要を図に示す。

Packed tower



洗浄集塵装置を効果的に働かせるには、それぞれの装置に適したガス流速と液ガス比を選定することが重要である。

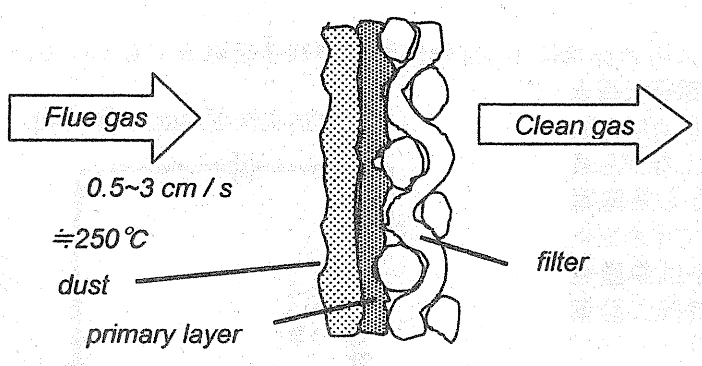
詳細についてはP.92～94を参照。

2-3 ろ過集塵装置

バグフイルター集塵装置は種々の集塵装置の中で最も広い適用範囲をもっている。バグフイルターは0．1μｍ粒径の粒子でも捕集できる。バグフイルターをガラス溶解炉の排煙ガス処理に使った場合、97～99%の集塵率を得ることができる。

集塵機構は、ろ布の表面に最初に付着した粒子でできた一次付着層が、微粒子を集塵するろ過層として利用される。ろ過層の排煙ガスの通過速度は、おおよそ0．5～3cm/cm である。したがって、大容量のガスを処理する場合は、多くのバグフイルターを並列に用いる多室集塵装置が使われる。

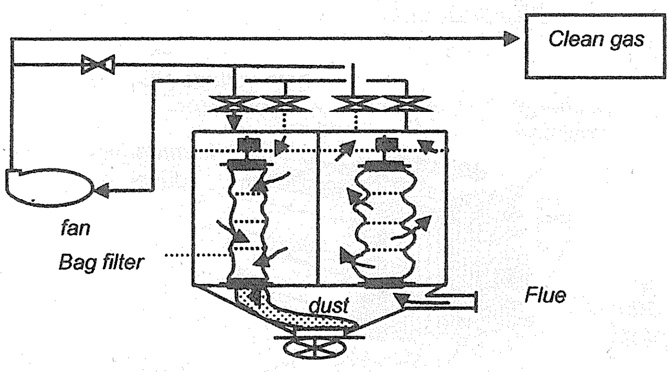
Filtration Action in Filter Cloth



ΔP≒150 mg Hg → dusting

例えば、溶解炉の排ガス35，000m^3/h （250℃）処理のバグフイルターは、6集塵室をもち、各室には直径30cm、長さ約600cm の円筒形フイルターが50～60本配置されている。この場合、6室の内の1室は、ある一定時間ダストの払落しがおこなわれ、残りの5室が除塵をおこなう。

ガラス溶解炉に使われるろ布は、200 ℃以下で結露による硫酸腐食が起こるので、ガラスファイバーが用いられる。



ろ布上にダストが蓄積して圧力損失が 150 mm Hg に達すると、ダストの払落しが必要である。ダストの払落しは、ガラス溶解炉の場合、最も一般的に使われている間歇式と、連続式がある。ダス

トの剥離除去は振動法か、逆気流法でおこなわれる。

Dusting frequency	*Dusting drive*
- intermittent	*- vibration*
- continuous	*- reverse air*

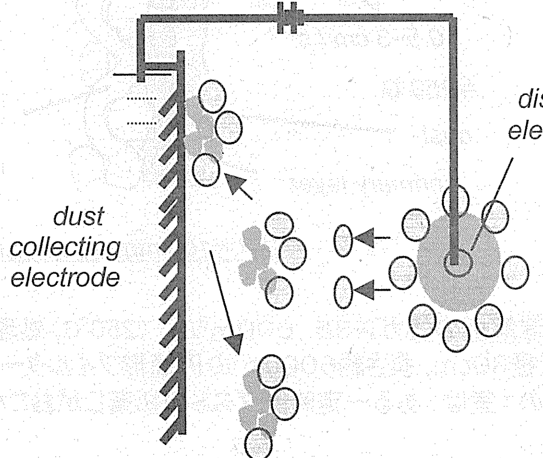
温度は、ろ布の耐熱温度を超えないように、また、硫酸の露点を避けるために200から250℃の間に保たれる。

詳細についてはP.94～95を参照。

2-4 電気集塵装置

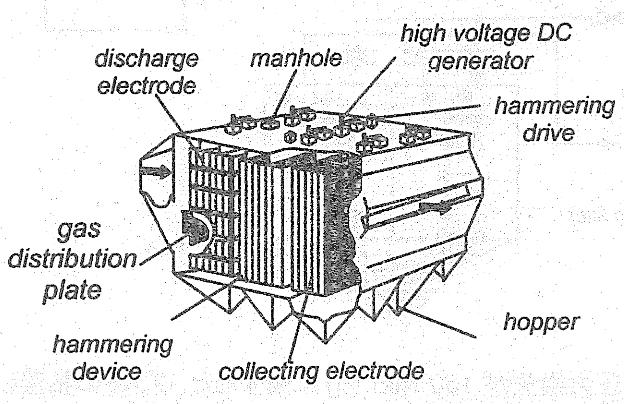
電気集塵装置(EP)は排ガス中の非常に小さな液体や固体粒子を除去するのに用いられる。装置は通常は心線の高電圧電極と板または管の接地陽電極の間にコロナ放電を発生させる。ここを衝突しながら通過する粒子は、放電電極から集塵電極に移動するイオンによってイオン化される。そしてこれらの粒子は集塵電極に引き寄せられ、集塵電極に静電力で保持される。

Principle of dust collection :



粒子は、槌打衝撃法または水洗によって定期的に取り除かれる。集塵装置は平板か管のどちらかを使うことができる。通常は、スライドに示すように多くの数の電極が付いている。

Structure of EP



EP はガスと粒子の性状にあまり左右されることは無く、高効率集塵が可能であり、圧力損失を伴

わずに集塵できる。

詳細については P.95～96を参照。

2-5 集塵装置の選定

集塵装置を選定する場合、スライドに示す粒子とガスの物性に注意をしなければならない:

Factors affecting Dust Collection:
dust concentration, particle size distribution, temperature of dust,
apparent electric resistance rate, due point, gas temperature,
composition of flue gas, gas volume, etc.

排煙ガス中のダストの粒子径と粒径分布はそれぞれの集塵装置の粒子除去性能に大きな影響をもっている。集塵装置で捕集できる粒子径を表に示す。目に見えない粒子濃度は 20 mg/Nm^3 であるといわれている。

高濃度のダストを含むガスに、ろ過集塵装置を適用すると、ダスト払落しを頻繁に行わなければならない。EP は排煙中のダスト濃度の影響をあまり受けない。

Applicable Range of Dust Collector

Type	Particle (μm)	Working (℃)	Cutback Level (%)	Pressure Drop (mm H2O)	Equipment Cost	Running Cost
Gravity	1000~50	d.p.~400	40~60	10~15	S	S
Inertia	100~10	d.p.~400	50~70	30~70	S	S
Centrifuge	100~3	d.p.~400	85~95	50~150	M	M
Scrubbing	100~0.1	no- limit	80~95	300~800	M	L
Filtration	20~0.1	no- limit	90~99	100~200	≧M	≧M
EP	20~0.05	d.p.~400	90~99.9	10~20	L	S~M

S: cheap, M: average, L: expensive

粉塵濃度に関しては、重力集塵装置と慣性力集塵装置の場合、大きな粒子と小さな粒子の凝集が促進されるので、粉塵ガス濃度が高くなるにしたがって、高い除去率が得られる。ベンチュリースクラバーとジエットスクラバーの場合、これらの煤塵を高濃度に含むガスに適用すると、ベンチュリーのスロート部が摩滅するので、ダスト濃度 10 g/ Nm^3 以下に適用すべきである。

詳細については P.97を参照。

3. Sox 除去技術

肥料製造工場では、ボイラー、乾燥機、焼成炉、溶解炉の燃料の燃焼により SOxが生成される。

Sources of SOx: Fuel SOx

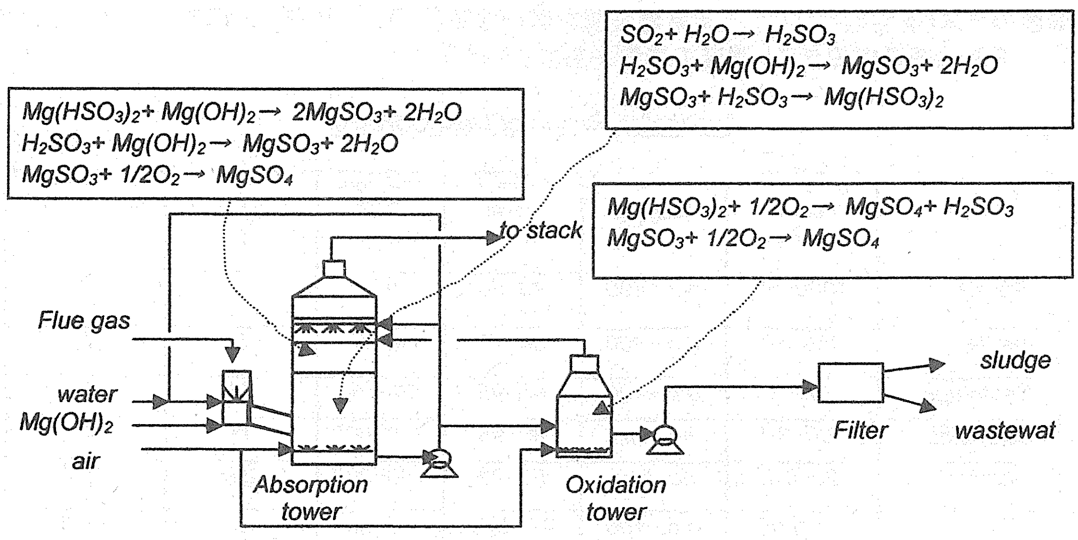
- Boiler - Dryer - Calcining furnace - Melting furnace

しかし、日本では排出基準や上乗せ排出基準を満たすために排煙脱硫装置を設置している肥料製造工場はないが、低硫黄燃料の使用によって基準に対処している。

排出基準が将来厳しくなれば、脱硫装置の設置が必要になってくるものと考えられる。排煙脱硫装置は湿式、乾式、半乾式に分類できる。これまでに設置された脱硫装置の数のほぼ70%以上が湿式法であり、処理ガス量では80%以上を占めている。

湿式法には、石灰吸収法、水酸化マグネシウム吸収法、アルカリ溶液吸収法、ダブルアルカリ法、酸化吸収法などがある。それらの中で、水酸化マグネシウム吸収法は中小規模のボイラー処理に適している。この処理方式は、スライドに示すように、建設費が安く、原料費が安く、毒性・腐食性が少なく、安全である。副生物は溶解性が高く、閉塞の問題を避けることができる。硫酸マグネシウムの副生物は肥料製造の原料として再利用することができる。

Wet Type Absorption



詳細についてはP.98～99を参照。

4. NOx除去技術

4-1 肥料工場におけるNOxの発生

NOxとは、酸化窒素(NO)と二酸化窒素(NO_2)の 2 種類の主な酸化物を意味する。燃焼では、NO が主であり、NO_2 は NO の主に下流側で派生する。燃焼行程における NOxの発生には主に二つのメカニズムがある。

(1)空気中の N_2 がバーナー室の高温の酸素と反応してできる、サーマル NOx

(2)燃料中の窒素が高温の酸素と反応してできる、ヒューエル NOx

空気比と理論燃焼温度で生成される NOx、いわゆるヒューエル NOxの濃度との関係を図に示す。肥料製造工場では、比較的窒素含有率の高い C 重油を使うが、ヒューエル NOxの発生はそれほ

ど高くない。肥料製造工場における主なNOxの生成はサーマルNOxと考えられる。

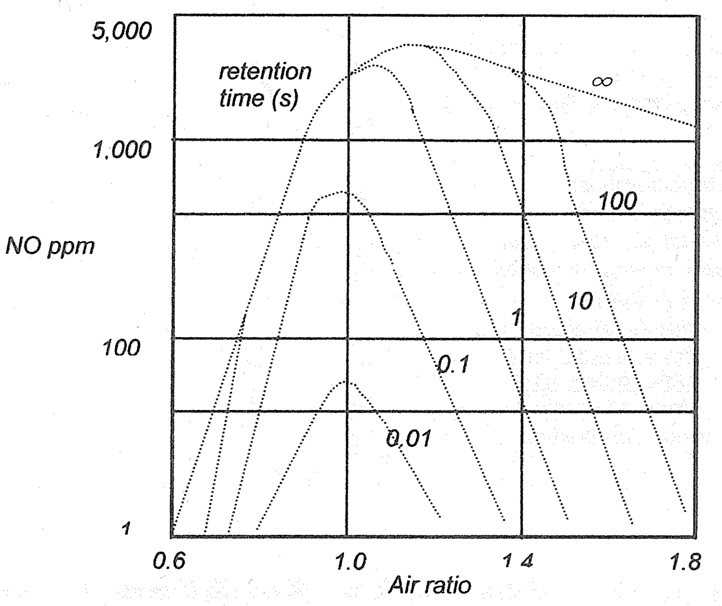
Thermal NOx ≫ Fuel NOx

次の運転状態になると、排煙中のNOx濃度は高くなる:

(1)燃焼温度が高い
(2)燃焼域の酸素濃度が高い
(3)高温燃焼域における燃焼ガスの長い滞留時間

理論燃焼温度におけるNOx生成と空気比と滞留時間の関係をスライドに示す。

Air ratio ~ Retention time ~Thermal NOx



空気比の増加の一定値までは、滞留時間が長くなるほど、NOx濃度は比例的に増加する。しかし、図から分かるように、空気比がある値より大きくなると、燃焼温度の低下に伴い、NOx濃度は減少し始める。

NOx concentration increases at:
- *higher temp. in combustion*
- *higher O_2 conc.*
- *longer retention in high temp. zone*

詳細についてはP.99～100を参照。

4-2 NOx 制御方法

これまでに述べてきた理論に基づく種々の NOx削減方法は、すでに開発され、表に示す制約条件の下で採用されている。図中の記号は:

◎; large effect is expected
○; not so large effect is expected
△; effects vary depending on the equipments
★; affecting on existing equipment is predicted
☆; careful application is required

NOx Reduction Methods		*Decreasing effect* Thermal NOx	Fuel NOx	*Remarks* lowering heat efficiency	lowering heat	enlarging equipment	enlarging
Improving	*operating*						
	Lower air ratio combustion	△	◎				☆
	Lower heat load	○	○		★	★	
	Decreasing pre-heat air temp.	○	○	★	★		☆
Improving equipment configuration							
	2-stege combustion	◎	◎				
	Rich-lean burner	○	○				☆
	Exhaust gas recirculation	◎	○	☆	☆		☆
	Steam or water injection		○	☆			
	Low NOx burner						
	<u>mixing accelerate type</u>	○	○				
	<u>flame-divided type</u>	○	◎				
	<u>self-circulate type</u>	○	○				
	<u>stepwise combustion type</u>	○	◎				☆
	Emulsion combustion	○	○	☆			

まとめ ― 肥料製造工場では、NOxの排出を減らすために次の対策が実施されている:

— 燃焼域の酸素濃度をできるだけ低くするための低空気比運転
— 燃焼室の温度と熱負荷をできるだけ低くするための低熱負荷運転
— 低 NOxバーナーの採用

詳細については P.101を参照。

5. 粉塵飛散防止
肥料工場で、大気汚染防止法により規制を受ける機器、設備は原料貯蔵所、ベルトコンベアー、バケットコンベアー、破砕機と篩である。

<u>Dust generating equipment & location designated by air pollution control law</u>
- belt conveyer
- bucket conveyer
- crusher, mill

- sieve
- ore stock yard

これら以外で、原料および製品サイロとホッパー、ベルトコンベアー、バケットコンベアーを除く輸送機器、包装機などは、基準に規定されていないが、労働者の健康リスクに対する作業環境安全を確保するために集塵装置が設置されている。

Equipment protected work shop environment from dust scattering
- silo, hopper for raw material & product
- transporting equipment except belt & bucket conveyer
- packing machine, etc.

原料は原則的に建物内に貯蔵される。例えば、リン鉱石のように屋外貯蔵される場合は、原料の表面をシートで覆い、ダストの飛散を防止している。

- outdoor stock
with sheet cover

(phosphate rock)

ベルトコンベアー、バケットコンベアー、破砕機、篩などの粉塵を発生する装置には、次のダスト飛散防止策が取られている:

(1)ダスト飛散防止構造の機器の設置と材料の屋内保管

(2)これらの機器を大気圧以下にブロワーで減圧吸引する密閉カバー構造の内に設置

(3)機器全体を覆ってしまい、吸引ブロワーで集塵

(4)ダスト発生箇所を部分的にフードカバーで吸引

- indoor allocation
- closed cover, negative pressure
- Sealed dust collecting cover
- dust collecting hood

これらの方法で捕集されたダストは、通常、サイクロンフイルターかバグフイルターに吸引される。

詳細については P.102を参照。

6. NH_3 除去技術

アンモニアは大気汚染防止法で、特定物質に指定されているが、排出基準値は定められていない。アンモニアの排出許容値は、悪臭防止法により敷地境界線上での規制と排出口での規制が

ある。敷地境界線値は自治体によって 1 から5ppmの間で定められる。排出口からの許容されるアンモニアの濃度はスライドに示す式によって計算される。

1. *Permissible NH_3 emission:*

1~ 5 ppm at boundary of premise (set forth by prefecture governors)

$Q = 0.108 \times He^2 \times Cm$

Q : gas volume (Nm3 / h)
He : effective height of exhausting outlet (m)
Cm: concentration at boundary line of premise (ppm)

肥料工場敷地内で発生するアンモニアの処理の例をスライドに示す。
The ammonia treatment in compound fertilizer plant, as an example, is shown in a slide.

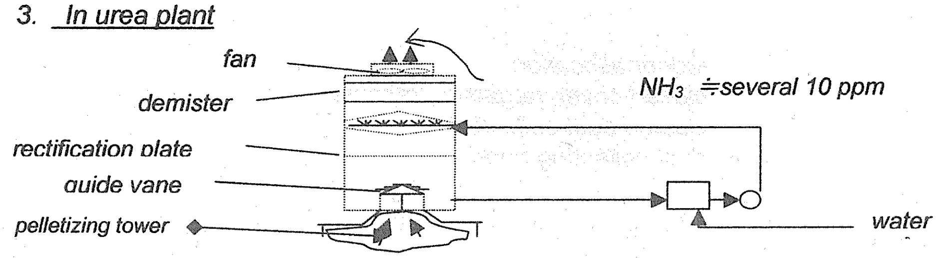
2. *In compound fertilizer plant :*

Process	Origin	Abatement
	$(NH_4)_2SO_4$	reservoir type wet scrubber
pelletizer & drying	$(NH_4)_3PO_4$	pressurized water scrubber
	$CO(NH_2)_2$	packed bed water scrubber
		(NH4 removal 70~90%, 20~50ppm)

アンモニアは造粒と乾燥工程から発生し、そこでは硫酸アンモニア、燐酸アンモニア、尿素などの原料の一部が、熱と原料同士の接触により分解される。これらのガス中のアンモニア濃度は薄く、粉体状の肥料ダストを含んでいるので、ガス中のアンモニアはスライドで示す湿式スクラバーで、水洗、あるいは希硫酸溶液、または燐酸溶液を用いてダストと一緒に吸収回収される。これらの方法によるアンモニアの除去率は70～90%の範囲にあって、排出アンモニア濃度は20～50ppmである。

尿素工場の造粒塔では、排ガス量が多く、1～5μm の微細な尿素粉末を含むので、特殊な集塵装置が使われる。造粒塔の上部に取付けられる集塵装置の構造をスライドに示す。集塵装置出口のアンモニア濃度は数十ppmである。

3. *In urea plant*



詳細についてはP.104～106を参照。

7. フッ素化合物除去技術

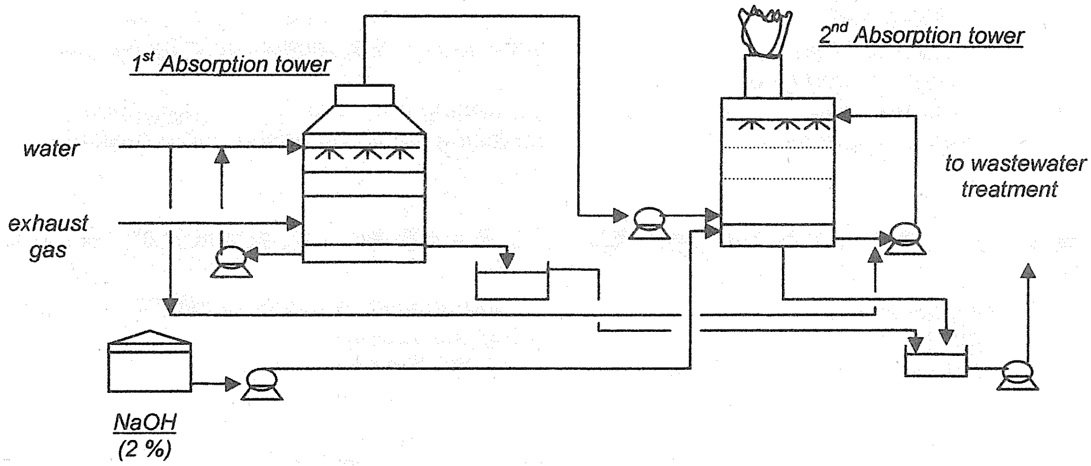
肥料工場では、フッ素化合物がフッ化水素((HF)と四フッ化ケイ素(SiF_4)の形で、原料の燐酸、過燐酸カルシウム($Ca(H_2PO_4)_2$ (原文 P.41 参照)の反応工程と濃縮工程、さらに、熔成リン肥、焼成リン肥などの溶解炉で生成される。

Generation of F
- reaction & condensation process for H3PO4 production
- reaction process for $Ca(H_2PO_4)_2$ production
- reaction furnace for fused P and calcined P production

フッ素化合物の処理には、HF と SiF_4 が共に水に強い親和性と比較的大きな溶解性をもっているので、湿式方式が採用されている。

HF, SiF4 → with greater hydrophile property

湿式集塵装置、充填層式湿式スクラバー、ジェットスクラバーなどが、フッ素化合物の処理に使われる。SiF_4 が水に吸収されると、酸化ケイ素(SiO_2)が形成され、付着と閉塞の問題を起こすので注意が必要である。除去剤としては水が一般的であるが、排ガス中のフッ化物濃度をさらに下げるときには、Na, Ca などのアルカリ剤を用いる。除去装置をスライドに示す。



詳細についてはP.102～104を参照。

8. 臭気除去技術

8-1 除去方式

臭いの特定または定量化は難しく、そのために特有の設計上の問題に特長される。臭いの制御は、発生源で行うのが最善策である。脱臭技術には幾つかの種類がある。

燃焼法の中で、直接燃焼方式は、臭い成分を、約800℃で、0．3～1．0秒間接触させて無臭の CO_2 と H_2O に替える。この方式は広く使われており、臭気除去に高い効果を持っている。蓄熱式脱臭装置は炉内に蓄熱装置をもっていて、臭気成分の燃焼によって加熱される。もし、臭気成分がトルエン換算で500ppm以上の熱量を持っていれば、燃料を加えずに燃焼することができる。この方式は構造が簡単であり、維持管理が容易であり、熱交換率は95%に達する。触媒燃焼方式は、触媒の存在下で悪臭成分を燃焼させ、無臭物質に変える。経済的な燃焼温度の200～300℃で、臭気の燃焼率は99%以上である。

Incineration method	*decompose to CO_2, H_2O by heat*
direct incineration	*at ≒800℃*
regenerative thermal oxidizer	*regeneration, heat efficiency ＞80%*
catalytic incineration	*using catalysis at 200~ 350 ℃, rem.＞99%*

スクラバー法では、臭気ガスは、スクラバーの中で、薬液または水によって洗浄される。この装置は安い上に、ガス中のミストとダストを同時に除去するころができる。

Scrubbing method	*scrubbing by chemical solution*
	water, acid, alkaline, oxidant, etc.

吸着法では、活性炭が吸着剤として、回収形、濃縮形あるいは交換式吸着形のいずれかの形で使われる。活性炭の再生は、水蒸気再生、加熱窒素ガス、酸化剤による酸化、あるいは取替えのいずれかの方法で行われる。

Adsorption method	
recovery type	
fixed bed	*activated carbon, steam regeneration*
fluidized bed	*activated c., heat regeneration by N2 gas*
concentration type	
honeycomb	*separating odor from low concentration gas*
replacement type	*replacing saturated adsorbent or oxidant*

生物法では、土壌ベッドあるいは生物膜充填材に生育する細菌により、臭気成分が分解される。

Biological method	*biodegradation by microorganisms*
soil bed	*using soil bacteria*
packed tower	*using bio-film on the media*

脱臭剤とマスキング剤は不快臭を、無害で不快臭のない成分に変える。

Deodorizer, masking agent	*deodorize or easing offending gas*

詳細についてはP.106を参照。

8-2 脱臭法における問題点(例)

各種の脱臭法における問題点をスライドに示す。

燃焼法の中で、直接燃焼法は高温で運転されるので、排出許容値を超える高濃度のNOxを生成する。蓄熱燃焼方式と触媒燃焼方式の場合、塩素成分を含む溶剤が混入すると、塩酸が生成される。ガス中に塗料が含まれると、閉塞の問題と、触媒の性能低下を引起すことがある。

Combustion method

Deodorizing Method	*Trigger*	*Trouble*
direct incineration	*NOx ↑*	*permission level ↑*
regenerative thermal ox.	*mixture of Cl_2, paint, etc.*	*HCl ↑, clogging*
catalytic incineration	*mixture of Cl_2, paint, S, etc.*	*catalyst deterioration*

吸着法では、ケトン、シクロヘキサンなどの溶剤が混入すると、活性炭が発火を起こし、排ガスの温度が上昇し、活性炭などの性能低下を来たす。

Adsorption method

Deodorizing Method	*Trigger*	*Trouble*
recovery type		
fixed bed	*mixture of ketone, high B.P. substance*	*firing, deterioration of activated carbon*
fluidized bed	*high temp. of exhaust gas*	*A.C. deterioration*
concentration type		
honeycomb	*mixture of cyclohexane*	*firing*
replacement type	*conc.＞ several ppm*	*short term A.C. replacement_*

生物法では、土壌が乾燥すると、分解性能が低下し、最終的には性能不能に陥る。充填塔の場合は、充填材表面に生物を育てるのに比較的長時間を要する。

Biological method

Deodorizing Method	*Trigger*	*Trouble*
soil bed	*drying of soil*	*malfunction*
packed tower	*slow acclimatization*	*slow starter*

スクラバー方式の場合は、散水量の低下が性能低下につながる。ガスがダストを多量に含む場合、スクラバー内部に閉塞の問題を起こすことがある。

Scrubbing		
	less sprinkling water	*malfunction*
	dust in gas	*clogging internals*

詳細についてはP.110～111を参照。

9. 溶剤回収と除去技術

有機溶剤の回収が必要になるのは、熱可塑性樹脂を使う被覆肥料の製造工程だけである。溶剤中の被覆剤の濃度は一般的におおよそ10%位である。

1. Sources of Generation
coated fertilizer (thermoplasticity resin)

排ガスからの溶剤の回収は、製品製造コストの経済性に大きな影響をもたらす。したがって、溶剤の回収は、環境管理としての対策以前に、コスト管理上から避けられない。そして、経済的理由から回収されずに残った溶剤は、大気汚染防止装置で除去される。

2. Abatement
recovery of solvent brings profit ⇒ production cost reduction
residual solvent value ≪ recovery cost ⇒ pollution control

大気汚染防止には、これまでに述べてきた除去方法が用いられる。冷却凝縮法では、溶剤蒸気が液体状態の蒸気圧よりも低い温度まで冷却される。この方法は分圧に見合った溶剤が残るのでそれほど実用的ではない。

3. Abatement Process
- cooling condensation method
cool down flue gas below vapor pressure

吸収・放散法では、除去対象の溶剤に対して高い溶解性と非常に低い蒸気圧をもった吸収剤が得られれば、この方法は適用できる。

- absorption & dispersion method
absorbing of solvent to absorbent with lower vapor pressure

吸着・放散法では、これらの方法は、蒸気圧の低い、競合吸着成分のない溶剤には適用できる。これらの装置は構造が簡単で、運転費用が安い。固定床、移動床、流動床の 3 種類の吸着装置がある。よく使われる吸着剤には、活性炭（粒状炭、粉末炭）、シリカゲル、モレクラシーブ、アルミゲルなどがある。吸着剤の再生は通常、ガス加熱、水蒸気加熱、伝熱、減圧抽出などで行われる。

- adsorption & dispersion method
- ☆ *applicable to compositions with low vapor pressure and non-existence of antagonist. Adsorbed at under pressure or lower temp..*
- ☆ *adsorber: fixed bed, moving bed, fluidized bed*
- ☆ *adsorbent: A.C., silica gel, molecular sieve, aluminum gel*
- ☆ *regeneration method: heated gas, steam, heat transfer, extraction under decompression*

詳細については P.112～114 を参照。

10. 環境管理システム

1. EMS: 環境管理システム（EMS）の傾向は、悪化の一途をたどる地球環境の状況下にあって、1992 年に開かれた環境と開発に関する国連会議で“持続可能な開発”が合意された。この決議に基づき、国際標準化機構（ISO）は 1996 年に“環境マネージメント・監査”を設定した。これにより、企業は企業活動が与える環境への影響と法規制に基づき、企業が持っている環境問題に対して、基本方針と目標を設定する。企業は、これを実行に移し、目標を達成するために、システムを修正し、監査していく。この作業は繰り返し行われ、仕組みは改善されていく。このサイクルは PDCA サイクル（Plan-Do-Check-Action）と呼ばれる。ISO 14000 は、環境管理を確立し推進していくために、適切な組織、義務、管理システムを作ることを要求している。

1. Environmental Management System
- Organization for Environmental Control
- ISO 14000 series----- PDCA cycle
- Responsible for environmental protection

ISO 14000

2. 環境管理はマニュアルに基づき管理され、それには汚染防止装置の運転方法、汚染防止装

置の点検方法、教育訓練、装置が停止した場合の緊急処置などが定められている。

2. Environmental Control Manual
- Operation Standard Manual

3. 従業員の教育訓練について、公害防止の担当者、管理者などは、環境管理に必要な資格を持たなければならない。したがって、計画的な教育訓練プログラムと環境管理マニュアルの点検が重要である。

3. Education & Training
- legally qualified expert of environment control
- training program and preparation of manual

4. 肥料工場では多くの無機粉体が取扱われるので、作業者の健康管理とロスの最小化のために、ダスト除去が重要である。

4. Environmental Control at Work Shop

5. 環境モニタリング： 事業者は法律で定められた大気汚染排出基準を守らなければならない。このためには、汚染物質の排出を、定期的に測定し、監視し、記録しなければならない。肥料工場に対する汚染防止法では、SOx、NOx、粉塵の排出が規制されている。

5. Environment Monitoring
- maintaining monitoring system
- monitoring of air pollution state
- legal emission permissible level

詳細についてはP.147～160を参照。

大気汚染防止技術パワーポイント解説書

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