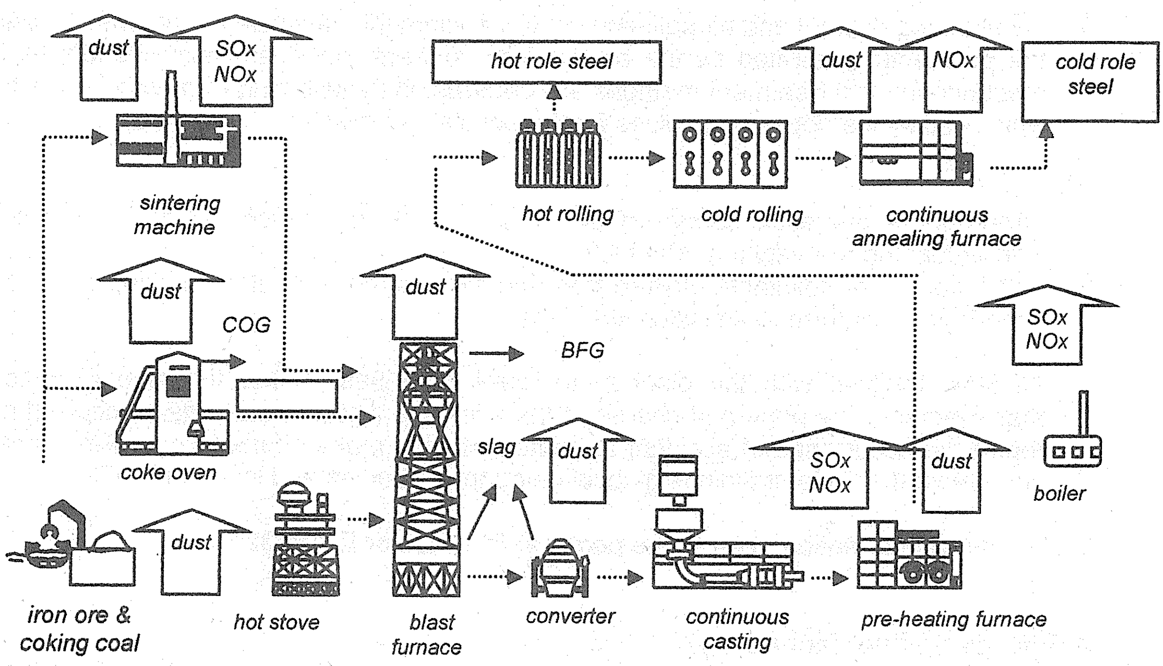
Ⅲ.Steel Industry

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.

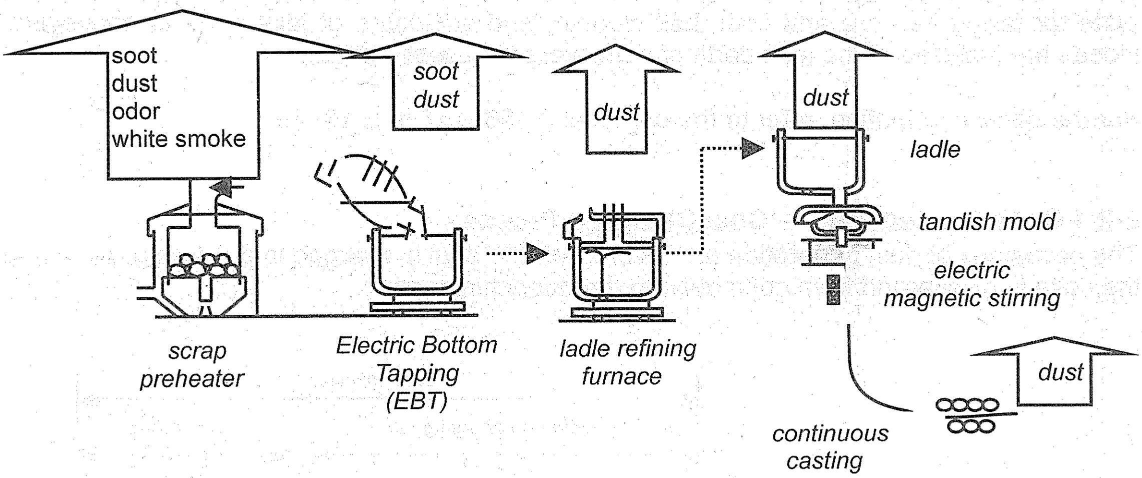
Other than these, boilers in the steel mill emit SOx and NOx too.

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.

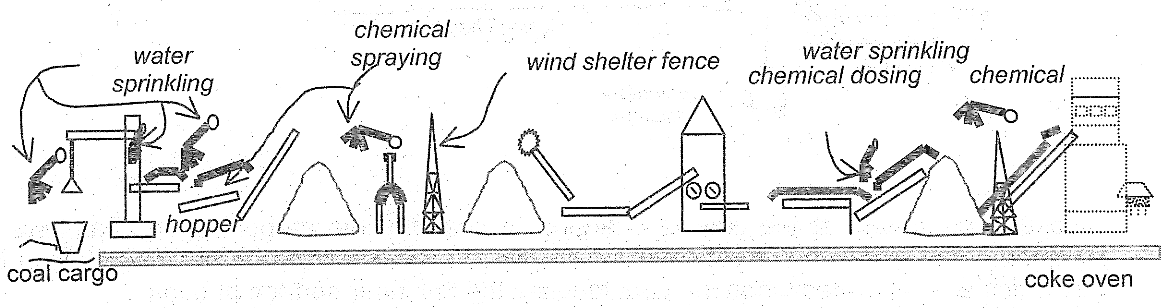
In the slide, typical process which is commonly adopted for the electric furnace steel factory to produce the ordinary steel and low alloy steel is shown.



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

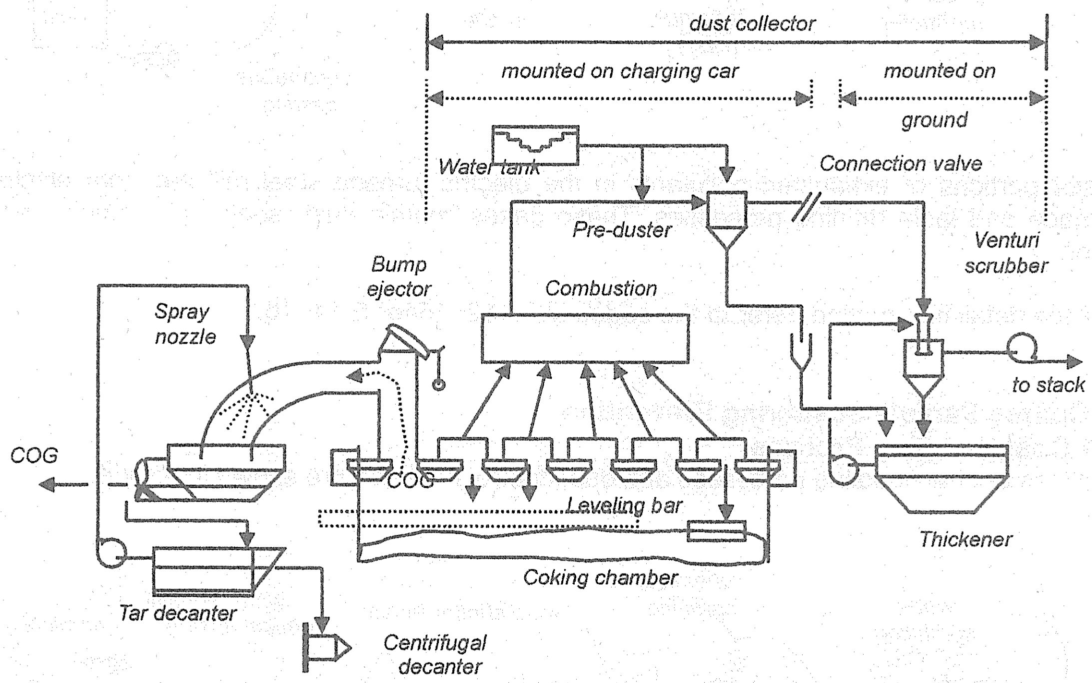
There are cases where the surface of piled raw materials is covered with net or sheet, or sometime be coated by chemicals such as polyvinyl acetate or tar. A wind shelter fence has been installed. A wind shelter fence of 7 m high with 40 % opening area could reportedly reduce the wind velocity by 50%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



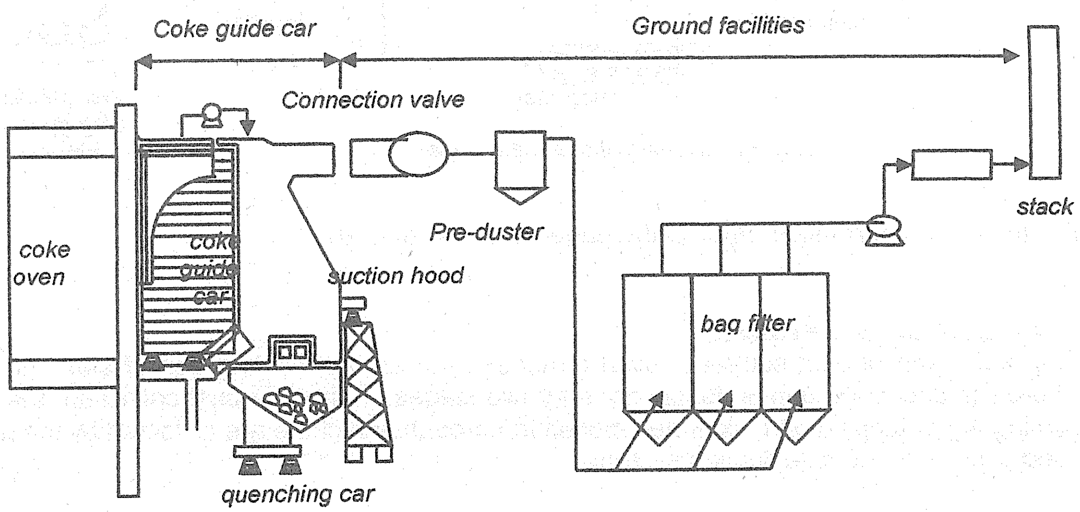
Smoke is generated at the time of charging of coal into the carbonization chambers by replacement of gases in the oven with coal, which contain steam and fine coal dust in the gas which are generated when the coal touches the hot inner surface of oven.

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.

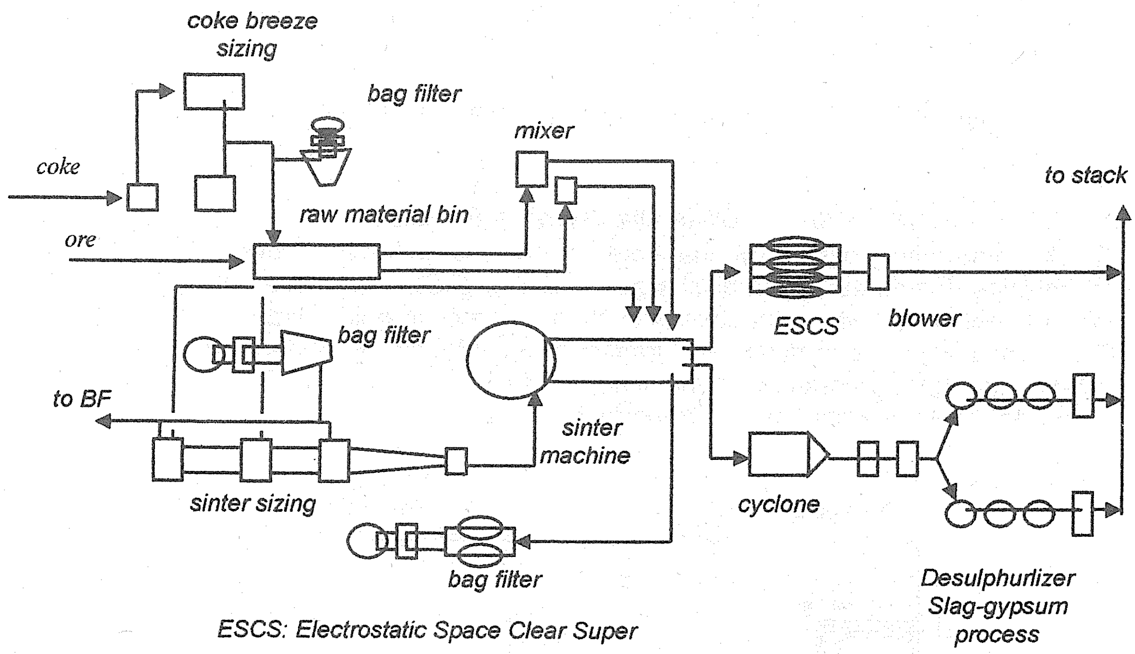
For the detail information, refer to the pages at P.156~157 or E.19.

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.

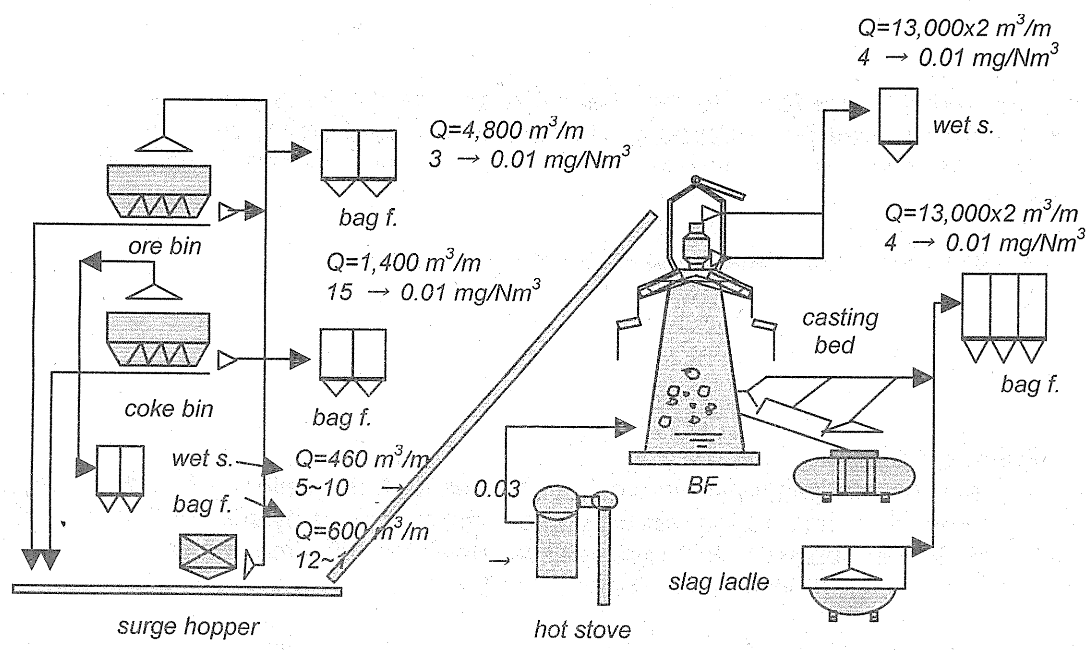


ESCS: Electrostatic Space Clear Super

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.

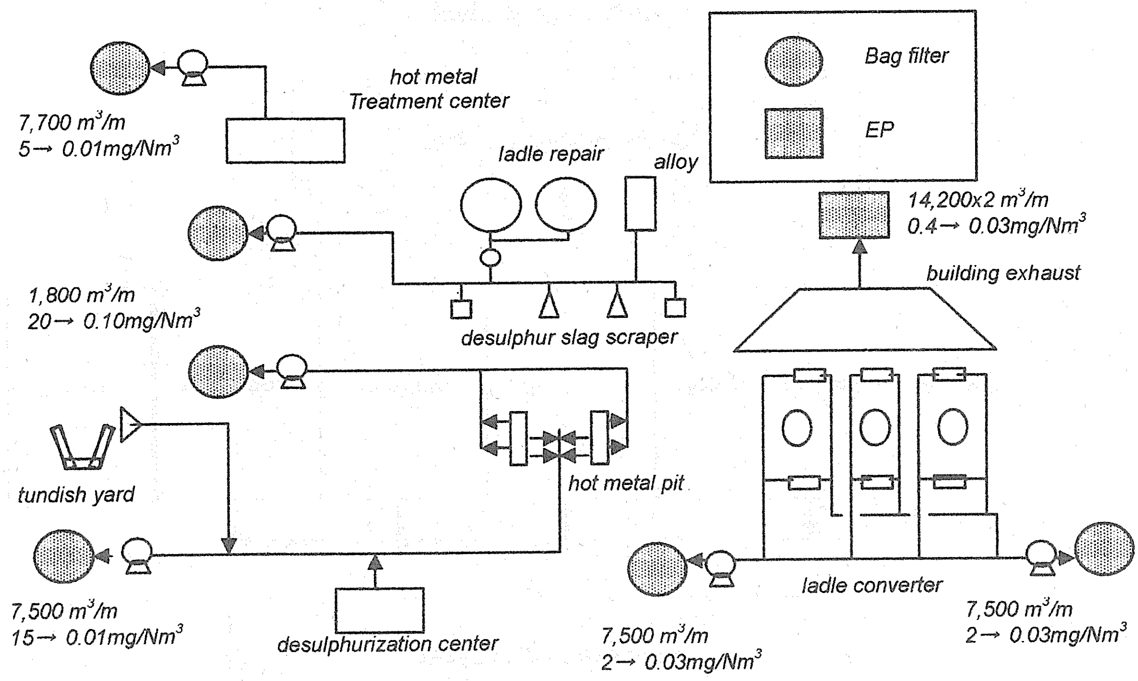
In the second dust collection, the dust which is not captured by the first stage collector system is gathered to small space at upper part of the casting bed as much as possible and collected. The second dust collection system is usually equipped with "storing system" or "curtain system" to cope with 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.

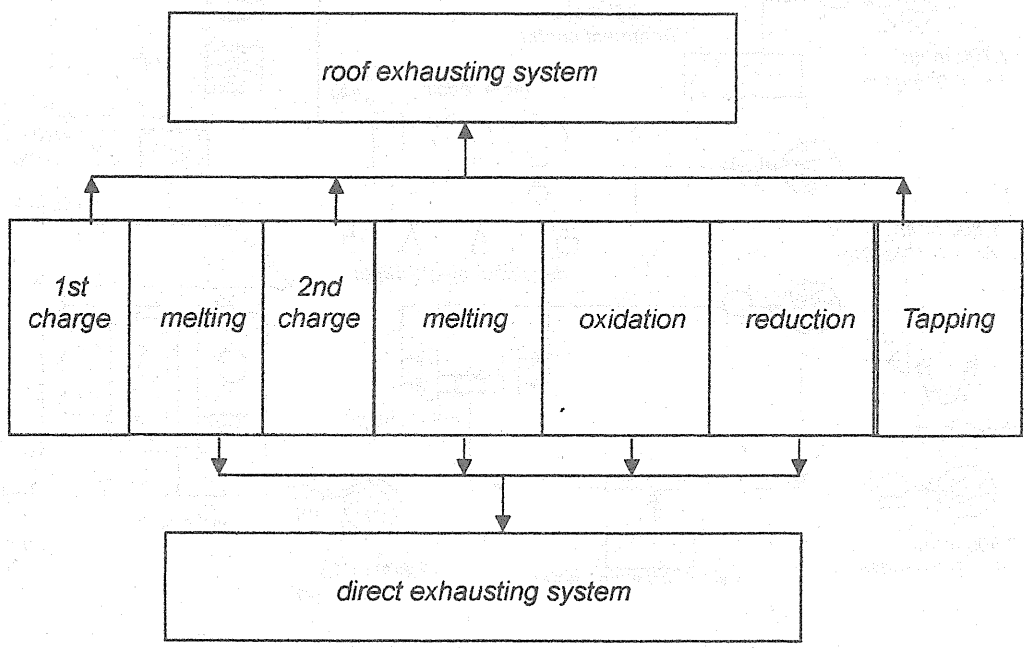
The wet type electrostatic precipitator installed on the rooftop or bag filter installed on the ground are used for dust collection of ladle converter building, though the dust collecting system of the building for converter has not so popular.
To prevent the sloping, stabilization of melting metal compositions 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.

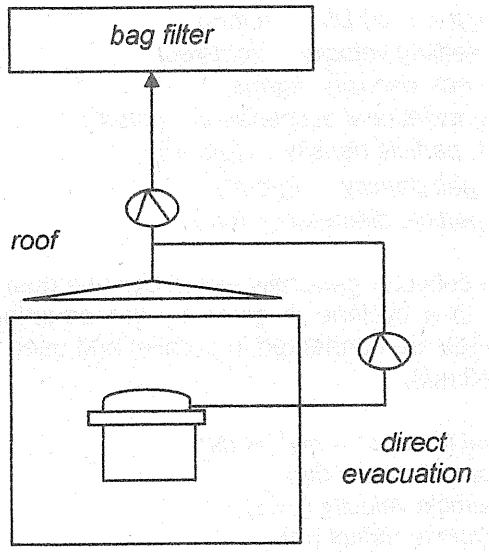
Conventional System



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

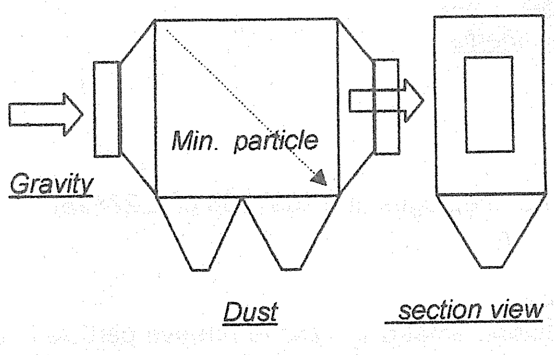
The electric furnace in steel mill plant produces not only a large amount of dust but also noise. For these troublesome, the dog house, which closes the whole electric furnace into the enclosed house, is very effective, and it makes possible to reduce substantially the collecting gas volume by 20~30%.

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/s^2)

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

ρ: gas density (g/cm^3)

D: particle diameter (cm)

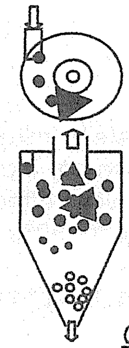
In the centrifugal force collector generally called cyclone dust separator, the centrifugal force exerted on a particle in a cyclone is given by the equation. For a large volume of gas treatment, small cyclones are connected in parallel and used as multi-cyclone. The inlet-gas velocity is set at 10 ~25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

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

m: particle mass (kg)

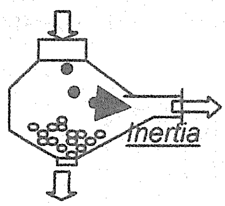
V: particle velocity (m/ s)

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.

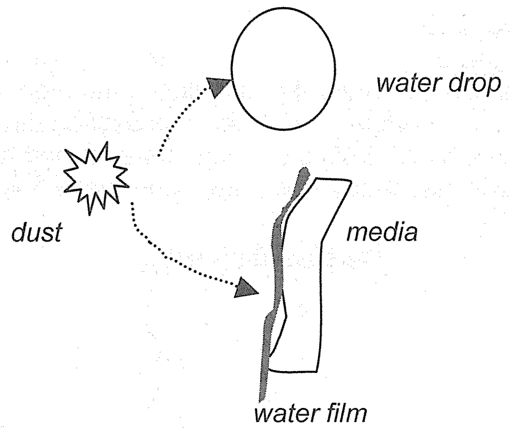


For the detail information, refer to the pages at P.165~166 or E.27~28.

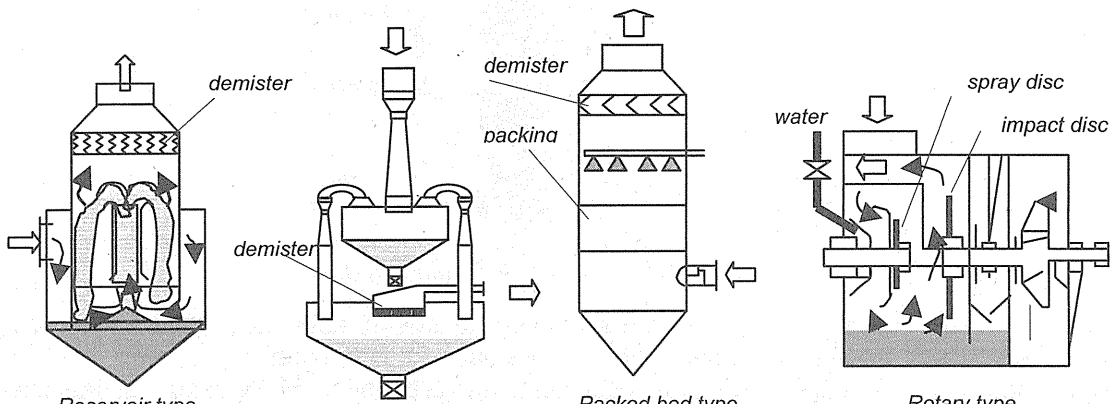
4-2 Scrubbing Dust collector

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.

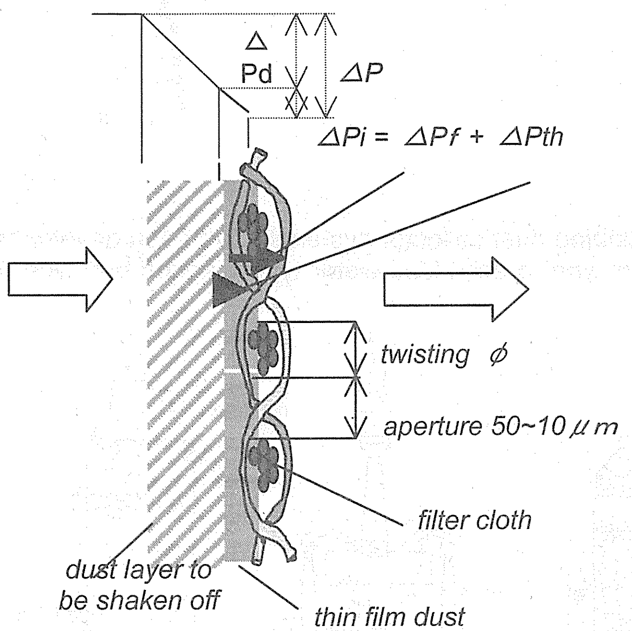
To achieve efficient performance of scrubbing dust collector, it is important to select a gas flow velocity and liquid to gas ratio suitable for the system.

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

4-3 Filter Type Dust Collector

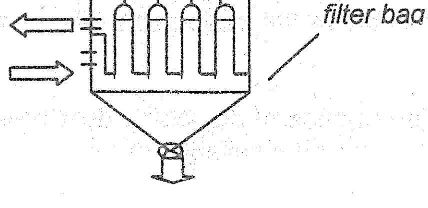
Principal types of filter type dust collectors are (1) the bag filter (2) the cartridge filter. The design of both is quite similar. However the bag filter is the more commonly used.
When gas contained dusts of certain particle sizes is passed through a filter cloth as shown in a slide, they adhere to 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.

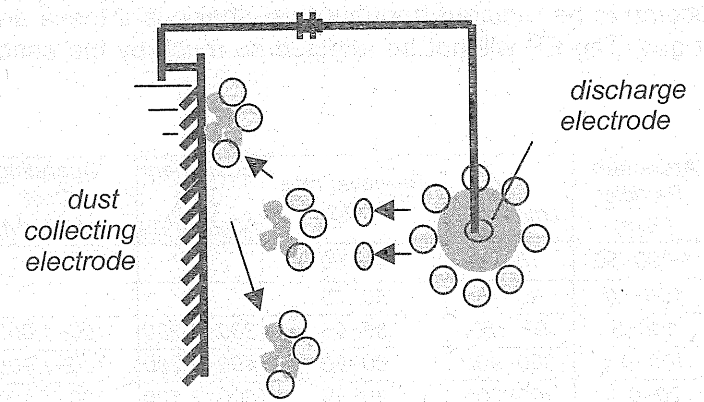
Type:	*Filter cloth:*	*Dust shake-off:*	*Apparent filtration rate:*
(1) bag filter	*(1) woven fabric*	*(1) intermittent*	*0.3~10cm/s*
(2) packed bed filter	*(2) nonwoven fabric*	*(2) continuous*	

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

4-4 Electrostatic Precipitator

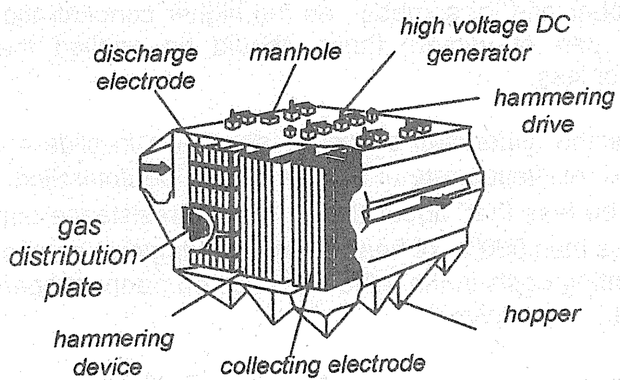
The electrostatic precipitators (EP) are used to remove very small liquid and solid particles from a gas stream. They operate by generating colonna discharge between high-voltage electrodes, usually a fine wire, and a passive earthed electrode, such as a plate or pipe. Particles passing through such 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 10^4~5×10^{10} Ωcm. The temperature should be less than about 250°C of heat resistance temperature of filter cloth for bag filter, and less than 500°C 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	$2NH_4OH+SO_2 \rightarrow (NH_4)_2SO_3+H_2O$ $(NH_4)_2SO_3+SO_3+SO_2+H_2O \rightarrow 2NH_4HSO_3+H_2$	$(NH_4)_2SO$
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.

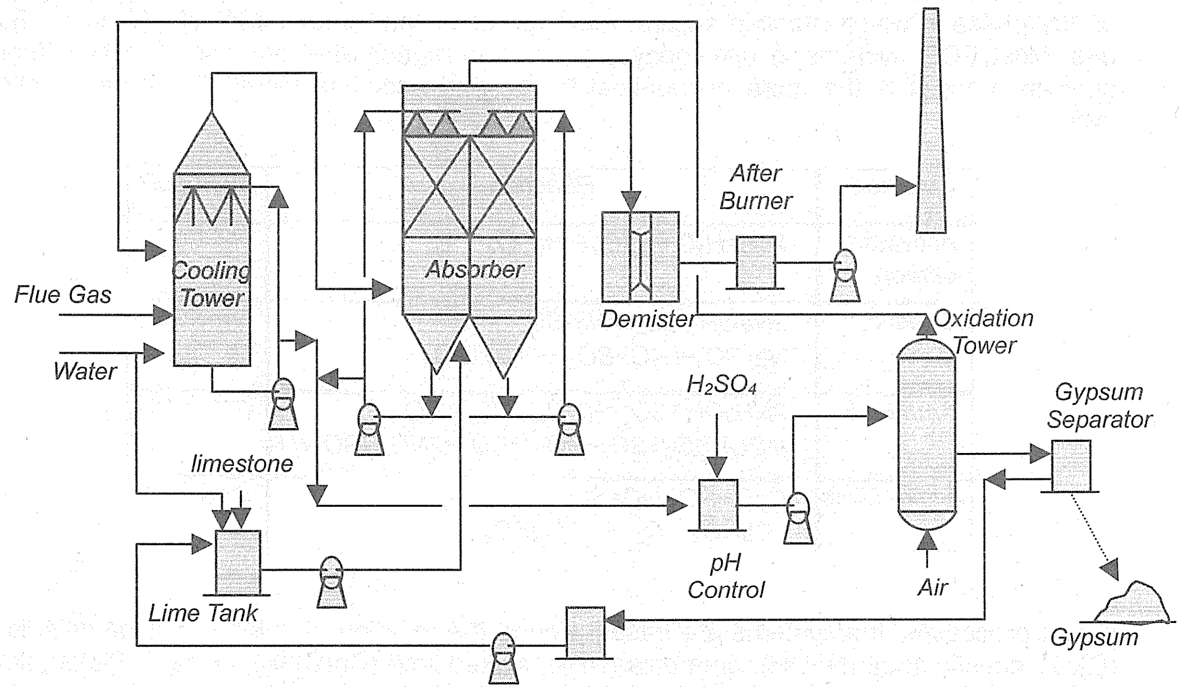
Limestone - Gypsum Process
SOx Rem. >90% ⟹ *most popularly used method In Japan*

- *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.

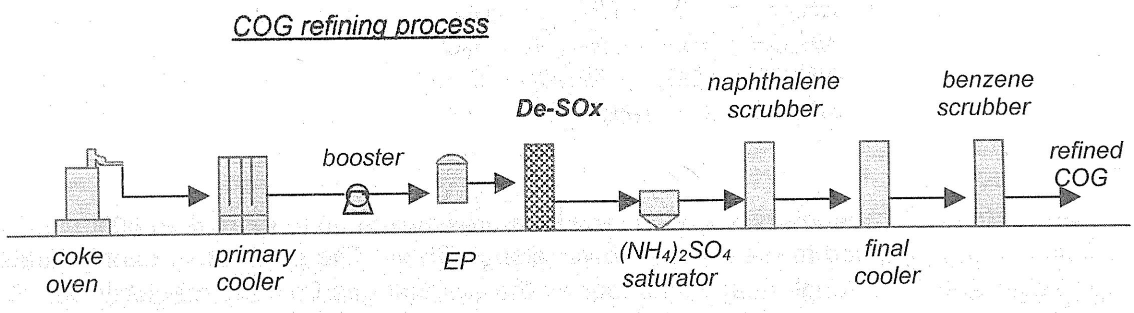
5-3 Coke Oven Gas Desulphurization Process

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.



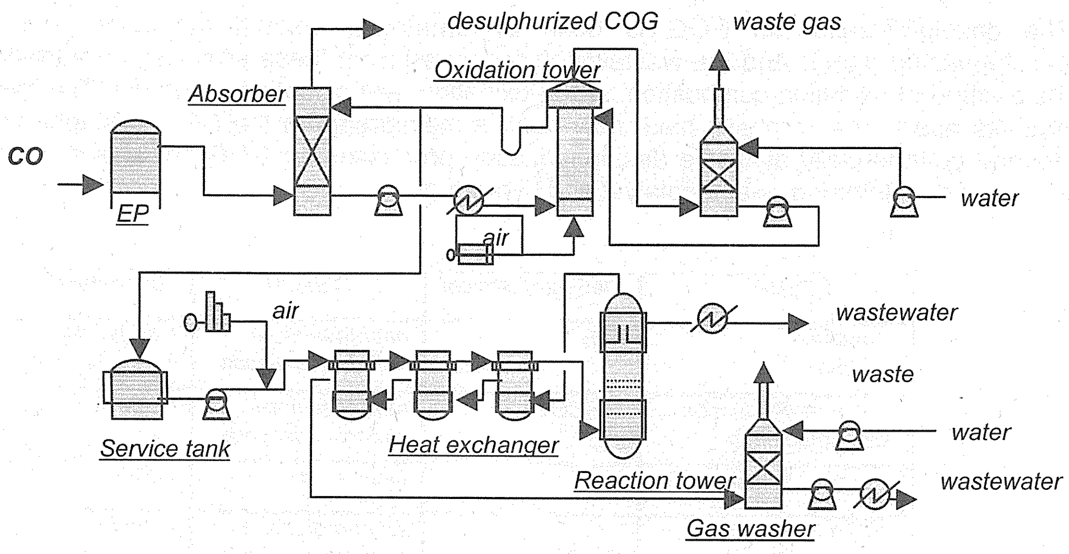
For the detail information, refer to the pages at P.188~189 or E.50~51.

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.

Takahax-Hirohax Process

Removal rate :S, CN > 90~99%



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

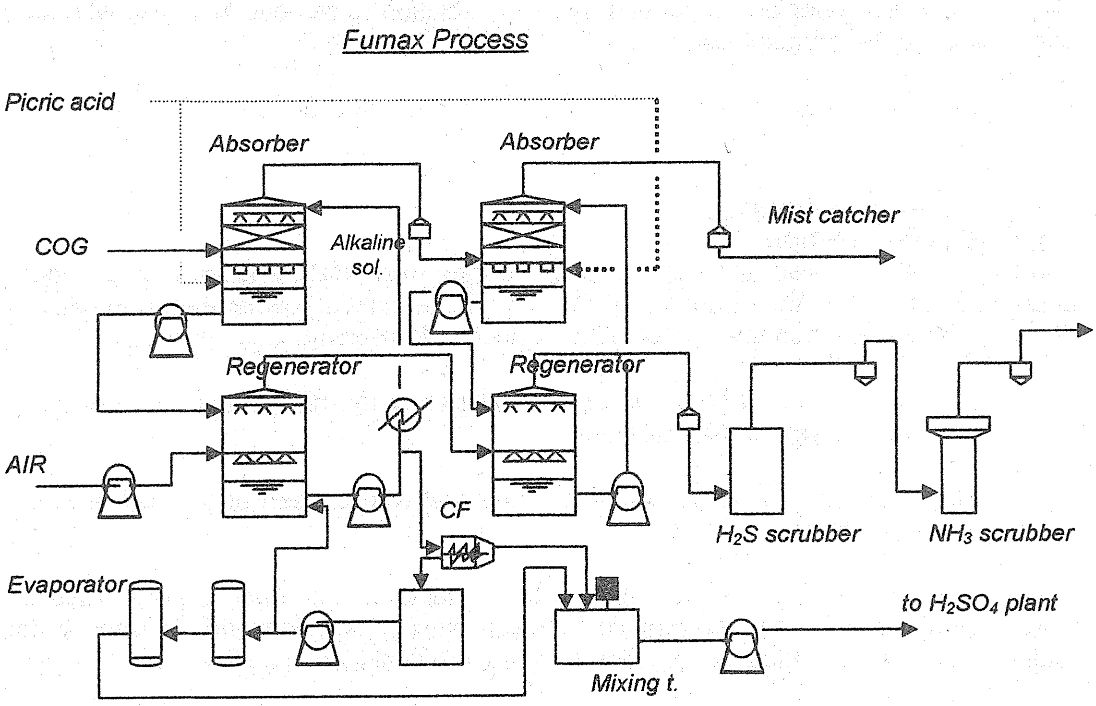
$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH + H_2S \rightarrow NH_4HS + H_2O$$
$$NH_4OH + HCN \rightarrow NH_4CN + H_2O$$
$$NH_4HS + 1/2O_2 \rightarrow NH_4OH + S$$
$$NH_4CN + S \rightarrow NH_4NCS$$

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.

<u>Absorption</u>

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

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.

<u>Regeneration</u>

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

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.

<u>H_2SO4 recovery</u>

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

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

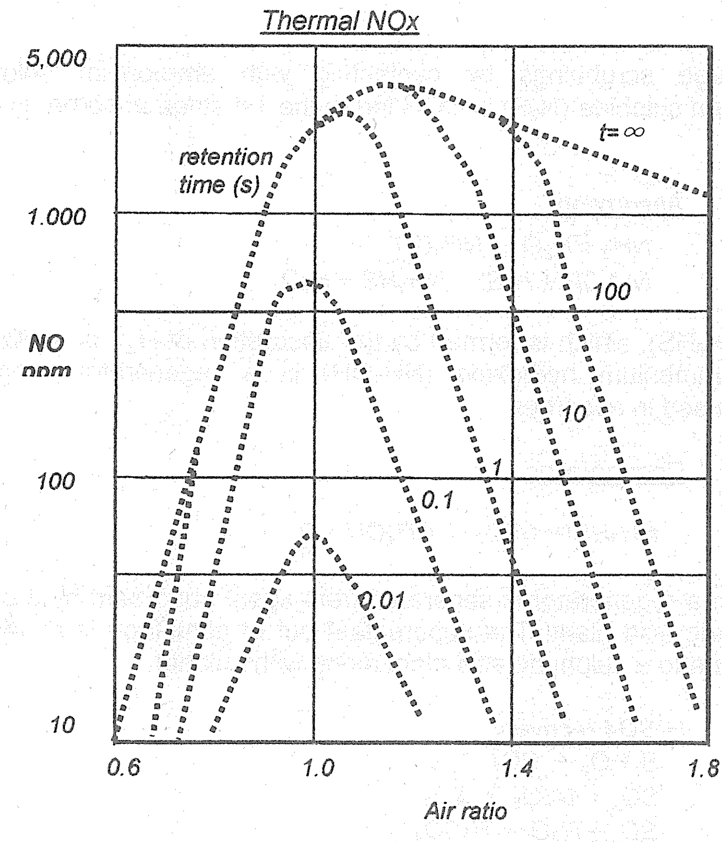
6-1-1 NOx Generation

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.



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/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

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

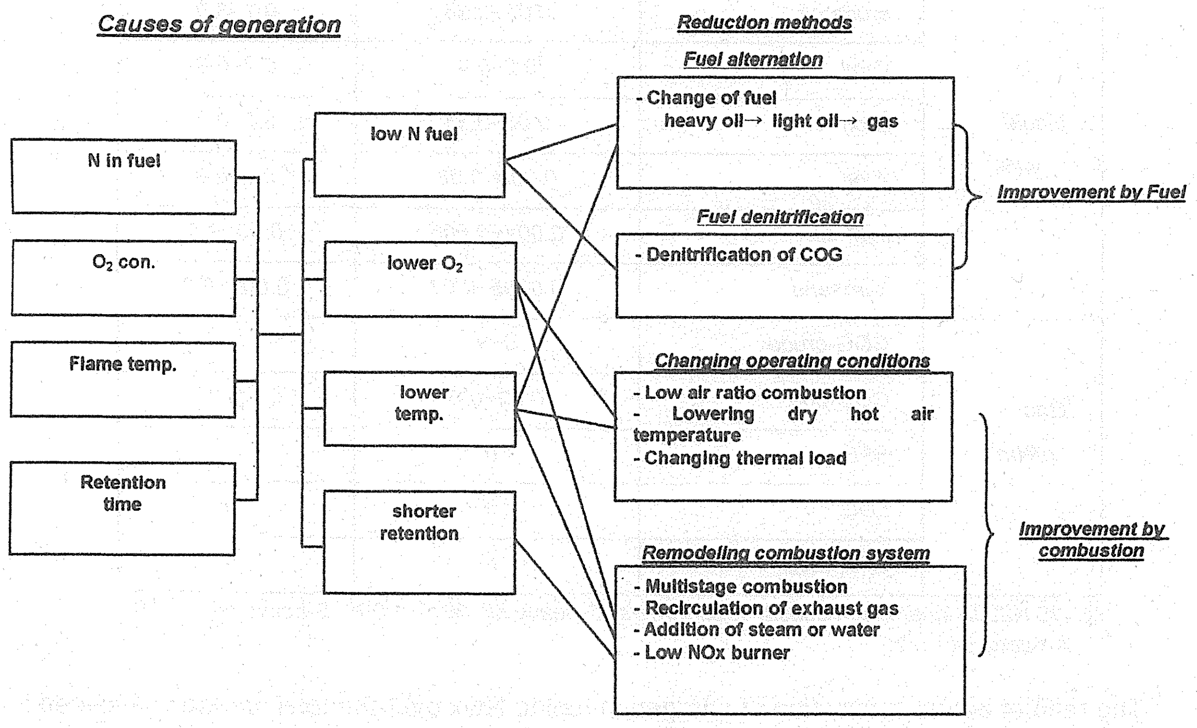
As measures to reduce NOx generation;

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 $\propto$ 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.

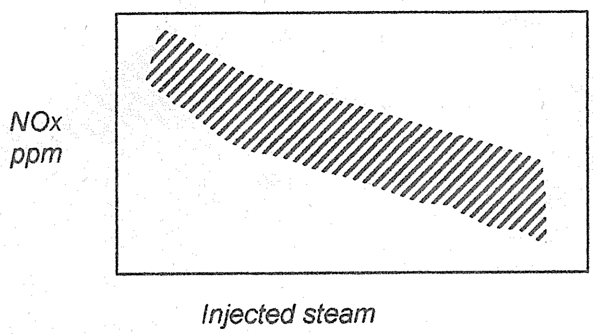
6-2-2 Combustion Improvement

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 — *1^{st} stage air ratio; 80~90%*
   rest air →2^{nd} stage combustion → NOx ≒▲20%

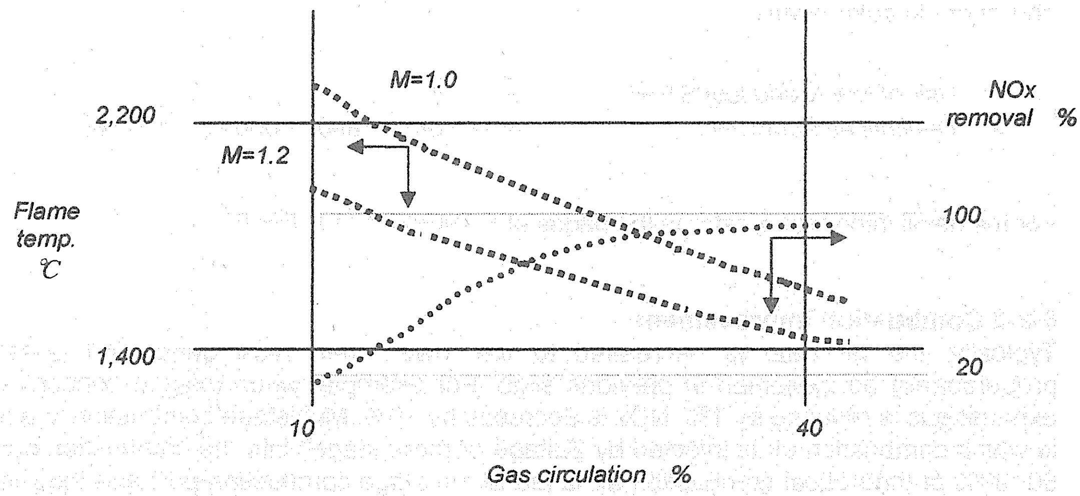
The figure shows the relations between a calories injected by steam and NOx generation.

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.

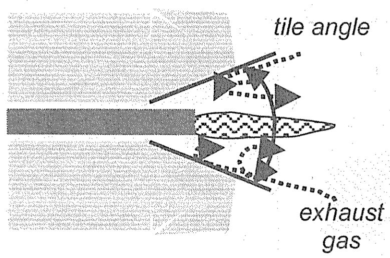
4. Exhaust gas circulation

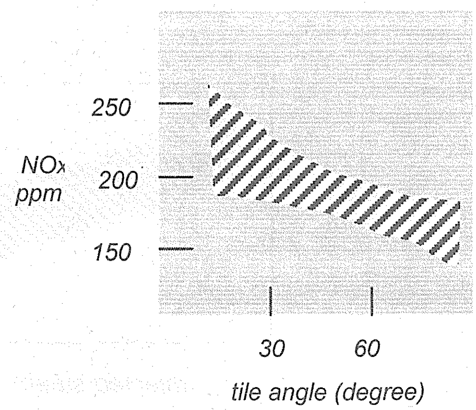


5. Low- NOx burner

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.

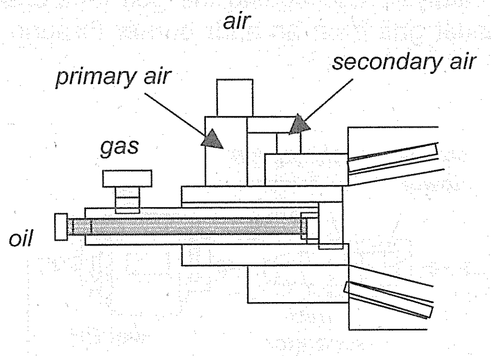
Wide-angle burner tile:
By widening the burner tile angle, the combustion exhaust gas near the tile is sucked within the tile angle by the kinetic energy of flame, by which the oxygen partial pressure of combustion air is decreased and simultaneously the flame temperature is lowered, leading to reduction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

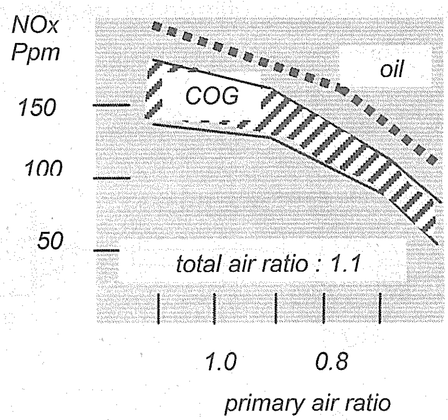




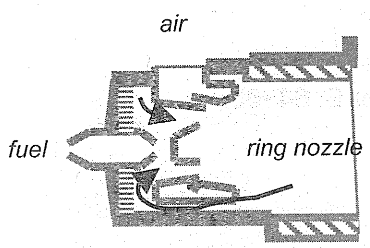
Double-stage combustion burner:
This is a method to provide a double-stage combustion in a burner so as to reduce the

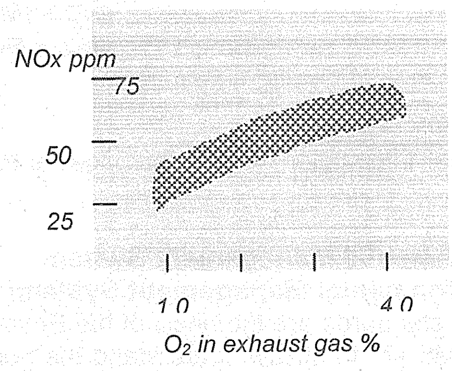
generation of NOx and , by forming a long flame, to lower the maximum temperature of the flame.





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.





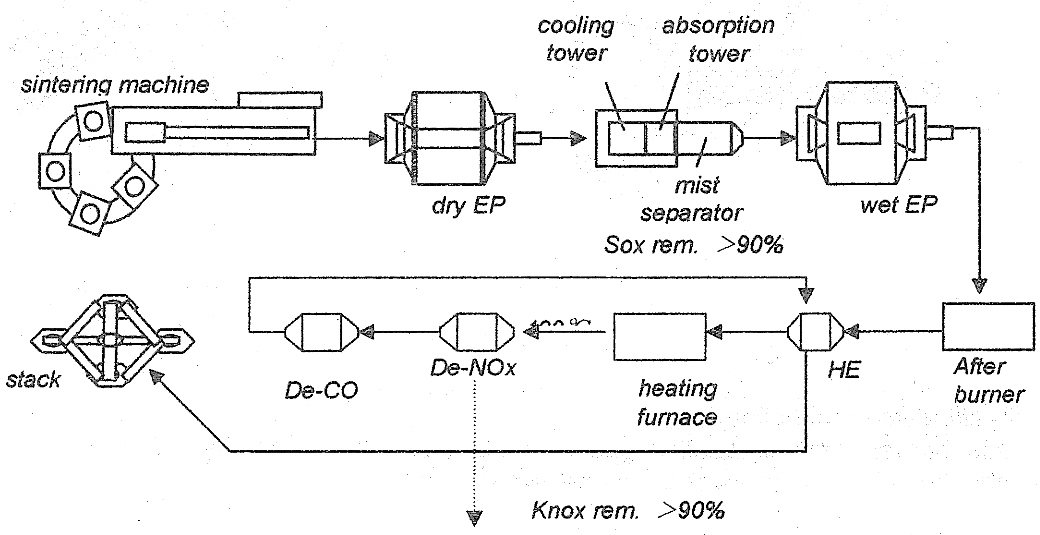
For the detail information, refer to the pages at P.196~202 or E.59~63.

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

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

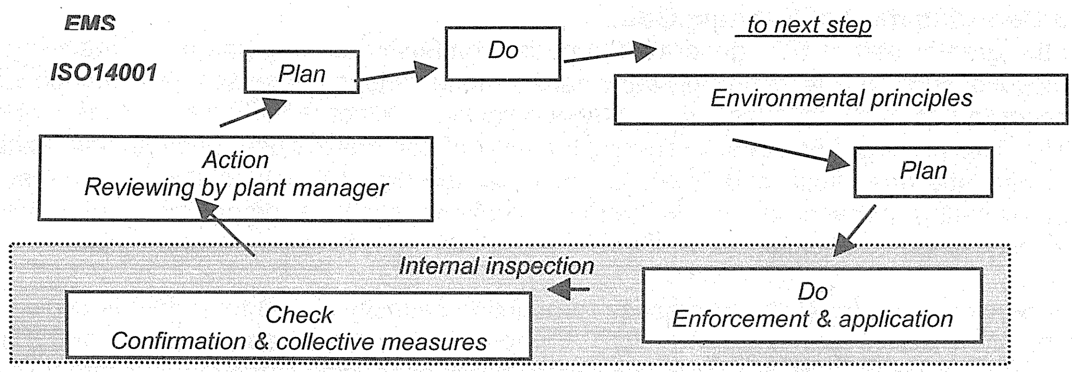
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

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.

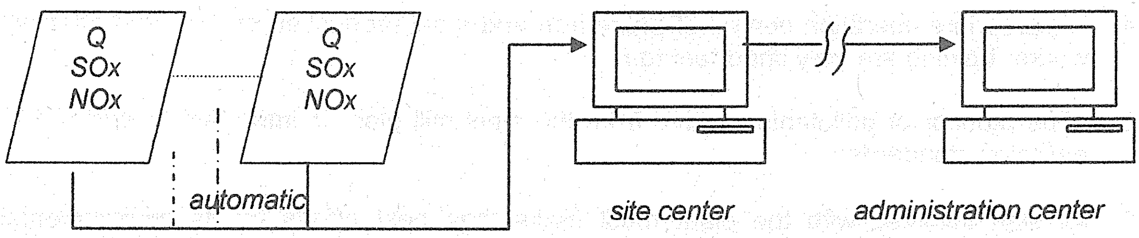
The air pollution quality monitoring in accordance with the Basic Environmental Law and the Air Pollution Control Law is broadly divided into two categories, one is the "monitoring emission quality" done by business, and the other is the "monitoring air pollution" done by local public corporation entities.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

Measurement Items

	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)

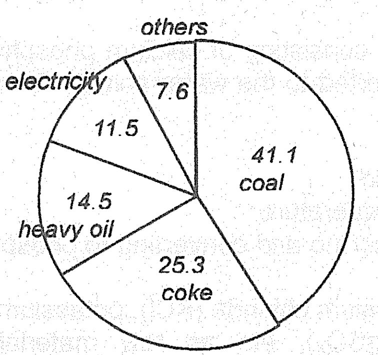
Process	Dry Dust Collector	Wet Dust Collector	Total
Material / Pig Iron	111,000	38,000	149,000 (61%)
Steel	33,000	60,000	93,000 (38%)
Rolling	2,700	300	3,000 (1%)
Total	146,700 (60%)	98,300 (40%)	245,000 (100%)

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

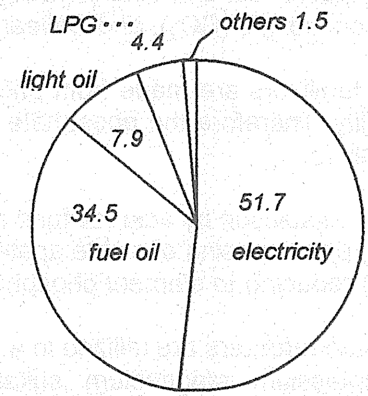
For the detail information, refer to the pages at P.205~206, E.67~68.

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.