

## 6.4 Metal Refinery

### 6.4.1 Introduction

Generally, the iron buried as oxides is a very important metal for the life of humankind, and the scale of its refinery process is very large. Also, the copper buried mainly as sulfide is important, and the scale of its refinery is relatively large too. Both processes have been the source of air pollution. Fluorine is used in the refinery of aluminum and chlorine is used for titanium and silicone. These are also causing air pollution problems.

### 6.4.2 Integrated Steel Works

#### (1) Ore

The earth is a planet abundant in iron, and hematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), etc. are used for the iron refining<sup>1)</sup>. Also, coal is required for the process, but Japan has little natural resources and is dependent on the import for those raw materials. Further, other materials such as limestone are also required, and the integrated steel work is usually provided with port facilities.

#### (2) Facility Outline<sup>2-4)</sup>

Large scale production of iron has been started since the invention of the blast furnace in the 15th century. At first, charcoal was used as reduction agent, and the lack of charcoal was a restriction for iron refining by the blast furnace, because forests were cut down. In 18th century, the desulfurization of coal by coaks oven became possible. So, today, a large scale integrated steel works with blast furnaces for iron refining using coal coke as reduction material which annual production capacity of, for example 12 million tons became possible to operate. And these integrated steel works consist of the material facilities and as the sintering furnace and coaks oven, the blast furnace and its associated facilities, the steel refining facility from pig iron such as converter or open-hearth furnace, the work furnace to make steel sheets or pipes, and the system for transportation and energy supply and control that connect with each other. Japan is the largest iron manufacturing country in the world with annual production capacity of 180 million tons of total iron and is refining 100 million tons of steel.

#### (3) Blast Furnace<sup>2-4)</sup>

The blast furnace is a symbol of the integrated steel works, and visitors of the plant will be deeply impressed by its sight rising high among other facilities. The blast furnace is, as shown in Fig.6.4.1, a tall cylindrical furnace, a little thicker at the lower part. It is consisted of a main body made by steel outer plate lined with brick its inside and a hot blast stove that sends hot air to the main furnace. A large blast furnace with a production capacity of 4,000 tons of pig iron per day is now in operation. Generally, the daily production rate of the blast furnace is about 0.8-1.0 ton per  $1 \text{ m}^3$  of inner volume of the furnace. The raw materials such as iron ore (sintered ore), coke, lime, fluorite, etc. are thrown in from the top of the blast furnace, and air, heated to about  $700^\circ\text{C}$  by a hot blast stove, is blown into the furnace from a lower tuyere to promote reduction reaction in the furnace. The blast furnace gas, mainly

composed of carbon monoxide, which is generated in the furnace and has a calorific value of about  $1,000 \text{ kcal/m}_N^3$  is used as a fuel for the hot blast stove.

A reduction environment is produced in the blast furnace, and there occurs such processes as the reduction of iron ore and melting of generated iron, the melting of limestone and fluorite and the dissolution of impurities such as sulfur and phosphorus contained in the melted iron into the melted limestone and fluorite. The separation of them occurs as heavy melted iron sinks to the bottom of the furnace and melted limestone rises over it. The temperature inside the furnace is about  $1,600^\circ\text{C}$ , and the situation resembles well with that of the age of first segregation of the earth when it was hot and the central core, mantle and crust were formed. The melted iron (pig iron) accumulated in the bottom of the furnace is taken out from a tap hole at the lower part of the furnace 5-7 times a day, and then the molten limestone (slag) floating over molten pig iron is also brought out from a slag hole alternately. Besides the exhaust gas from the hot blast stove, air pollutants discharged from the blast furnace include dust and fume formed when taking out the pig iron and slag and the leak from the furnace top. The concentration of nitrogen oxides in the exhaust gas of hot blast stove is 6.27-1.11 ppm converting to 0% oxygen when the blast furnace gas is used as a fuel, and is 34.8-97.7 ppm when the mixture of the blast oven gas and the coke furnace gas is used as a fuel <sup>2)</sup>.

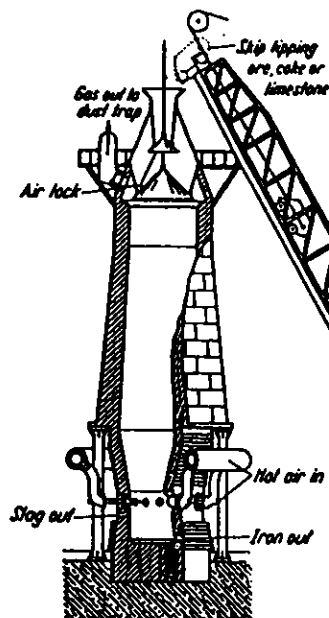


Fig.6.4.1 Blast Furnace

#### (4) Cokes Oven <sup>2)4)</sup>

The cokes oven is a facility to obtain coke by carbonization of coal, and is made of bricks. It is composed of a carbonization part and a combustion part. Coal is charged into the former and the coke furnace gas generated in it is burnt in the latter to make coke through heating and carbonization while shutting down the air.

About a hundred coke furnaces are usually constructed side by side, each of which the size of carbonization part is 400-450 mm wide, total length 8-6 m, total height 4-6 m and the amount of charged coal 8-27 tons. The temperature of combustion part is about  $950-1,300^\circ\text{C}$  and the coal is made into coke in 14-24 hours <sup>2)4)</sup>. The wet

quenching method has been used before in which coke is pushed out from each oven one by one and quenched by sprayed water, but the dry quenching method is recently used that quenches coke by taking it out into a steel vessel and quenching it with nitrogen gas under a tightly closed condition. The latter method has advantages because thermal energy can be recovered and the discharge of dust from steam exhaust does not occur. Besides dust produced at the wet quenching process, air pollutants from the combustion of cokes oven gas are generated in this method. Sulfur oxides is not produced in the combustion part of cokes oven gas as it is well refined, and also dust is not produced because the process is a gas phase combustion. However, the nitrogen oxides is a problem. There is data that the concentration of nitrogen oxides in the cokes oven exhaust gas is about 284-1,844 ppm when the coke oven gas is used as a fuel periodically in accordance with a cycle of taking out coke from the furnace.<sup>2)</sup>

#### (5) Sintering Furnace Machine <sup>2) 4)</sup>

The shape of iron ore for iron refining is not always uniform, and much powdery ore is also included. Therefore, the temperature distribution in the blast furnace becomes not uniform and the ventilation of the furnace is deteriorated if the raw iron ore is introduced in the furnace as it is. Furthermore, sulfur contained in the iron ore enters into the pig iron and also deteriorates its characteristics. Accordingly, the ore is sintered so that the raw materials are utilized efficiently by adjusting their particle size and improving the ventilation of the furnace, and sulfur is removed. In the sintering process, powder ore, sulfuric acid slag, iron sand, mill scale, blast furnace dust, scrap, etc. are mixed with limestone, converter slag, etc., and coke is also mixed in them as a fuel. The mixture is sent into one end of the sintering furnace, and transferred through it on the belt of the pallet that travels between two sprockets. It is quenched by air when the belt moves to the other end of the sintering furnace and the sintering process is completed<sup>2) 4)</sup>. The primary air pollutant emitted from the sintering process is oxides of sulfur, and about 71% of sulfur contained in the raw iron ore is discharged as sulfur oxides. This amount corresponds to a major part of the discharge of sulfur oxides from the integrated steel work, and its concentration is said to be about the same as that of the exhaust gas from heavy oil combustion<sup>4)</sup>. Also, there is data that the amount of nitrogen oxides discharged, when converted to NO<sub>2</sub>, is 76.2-369 kg per 1 ton of ore sintered<sup>2)</sup>.

#### (6) Converter, Heating Furnace, Etc. <sup>2) 4)</sup>

In the integrated steel work, there are many combustion facilities including the converter, open-hearth furnace, electric furnace, working furnace for steel, and boiler. The converter, shown in Fig. 6.4.2, is a pear-shaped furnace with an opening on the top, and is a typical facility in the integrated steel work along with the blast furnace.

As shown on the left of Fig. 6.4.2, it can be tilted to take out the melted steel and slag in its inside. In the basic oxygen process of steel manufacturing, which succeeded to improve the efficiency and is shown in Fig. 6.4.2 for the case of an upward oxygen blowing converter (LD converter), fine iron oxide fume of about 0.2  $\mu$  m in diameter is discharged, and the release of red cloud of high concentration, as high as 70-80 g/m<sup>3</sup>, rising high in the sky, has attracted much attention. However, this problem is almost solved by the dust collector at the present, and it is highly appraised as a great achievement of air pollution measures in the steel industry. In other cases of air pollution measures in the integrated steel work, the electrostatic precipitator and desulfurization/denitration equipment have been successfully applied. In Japan, high quality steel products can be refined quickly in the LD

converter, and the open-hearth furnace is not used now.

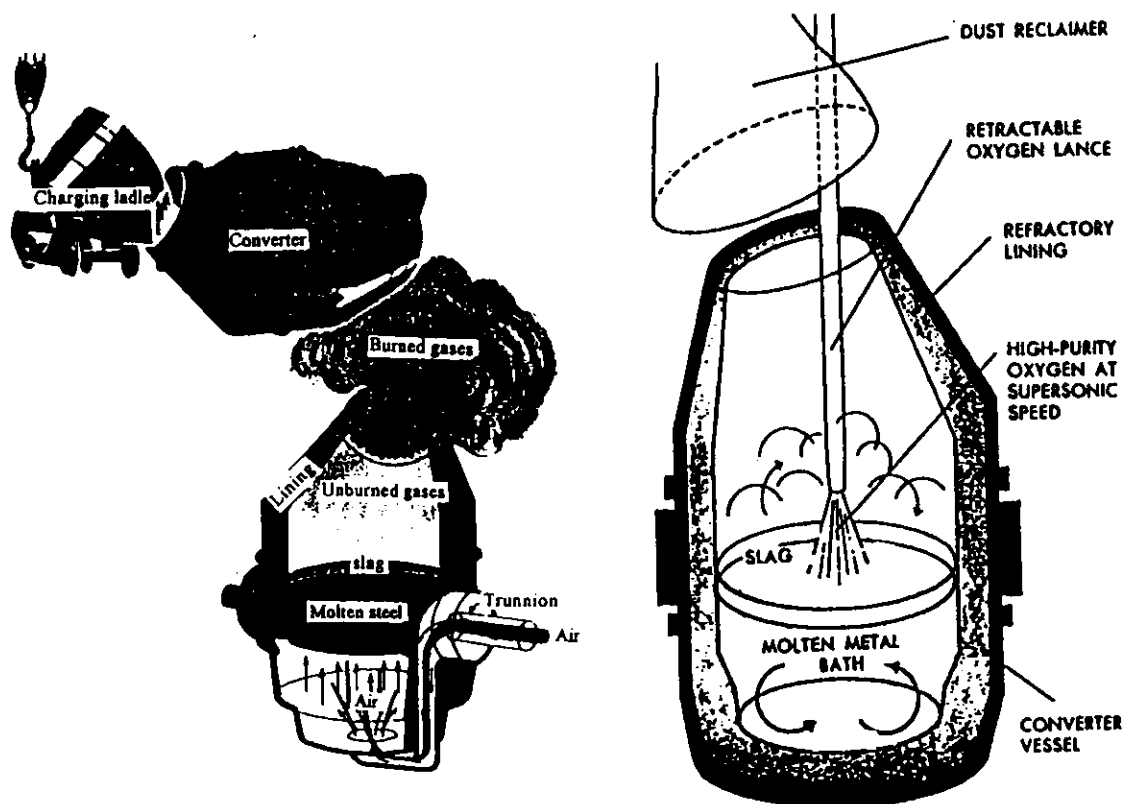


Fig. 6.4.2 Converter Furnace

### 6.4.3 Copper Refinery <sup>5)</sup>

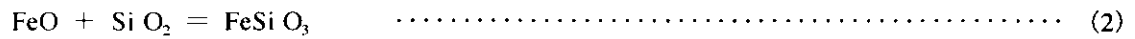
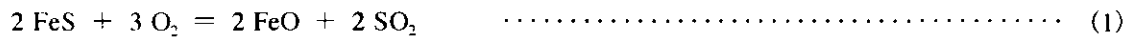
Copper is most abundantly mined as sulfide ore such as iron containing chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ) and covellite ( $\text{CuS}$ ), although it is also mined as native copper ( $\text{Cu}$ ) or cuprite ( $\text{Cu}_2\text{O}$ ) <sup>1) 5)</sup>. As a content of copper in the copper ore is very small, the refined ore obtained by flotation process to separate useful ores from the mother ore is dried and roasted in the multi-stage roasting furnace to burn excess sulfur, arsenic, antimony, etc.. In this process, all of the copper and most of the sulfur combined with iron are retained in the ore and excess sulfur is discharged in the atmosphere as sulfur dioxide. Then, the roasted ore obtained from the roasting process is heated and melted in the reverberatory furnace or self-melting furnace at  $1,370\text{-}1,500^\circ\text{C}$  by burning coal or heavy oil. Impurities are removed as a slag and the copper content is increased.

Through this process, copper is converted to cuprous sulfide and iron to ferrous sulfide. Those are melted together to form a matte containing 38-45% copper. Then, this matte is changed into the converter along with silica and alumina.

In the first stage of the converter process, ferrous sulfide is oxidized by air blown into the converter, and sulfur dioxide is formed. This sulfur dioxide then combines with silica and alumina to form a slag, and pure cuprous sulfide is left in the bottom of the furnace.

The slag is removed by tilting the converter, and then refining is continued by raising it upright. Cuprous

sulfide is decomposed to remove sulfur as sulfur dioxide, and the melted copper in the furnace is taken out. Major chemical reactions in the copper refining process are shown in Eq. (1) to (3). Blister copper obtained in the converter is further refined by electrolytic refining to obtain pure copper <sup>5)</sup>.



Major air pollutants from the copper refinery process are sulfur dioxide and particles. In the exhaust gas of the self-melting furnace, 20-30 /m<sub>N</sub><sup>3</sup> of particles are contained and collected by the cyclone or electrostatic precipitator.

#### 6.4.4 Zinc Refinery

The major ore containing zinc is zinc blende (ZnS), so zinc is also mined as a sulfide ore like copper. In the refinery of zinc blende, the refined ore obtained through the concentration process is roasted to remove sulfur as sulfur dioxide, as shown in Fig.6.4.3. As sulfur dioxide is an air pollutant, it is used to manufacture sulfuric acid. However, if its concentration is small, it is converted to plaster by the exhaust gas desulfurization equipment. Zinc is then sent to the exuding/dissolution process and refined by electrolysis as Fig.6.4.3.

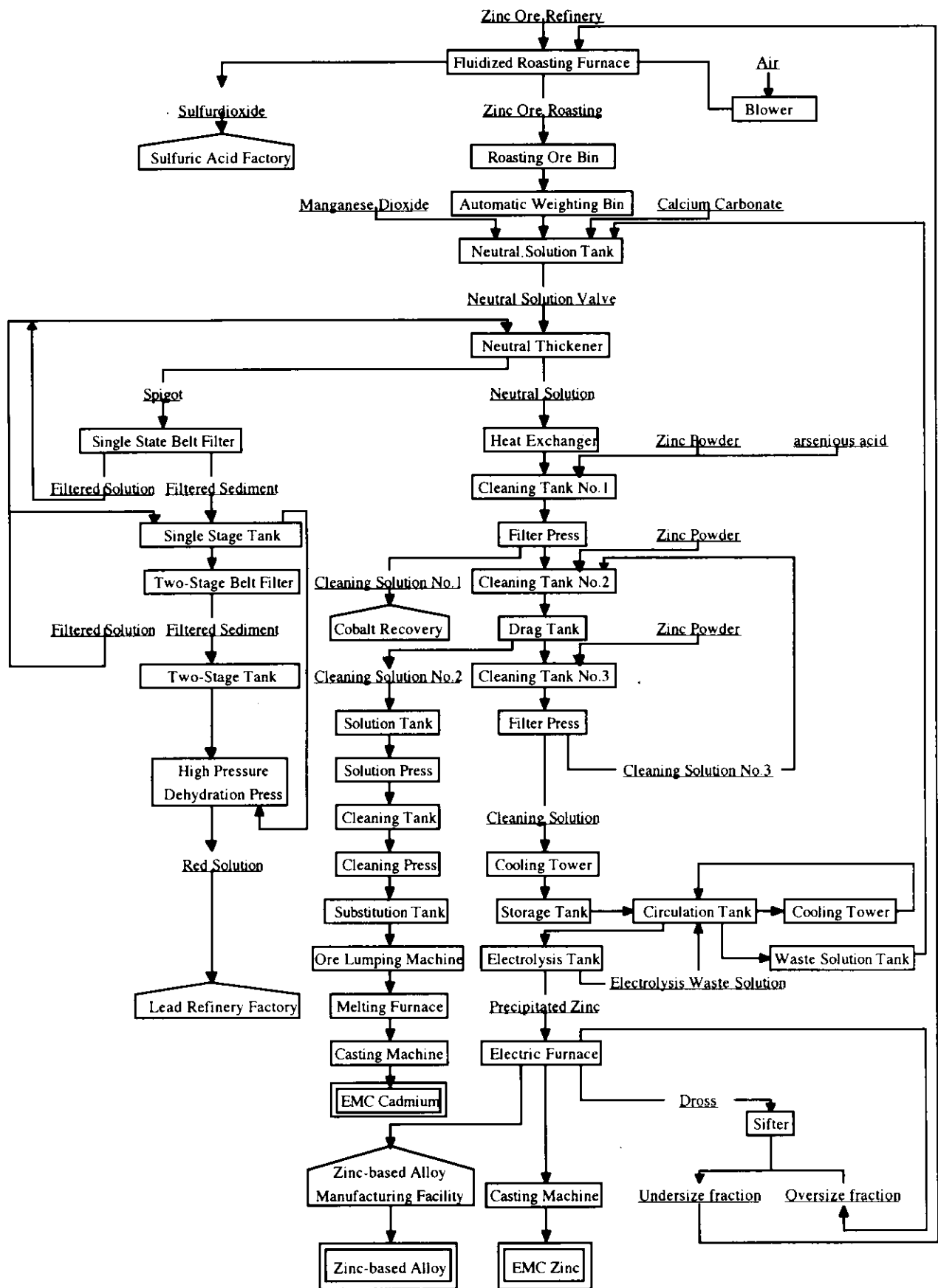


Fig.6.4.3 Zinc Refinery

#### 6.4.5 Aluminum Refinery <sup>6)</sup>

The major ore for aluminum production is bauxite ( $\{HAlO_2\}_2 \cdot H_2O = Al_2O_3 \cdot 2H_2O$ ) <sup>1)</sup>.

Bauxite is converted first into sodium aluminate by dissolution process with sodium hydroxide solution. Then, alumina ( $Al_2O_3$ ) is obtained by Bayer process, in which aluminum hydroxide obtained by hydrolysis of sodium aluminate is calcinated, and it is then refined by electrolysis under the bath of molten salt containing fluorine. This process had been widely used in Japan before, but is now almost abandoned since the energy crisis because the price of electricity increased. The refinery has been transferred to overseas, and the domestic work of aluminum industry is restricted to only working process now.

This refinery work has discharged hydrogen fluoride in the molten salt electrolytic process and caused air pollution problems. The electrolytic refinery is proceeded by melting alumina in the high temperature molten bath of cryolite ( $AlF_3 \cdot 3NaF$ ), which is a double fluoride of aluminum and sodium, and running the electricity between cathode (carbon) placed in the lower part of electrolytic furnace and carbon anode inserted into the upper part of the furnace. Here, the operating voltage is 4.7 volts and the temperature of electrolysis is about 950°C. The anode is oxidized and consumed by oxygen contained in alumina. Either the soderberg type anode which is forming an electrode by burning carbon paste or the Prebake type anode which uses an electrode burned in advance is used. The amount of air pollutants emission is less for the latter type. The specific weight of molten bath at melted condition is 2.08-1.96, and that of aluminum is 2.28-2.24. Thus, the aluminum generated is separated from the molten bath. Carbon monoxide, tar, alumina particles, and hydrogen fluoride are generated in this process, and, for example, it is reported that 40 mg/m<sup>3</sup> of hydrogen fluoride, 100 mg/m<sup>3</sup> of tar, 90 mg/m<sup>3</sup> of particles are contained in the exhaust gas of the electrolytic furnace and are controlled <sup>6)</sup>.

#### 6.4.6 Refinery of Titanium and Silicon

Titanium is a super heat resisting metal with an excellent anti-corrosion characteristics, and its alloy is used as a material for gas turbine blade. Also, silicon, germanium, and zirconium are quite useful as a material for semiconductors and special purpose materials. Those elements are easily combined with chlorine to form chloride, and the chlorides of these elements are refined by hydrogen reduction after removing impurities through distillation. Primary air pollutant emission by those refinery processes is chlorine.