6.3 Chemical Process

6.3.1 Introduction

The chemical industry is an essential factor for the prosperity of humankind, but it has been causing many air pollution problems because it deals with various chemical substances. As the kind of chemical industry is diverse, only some typical examples of incidence of the emission of air pollutant will be described below.

6.3.2 Cement Industry

Dust scattering from the cement industry has been often a subject of claims. Cement is a generic name of inorganic colloid containing plaster, lime, magnesia, volcanic ashes, etc. The currently so called cement is the Portland cement or the mixed cement, which is mainly composed of the former, and its manufacturing method is summarized as, "to thoroughly mix mainly lime material and magnesia material in proper proportion, then to obtain clinker by firing it until part of it will melt, and to pulverize or crush it while adding some gypsum." There are a dry process and a wet process in the manufacturing method of cement.

(1) Dry Process

In the dry process, lime stone and clay are dried by a rotary dryer, such as shown in Fig. 6.3.1, until their water content becomes less than 1%. Then, mixing them at an appropriate ratio considering their composition, the clinker is produced by firing them in the rotary kiln. The heat source of the rotary dryer is the combustion gas of coal or oil, and the raw materials is continuously fed into one end of the cylindrical rotary furnace and the dried material is brought out from the other end. In this case, the exhaust gas of the rotary kiln is sometimes used as a heat source. Dried materials for cement is then continuously fired in the rotary kiln, shown in Fig. 6.3.2, which is made of a steel cylinder, lined with fire bricks and inclined by 3-5 degrees from the horizontal. That is, the materials fed from the upper end of the kiln will move downward in the furnace which is rotating at 1-2 rpm, and burned at the lower end at a temperature of about 1,450°C for 1-4 hours until they are partly melted. The cement clinker formed will be discharged from the lower end of the kiln at a temperature of about 1,100°C.

Heat is recovered by the boiler and suspension heater attached to the kiln. The rotary kiln, shown in Fig. 6.3.2, is attached with a suspension heater that exchanges heat by flowing the materials and burnt gas through a chain of several cyclones. The rotary kiln is the largest source of air pollutant in the cement industry, and generates air pollutants such as cement dust, sulfur oxides, nitrogen oxides and heavy metal fumes.

(2) Wet, Lepol Process

In the wet process, the product is manufactured by crushing and mixing the materials as a slurry of about 35% water content, without drying, with ball mill or compartment mill, and burning with the rotary kiln.

In the Lepol process, 10-14% of water is added to the material obtained from the mixing process of the dry process, and pellets of 2.5-5 cm in diameter are made by the pelleting machine. Then the pellet is dried and fired
by the exhaust gas of the rotary kiln to obtain clinker.

Fig. 6.3.1 Rotary Dryer

Fig. 6.3.2 Rotary Kiln
(3) Cement Manufacturing

The clinker obtained from the burning process using kiln is cooled to a room temperature by the air quenching cooler, and then cement is obtained by adding 4-6% of gypsum and crushing them with a ball mill or a tube mill. Here, the gypsum is added as a coagulation retarder for the cement. The cement industry is attracting attention, because it acts as a receiver of gypsum obtained by desulfurization plant for flue gas with excellent environmental stability, as described in Chapter 7, and also it uses scrapped tires as a fuel or flyash as a raw material.

(4) Air Pollutants

The major air pollutant in this industry is the dust generated from processes such as crushing and mixing, silo storage, transportation, burning process, and drying, and the sulfur oxides and nitrogen oxides are also generated from the rotary kiln and rotary dryer. Particularly, the concentration of nitrogen oxides in the exhaust gas of the rotary kiln is quite high. The pollutant, that is attracting much attention recently, is the particle, and it is presently handled by the electrostatic precipitator. The sulfur oxides due to fuel containing sulfur are absorbed by the raw materials for cement, and the ash enters into the cement if coal is used as a fuel. The concentration of dust from the rotary kiln in the dry method is 25-130 g/m³ and the dust is collected by the electrostatic precipitator.

In the case of the wet process, it is reported that the dust of 84.5 g/m³ discharge concentration has been processed by an electrostatic precipitator to achieve the collection efficiency of 97.8%. Also, there is data that, in the case of rotary dryer, the dust collection efficiency is 99.93% for the exhaust concentration of 42.9 g/m³. Also, data is reported that the concentration of nitrogen oxides in the exhaust gas of the rotary kiln is 158-1,469 ppm for the dry process and 503-1,927 ppm for the wet process, converting to the concentration for 0% oxygen.

6.3.3 Sulfuric Acid Industry

In the production of sulfuric acid, the contact process is adopted. In this process, the elemental sulfur is oxidized by air to sulfur dioxide, then the latter is oxidized to sulfur trioxide using vanadium pentoxide as a catalyst. Then it is made into contact with sulfuric acid to obtain highly concentrated sulfuric acid. Sulfur oxides has been obtained by burning iron sulfide before, but is now obtained by the method using elemental sulfur which is a byproduct of desulfurization of the heavy oil.

The primary chemical reaction of this process proceeds as Eq.(1) to (3) below:

\[
S + O_2 = SO_2 \hspace{2cm} (1)
\]

\[
2SO_2 + O_2 = 2SO_3 \hspace{2cm} (2)
\]

\[
SO_2 + H_2O = H_2SO_4 \hspace{2cm} (3)
\]

The major air pollutants produced are sulfur dioxide and acid mist, and the amount of sulfur dioxide emission is about 20-70 pounds (1 pound is equivalent to 0.4536 kg) per 1t of acid production, and that of acid mist is 0.3-
7.5 pounds per 1 t of acid production if there is no removal system. However, the latter is reduced to 0.02-0.2 pounds if the removal system is installed. 4,5

6.3.4 Nitric Acid Industry 4,5

In the production of nitric acid, a method using ammonia as a raw material is adopted. In this process, ammonia is oxidized by air in high temperature to form nitrogen monoxide, at the existence of platinum catalyst. Nitrogen dioxide, obtained by oxidizing the mixture of this nitrogen monoxide and air, is then absorbed into the water to form nitric acid. The primary chemical reactions of this process are shown in Eq.(4) and (5): 5

\[
4 \text{NH}_3 + 5 \text{O}_2 = 4 \text{NO} + 6 \text{H}_2\text{O} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (4)
\]

\[
3 \text{NO}_2 + \text{H}_2\text{O} = 2 \text{HNO}_3 + \text{NO} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (5)
\]

The major air pollutants emitted from this process are nitrogen monoxide and nitrogen dioxide exhausted from the absorption tower. The amount emitted is, converting it to nitrogen dioxide, about 57 pounds per 1 t of 100% nitric acid production. Besides, it is reported that about 10 pounds of nitrogen dioxide equivalent per 1,000 pounds of strong acid production is discharged from the nitric acid concentrator.

The removal efficiency of a catalytic burner for processing the exhaust gas from the absorption tower is reported as 36-99.8% with average 80%, and that of an alkali scrubber is reported as 90%. 4,5

6.3.5 Chlorine Production 4,5

Chlorine is produced by the electrolysis of sodium chloride water solution, and it is formed at the positive electrode. Fig.6.3.3 shows a schematic of the diaphragm method. High temperature chlorine formed is cooled, and then washed by nitric acid to dry. It is then liquefied and shipped. Major cause of chlorine release is the discharge of gas that is not liquefied. When there is no protection system, the amount of chlorine emission is 2,000-16,000 pounds per 100 t of liquefied chlorine production for the mercury method (concentration of 20-50 ppm), and 2,000-10,000 pounds for the diaphragm method. Other than that, it is reported that 400 pounds of chlorine is discharged from the water absorption tower, 450 pounds from the vent hole of tank trucks, and 1,200 pounds from the vent hole of storage tank. 4,5

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Fig.6.3.3  Process of Sodium Chloride Water Solution Electrolysis