7.7 Flue Gas Desulfurization Equipment and By-Products

In Japan, the rapid popularization of flue gas desulfurization equipment began in the 1970's. Environment Agency calculations in 1993 showed that 2,140 such units were in operation, processing a total raw gas flow of 217 million $m^3{}_N/h$.

Flue gas desulfurization is categorized into two separate procedures, the wet method and the dry process. The majority of equipment which is currently in operation utilizes the wet method. The desulfurization ratio of the wet method is effective. Stable desulfurization results are obtainable even in conditions of load fluctuation. Technically it is a well established method. The lime gypsum method is the main technique used for large capacity power plant boilers, such as coal fired thermal power stations utilized by electric companies. For independent power plant boilers used for general industrial purposes, the magnesium hydroxide method is widely used.

Table 7.7.1 illustrates the different types of flue gas desulfurization methods in use or under development and their related by-products.

The following sections describe major desulfurization processes, their unique characteristics and their by-products.

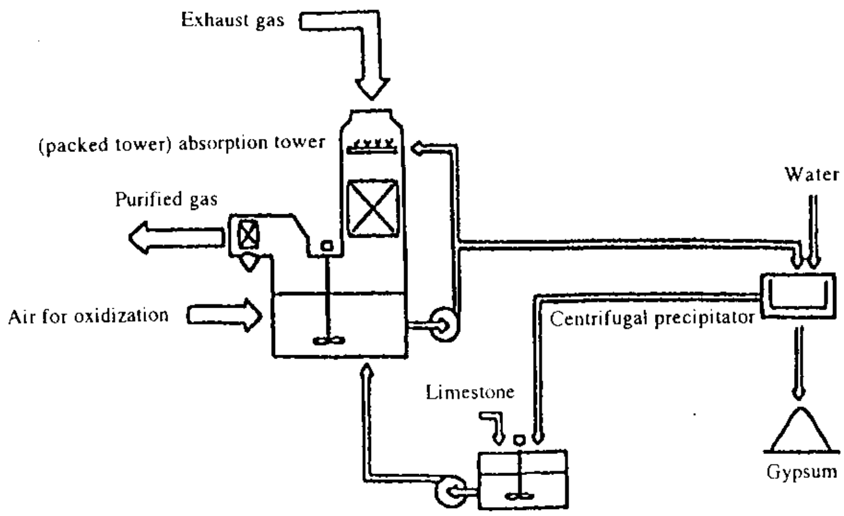
Table 7.7.1 Desulfurization Process and By-products

Process	Absorbing Agent	By-products	Usage
Lime gypsum Method	Limestone Slaked Lime	Gypsum	Gypsum Board Cement
Magnesium Hydroxide Method	Magnesium Hydroxide	Magnesium Sulfate	Discharge
Ammonia Method	Ammonia	Ammonium Sulfate	Fertilizer
Electron beam Method	Ammonia	Ammonium Sulfate	Fertilizer
Sodium Method	Sodium Hydroxide	Sulfur Soda Mirabilite	Pulp Dispersion Agent Chemicals
Simple Desulfurization Methods	Limestone, Slaked Lime	Gypsum + Coal Ash	Soil Melioration Agent Roadbed Agent

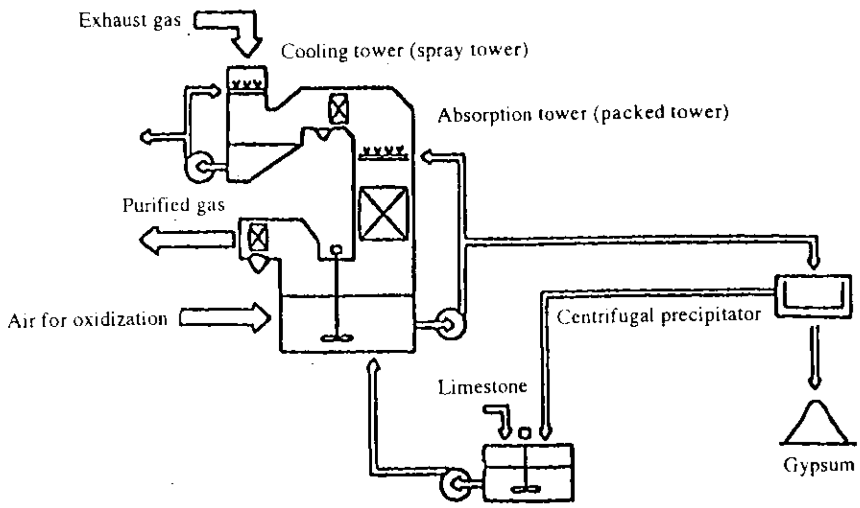
7.7.1 Various Processes of Desulfurization

(1) Lime Gypsum Process

Limestone and calcium hydroxide (slaked lime) particles, in the form of a slurry liquid, absorb SO_2, creating a gypsum by-product. During the initial stages, there was scaling trouble as a result of gypsum adhering to the inner surface of the absorption tower. This was due to the low solubility of limestone and slaked lime. This problem has nearly been solved and this method has become the current mainstream of large-scale flue gas desulfurization equipment. The basic process consists of cooling the exhaust gas and absorbing SO_2 within the absorption tower. The created calcium sulfite is aerated in the oxidizer and the by-product is then retrieved as gypsum (2 tower type). In recent years, many systems utilize a method in which cooling, absorption, and oxidation is all performed in one tower. As illustrated in Fig.7.7.1, the cooling tower can also be set up separately depending on the circumstances.



(a) Absorption oxidization one tower method (soot mixture one tower method)



(b) Cooling tower method (soot separation two tower method)

Fig.7.7.1 Standard Process for Lime Gypsum Method [2)]

As this procedure, which utilizes only one tower, immediately oxidizes the absorbed SO_2 within the absorption tower, turning it into gypsum, the partial pressure level of the SO_2 is reduced. The absorbed SO_2 is reduced desorption. Even if the pH level of the absorption liquid falls into a lower domain of around 4.5~5, the absorption reaction of the SO_2 still continues to progress. Also, the advantage of this one tower system is that it produces a smaller amount of the substance responsible for COD (Chemical Oxygen Demand) within the wastwater. This characteristic allows for a reduction the equipment for wastewater treatment. The purity of the gypsum, in comparison with methods which establish two separate towers for the cooling unit and oxidizer, declines slightly. However, the cost of the facility itself is reduced by 50~60% over the cost of conventional methods.

The construction of a separate cooling tower is determined by considering such factors as the properties of the exhaust gas and the purity level of the recovered gypsum. However, in the event that a separate cooling tower is built, the purity of the gypsum is over 95% and the dust collection efficiency is over 90%. Therefore from the standpoint of recovering a gypsum by-product this method is more advantageous. On the other hand, capital costs is higher and there is an increase in the amount of wastewater and sludge.
For absorption devices, packed towers or spray towers of a device with little pressure loss are frequently used. Moretana-tower (perforated plate-type tower) and jet bubbling devices are also utilized (Fig.7.7.2).

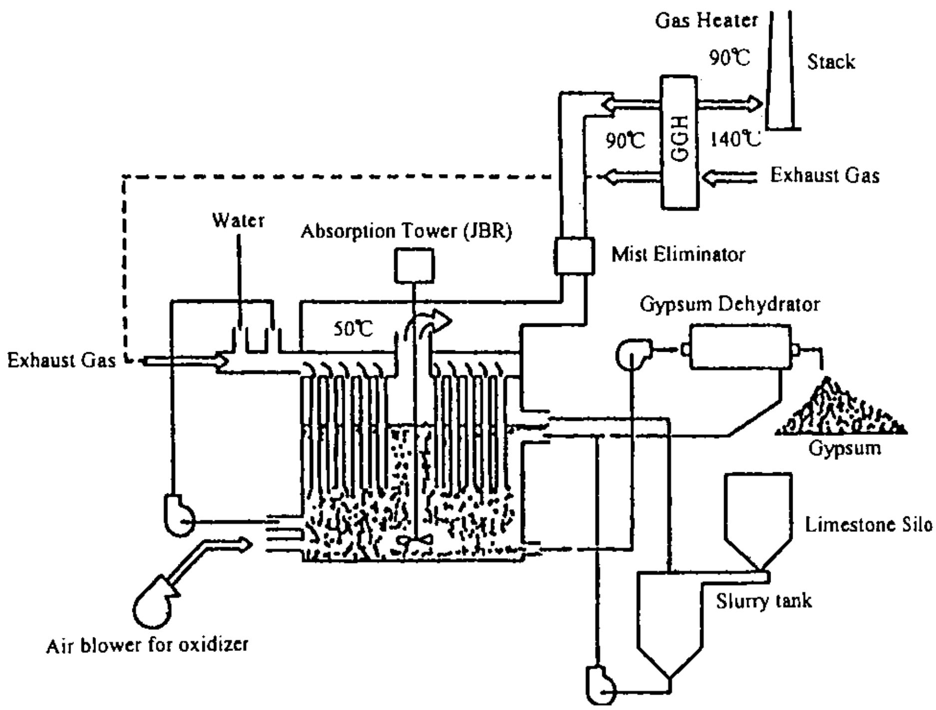


Fig.7.7.2 Jet Bubbling Reactor [3)]

(2) Magnesium Hydroxide Process

The magnesium hydroxide absorbing agent, in the form of slurry, reacts with the SO_2 and creates magnesium sulfite. Furthermore, once oxidized, it changes into magnesium sulfate which is harmless and highly soluble with water. This makes is possible to dispose of the drain-off or effluent. In comparison with sodium hydroxide, magnesium hydroxide is less harmful to the human body and a comparatively cheaper product to use. It is widely used in small to medium sized flue gas processors ranging in capacity of about 5~400,000 m^3_N/h. Set up of the systems are prevalent especially in coastal areas where the absorbing agent can be drained. In Japan, there is a growing influence to make this a popular method alongside that of the lime gypsum method. The processing equipment consists of a system which unifies both the absorption tower and oxidizer into one unit. Furthermore, another method which incorporates a stack into this unit is also being adopted (Fig.7.7.3).

(3) Sodium Scrubbing Process

This process utilizes sodium hydroxide or sodium carbonates as the absorbing agent. These substances are both highly soluble and can be used as an aqueous solution. There is no worry in regards to scaling and the both have a high absorption rate. Much of its achievements have been made in use with small scale flue gas desulfurization devices of less than 20,000 m^3_N/h. In particular, its sodium sulfite and sodium sulfate by-products are used largely in paper and pulp factories.

(4) Ammonia Scrubbing Process

(4-1) Ammonium hydroxide process

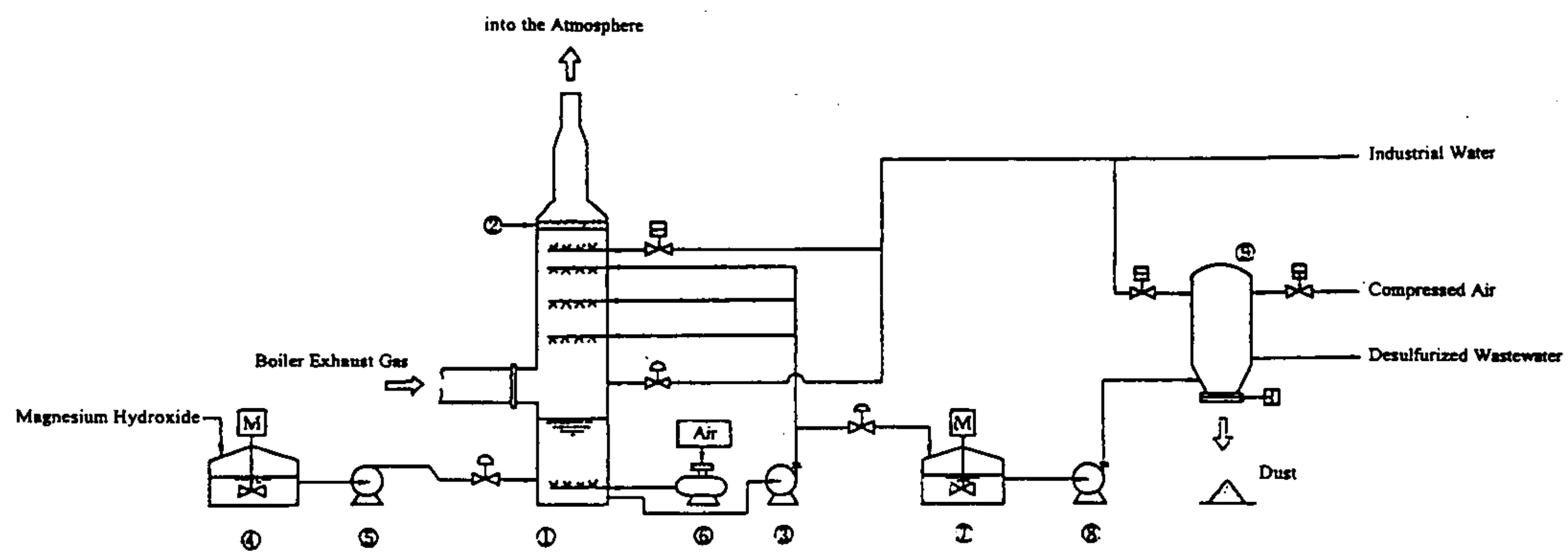
This process utilizes an aqueous agent consisting of ammonium hydroxide and absorbs the SO_2 while producing an ammonium sulfate by-product. In order to use the newly created ammonium sulfate aqueous agent as fertilizer, it must first be solidified. In order to do this a vast amount of energy is required. With the exception of facilities which use an excessive amount of ammonia, nearly no new facilities for this process have not built in recent years.

(4-2) Desulfurization by electron beam irradiation process

This desulfurization and denitrification process cools the exhaust gas down to 70~90℃. Ammonia is then injected into the gas, at the same time being irradiated by an electron beam. SO_2 and NOx found within the exhaust gas is used as fertilizer for the ammonium sulfate and ammonium nitrate, after which it is recovered by a dust collector. This process was developed in Japan. Substantiative testing is being performed in the US and Germany but it has yet to be used for practical application in the field. The unique characteristic of this process is that a fertilizer by-product is produced and there is no waste or wastewater. In the future al large-scale electron beam irradiation device will be manufactured. If a reduction in the system's energy consumption can be achieved, there may be high expectation placed in this method from the standpoint of its use of resources such as fertilizer.

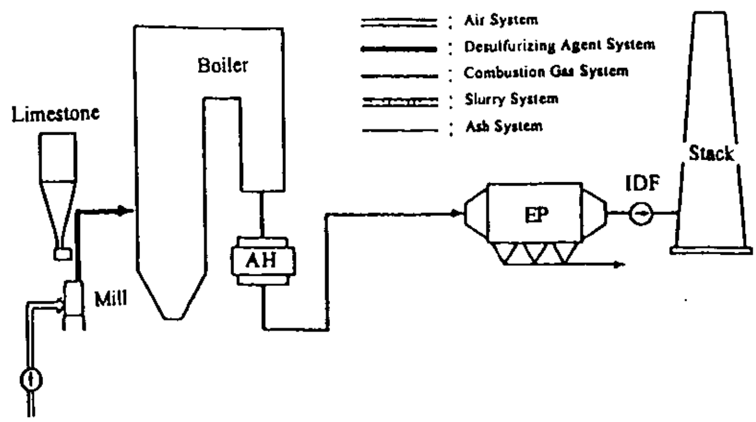
(5) Dry process, Semi dry process

While its rate of desulfurization is somewhat lower, the dry process and semi dry process was developed as a low cost simple process for desulfurization. There are two process: ① absorption of the SO_2 by limestone infused into a furnace heated to 900～1,200℃ ② slaked lime slurry is sprayed into the flue where the SO_2 is absorbed and the by-product is collected along with the dust by a dust collector. Both of there process include such methods as spraying water after desulfurization or recirculate the dust collected by dust collecting equipments, substances which did not react to the absorbing agent, as absorber (Fig.7.7.4). While the equipment and facilities are relatively simple, reaction efficiency is low. There are also not many uses for the by-product produced. Also disposal is limited to certain areas.

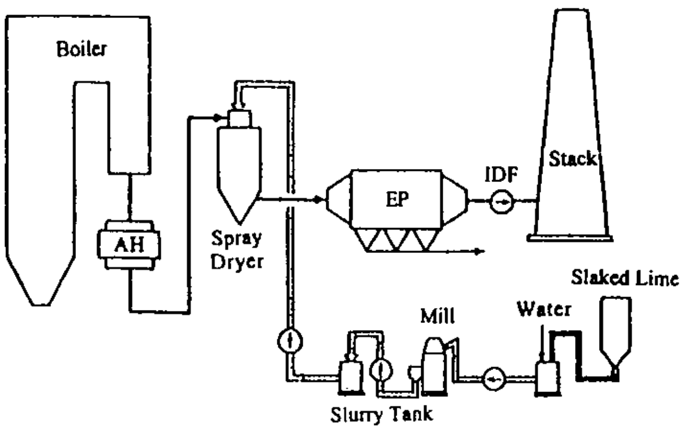


① : Absorption Tower
② : Mist Eliminator
③ : Absorption Tower Circulation Pump
④ : Magnesium Hydroxide Tank
⑤ : Magnesium Hydroxide Pump
⑥ : Air Blower for Oxidizer
⑦ : Filter Supply Tank
⑧ : Filter Supply Pump
⑨ : Filter

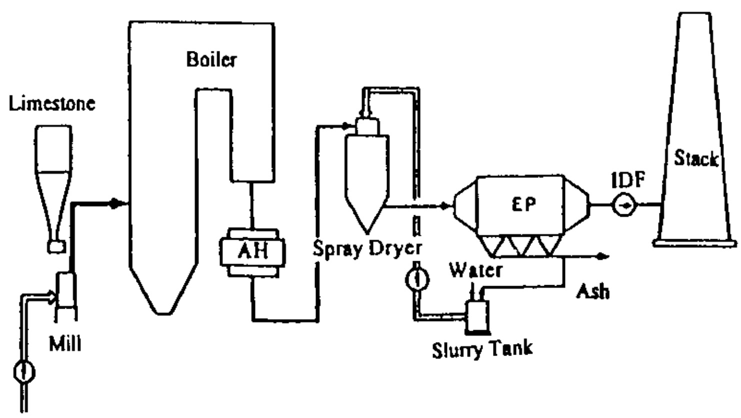
Fig.7.7.3 Magnesium Hydroxide Method Desulfurization/Denitration Process Flow Sheet [4)]



(a) Desulfurization within the furnace System



(b) Semi Dry Desulfurization System



(c) Dust Recirculation Semi Dry Desulfurization System

Fig.7.7.4 Simple·Dry, Semi Dry Desulfurization [5)]

(6) Desulfurization using activated carbon

The development of this process is being furthered in Japan and Germany. This desulfurization, denitration method, splits the activated carbon in to two layers. The first layer absorbs the SO_2, while ammonia is injected into the second layer, utilizing the activated carbon as the catalyst for denitration in order to change the NOx into nitrogen. The absorbed SO_2 is recovered as sulfur or sulfuric acid. The construction costs of the activated carbon process are lower in comparison with that of other wet processes but operating costs run high.

7.7.2 Future Trends for Flue Gas Desulfurization

It is believed that for the time being the majority of flue gas desulfurization will be done by the lime gypsum method. In the future, there will be requests for more compact gas treatment, including wastewater treatment facilities. And, as the majority of the coal combustion in Japan utilizes coal with low sulfur content, there will also be demands for reduced emission levels, and improvements in the desulfurization efficiency. As one step in energy saving measures, methods for utilizing waste heat and reheating exhaust gas to prevent steam plume are being investigated. As a way to reduce the wastewater processing plants, the non-wastewater process is being examined. There are two methods which have been developed. One such process calls for the use of heat from exhaust gas to vaporize the wastewater, after which a dust collector is utilized to remove solid particles within the wastewater. Another method separates solids and liquids using electrodialysis on the waste water.

It is believed that there is an increase in the number of flue gas desulfurization units also in developing nations. However, there is an inclination to buy cheaper units and sacrifice the desulfurization efficiency. Facilities which produce sulfur or sulfuric acid by-products or directly produce fertilizer by-products all have high facility costs. As by-products are recovered mixed with coal, when using the dry process which uses limestone and slaked lime, and also the simple semi dry desulfurization method, the effective use of these compositions will be an important issue in the future.