

10.1. Introduction. 10.2. Non-regenerative or Throwaway Type Scrubbers. 10.3. Methods to Upgrade the Performance of Conventional Limestone FGD System. 10.4. Non-conventional Wet System. (Lime or Lime stone Absorption). 10.5. Spray Dryers (Dry Scrubbers). 10.6. Different Types of Absorbers. 10.7. Sealing and Corrosion of Scrubbers and their Prevention. 10.8. Non-conventional Throwaway Scrubbers. 10.9. Advantages and Disadvantages of Wet Scrubbers. 10.10. Regenerative Type Scrubbers (FGD Systems). 10.11. Dry Scrubbing System. 10.12. Sludge Disposal and Its Uses.

10.1. INTRODUCTION

Coal is re-emerging as the dominant fuel for power generation for the intermediate term (15-20 years). Use of coal today requires emission control devices different from those used in the last era of coal dominance. The main objectionable emission among all is SO_2 which is highly injurious to human, animal and agricultural life. The present strict restrictions on emissions by the Government have forced this industry to remove SO_2 from exhaust gases to a permissible level. The flue gas desulfurization (FGD) has become the basic necessity of the power plant as most of the inferior coal available for power generation throughout the world contains 3 to 4% sulphur. The equipment used for removing SO_2 is known as scrubber, a major equipment feature of coal-fired power plant design and construction.

Sulphur in coal cannot be destroyed, it can only be converted to one form or other. The technology of FGD is therefore one of conversion. The technology used is generally split according to the type of end product generated, rather than by the exact chemical route used. This technology is generally classified as *Non-Regenerable* or throwaway process which produces sulphate salts which are worthless and discharged and *Regenerable process* which produces sulphur or H_2SO_4 from the collected material.

The throwaway system has been developed and most widely used type today. As per 1978 estimates, nearly 94% of the total generation used this type of scrubbing system for an effective removal of SO_2 . The basic attraction is the requirement of simple equipment, easy pH control and cheap raw materials used makes this system most popular and economic among all the presently available techniques. Therefore, this chapter will deal with this type of system in more detail and other systems will be just introduced as they are not yet used on commercial basis.

Fundamentally, all flue gas desulfurization processes rely upon absorption or adsorption. Absorption is the transfer of a substance, such as SO_2 from a mixture of gases into a liquid with which, the gas phase is brought into intimate contact. This phenomenon is the one on which most of the today's FGD technology is used. Adsorption is the adhesion of very thin film of substance on another substance with which it is contacted. The capture of SO_2 by activated carbon is an example of this process which is rarely used for SO_2 removal from flue gases.

The common methods which are used are of absorption type. The materials used for absorption include lime, lime-stone, MgO , dual alkali and carbonates. All these materials are dissolved in water and then they are sprayed in a box like tower where the flue gases enter. By making the intimate contact of both, the efficiency of absorption is increased. The absorption capacity depends upon the surface of absorption exposed to flue gases, relative velocity of two and residence time and many others. This process is made more effective if a material with which SO_2 can react chemically is present in the phase into which it is transferred. If alkali is present in water with which the flue gas is contacted, the absorption of SO_2 is greatly enhanced.

10.2. NON-GENERATIVE OR THROWAWAY SYSTEM (LIME OR LIME STONE ABSORPTION TYPE SCRUBBER)

Presently 95% scrubbers used in the power industry fall under this category as this technique and design are very well developed during last 20 years.

The concern of the designer of a utility, FGD system today is two-fold. He must design a system to satisfy all local emission levels ; while simultaneously meeting waste disposal requirements. In addition

to this, he must also find ways to minimise the energy requirements of an essentially this non-productive process.

The basic closed-loop scrubber system commonly used is shown in Fig. 10.1. Flue gas, after fly ash has been removed in electrostatic precipitator, enters the bottom of the absorber and exits at the top. A water slurry of an alkali reagent, such as lime stone, is sprayed down against the gas through a series of nozzles. This slurry falls to bottom, absorbing SO_2 as it travels down. It drains out of the bottom of the tower into a reaction tank to complete the conversion to calcium sulphate (CaSO_4) popularly known as gypsum and then recycled back to the nozzles for another pass.

Some type of packing is often built into the tower to improve the gas-liquid contacting. This could be either a mobile packing, such as plastic balls or glass marbles or a fixed packing, such as plastic punch plates.

The flue gas coming out of absorber after removing SO_2 , the gas is reheated in order to protect the booster fans, provide added buoyancy to the plume and increase visibility. The reheating is generally achieved with an extraction steam. Soot-blowers are also provided to keep the heat exchangers clean.

Limestone slurry is supplied from a storage and grinding facility. Waste slurry is periodically blown down from each absorber, concentrated in thickeners and then pumped to a pond—an ultimate disposal area. Water is recovered and recycled back into the system at several locations as shown in figure 10.1. Some make-up water is always required to overcome the losses in the system. The scrubbing system includes reagent preparation, water treatment and waste disposal.

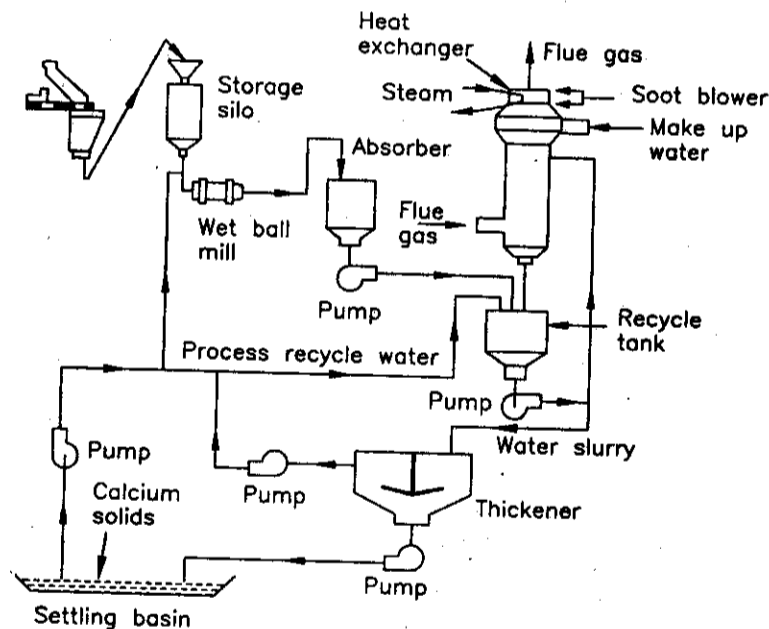


Fig. 10.1. Schematic diagram for closed loop operation.

Lime-stone (CaCO_2) is not as reactive as lime (CaO) and a higher stoichiometric (mole ratio of $\text{CaCO}_3 : \text{SO}_2$) addition is necessary which affects solid disposal problem as well as raw material costs. Even though lime-stone is favoured because of its relative simplicity and major development work has been done with lime-stone.

The degree of SO_2 removal which can be achieved with lime-stone is limited by the cost of stages, spraying rates, fineness of limestone grind, gas side pressure drop and slurry retention time, both in the scrubber and holding tanks.

The liquid gas ratio (L/G) generally used lies between 40-100 gallons of slurry per 1000 ft³ of gas at a stoichiometric ratio of 1.5 and removes 90% SO₂ from the flue gases. The effect of L/G ratio on the efficiency of SO₂ removed is shown in Fig. (10.2) for the two different pH-values.

One of the major advantages of lime-stone scrubbing is the potential for removal of particulates as well as SO₂ from power plant stack gas and thereby eliminates the need for electrostatic precipitators which are considered responsible for many outages of the power plant.

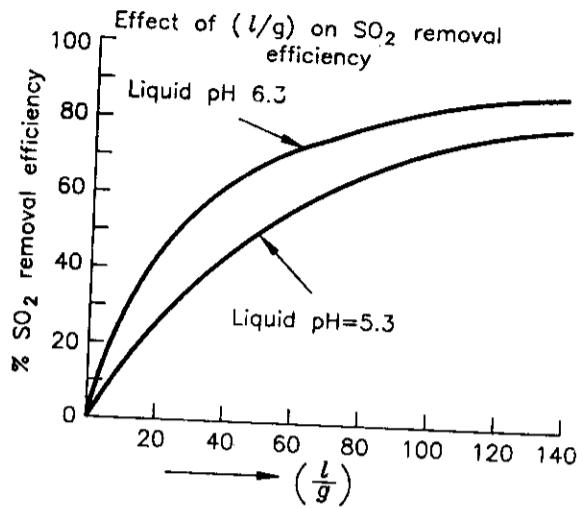


Fig. 10.2.

The most controversial aspects of FGD is cost which includes capital as well as running cost. The required capital cost \$/kW and in terms of percentage of power plant cost are shown in Fig. 10.3 (a) and Fig. 10.3 (b) for three different capacity plants. The Figure shows that the capital cost is very high which many times prevents the use of FGD system in the power plant.

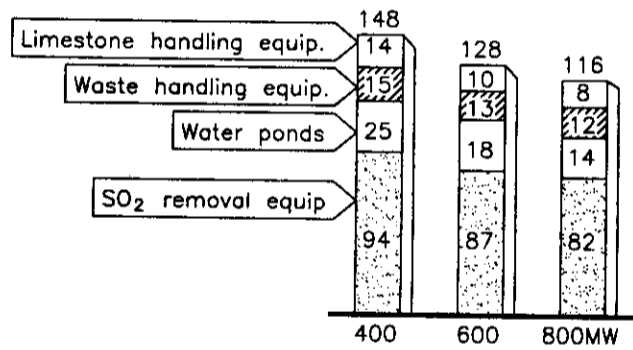


Fig. 10.3. (a) Capital cost in \$/kW for SO₂ removal compared with other equipments.

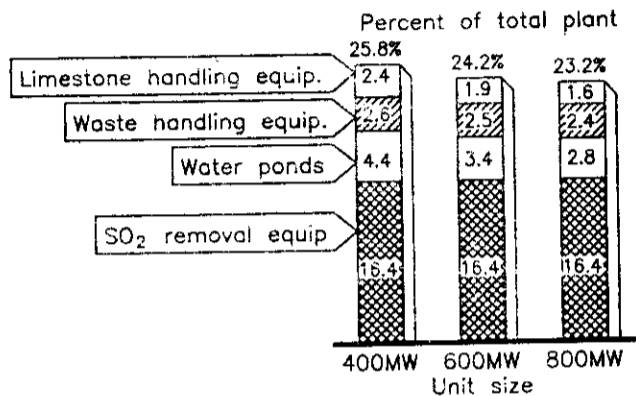


Fig. 10.3. (b) Percentage cost for the removal of SO₂ compared with other systems.

In addition to capital investment, there are substantial operating costs associated with FGD system. The system will consume 2% of the generating capacity, 7 tons of limestone for each 100 tons coal burned and requires an additional 20 to 40 people for the operation of the plant. The overall operating cost lies between 5 to 9 mills/kWh depending upon the capacity of the plant and capacity factor.

This system is generally preferred where large area is available for solid waste disposal, calcium is easily available at lowest cost and ample water supplies are existing at the site.

Chemistry of Lime-stone Wet Scrubber System. The absorption of SO₂ in the lime-stone scrubber occurs as per the chemical reactions listed below.



The second reaction above takes place only in a low pH environment.

Absorber reactivity depends on calcium ion availability in the scrubber spraying fluid. The *pH* of the fluid is a measure of free hydrogen ions, and can be considered as the measure of calcium ion availability as high pH denotes high availability. In conventional scrubbing system, there are very few calcium ions present to accomplish the removal of SO₂. Therefore, a slurry containing excess calcium in the form of Ca(OH)₂ is necessary to replenish the calcium ion that has undergone reaction. The unreacted solids in the slurry are recirculated through the scrubber requiring high pumping energy, high liquid to gas ratio, and extensive cleaning of scrubber and mist eliminator.

In any lime system when SO₂ is absorbed, the sulphite and bisulphite ions (SO₃⁻¹HSO₃⁻¹) remain in equilibrium in the reacted scrubber fluid.



In scrubber system, the pH of slurry must be closely regulated since a high pH will shift the equilibrium in the equation 5 to the right encouraging the formation of excess CaSO₃. The insoluble CaSO₃ crystals are very small, do not settle readily and cause plugging, scaling and erosion of the scrubber pumps and constant maintenance problem. On the other hand, if the pH of the slurry drops too low, the presence of Ca(HSO₃)₂ which can be easily oxidized results in the formation of gypsum inside the scrubber as per the equation 3. Therefore, the pH of lime-system is regulated to a value of 7 at the scrubber inlet and kept within the narrow range of ±0.5 between inlet and outlet of the scrubber.

10.3. METHODS TO UPGRADE THE PERFORMANCE OF CONVENTIONAL LIME-STONE FGD-SYSTEM

Many more methods are introduced to upgrade the performance of lime-stone wet FGD system. A few of them which are important are discussed here :

1. Use of Magnesium. The use of magnesium in the scrubber loop in the form of *thiosorbic lime* changes the nature of chemical reactions in the scrubber significantly. The solubility of $MgSO_3$ is more than two orders of magnitude greater than that of $CaSO_3$, so there will be an increase in dissolved Mg . The resulting increase in sulphite concentration and dissolved alkalinity boosts the SO_2 removal efficiency of the scrubber as shown in Fig. 10.4. It is possible to remove 90 to 95% of SO_2 from the gases even if high sulphur coal is used as fuel. The use of magnesium reduces the L/G ratio considerably and scrubber may be operated in subsaturated condition with respect to gypsum which is not at all possible with lime-stone system.

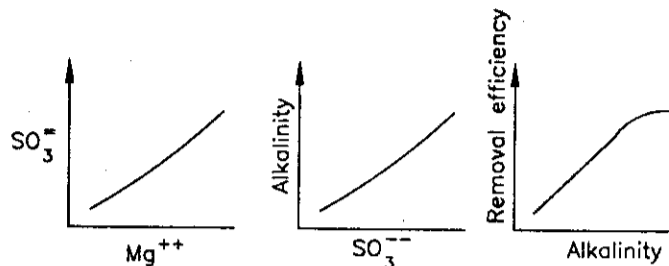


Fig. 10.4. Effect of Mg on the removal efficiency of lime scrubber. (The presence of soluble Mg^{++} ions increases SO_3^{--} concentration and alkalinity)

However, concentration of Mg solution must be carefully controlled because high Mg concentration at high pH causes the formation of $Mg(OH)_2$ gel which plugs sludge filtering equipment and interferes with sludge setting. Presently this type of system is used at six power stations in USA.

2. Use of Adipic Acid. The addition of adipic acid to lime-stone system enhances the chemical reaction process similar to that of Mg. Adipic acid buffers the pH drop in the range of 4 to 5 at the gas-liquid interface during SO_2 absorption. This results in higher SO_2 concentrations in the surface film and accelerates the mass transfer. 90% removal of SO_2 is also possible with this method. Lee Catalano has developed the following equation to estimate the required adipic acid concentration in the scrubber system to achieve a given SO_2 removal.

$$\begin{aligned} & \text{Fraction of } SO_2 \text{ removed} \\ & = 1 - \exp \left[-0.0013 \text{ Cad} - 0.00216 \exp (pH) - 0.0995 \left(\frac{L}{G} \right) \right] \end{aligned}$$

where, Cad = adipic acid concentration (ppm)

pH = pH of the scrubber feed liquid

L/G = Liquid to Gas ratio.

The arrangement of the components of such a system used at Springfield power station is shown in Fig. 10.5.

3. Use of Calcium Chloride with Formic Acid. This is another successful system used for scrubbing purposes on commercial basis. Since calcium chloride is soluble, the scrubbing liquor is a solution and not a slurry. The pH value of the liquid used lies in the range of 4 to 5, and encourages the formation of $Ca(HSO_3)_2$. This is the only soluble sulphite and the one most easily oxidized to gypsum under controlled conditions.

4. Double-Alkali System. This system is superior to conventional scrubbers, as it uses dual alkalies in the system. This system uses two operating loops—one for scrubbing and one for regeneration of chemicals as shown in Fig.10.6.

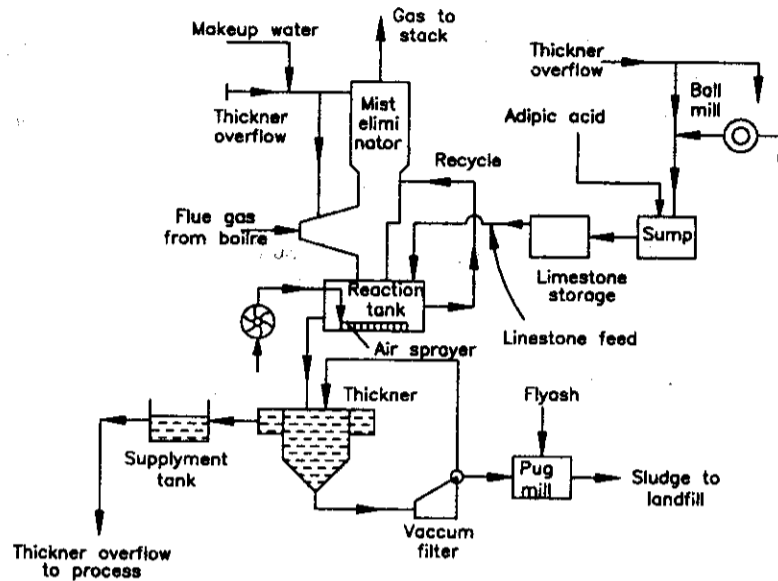


Fig. 10.5. Springfield power plant using Adipic Facility.

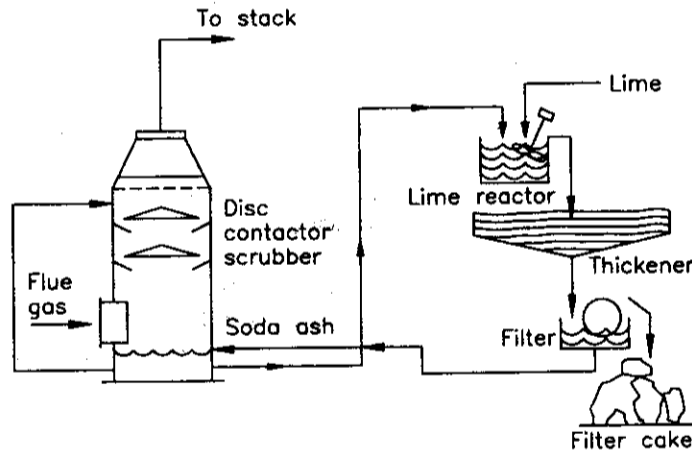
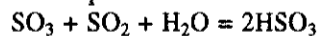


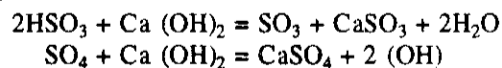
Fig. 10.6. Double-Alkali process.

Sodium as a scrubber reagent overcomes some of the problems associated with calcium. In the sodium calcium dual alkali system, soluble Na_2SO_3 reacts with SO_2 in the scrubber to produce NaHSO_3 .

Sulphite and sulphate \rightarrow sulphite



The lime-stone slurry is added in the regenerative loop to form CaSO_3 and regenerate Na_2SO_3 . The regeneration reaction is



Sulphate precipitates as a hydrated mixed crystal or as a gypsum plus a hydrated mixed crystal depending on concentrations of the dissolved species. The 90 to 95% SO_2 removal is possible with this system using L/G ratios as low as 10 to 15 gallons/1000 ft^3 gas. The other advantages of the system are listed below

1. There is no calcium in the scrubber loop which is mainly responsible for scaling.

2. In the regeneration loop, the pH is above 8 but there is no scaling problem.
3. High removal efficiency (>95%) is achievable at low L/G ratio and virtually 100% absorbent utilization takes place.
4. The maintenance is minimum as soft scrubbing solution is used instead of an abrasive, low pH slurry.
5. The equipment size is 50% of conventional due to high reactivity of the insoluble sodium solution, vessel and piping are smaller and power requirement is reduced by 60%.
6. This system produces mechanically stable filter cakes that is easily conveyed and can be used for landfill without adding chemicals for fixation.

Disposal costs are also significantly reduced due to excellent settling and filtration characteristics of generated solids.

Three dual alkali units for 1100 MW capacity power plants are operating in USA from 1980.

The SO_2 removal efficiency and system availability were found 95% for the scrubber plant of this type established at Gulf Power Station. No plugging or scaling were experienced despite the fact that no washing was done.

5. Davy S-H Process. This process takes a completely different approach to control the pH of the scrubber liquid. The main feature of the system is the controlled use of chlorides. The arrangement of the components is shown in Fig. 10.7

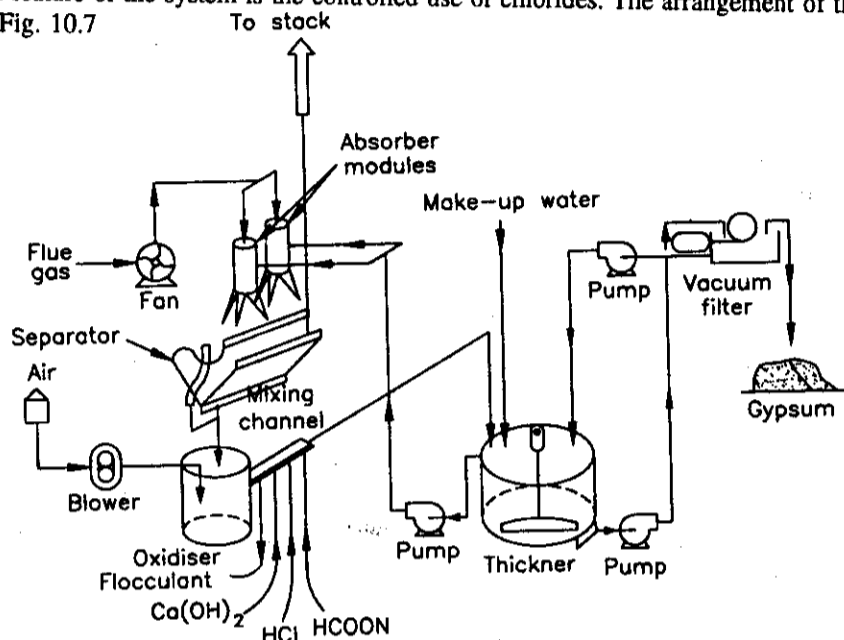
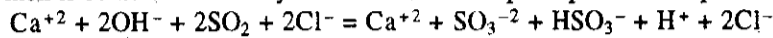


Fig. 10.7. Davy S-H Process.

A small amount of hydrochloric acid (HCl) is added to $Ca(OH)_2$ along with formic acid (HCOOH), as a buffering agent, to form clear alkaline solution. The formed chloride ($CaCl_2$) increases the concentration of available calcium ions in the scrubber solution due to its high dissociation property. This eliminates the need for recycle of the solution, like in conventional systems and allows to use lower (L/G) ratio (10 to 14). The scrubber washing solution can be adjusted to high pH value between 10 to 11 at the scrubber inlet, depending on the SO_2 concentration in the gas, and degree of desulfurization required.

In conventional lime system, the pH from inlet to outlet of the scrubber is held within a very narrow range whereas in Davy S-H process, the drop in pH is desirable because it favours the formation of

bisulphite ions which is soluble and readily oxidized. The absorption proceeds as per following equation :



at a pH value between 8 and 11. The chloride ions present in the solution act as intermediate carriers and remain in the cycle in the form of CaCl_2 in the solution.

As the reaction proceeds, the OH^- ions from the solution are used up and an abundance of H^+ ions is made available. The pH of the solution drops rapidly to 4.5. To control this drop, the formate ions from the addition of formic acid as a buffer absorbing the H^+ ions to form molecular HCOOH . This always keeps the pH value between 4 and 5 assuring the formation of calcium bisulphite. By preventing a rapid drop in pH, high SO_2 removal can be achieved in the pH range of 4 to 5.8. After the formate ions are largely consumed, the buffer effect is weakened and pH of the solution falls to 4 which is the optimum value for oxidation of calcium bisulphite to gypsum.

40 MW Weither power station in Germany is equipped with this system and operating successfully from 1974 onwards.

Advantages of this System are listed below :

- * The conventional lime-stone process cannot tolerate chlorides in gas stream and therefore pre-scrubbing is necessary. But Davy S-H process not only tolerates the chloride but the presences of chlorides enhances the process without any corrosion problem.

- * Complete oxidation in gypsum is very essential in any type of scrubbing process. In Davy S-H process, the washing fluid leaves the system at an ideal pH range for oxidation, therefore, an additional acidifying step is not essential. The formation of the large gypsum particles compared to fine sulphite particles, allows the liquid to be easily separated from the gypsum in the thickener.

- * Scrubber recirculation pumps and agitation equipments to maintain a slurry is eliminated from the system.

- * The possibility of scale formation and plugging is totally eliminated.

- * The maintenance of the system components due to erosion is also eliminated.

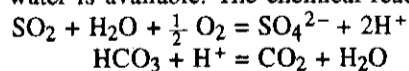
- * Power consumption is greatly reduced due to low (L/G) ratio used in this system.

- * Stable gypsum is formed due to oxidation as stable gypsum can be used for making wall boards and ceiling panels. The stable gypsum can be easily dewatered and stacked. Loss of additives is also reduced due to better dewatering properties of stable gypsum.

The system is simple in operation, requires less maintenance, therefore the availability of the system is considerably high compared with all other systems. In addition to this, the process has maintained high desulfurization efficiency (95%) over a wide range of SO_2 emitted from the boiler and carried with the gases.

10.4. NON-CONVENTIONAL WET SCRUBBER

Another wet process available is sea water scrubbing. Advantage of using sea water is, it is alkaline and SO_2 is absorbed by sea water and forms sulphate ions, a natural constituent of sea water. This process can be used where sea water is available. The chemical reactions are listed below.



It forms sulphate and H_2 ions, increases concentration and lowers the pH-value. Bicarbonate ions of sea water reacting with H_2 ions releases CO_2 .

Spent sea water collected at the bottom of the scrubber is led to the mixing tank for treatment where fresh sea water and O_2 is mixed and finally discharged to sea. The advantages of this system are (i) the method is simple as no chemical is added (ii) No problem of clogging and (iii) No land disposal problem is faced.

This type of plant is in operation at Tata Electric, Bombay.

10.5. SPRAY DRYERS (DRY-SCRUBBERS)

Another successful FGD-system is the spray dryers. The dryer FGD system have proved commercially viable particularly in Europe. The general outline of the process is shown in Fig. 10.8. Reagent is pumped to the absorber and sprayed as a fine mist which mixes intimately with flue gases. Water is evaporated with the heat of the gas while SO₂ and SO₃ are absorbed. A dry powder is formed as the flue gases cool. The most popular design makes the use of high speed rotary atomiser placed at the top centre of the vessel.

The performance of the dryer depends upon the temperature differential across the absorber but especially on how close the exit gas temperature gets to the adiabatic saturation temperature (approach temperature). It is necessary to increase the lime-reagent to increase the efficiency. Either thicker slurries must be used or greater amount of water must be evaporated.

At the inlet, higher gas temperature may begin to reduce efficiency of upstream heat transfer devices. At the outlet, the closer the system gets to the approach temperature, greater is the potential for solid deposition and corrosion in the spray dryer.

The presence of chlorides in the flue gas has enhanced SO₂ removal. But they aggravate corrosion tendencies. The injection of NH₃ upstream of the dryer also promotes removal of SO₂ at lower reagent utilization rates.

Even though spray dryers are simpler in design and operation than wet scrubbers, the technology is not so well developed. It was also observed that the residence time was often inadequate to suitably dry the solids. The atomizer tips require silicon carbide to provide reliable service which increases the cost of the system.

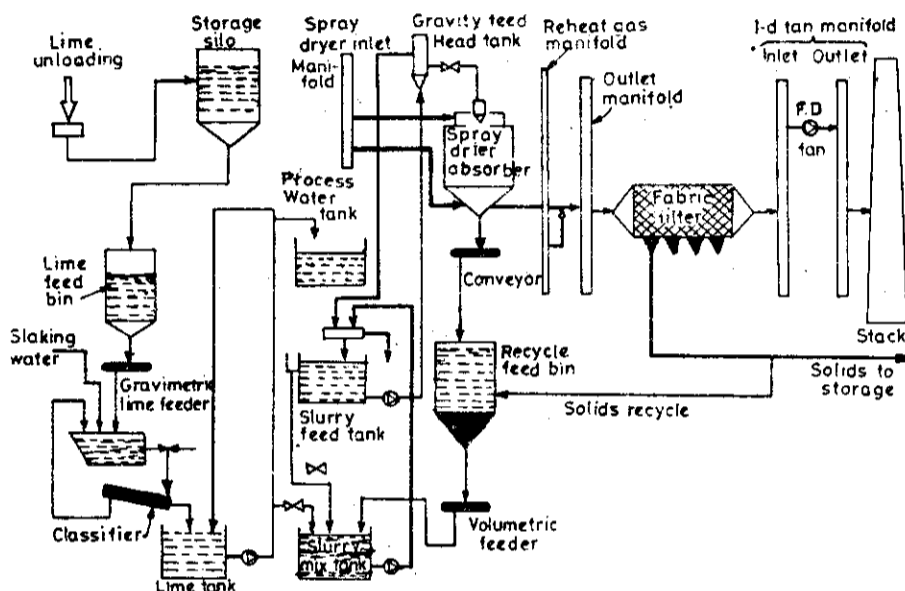


Fig. 10.8. Spray-dryer used for low-sulfur coal and equipped with fabric filters.

Deposition on the vessel walls was another problem caused by poor process control and many installations have experienced difficulties in handling and transporting spray dryer solids. Presently, most of the problems are successfully solved and like wet scrubber, operation experience has been translated into successful utilities of the spray-dryers.

These types of units are used, particularly in Europe, to remove 90% to 95% of SO₂ generated.

Some of the difficulties experienced in U.S.A. are listed below :

(1) The upstream location (before ESP) of dryer was unable to handle 2 to 5 times increase in solid loading.

(2) The line used in spray drier is much costlier than the lime-stone used in wet drier.

(3) The solid waste from spray drier, although dry, is not fully oxidised.

(4) Existing solid handling systems may be undersized.

(5) Long-term reliable operation for the removal of SO_2 at 90% has not been established.

(6) The technique becomes uneconomic with sulfur content in the coal higher than 3%.

The advantages of the sodium process are, SO_2 scrubbing efficiencies of 90 – 95% are achievable with lower energy consumption resulting from the lack of need for reheat and almost no make-up water requirements. The process combines the advantages and efficiency of sodium scrubbing in dry scrubber system, but Na_2SO_4 produced is highly soluble which may present a leaching problem at the disposal site.

On the other hand, the regenerable closed loop system yields elemental sulfur, a marketable product, but the system complexity makes operating and capital costs much higher than for the throwaway process.

The spray dryer used in the Rockwell International System is somewhat different than described above. A multiple atomizer concept as shown in Fig. 10.9 provides turn down capabilities greater than 5 : 1 by shutting off one or more of the atomisers. Use of a roof disperser imparts spin to gas that is counter to atomizer spin and helps to ensure complete gas mixing. Multiple discharge points in the dryer chamber are not used in this system.

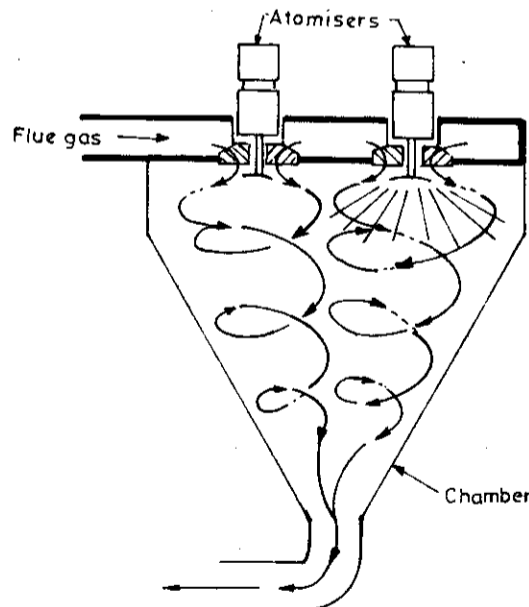


Fig. 10.10. Bowen's dryer (right) uses multiple atomizers and a roof disperser, relying on rigid temperature control to prevent agglomeration of damp product.

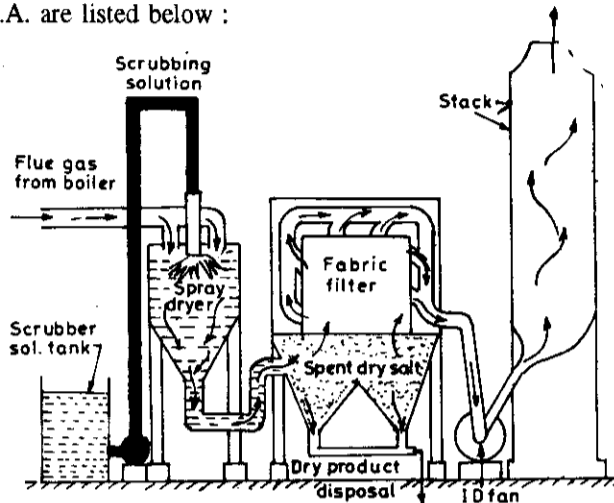


Fig. 10.9. Niro's dryer design (left) uses a single atomizer and compound gas disperser to achieve mixing. Multiple discharge of product removes agglomeration. Bowen's dryer (right) uses multiple atomizers and a roof disperser, relying on rigid temperature control to prevent agglomeration of damp product.

As with dry-system, scrubbing with calcium, Liquid/Gas ratios are low (0.3 gal/1000 cuft). The control is achieved by measuring the outlet temperature and SO₂ content of the inlet gas. These measurements are used to regulate the solution flow rate and solution concentration to the spray dryer.

10.6. DIFFERENT TYPES OF ABSORBERS

Few different types of wet collectors are discussed below :

1. Packed Type Scrubber. Scrubber is designed to make an intimate contact between the slurry and gas. The slurry used may be broken up into fine drops or particles by spray nozzles as in the case of spray tower and may be divided into thin film by passing through a bed of tower packing. The slurry which comes out of scrubber becomes highly corrosive therefore it is necessary to construct the scrubber of high corrosion resistant material (fibre-reinforced plastic). The thickness of the packing lies between 1 to 3 metres. However many scrubbers use 5 to 10 metres of packing for scrubbing less soluble gases like SO₂ and H₂S. The arrangement of different components used is shown in Fig. 10.11.

The selection of the proper tower packing media will have a significant effect on the design and efficiency of a scrubber. High density polyethylene which has high resistance to corrosion is used as a packing material.

The minimum scrubbing liquid flow rate that gives good wetting of the packing is used in the design of packed scrubber. This minimum flow required depends upon the type of flow (counter or cross).

At the gas flow rate of 5000 kg/hr-m², the liquid input rate is reduced from 2000 litres/min for counter flow scrubber to 800 litres/min for cross-flow design.

2. Spray Type Scrubber. These are the simplest wet type collectors. The liquid is sprayed through the nozzles into the gas stream through the towers. The liquid particles wet the dust particles which then agglomerate and drop out. The eliminators are provided at the outlet of the tower to avoid the spray droplets entrainment and carry-over. The eliminators are particularly essential when the gas velocity exceeds 2 m/sec. The use of spray towers is usually limited to the collectors of particles of 10 μ or larger. The arrangement of the different components used is shown in Fig. 10.12. Spray towers have the advantage of almost negligible gas side pressure drop and simplified internals. However, they require higher liquid to gas ratios and more height than the conventional marble bed scrubbers or packed towers.

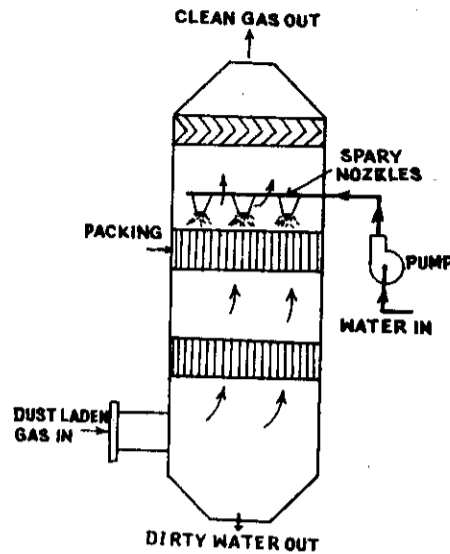


Fig. 10.11. Packed type wet collector.

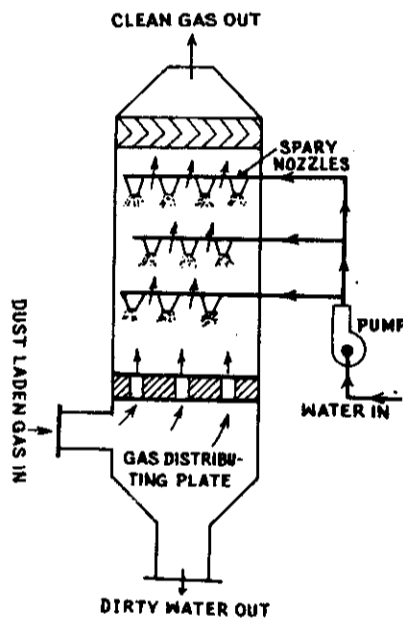


Fig. 10.12. Spray type wet collector.

A two-stage spray tower scrubber system using a rod scrubber for particulate removal and spray tower for SO_2 removed as shown in Fig 10.13. (a) is preferred over a single spray tower. In this system, each stage has its own first stage reaction tank, thereby supplying the seed crystals necessary to prevent calcium sulphate scaling. This process design means that no flyash will be present in the SO_2 absorber.

An actual system of two stage scrubber at Sherburne is shown in Fig. 10.13. (b), a slurry of pulverised lime stone enters directly into the reaction tank (located at the bottom of the scrubber). Recirculation pumps convey the scrubbing slurry from the reaction tank to underbed spray nozzles. The incoming gas, laden with dust and SO_2 contacts the sprayed slurry. The removal of SO_2 and particulate matter occurs in the bed. The scrubbing cycle continues with the reacted materials draining to the reaction tank which is designed to provide the completion of chemical reactions and precipitation of solids. From the reaction tank, pumps recirculate the scrubbing solution as shown in figure. A bleed line provides the necessary solids removal to a pond. Here, solids settle and classified water is available for recirculation. The cleaned flue gas passes through a mist eliminator for removal of the remaining water particles and is then reheated for induced draft fan protection and plume control.

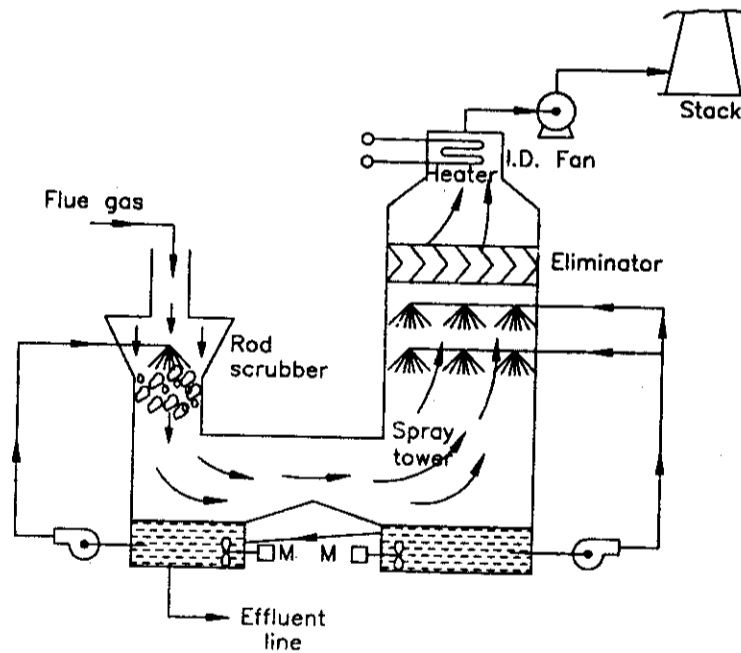


Fig. 10.13. (a) Two-stage spray tower scrubber system.

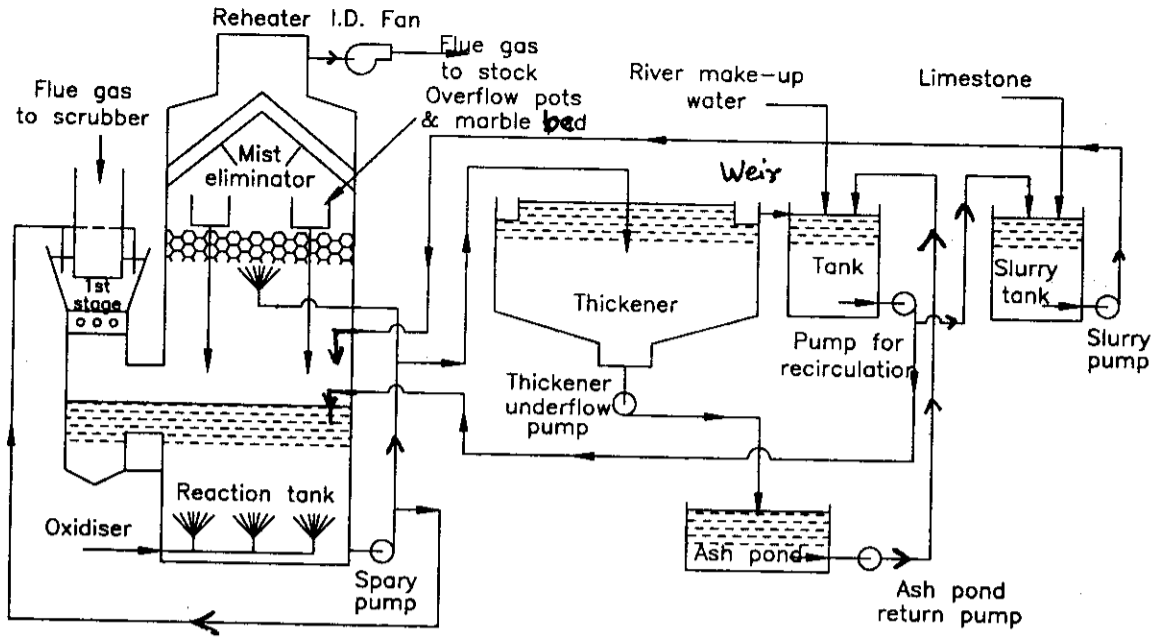


Fig. 10.13. (b) Sherburne County scrubber system.

The primary function of the scrubber is to transfer SO_2 from the flue gas into the liquid. The marble bed scrubber acts as an absorption tray. The SO_2 is absorbed by the scrubbing liquid and is converted to solid sulphur compounds in the reacting tank.

3. Cyclone Scrubber. The efficiency of the collector is increased by the turbulent motion of gas and water. In cyclone scrubber, the gas enters tangentially like dry cyclone separator and the slurry is injected through the nozzles towards the wall of the shell as shown in Fig. 10.14.

The gas enters into the cylindrical scrubber through a tangential inlet near the base as shown in figure and swirls upward to the outlet at the top. Dust particles are carried to settling tank by falling droplets of water flowing down along the scrubber wall.

The efficiency of this collector is high and the major advantage is, it absorbs 90% soluble gases (H_2S , SO_2) more efficiently than other collectors.

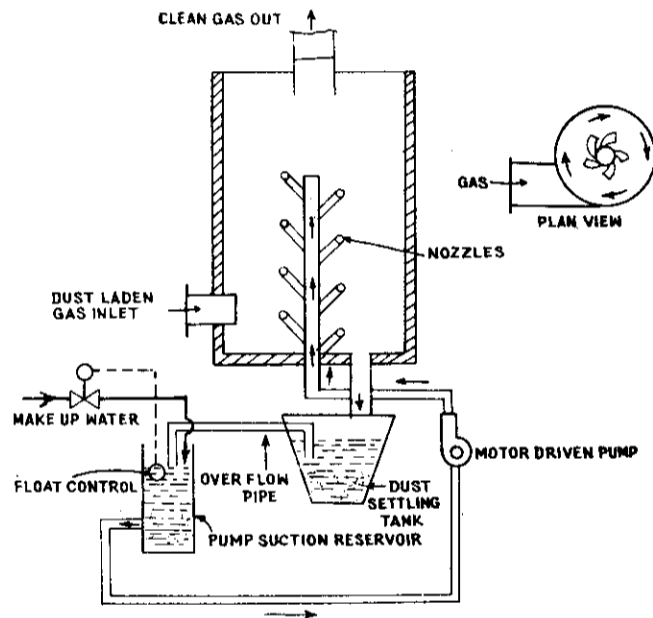


Fig. 10.14. Wet-cyclone Scrubber.

The water is recirculated as shown in figure and make-up water is added by level control. The make-up water required is 25 to 30 litres/min per 1000 m³/min of gas handled. The pressure of the water required varies from 2 to 20 bar. The draught loss is in the order of 4 cm of water at full rating. Considerable wet gas scrubbing is practised in England.

The SO₂ content is reduced from 862 to 385, 658 to 125 and 617 to 118 ppm in many wet scrubbers tested by Northern States Power Company.

4. Venturi Scrubber. Venturi scrubber differs from all other wet scrubber as it can give high efficiency. Air carrying SO₂ is passed at a high velocity through the venturi-section comprising a tapered converging inlet, parallel throat and divergent exit cone. Slurry is introduced at the throat where the air velocity reaches 60 to 90 m/sec.

The high velocity of gas stream atomises the water into relatively small droplets and gas and dust particles are captured within the droplets. The diverging outlet cone also provides further opportunity for collection during the period of deceleration. By the time, the mixture of water slurry and gas leaves the venturi, the most of the gas and dust particles are trapped within the droplets.

The flooded disk (variable throat) shown in Fig. 10.15 is a recent development. The scrubbing liquid is fed to the centre of the orifice plate which serves to distribute the liquid across the throat. The slurry coming out of scrubber is collected after passing through a cyclone collector as shown in figure. Very high scrubbing efficiency as 95 to 99% is achieved by this type of absorber but at the cost of high pressure drop. Therefore its running cost is considerably high.

5. Mobile Bed Scrubber. The arrangement of the scrubber is shown in Fig. 10.16. The bed is made of mobile packing like glass spheres or marble pieces and slurry is sprayed over it and gas is passed from the bottom as shown in Fig. 10.16. The specific feature of this absorber is rapid absorption action, low liquid side pressure drop and good flyash and SO₂ removal.

10.7. SCALING AND CORROSION OF SCRUBBERS AND THEIR PREVENTION

The worst problems associated with wet scrubbing are scaling, plugging and corrosion and erosion of the scrubber parts. These factors are responsible for inefficient operation of the plant and high maintenance costs.

1. Scaling. Scaling occurs when the solutions are supersaturated to point where crystallization takes place, whereby large crystal masses are formed on system components such as walls, piping and nozzles. These scale formations are of two types as described below :

(a) **Calcium Sulphite Scaling** (CaSO₄·½ H₂O). It is formed in the scrubber under certain pH conditions.

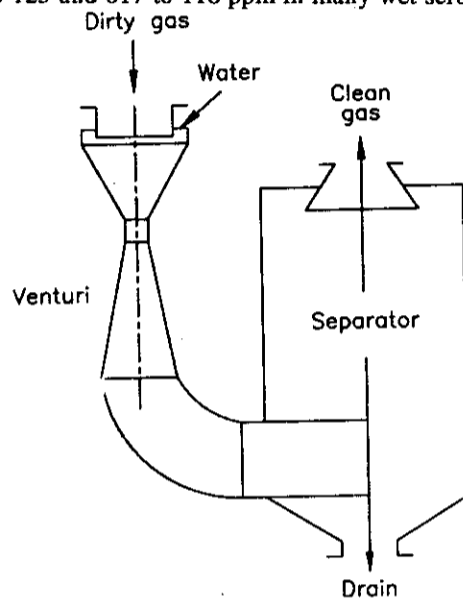


Fig. 10.15. Venturi Scrubber.

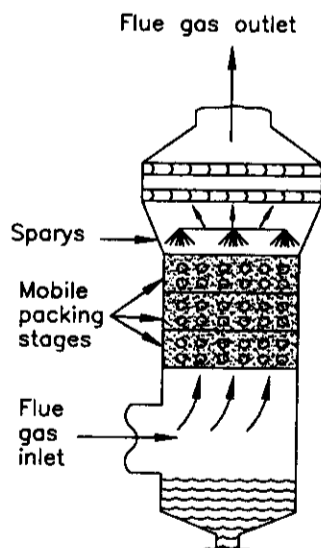


Fig. 10.16. Mobile bed scrubber.

Extremely soluble bisulphite in solution changes the relatively insoluble sulphite when the solution pH shifts from 4 to 10. When SO_2 is absorbed, the scrubber solution is usually between pH 4 to 6 and, therefore, the predominant species are bisulphite. When the pH is suddenly raised either in localized areas or in a reaction tank, crystallization of calcium sulphite will occur. It has been experienced that sulphite scaling occurs in the scrubber bed when free hydroxide is introduced thus causing bed pH to rise. By proper control of pH of the spray slurry (<10) entering the scrubber, calcium sulphite scaling can be controlled in the scrubber. This scaling is self-controlled in limestone system by maintaining pH between 5 and 7 due to the buffering action of the carbonate-bicarbonate couple.

(b) **Calcium Sulphate Scaling ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).** It is formed in the system due to oxidation in the scrubber, reaction tanks and thickeners which increases the sulphate ion concentration in the system. The scaling can be minimized by circulating calcium sulphate seed crystals. The seed crystals provide nucleation sites for non-scaling forming homogeneous precipitation of calcium sulphate.

The seed crystal recirculation and mixing in the reaction tank is supplemented by forced oxidation to prevent calcium sulphate scaling in limestone systems. In a forced oxidation system, air is bubbled into the reaction tank to oxidize the sulphite to sulphate. The forcibly and naturally oxidized sulphate is precipitated in the reaction tank. Forced oxidation essentially eliminates the dissolved sulphate returned to the scrubber, thereby minimizing the potential for oxidation of sulphite to sulphate by the oxygen in flue gas and resultant scaling. A reduction in overall solids concentration is an added benefit with forced oxidation as the majority of solids are gypsum and seed crystals.

2. Plugging. It is similar to scaling but consists of soft deposits formed by chemical reactions. These deposits generally buildup in the demister (mist eliminator) and severely restrict the gas flow and increase the pressure loss. As much as 30 gpm of scrubber liquid is entrained in the gas passing through the demister and forms the plugging deposits.

The plugging problem can be solved by any one method or combination of the following :

- * Installation of an intermediate wash tray to lower the concentration of the slurry solids in the gas before entering into the demister.
- * Providing the orientation of demisters to cross-flow conditions, with gas flowing horizontally and demister draining vertically.
- * Providing intermittent back washing of the demister.

The plugging problem can be corrected by washing the demister if the deposits are soft. But if the deposits are made of soft and hard scale formed by the precipitation of CaSO_4 from super saturated liquid, then some other technique must be used in addition to washing.

Several manufacturers, presently, are using spray towers for desulfurisation systems to avoid plugging problems.

3. Corrosion. Most high efficiency scrubbers quench the flue gas to its saturation temperature. As gas is humidified, serious corrosion problems can develop. Corrosive attacks are further accelerated by high gas inlet temperature, high solid contents, acid content of recycle liquor streams and high gas and liquor velocities often necessary to effect good scrubber performance. Acid is formed because, gas becomes wet and can rapidly attack alloys used. In addition to the scrubber, auxiliary equipment such as fan, pumps and heat exchangers are subjected to corrosion attack. Therefore, the major problem faced for the successful operation of wet scrubbers is the corrosion of the metal part used in scrubbers.

When the flue gases containing SO_2 and SO_3 are brought directly into the scrubber, an ill-defined junction of wet and dry gases results. In this junction, scrubbing liquor is readily pulled into the inlet duct by eddy currents, causing high localized acid concentrations. To avoid the disadvantages of this type of entry, gases are prequenched before coming to main scrubber spray tower. Thus, the gases are already saturated when they enter the scrubber and the interface and eddy current problems are avoided.

Providing reheat of the gases prevents corrosion of downstream of the scrubber, avoids a visible plume from stack and provides better dispersion of the pollutants.

Materials Used for Scrubbers. The common materials which are used for scrubber construction are stainless steel and fibreglass reinforced plastic (FRP). These materials are further provided with lining to resist the corrosion and increase the plant life. The common materials which are used for the lining of the stainless steel are acid resistant brick material and ceillcote.

The acid brick lining provides an acid resistant, abrasion resistant and furnishes thermal protection. Brick linings have their limitations as fireclay acid brick cannot sustain temperature above 450° to 550°C. This is because when the droplets of scrubbing liquor impinge on acid brick lining at gas temperature above 400°C, spalling takes place. Silicon carbide brick has the best spalling resistance even at 1400°C but its high installation cost limits its use. Brick lining restricts the shape of the scrubber vessel, greatly increases weight, makes vessel access difficult, and are costly to instal. Despite these serious limitations, these are frequently used to the critical zones of the scrubber.

10.8. NON-CONVENTIONAL THROWAWAY SCRUBBERS

1. Lime and Alkali-Flyash Process. This system can be used with coal containing low sulphur and its ash containing high percentages of CaO and MgO.

The alkaline fly ash can be added to the system either by collecting flyash separately in electrostatic precipitators, slurring and pumping to the scrubber circuit or by scrubbing flyash directly from flue gases by recirculating a slurry of flyash and water.

The second type scrubber system mentioned above is used at Montana Power plant of 360 MW capacity where ventury type absorber is used. The flyash loading is also reduced considerably in this scrubber avoiding the use of electrostatic precipitator and reducing the major cost factor. A provision for washing the mist eliminator is also made and very low level of suspended solids is maintained in the liquid circulated.

This type of system is very economical as it utilises the natural alkalies from the ash carried with gas and reduces the cost of reagent completely.

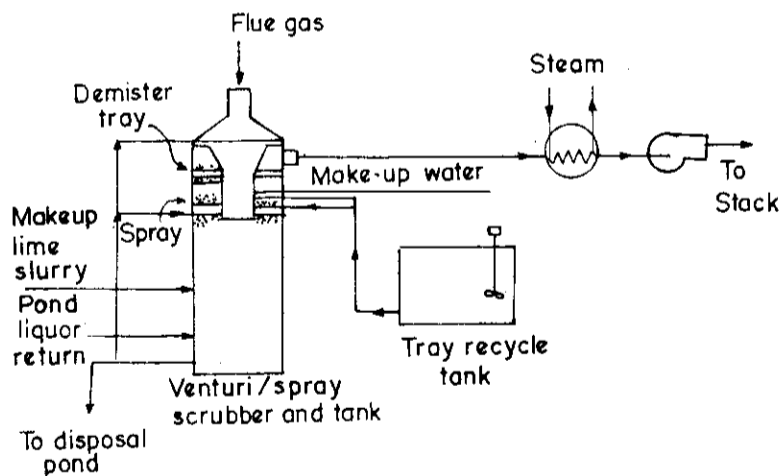


Fig. 10.17. Typical Lime/Alkali Flyash Process.

2. Sodium Scrubbing. The sodium scrubbing system used at Nevada Power Plant is shown in Fig. 10.18. This system uses locally mined trona as scrubbing solution instead of commercial grade *soda ash*. The system uses venturi scrubber and tray type absorber to control the stack gas standard of 50 ppm SO₂. The waste effluents are disposed to solar evaporation tanks. The salts in the tank consist of a mixture of *sodium carbonate* and *sodium chloride* which is environmentally acceptable disposal.

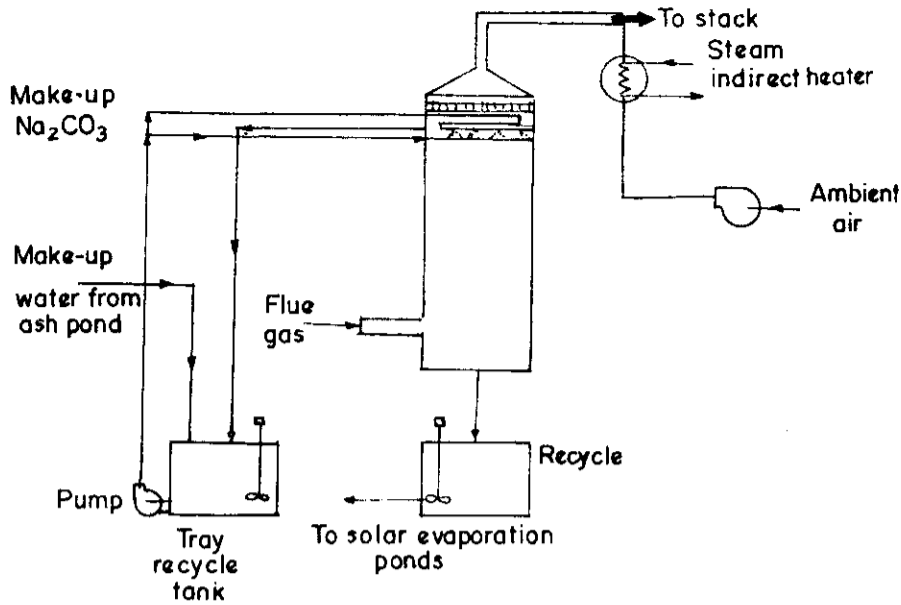


Fig. 10.18. Typical Sodium Scrubbing Process.

This system is generally preferred at desert location where water availability is low, coal used contains low sulphur, the natural evaporation rate is high and sodium carbonate is locally available.

The benefits of this system are listed below :

- * The capital cost is low.
- * Use of soluble sodium salts instead of calcium slurries insures higher reliability with reduced maintenance costs by avoiding plugging and scaling.
- * Sodium scrubbing avoids the high liquid to gas ratios and reduces the size of the plant considerably.
- * Waste disposal is economical and environmentally attractive.

10.9. ADVANTAGES AND DISADVANTAGES OF WET SCRUBBERS

Advantages. (1) It can handle any type of fuel and cope up with varying furnace conditions by changing the power input.

- (2) It requires small space.
- (3) There is no limit on flue gas temperature and moisture content.
- (4) It has an ability to remove SO_2 as well as particulates.
- (5) It can collect submicron as well as coarse particles.

Disadvantages. (1) Slurry disposal poses a difficult problem.

- (2) The plume buoyancy is reduced due to entrained mist and to overcome this, reheat is necessary.
- (3) The corrosion is quite heavy as SO_2 produces acidic mist.
- (4) The power requirement as well as capital costs are high. The running cost is 5 times of ESP.
- (5) Scaling and plugging are the main problems in the operation of the scrubbers.
- (6) Start up of a scrubber and getting it into the full operation is fairly complex and time-consuming procedure, therefore, scrubbers should be used with the plants that operate continuously at constant load.
- (7) The cost of the scrubber does not decrease very much with respect to plant size as in boiler and turbine.
- (8) It requires large quantity of water for cleaning as well as disposal of sludge.
- (9) Wet scrubbing requires special metals for construction of scrubber parts and costly lining due to high risk of corrosion.

10.10. REGENERATIVE TYPE SCRUBBERS (FGD SYSTEMS)

The problem of the waste disposal with conventional lime stone system is very critical as large quantity of gypsum as a byproduct is produced and it requires several hundred acres of land for its permanent impoundment. Wet gypsum generally lacks in structural strength and makes it difficult to reclaim the disposal area when the plant is decommissioned. Gypsum is also water soluble and presents the potential for leaching away the ground water over a long period.

A regenerative type process is considered as an alternative to the conventional system as it not only avoids the problem of disposal but produces sulphur and H_2SO_4 as by-product also.

Fig. 10.19 shows the possible amounts of byproducts produced by a regenerative process from a 600 MW plant burning coal containing 3% sulphur. It can produce 1 million tons of sulphur, 3 million tons of H_2SO_4 and 6 million tons of stable gypsum during life period of the plant of 30 years. Whereas, a limestone system will throw away 10 million tons of wet sludge containing gypsum, calcium sulphite, untreated limestone and substantial quantity of water. In USA, 200 million tons of these materials were disposed off in the year 1980. This is creating a waste management problem of monumental proportions.

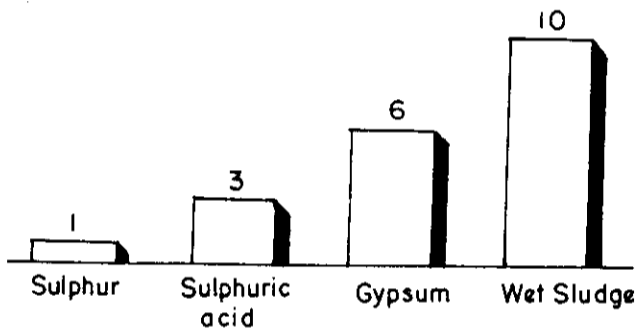


Fig. 10.19. Byproduct quantities from regenerable FGD process.

There are more processes of regenerative type but well-developed and adopted is only Wellman-Lord process which is only discussed here.

1. Wellman-Lord Process. It is most widely used regenerative type system. It has operated reliably and with SO_2 removal efficiently in oil and coal-fired plants. The block diagram of the components is shown

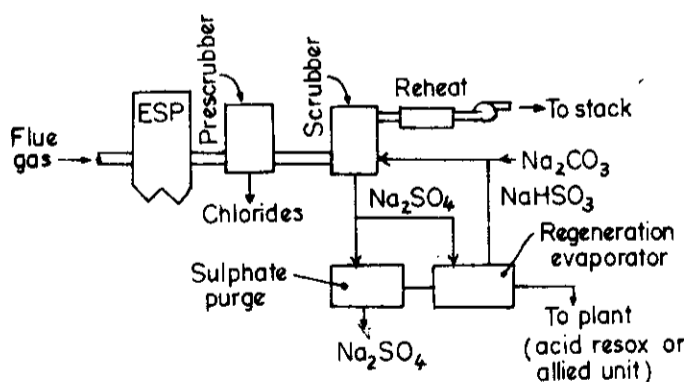
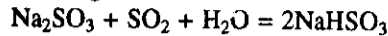


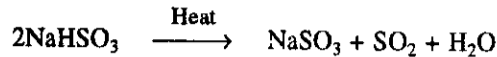
Fig. 10.20. Wellman-Lord Process.

in Fig. 10.20. The process uses sodium sulfite as the scrubbing medium. Reaction with SO_2 produces sodium bisulphite which is heated to evolve SO_2 and regenerate Na_2SO_3 . The evolved SO_2 from regeneration is compressed and liquified or catalytically oxidized to produce H_2SO_4 or reduced to elemental sulphur. This process scrubs with an aqueous sodium solution instead of slurry and keeps the scaling and plugging to a minimum.

Absorption reaction is given as



The regenerative reaction is given as



As water condenses from SO_2 steam mixture, a wet enriched SO_2 gas stream is produced for further processing.

Nagoya station of 115 MW in Japan and Nipsco plant in USA are the examples where Wellman-Lord process is used for removing SO_2 from flue gases. Another notable plant of 1700 MW capacity where this process is used is San Juan station at New Mexico.

2. Magnesium Oxide Scrubber. This is most economical regenerative type of method among all available today. The system components are shown in Fig. 10.21. The system uses highly reactive MgO to absorb SO_2 and forms magnesium sulfite which is then shipped to regeneration plant where SO_2 is released and MgO is returned back to the scrubber. Eddystone station of 696 MW capacity and Cromby station of 150 MW in USA are using this type of scrubber.

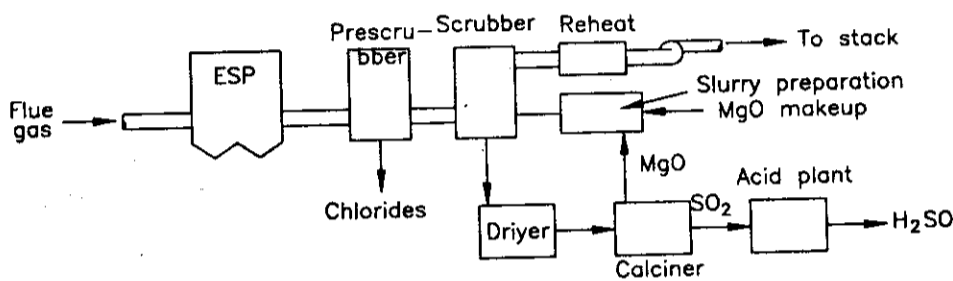


Fig. 10.21. Magnesium Oxide Scrubber.

Regenerative desulfurization systems have never enjoyed wide applications compared with lime stone and dry FGD systems because these systems are more complex, have higher capital costs, require more energy to run and requires tight process control which are quite difficult and costly problems.

10.11. DRY SCRUBBING SYSTEMS

Dry Scrubbing for the combined removal of both SO_2 and particulates from flue gases is one of the most promising directions being taken in FGD technology today. The waste handling problems associated with wet scrubbing have long been calling for the development of dry technology. The fabric filter, with its ability to remove very fine particulates (50 to 100 μ) at high collection efficiency (99%) was mostly responsible for dry scrubbing development. Addition of spray drier upstream of the fabric filter as primary absorber stage marked the emergence of the combined system as a dual purpose dry scrubber.

Dry Scrubbers offer potential advantages over wet scrubbers, especially in the areas of energy savings and capital costs. Further, the design of dry-system is relatively simple, stack gas reheat is greatly reduced and the disposal product is dry rather than a wet sludge. The major disadvantage of dry scrubber is the use of an expensive alkali compared with limestone. Many times high cost of alkali absorbent may offset the saving in capital costs and maintenance charges.

There are mainly three types of dry scrubbers as spray, drying dry injection and combustion of fuel with lime-stone mixture. The third type is discussed in more detail in the chapter on FBC system. Among the remaining two, spray drying is the only one presently being offered on a commercial scale.

The system arrangement for spray drying system is shown in Fig. 10.22. The basic components are spray drier and fabric filter. In this process, the slurry of the absorbent solution is atomised into the incoming gas-stream to increase the liquid gas interface and to promote the mass transfer of SO_2 from gas to liquid. The thermal energy of the gas also helps to evaporate the water and produce a dry powdered mixture of sulfite-sulphate and some untreated alkali. The gas is further passed through fabric filter where most of the particulates carried by the gas and dry powder formed in the scrubber section is removed. Since the flue gas is not saturated and does not contain liquid carryover, troublesome mist eliminators are not required.

Earlier, powdered nahcolite (a mineral form of sodium bicarbonate) was used instead of sodium bicarbonate because of the tendency for the bicarbonate to form a porous carbonate with significantly greater specific area than commercial soda ash when heated. But these absorbents were not used due to prohibitive cost in the throwaway system.

Other alkalis such as calcium and NH_3 were too temperature dependent and high temperatures for maximum absorption efficiency necessitated the development of fabric filters that could withstand hot gases ($150\text{-}200^\circ\text{C}$). Soda ash, trona and calcium in the form of lime are now acceptable reagents.

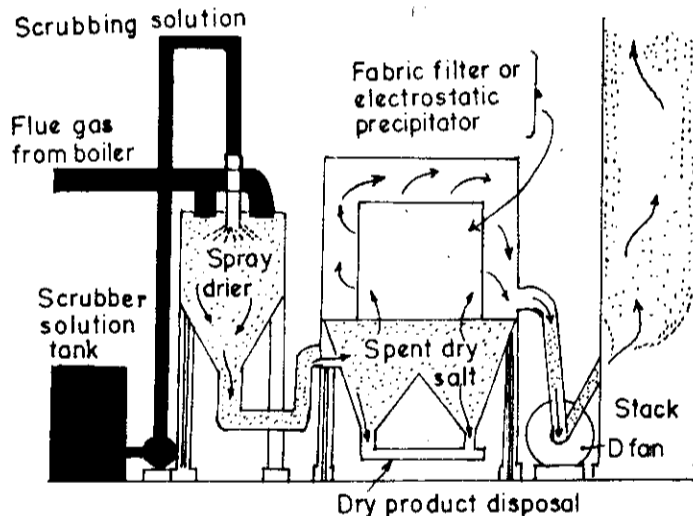


Fig. 10.22. Spray type dry scrubbing system.

The factors which are responsible for the efficiency of the system are atomization of the absorbent, intimate mixing of gas and absorbent and residence time of both in the absorbent and stoichiometric* ratio of the absorbent.

To economise the above described system, the reagent discharged at the base of the absorber and fabric filter is partly recirculated with the fresh feed material. This helps to use again the non-reacted absorbent. This further provides inert particles upon which fresh absorbent is dispersed. Alkaline material in the flyash is also made available for SO_2 absorption. Such system used at Antelope Valley Station of 440 MW capacity in North Dakota, first of its kind in USA is shown in Fig. 10.23. This plant handles 2800 tons of gas per hour burning 375 tons of coal per hour and reduces SO_2 level from 800 ppm to 304 ppm.

*Stoichiometric ratio is defined as the ratio of the actual absorbent required to the theoretical requirement in terms of molar equivalents at a stoichiometric ratio of 1.

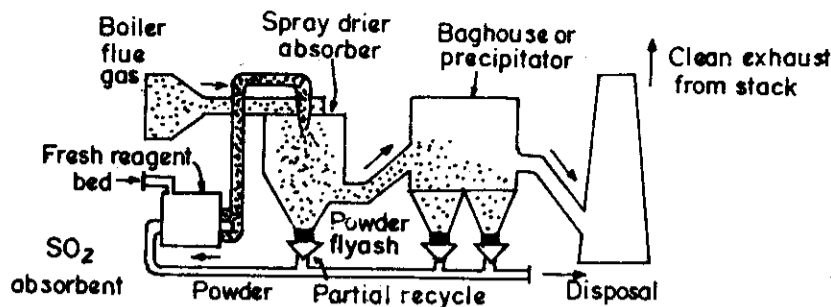


Fig. 10.23.

Comparison of Wet Versus Dry Scrubbers

1. A dry system has less equipment than wet system. Thickeners, centrifuges, vacuum filters and mixers are not required to handle the waste in dry system.
2. Waste products from dry scrubber are collected along with flyash and can be handled with conventional dry material handling.
3. Scaling and plugging are not the problems with the dry systems.
4. Corrosion is also not experienced in dry systems.
5. There is large flexibility in the operation of the dry system. Feed rate can be easily adjusted as it has little concern of pH control in the scrubber.
6. The size of the plant is much smaller and therefore the capital cost as well as operating and maintenance costs are also less than wet system.
7. The energy requirement of dry system is hardly 25% of the wet system to operate the equipments used.
8. The I.D. fan can be safely located ahead of the stack without fear of fan corrosion and without need of reheat.
9. The water requirements of dry system are much less than for a wet system.
10. The gas volumes of the spray dryer are reduced below those leaving the air heater with resultant saving in cost for particulate collection.

A ceilmate corrosion resistant monolithic lining showed the best resistance to corrosion as well as to erosion. These linings are formulated of thermosetting resins, usually epoxy or polyester. They can be reinforced with glass mat or cloth to increase the tensile strength and to lower the coefficient of thermal expansion of the lining. The lining range in thickness varies from 4 to 12 mm. It has been estimated that these linings give satisfactory protection at least for ten years under severe operating conditions such as high temperature, severe chemical reaction, thermal shock, impact and abrasion.

Recently scrubbers are fabricated of fibreglass reinforced plastic (FRP) to resist the attack by corrosive gases and liquids. With FRP construction, it is advisable to use fire-retardant resins. Temperature limitations of FRP are overcome by using an inlet spray quench section to keep the gas temperature below 150°C.

No problems are encountered with stack lining as only dry flue gases are exhausted. But if the gases are not heated to 60°C, stack should be assembled with acid resistant mortar.

10.12. SLUDGE DISPOSAL AND ITS USES

One of the major challenges associated with lime stone scrubbing is the large amount of byproduct material requiring disposal and recovery.

The chemical constituents of the sludge formed are mainly responsible for unique handling and disposal difficulties. The FGD sludge is composed of calcium, sulphur salts, along with varying amount of calcium

carbonates (CaCO_3) and untreated lime. Most of the sludge contains calcium sulphite hemi-hydrate ($\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$) and some calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)—known as gypsum—and small amount of free lime (CaO). As this slurry has pH of 7 to 9, most of the untreated lime forms CaCO_3 with the CO_2 from the flue gases. In lime-stone scrubbers, the low pH of slurry encourages the oxidation of some SO_2 to SO_4 promoting the precipitation of gypsum. The degree of oxidation depends on the excess air in the boiler, sulphur content in the coal and presence of O_2 with the flue gases.

The choice of site for its disposal is also a major consideration as the volume of sludge is extremely large. The factors which are responsible for the choice of site are surface water contamination; fugitive particulate emission and physical stability of the sludge. Economic factors alone cannot control site selection but environmental regulations also play the leading role. The effluent cannot be discharged to river as river authorities usually do not allow reducing matter to enter a river.

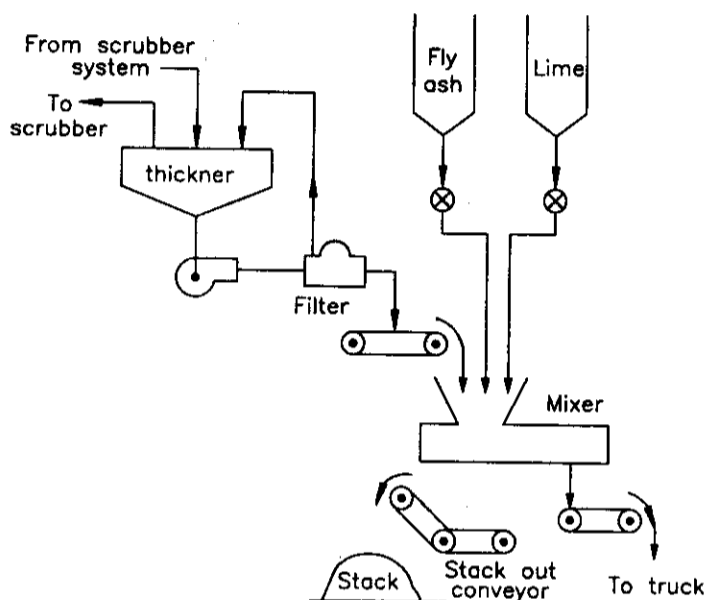


Fig. 10.21. Sludge disposal system.

There are mainly three methods of disposal as wet ponding, dry impoundment and mine disposal.

Wet ponding is most widely presently used method but it requires large areas of land (0.2 to 1 acre-ft/MW-year) as sludge contains large amount of water. Because the sludge is highly thixotropic, ponds are unstructural sites and not amenable to reclamation. Leaching from wet pond is another important environmental issue for locating the site for disposal.

Dry impoundment methods include mechanical dewatering or blending with flyash and land filling and sludge stabilization.

One consideration that affects all the above methods is the physical instability of the sludge which is dependent on many factors like waste density, effective cohesion, densing or swelling property and many others. There are many methods which are used for increasing the stability of the sludge, some popular are blending, forced oxidation and chemical fixation.

It has been estimated that capital and operating cost of sludge stabilization and disposal are as high as \$ 3.2 per ton of coal fired. An environmentally stable waste byproduct will be a major consideration for any new FGD system. Future demand of high SO_2 removal will make second generation lime system such as Davy S-H process a viable alternative to lime-stone wet scrubbing.

Uses of Waste-Sludge. The sludge upgraded either by oxidation method or by blending with ash or other stabilizing agents can be used for many useful processes.

The strength of the sludge can be increased by pozzolanic reactions. The final mass formed gets strength with age and is essentially impermeable to water after being fully hardened. The solid mass formed is used

as road base material as concrete like blocks in the creation of artificial ocean reefs and light weight aggregate in the construction industry.

Forced oxidation process with gypsum as byproduct recovery has been widely used presently particularly in Japan and Germany. The gypsum may have a future sale potential as raw material for making wall board and in cement industry as a set retarder. The gypsum produced has a high degree of purity (95 – 97% CaSO_4) so the wall boards made out of this have a 10% lower specific gravity than that made from mined gypsum with 50% greater strength. If the gypsum cannot be sold and must be stockpiled it is easily dewatered to 80% solids and can be easily stacked, using only 60% of the land necessary for sludge disposal. The handling of the gypsum is more easy and it is chemically stable and environmentally acceptable than $\text{CaSO}_3/\text{CaSO}_4$ sludge.

A long road was constructed in Pennsylvania in 1977 from stabilized sludge. The strength is increased three-fold during 3 years period as a result of ongoing sulfo-pozzolanic reactions. An artificial reef built along the Island of New York in 1980 using 15000 blocks made of stabilized sludge, to help an aquatic life is another example of the use of stabilized sludge.

An alternative to byproduct disposal is the byproduct recovery involving regeneration of sulphur and recycling of the calcium additive as mentioned earlier. Several European plants are using such processes on large scale.

EXERCISES

- 10.1. What is the main function of a scrubber ? When it is preferred in the thermal power plants ?
- 10.2. What is the difference between non-regenerative and regenerative type of scrubbers ? Discuss their relative merits and demerits.
- 10.3. Draw a line-diagram of a limestone absorbing type scrubber and explain its working. List out the chemical reactions of limestone scrubber.
- 10.4. What is the importance of regulating the pH value of the scrubber slurry ? What is its range and why this particular range is used to effective working of a scrubber ?
- 10.5. What are the different methods used to upgrade the performance of lime-stone scrubber system ? Explain any one with a neat sketch.
- 10.6. Draw a line diagram of double alkali system of scrubbing and discuss its merits over other types of scrubbing methods.
- 10.7. Describe the working of Davy S-H process with a neat sketch and list out its outstanding features.
- 10.8. What are the different types of absorbers used in scrubbing system ? Explain the working of cyclone type with a neat sketch.
- 10.9. Draw a neat line diagram of two stage spray type scrubber system and explain its working.
- 10.10. Discuss the relative merits and demerits of venturi and mobile bed absorber type scrubbers.
- 10.11. Discuss the relative merits and demerits of wet type scrubbers.
- 10.12. What are the basic causes of scaling and corrosion of scrubbers ? What different methods are adopted to reduce the same ?
- 10.13. Draw a neat line diagram of Wellman-Lord Process and explain its working. What are its outstanding features ?
- 10.14. What do you understand by dry scrubbing ? Draw a neat diagram of a dry scrubbing system and explain its working.
- 10.15. Explain the different uses of sludges coming out of scrubbers.



Control of Nitrogen Oxides

11.1. Introduction. 11.2. Effects of Nitrogen Oxides. 11.3. Factors affecting NO_x Formation. 11.4. Reducing NO_x by Furnace and Burner Design. 11.5. Reducing NO_x by Two-Stage Combustion. 11.6. Control of NO_x by Flue Gas Recirculation (FGR). 11.7. Exhaust Gas Denitrification. 11.8. Simultaneous Desulphurization and Denitrification. 11.9. Control of NO_x in Gas Turbine Plant.

11.1. INTRODUCTION

The regulations on the nitrogen oxide emissions are becoming hard as it is one of the most offensive pollutants produced by combustion process. An increased power generation activity has increased NO_x emission and it has become essential to limit its emission level as it has many bad effects on the human health. The oxides of nitrogen are the second most abundant air contaminants found in the thermal power exhaust. The control of NO_x pollution has proved to be difficult and no widely applicable method has so far been developed on commercial basis. Measures are taken at different stages to reduce its emission before the gases are exhausted to atmosphere.

11.2. EFFECTS OF NITROGEN OXIDES

NO_x is produced in all combustion processes using air. It forms chiefly as nitric oxide (NO) which later gradually combines with atmospheric O₂ to form nitrogen dioxide (NO₂). The NO₂, in turn, reacts with hydrocarbons and O₃ in the presence of sunlight to produce smog and compounds that irritate eyes, may aggravate certain respiratory diseases and infuse plant life. In combination with moisture in atmosphere, NO₂ forms droplets of nitric acid. These acid mists cause corrosion to metallic structures in the plant and its vicinity.

It is also believed that NO_x contributes significantly to rain acid problem. It has also become essential to restrict further NO_x emission to achieve compliance with O₃ regulations. It creates health hazards only in densely populated and smog prone areas, therefore the regulations are strictly followed for the power plants situated in city like areas. The job of establishing emission limits is complicated by different boiler designs and types of fuel used. Both of these variables influence significantly the amount and nature of NO_x emissions. Therefore it is not possible to apply the same emission rules throughout the country or state and it is mostly dependent on fuel properties.

The NO_x emission standards have been set for large capacity thermal power plants. The present standard in USA is 0.3 kg/million kJ of heat generated for bituminous coal and 0.25 kg/million kJ for sub-bituminous coal. For oil and gas fired plants these limits are 0.15 and 0.1 respectively. These restricted standards demand 60 to 70% of reduction of NO_x from the total NO_x generated.

It has been observed that the plant life is damaged when NO_x exceeds 25 ppm. and safe limit for human beings is 5 ppm.

In boilers, NO_x is derived from two sources, nitrogen in the combustion air (thermal NO_x) and N₂ chemically combined with fuel (fuel NO_x). For fuels like natural gas and light oils containing low amounts of nitrogen, thermal NO_x is predominant in the total NO_x formed. But for heavy oil fuels and coals, fuel NO_x predominates in the total NO_x.

Typically, between 60% and 80% of all NO_x generated from the combustion of coal is attributed to fuel nitrogen. It has become necessary to focus attention to both thermal and fuel sources, much of the present low-NO_x combustion development is directed at controlling fuel NO_x.

11.3. FACTORS AFFECTING THE NO_x FORMATION

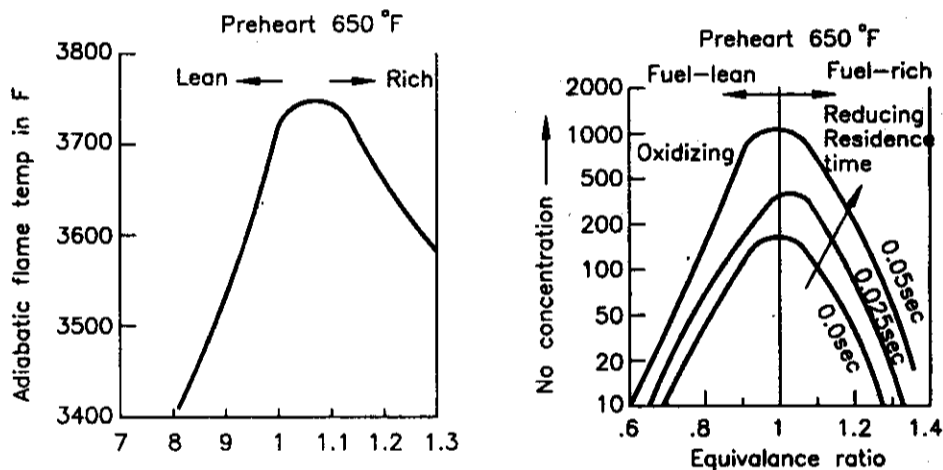
The nitrogen oxides are produced in all fossil fuel combustion processes using air as the oxidant. The amount of NO_x formed is strongly dependent on peak flame temperature and residence time at the peak temperature. Other factors such as heat and mass transfer rates, fuel type and composition and operating and design variables contribute significantly to the amounts of NO_x produced.

Amount of NO_x emitted by the boiler may be controlled by the proper design of boiler furnace and burner setting, use of combustion modification by providing rich mixture in the combustion and allowing less time to remain in high temperature zone (as lean mixture and more residence time are inductive for NO_x formation) and by scrubbing of stack gases for NO_x . In actual practice, a single or a combination of the methods mentioned above are used for controlling NO_x emission.

The NO_x formation can be decreased by reducing the concentration of O_2 in the combustion zone, controlling the peak temperature in the combustion zone or reducing the residence time of N_2 and O_2 in peak temperature zone as NO_x is formed only at high temperature ($\geq 1200^\circ\text{C}$) and in lean air-fuel mixture. The effect of air-fuel ratio on the peak flame temperature and NO_x formation taking residence time as parameters are shown in Fig. 11.1 (a) and Fig. 11.1 (b).

The flame temperature can be controlled by controlling heat release rate, burner setting and by adjusting flue gas recirculation. Low NO_x burners are another alternative. They control fuel and air mixing in such a way that the flame temperature is kept low by dissipating heat quickly.

The quantity of O_2 can be controlled through proper excess air operation. Firing with low excess air has presently become standard practice on oil and gas fired boilers. NO_x reduction with this technique alone has reduced NO_x formation by 15 to 20%.



(a) Effect of equivalence ratio on flame temperature.

(b) Effect of equivalence ratio on NO_x concentration.

Fig. 11.1.

Generally three methods are commonly used to reduce the production of NO_x in the boiler during combustion of fuel :

- (1) The O_2 concentration is reduced or oil concentration is increased.
- (2) The temperature of the combustion zone is reduced.
- (3) The residence time of the products in the high temperature zone is reduced.

To reduce the maximum temperature of combustion, the combustion products are recirculated, promoting equalization of temperature field in the furnace. Two side screens are installed in the flame zone which are cooled by gaseous stream and reduce the temperature in the flame zone.

A reduction in time of residence of the combustion products in the high temperature zone is ensured by burning the fuel under conditions close to stoichiometric. This is most promising method as it reduces the other combustion products as CO, formaldehyde, aromatic hydrocarbons and SO_2 to minimum.

11.4. REDUCING NO_x BY FURNACE AND BURNER DESIGN

The formation of NO_x depends on the quantity of O_2 and N_2 in the products of combustion and heat of combustion. Boiler and burner design can significantly affect NO_x formation because peak flame temperatures, air-fuel ratio, residence time and quenching rate of combustion gases in the furnace are affected by many parameters.

Firing with low excess air is now standard practice. Reductions in NO_x levels have registered between 15-20%. Operating with 10% excess air can increase NO_x emissions by 10 to 20%. But decrease in the combustion air can be made until CO values reach a level of about 200 ppm. Reducing excess air beyond this normally increases smoke to unacceptable level in oil-fired boilers with carbon carryover, the main culprit with coal-fired units.

Burner spacing can affect the intensity of combustion and ability of bulk gases to circulate into the primary zone and quench the NO_x formation reaction. Units with closed spaced burners and low surface to volume ratios have been observed to have higher NO_x emission than units with less closely spaced burners and lower burner zone heat release rates. This is because interaction of closely spaced burners increases the peak and average flame temperatures. In addition to space between burners, the location of the burners in the furnace walls affects the interaction of flames and thus the peak and average temperature in the firebox. Generally the flames of wall fired units have higher peak temperatures and lower quenching rates than corner or tangentially fired units. Thus, wall fired boilers usually have greater NO_x emissions than corner fired units.

Boiler and firing system geometries play a significant part in controlling NO_x emissions. Designers have lowered burner zone heat release rates by 30-50% to reduce the NO_x formation and minimising slagging.

A turbo furnace as shown in Fig. 11.2 with burners on opposite walls allows ample residence time and is conducive for slow mixing. Low swirl burners further delay the mixing of secondary air into the fuel which produces low temperature diffusion flame which inhibits NO_x formation. Low NO_x can also be achieved by directing the fuel and less than 20% of the secondary air into the centre of the furnace, with remaining secondary air directed parallel to the furnace walls. The delayed mixing of the wall air into the vortex causes a fuel rich combustion zone reducing formation of NO_x . This is known as rich fire ball concept as shown in Fig. 11.3.

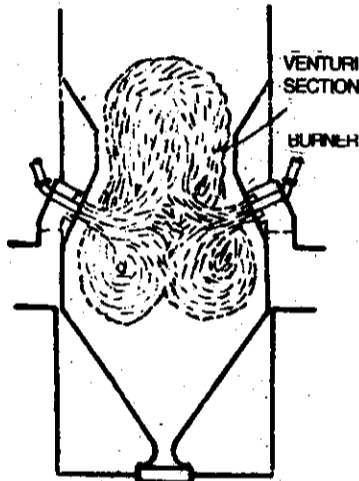


Fig. 11.2. Turbo furnace.

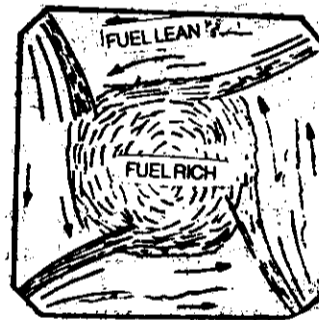


Fig. 11.3. Fire ball furnace.

Low NO_x burners control mixing of fuel and air in a pattern that keeps flame temperature down and dissipates heat quickly. One commercial unit, known as self-recirculation system as shown in Fig. 11.4, uses

gas recirculation and two stage combustion, all within the burner. The key feature of this burner is the creation of a strong recirculation of the combustion products in the burner throat as shown in figure.

Modified furnace designs as a means of lowering NO_x emissions include the primary combustion furnace, an arch fired furnace and the compensated wind box.

The primary combustion furnace confines fuel-rich flame zone outside the main furnace. This has reduced NO_x formation considerably.

In arch fired furnaces, the coal is introduced downward from the arch into the furnace, with the bulk of combustion air added through the front wall, perpendicular to the flame jet. This creates a slowly mixing diffusion flame which reduces NO_x formation.

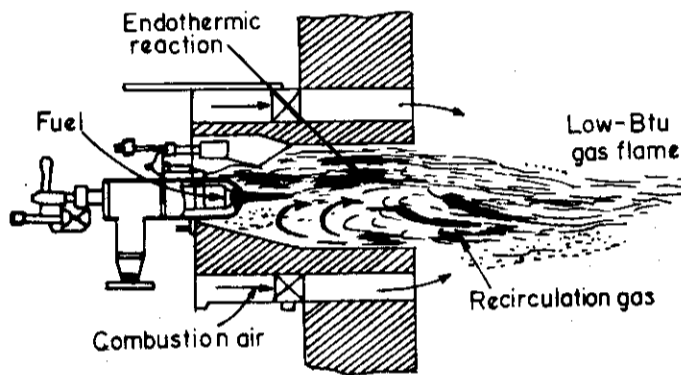


Fig. 11.4. Gas recirculation with two stage combustion with the burner.

The compensated windbox is used for closer control of excess air in multi-burner pulverised coal fired boilers. These units are equipped with tertiary parts to provide air above the burner so formation of NO_x can be minimised by staged combustion technique.

The selection of NO_x control system for a given installation is influenced by boiler size and type of fuel used, applicable regulations and characteristics of control equipments. The optimum system is one that meets the emission regulations at the lowest cost and at the same time provides flexibility for changes in fuel or regulations over the plants design life time.

11.5. REDUCING NO_x BY TWO STAGE COMBUSTION

Coal fired boilers of a decade ago were designed to save capital costs by minimising boiler furnace volume. To compensate decreased size, highly turbulent combustions were developed, using large amount of excess air to obtain total carbon burn up. This design created ideal conditions for the formation of NO_x . But with the new acts of pollutions, this level of NO_x emission cannot be accepted and some other methods to reduce NO_x emission must be adopted.

Stage combustion is perhaps the single most effective NO_x control scheme for new or existing boilers with heat input rate above 200 million kJ/hr. In this system, localised fuel rich mixture conditions are created so NO_x formation is minimised. Reduction of 70% with gas and 40% with coal can be achieved with this method.

By combining two stage system of combustion, the NO_x content in the flue gases can be reduced to 50-100 ppm. The main disadvantage of this system is the higher CO content in the products of combustion and special measures should be taken to after burn the CO at the end of the furnace.

Staged combustion can be achieved by several ways. A common method is to operate top burners with air only on air-rich mixture and bottom burners with fuel-rich mixture. In some applications, overfire air ports are added above the top burner row with the burners firing at or near fuel-rich conditions.

Staged combustion can create some operational problems when it is to be applied to the existing boilers. Staged combustion may result in longer flames which, if not properly controlled, can lead to flame

impingement, slagging and tube's corrosion in the lower region of the boiler. Therefore, the degree of staging for existing and new boilers is limited by excessive CO when firing residual oil and unburned carbon and slagging when firing coal.

The use of staging is limited for utility boilers and it cannot be used for industrial units as they are equipped with only one or two burners and have not room for overfire air ports.

Recently, duel register pulverised coal burners which produce limited turbulence and controlled diffusion flame are introduced for application. A venturi mixing device which provides a homogeneous mixture of coal and primary air to burner is shown in Fig. 11.5. Secondary air is introduced through two concentric air zones surrounding the coal nozzle. Air flow to each zone is controlled by inner and outer registers independently. Another type of duel register burner is shown in Fig. 11.6. 65% of NO_x reduction is achieved by this register maintaining the NO_x level around 0.2 kg/million-kJ.

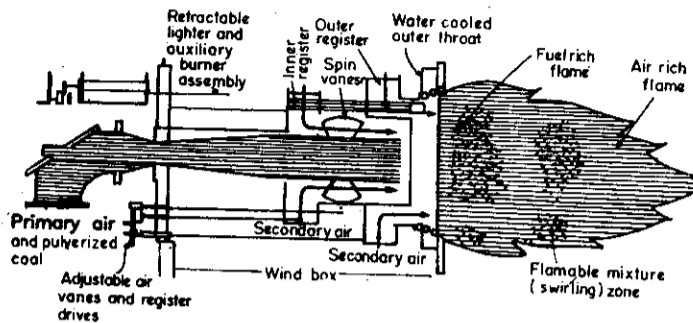


Fig. 11.5. Venturi type burner.

Some of the advantages using duel register burners are listed below :

1. A flame splitting distribution tip which causes a flower petal flame pattern minimises mixing between coal and primary air.
2. A perforated air plate that measures air flow, improves secondary air distribution.
3. Nozzle velocity can be varied to minimize shear induced turbulence and hence NO_x emissions.
4. The total air required is less and carbon burnout is more complete.

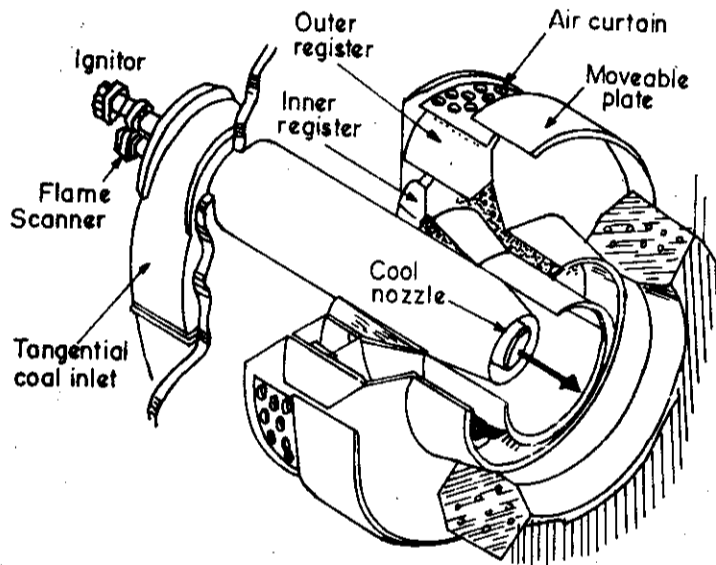


Fig. 11.6. Duel register burner.

11.6. CONTROL OF NO_x BY FLUE GAS RECIRCULATION (FGR)

Flue gas recirculation (FGR) has been successfully used for oil and pulverised coal fired boilers to reduce thermal NO_x formation.

The fuel and air usually do not have adequate time to mix properly when stoker firing is used. Even use of overfire air and different grate designs have not solved the problem completely. The FGR system has been recently used to reduce NO_x emission and to improve the operating efficiency of the boiler. The arrangement of the system is shown in Fig. 11.7. Flue gas is extracted after the convective section of the boiler and is injected into the stoker undergrate air duct downstream of the forced draft fan. A flow control damper on the discharge of the recirculation fan is automatically controlled after receiving the signal from the controller mounted on the boiler to set the ratio of recirculated flue gas to combustion air.

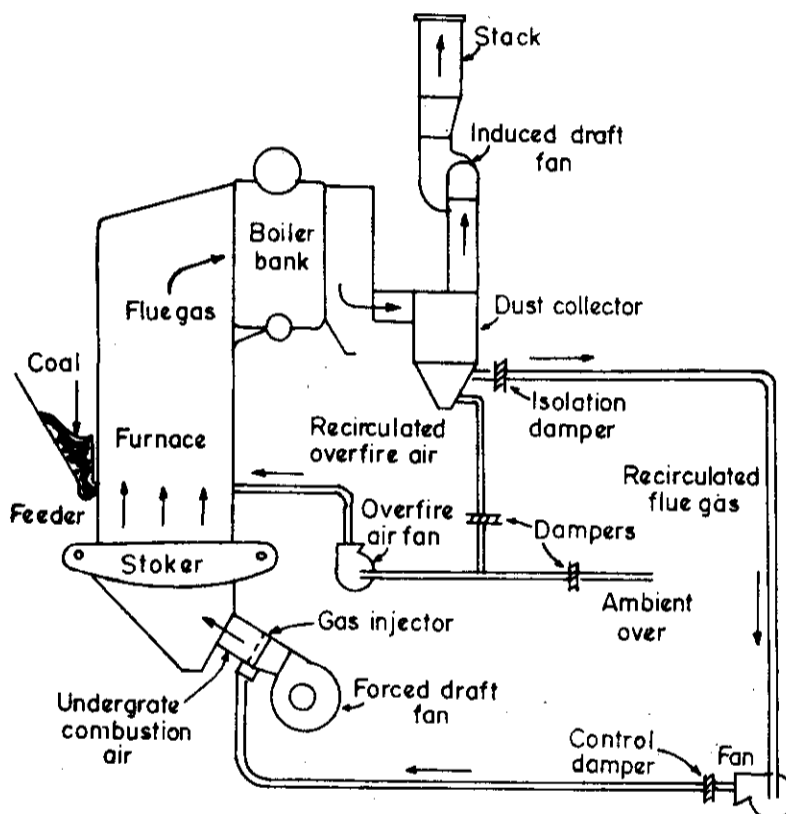


Fig. 11.7. Flue gas recirculation system.

The advantages of this system are listed below :

1. The flue gas recirculation provides smoother operation over time. The excess oxygen required is reduced considerably at all boiler loads as shown in Fig. 11.8 (a). Lower excess air saves the fuel requirement and reduces the chances of NO_x formation.
2. The excess air reduction also reduces the NO_x emission as shown in Fig. 11.8 (b). 20 to 50% of NO_x reduction can be achieved by 20-40% flue gas recirculation.
3. The FGR reduces the particulate emission as large as 35% and opacity also. An opacity as a function of boiler load with and without recirculation is shown in Fig. 11.8 (c). Earlier, the boiler capacity was limited by opacity regulations to 40 tons/hr. Flue gas recirculation extended the boiler capacity to 60 tons/hr without exceeding capacity limits.

4. The moisture in the flue gas improves the reactivity of the carbon in the coal via a water-gas reaction which improves carbon utilisation in the furnace. It also helps to keep the fuel bed cool by absorbing additional heat.

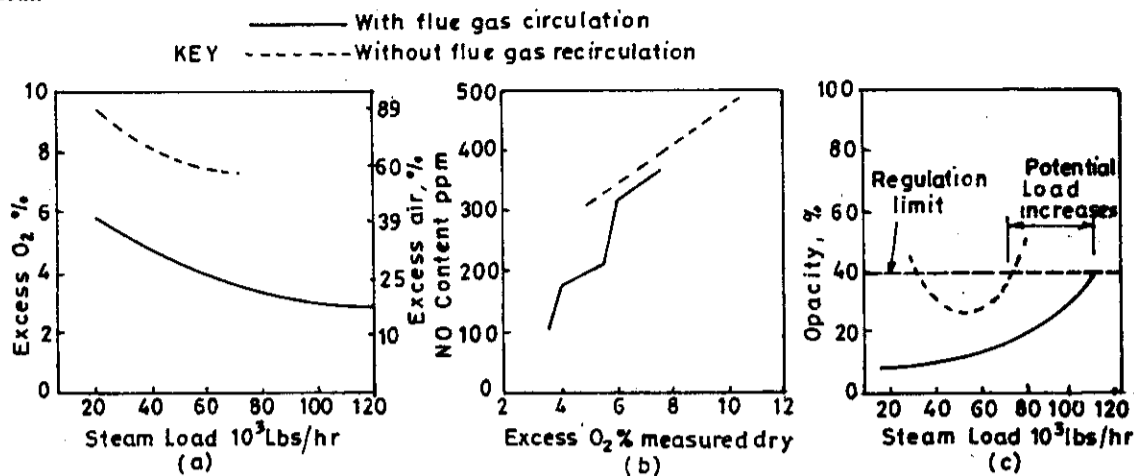


Fig. 11.8.

5. A reduction in the size of equipment downstream of the boiler-duct work, dust collection equipment and scrubbers can be achieved because of reduced stack gas flow.

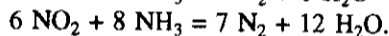
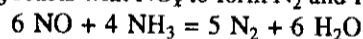
The above-mentioned benefits may combine with the traditional advantages of stoker fired boilers, greater solid fuel flexibility and lower capital cost—to keep them competitive with pulverised coal fired and fluidized bed boilers.

The only limiting factor to use this technique in any of the combustion systems is the change in the distribution of heat transfer. Radiation heat transfer is reduced in the furnace because of low gas temperature and convective heat transfer is increased in the connection section because of greater mass flow. FGR increases the super-heat and reheat sometimes excessively. In addition to this, increasing the amount of FGR will increase furnace pressure and to maintain the furnace pressure below trip pressure requires changes in the gas flow pattern and changes in the area of superheat and reheat sections.

11.7. EXHAUST GAS DENITRIFICATION

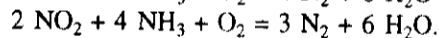
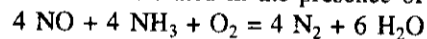
Post-combustion techniques have been proposed and used for control of NO_x emissions to levels significantly below than the present standard laid down by the Regulating Authority 0.05 kg/million kJ. There is growing trend in this industry to consider this mode of NO_x reduction as the ultimate vehicle for reducing NO_x emission in the power plants. This is most promising technique as it is proved that this can remove 80-90% NO_x from the exhaust gases and maintains the NO_x emission well below the allowable level. This system is well developed in Japan and used on many power plants very successfully. Selective Catalytic Reduction (SCR) is going to be viable NO_x control technique.

Among all, NH₃ is considered most effective NO_x removal and presently used in Japan. In this process, NH₃ is injected into the flue gas, between the economiser and air heater. The mixture then passes through a catalyst bed where the NH₃ reacts with NO_x to form N₂ and H₂O vapour as per the reactions listed below :



Here, the first reaction dominates, since 95% of the NO_x in the flue gas is in the form of NO.

The above reactions are accelerated in the presence of O₂ in the flue gases as listed below :



Among the critical variables, which affect the above reactions is the reaction temperature. These reactions take place around 550°C without catalyst but this temperature can be reduced to 150 to 250°C by the addition of catalyst which is well within the range of exhaust gas temperature of power plant as shown

in Fig. 11.9. A small amount of NH_3 invariably passes through the catalyst and exists in the reactor mixed with flue gases due to incomplete reaction between NO_x and NH_3 . It is the operation experience of the reactor that NH_3 slip is negligible when NO_x removal is below 80%. If the removal is made 90%, NH_3 slip becomes 10-20 ppm or higher. Control of NH_3 slip is very important because it forms ammonium sulphate and bisulphate which can plug the downstream air preheaters.

Japan design considers 80% NO_x removal as most economic and optimum control level because it minimizes capital and operating costs and environmental impact while maximizing system life. NO_x removal efficiency of 90% can be achieved but it costs significantly more than 80% removal. Because about 30% more catalyst and a slightly higher $\text{NH}_3 : \text{NO}_x$ mole ratio are required.

Catalysts consisting of small amounts of vanadium oxide (V_2O_5) or titanium oxide (TiO_2) base are used almost universally as they are highly resistant to SO_2 poisoning. Honeycom, pipe and plate catalytic elements are generally used for oil and coal fired boilers to avoid the possibility of plugging by particulates. The catalyst life ranges from 1 to 3 years as the fuel used-gas, oil or coal and the percentage of sulphur in the coal is 1 to 3%.

The process being dry, does not pose any waste water problems. However, the main difficulties experienced in adopting this system are optimum temperature range (300-400°C) for its successful operation, reduction of catalyst activity by SO_2 and plugging of catalyst bed particulates.

Despite potential problems, SCR processes have been incorporated in Japan on 62 power plants (26 plants are larger than 33 MW and seven are larger than 330 MW), 156 MW Chugoku power station and 90 MW Hokkaido plants in Japan and 215 MW California Edison CO. in US, are the examples where this system is successfully used to control NO_x emission.

11.8. SIMULTANEOUS DESULPHURIZATION AND DENITRIFICATION

Recently few techniques are developed for simultaneous desulphurization and denitrification.

A process of this type uses a copper oxide CuO for SO_x removal and the product of reaction between CuO and SO_x which is copper sulphate (CuSO_4) is used as catalyst for the removal of NO_x . CuO and CuSO_4 both work as catalyst for NO_x reduction to N_2 and water by reaction with NH_3 . Subsequent regeneration of the catalyst beds which requires a reducing gas, such as H_2 produces a SO_2 rich stream that can be used to produce various byproducts, like H_2SO_4 .

Combustion of fossil fuels in a fluidised bed of limestone has been successfully used for SO_2 removal and such system also helps to retard the formation of NO_x as the bed temperature is considerably low (1000°C) compared with pulverised and other system of combustion. In addition to this, the product of dolomite and SO_2 formed also helps to remove formed NO_x .

The reactions involved are

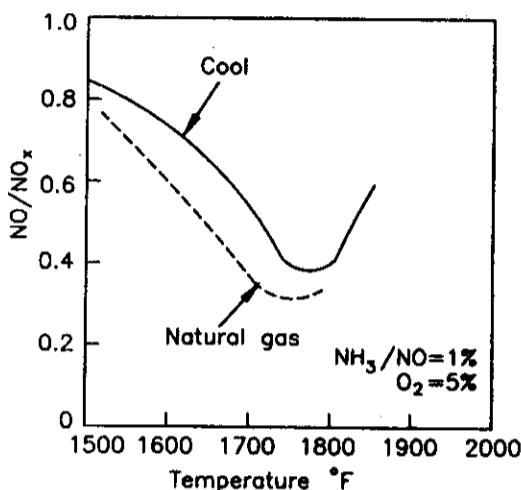
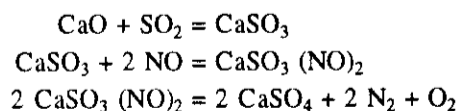


Fig. 11.9.

Honeycom, pipe and plate catalytic elements are generally used for oil and coal fired boilers to avoid the possibility of plugging by particulates. The catalyst life ranges from 1 to 3 years as the fuel used-gas, oil or coal and the percentage of sulphur in the coal is 1 to 3%.

The use of low nitrogen fuels, cleaning of exhaust gases through the use of catalytic converters, improved methods of combustion and combustion chamber and remodelling are some of the methods to reduce NO_x emission to the atmosphere.

11.9. CONTROL OF NO_x IN GAS TURBINE POWER PLANT

An appreciable amount of toxic NO_x forms with the combustion of fuels in the gas turbine plants. The problem of NO_x removal has become more important as the plant capacity has increased to 100 MW and more.

In the combustion chamber of gas turbine, high local flame temperature (1700 – 1850°C) and high pressure facilitate the formation of NO. The long exhaust path, high excess air and high pressure downstream of combustion chamber induce oxidation of NO to NO_2 . The concentration of NO_2 in the flue gases is responsible for exhaust gases having a peculiar brown colour.

One of the effective methods for decreasing NO_x in the exhaust of gas turbine power plant is to maintain low α_a and provide effective mixing in the front zone of the combustion chamber. Effective mixing at $\alpha_a > 1.6$ makes it possible to decrease local maximum temperature as well as to decrease the time for burning out the fuel. This reduces the formation of NO_x because increase in burning time of fuel appreciably increases the yield of NO_x .

Despite the fact that exhausts from peak load gas turbine plants are of short duration (2 to 3 hrs), the necessity of dispersing the exhausts to the limit of allowable concentration (0.085 mg/m³) leads to increased height of the chimney and increased cost of the whole plant. Presently, there is need to develop methods for dispersing harmful NO_x instead of its removal as the gas turbine plants are used as peak load plants for short duration of time.

EXERCISES

- 11.1. What are the bad effects of NO_x emission ?
- 11.2. What factors affect the formation of NO_x ?
- 11.3. How NO_x formation is reduced by adopting specific burner and furnace designs ? Illustrate the answers with neat sketches.
- 11.4. What do you understand by two stage combustion ? Draw a neat diagram of duel type resistor burner to reduce the formation of NO_x . List out the advantages of such burner.
- 11.5. Draw a neat line diagram used to control NO_x formation by flue gas recirculation. What are the major advantages of this system over other systems ?
- 11.6. How NO_x is reduced in the flue gases ? Explain with chemical reactions the use of NH_3 to control the NO_x in the flue gases.
- 11.7. What are the specific problems faced for controlling NO_x formation in Gas Turbine power plants ?

* α_a = (Actual air used per kg of Fuel/Air required per kg of fuel for complete combustion).



