

One example is the United States Department of Energy's Vision 21 Program, which aims to develop the ultimate energy facility. The Vision 21 plant will have zero emissions and no net discharges of wastewater, solid waste, sulfur dioxide, nitrous oxide or carbon dioxide. If required, the plant will capture and store (sequester) carbon dioxide to achieve zero emissions.

In this concept, hydrogen is produced from coal and water in the absence of air or oxygen. The hydrogen is used to produce electricity in a solid oxide fuel cell. The carbonation of calcium oxide (CaO) to calcium carbonate (CaCO₃) sequesters CO₂ and assists in increasing the hydrogen yield. The calcium carbonate is dissociated back into calcium oxide and a concentrated stream of carbon dioxide (CO₂) by the waste heat from the fuel cell. The carbon dioxide can then be injected into ocean, or other geological reservoir, such as used-up natural gas reservoir. Also calcium carbonate can be stored as solid waste. The basic schematic of a hypothesized zero emission coal power plant is shown in Fig. 6.17.

6.12 Pollution Control from Coal Combustion

The major pollutants emitted during coal combustions are SO₂, NO_x, and particulates. However, one of the objectives of clean coal technology is to capture CO₂ too. Sulfur compounds present in coal convert to SO₂ during the combustion process. Although attempts have been made to remove sulfur compounds from coal prior to combustion, post combustion flue gas desulphurization appears to be more economical and technologically less challenging. Sulfur present in coal may be broadly grouped into the following three categories:

- Organic
30–70% of the total sulfur in coal are in this form and cannot be removed by direct physical separation.
- Sulfate
Less than 0.05% of total sulfur in coal is present as sulfates, which are generally soluble in water.
- Pyritic
0.5–3% of total sulfur in coal is in this form and is generally removed from the coal during cleaning process and size reduction using gravity separation.

6.12.1 Removal of Organic Sulfur

Organic sulfur species in coals are mainly thiols, sulfides, disulfides, thiophenes and their derivatives. A number of methods have been explored for removal of organic sulfur prior to combustion. These include:

1. Solvent partitioning
2. Neutralization method
3. Hydrogenation reaction or sulfur reduction
4. Thermal decomposition
5. Oxidation
6. Sodium hydroxide treatment or nucleophilic displacement, and
7. Microbial removal

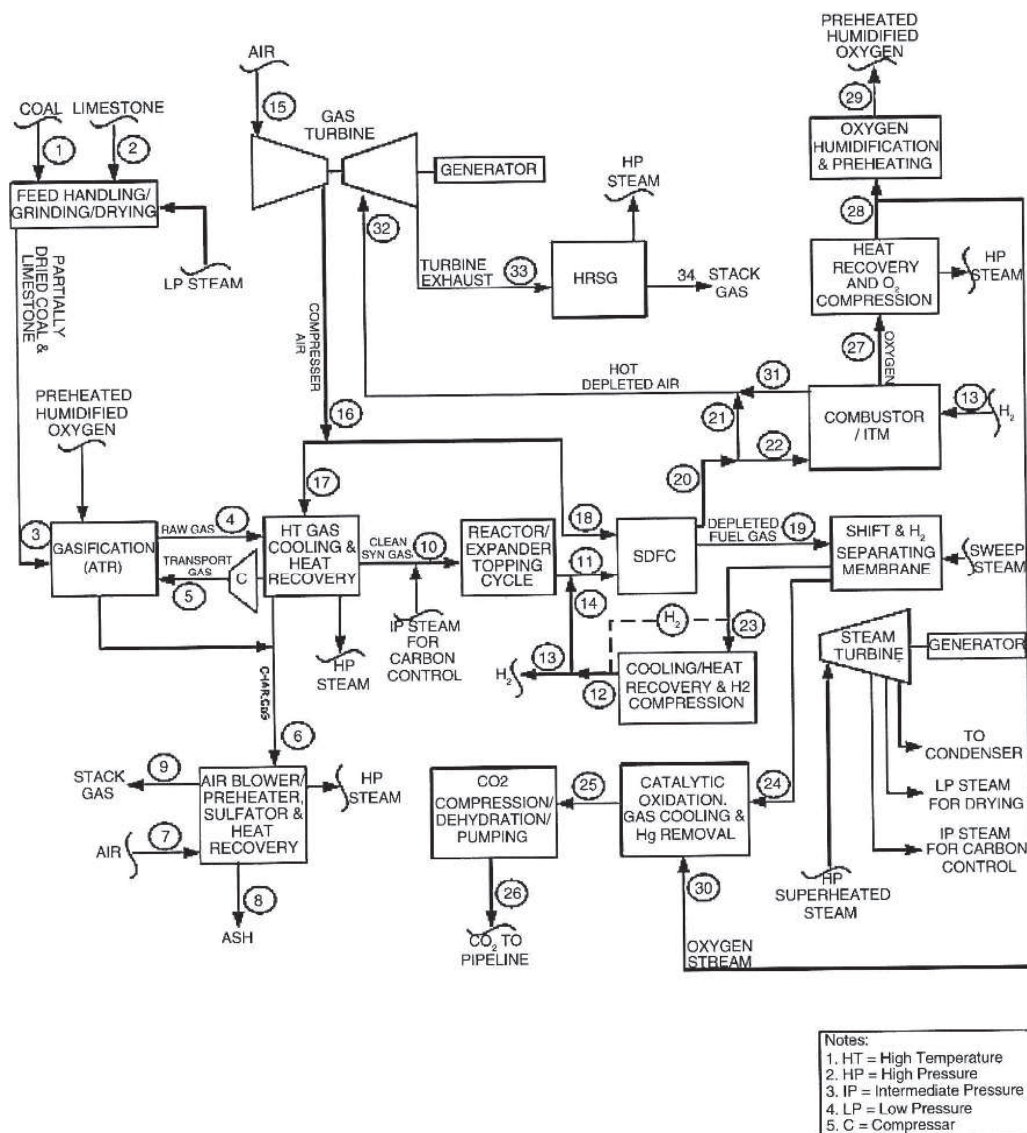


Fig. 6.17. Conceptual system for zero emission coal power plant. (Printed with permission from [560]).

6.12.1.1 Solvent Partitioning

In this method, an organic solvent is used to dissolve the organic portion of the sulfur compounds that are present in the coal. The solvent is regenerated and recycled for economic operation. A number of solvents have been tested for removal of

organic sulfur and are listed in Table 6.19. Some of the solvents were also used at supercritical conditions to enhance the extraction process.

Table 6.19. Solvents proposed for removal of organic sulfur by solvent partitioning method.

Solvent	Operating temperature	% of organic sulfur removed
n-Propanol [571]	30	43–61%
Tetrachloroethylene [572] ^a	120	43
Tetrachloroethylene [573]	120	50
Hydrogen peroxide (15%) [574]	15–40	76% pyritic, 70% sulfate, 5% organic
Hydrogen peroxide + 0.1N H ₂ SO ₄ [574]	15–40	~100% pyritic, ~100% sulfate, 26% organic
Methanol/water and methanol/KOH [575]	–	33–62 total sulfur
Methanol [576]	500	86% total, 90% organic
Perchloroethylene [577–581]	120	5–30% fresh coal 30–60% weathered coal
Perchloroethylene [582]	120	70
Trichloroethane [583]		
Potassium permanganate (6%) [584]	Room temp	90% pyritic; 87% organic
Methanol/KOH (5% wt) [585]	350	>90%
Methanol and ethanol [586, 587]	Supercritical	–
Acetone+water [588]	Supercritical	61
Methanol + water and ethanol + water [589]	Supercritical	60% pyritic; 97% sulfate; 28% organic
CO ₂	450 (supercritical CO ₂)	50 Total
CO ₂ + H ₃ PO ₄		80 Total
CO ₂ + methanol (10%) [590] ^b		60% Organic

Source: Reference [570].

^aProcess involved copper chloride oxidation followed by tetrachloroethylene extraction.

^bSupercritical extraction under pyrolysis condition.

6.12.1.2 Neutralization Method

Thiols and mercaptans may be neutralized using an alkaline solution due to the acidic nature of these two compounds. However, it should be noted that other organic sulfur compounds, such as sulfides and disulfides, cannot be removed by this method [591].

6.12.1.3 Hydrogenation Reaction

Sulfur compounds react with hydrogen producing hydrogen sulfide, which is then scrubbed from the gas stream using an acid gas treatment process. The chemical reactions of hydrogen with thiol compounds are shown below [591].



6.12.1.4 Thermal Decomposition

In this method, coal is heated to a high temperature in the absence of oxygen. Sulfur containing compounds undergo the decomposition reaction liberating sulfur as SO_2 or H_2S . In most of the cases, H_2S is released. A number of researchers proposed the use of a catalyst to lower the decomposition temperature for sulfur compounds. Other compounds present in the coal are found to decompose at this temperature [592–598].



6.12.1.5 Oxidation Reaction

Sulfur compounds may be reacted directly with oxygen or other oxidizing agents to convert them to water soluble sulfate compounds [599–601].



where 'R' represents CH_3CH_2 or $(\text{CH}_3)_2\text{CH}$ groups.

6.12.1.6 Reaction with Sodium Hydroxide

Sodium hydroxide can react with sulfur compounds forming water soluble sodium sulfide. A typical reaction with NaOH is shown below [602–607].



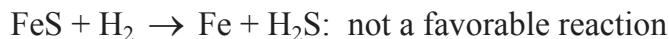
6.12.1.7 Microbial Removal

Certain microorganisms have the potential to remove sulfur from coal [608–622]. Microbial desulfurization of coal has shown various advantages including a higher

pyrite removal efficiency and lower coal wastage compared to physical methods. The costs are also lower compared to chemical methods because microbial methods operate at ambient conditions with fewer chemicals. However, microbial processes are slower, requiring days to complete. The best known pyrite-oxidizing bacteria is *Thiobacillus ferrooxidans*, a gram-negative iron-, sulfur and metal sulfide-oxidizing bacterium. Certain thermophilic bacteria have also shown to remove pyritic sulfur from coal. These include *Sulfolobus acidocaldarius*. *Sulfolobus*, a member of archaeobacteria, oxidizes pyrite, elemental sulfur, certain metal sulfides and organic compounds at temperature of up to 85°C. Other microorganisms capable of desulfurization of coal include *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*.

6.12.2 Removal of Pyritic Sulfur

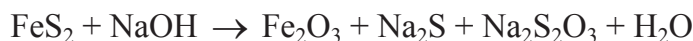
Pyritic sulfur can be removed from coal prior to combustion by reacting it with hydrogen, NaOH, or oxygen. The hydrogenation Reaction can be written as:



Oxidation Reaction



Reaction with sodium hydroxide (NaOH)



Various other methods have been proposed to remove sulfur from coal prior to combustion, however, all these processes still would require a post combustion flue gas clean up system. As a result most of the current focus is to develop a better flue gas desulfurization system to capture sulfur dioxide in the combustor as soon as it is released.

6.12.3 Sulfate Sulfur

Most of the coals contain a very small percentage of sulfur in the sulfate form. Most of the sulfates are also water soluble and generally are removed during the coal cleaning process.

6.13 Flue Gas Desulfurization and NOx Removal

A number of technologies have been proposed for flue gas cleaning. Several processes are already in use commercially. A review of these processes has been provided by a number of researchers [623–627]. Figure 6.18 shows these processes. Based on the working principles of these technologies, they can be classified first into two main categories: Once Through and Regenerable.

In the Once Through process, SO_2 reacts with the sorbent, which is generally disposed of as a waste. Most of the processes generate CaSO_4 , or better known as gypsum, that can be used for other applications, such as soil treatment and plaster.

In the regenerable processes, sorbent is regenerated and recycled back to the system. However, the main issue with the regenerable processes is how to store the released SO_2 .

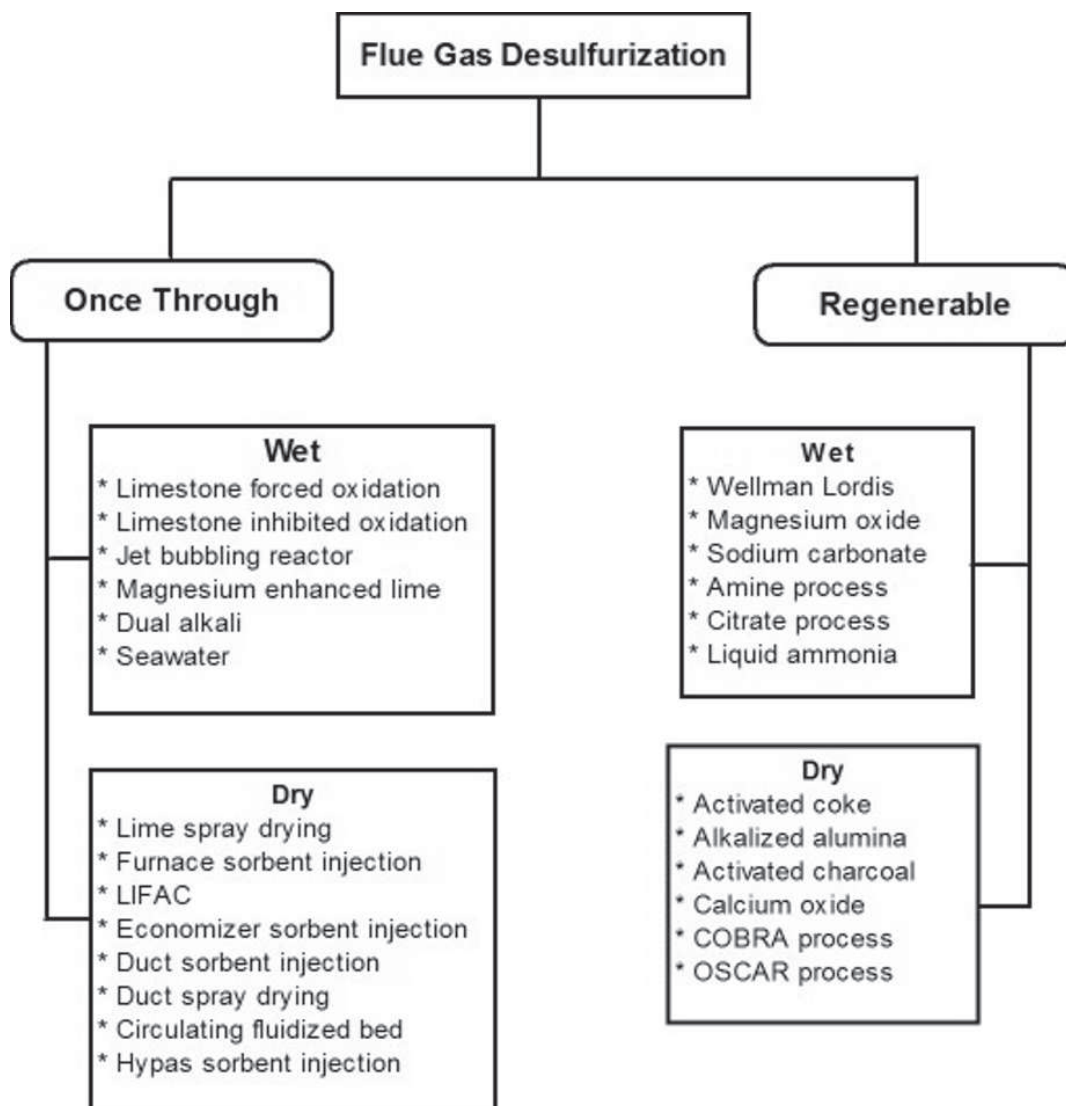


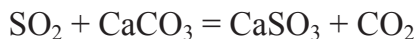
Fig. 6.18. Various methods for flue gas desulfurization. (Adapted with permission from [623]).

Among the processes mentioned in Fig. 6.18, the following processes have been employed commercially so far. The other processes are either in the experimental or pilot plant stage. The Flue Gas Desulfurization (FGD) methods currently used in the industry are listed below.

- Lime and limestone FGD
- Spray dryer absorption
- Furnace injection of calcium sorbent (LIMB)
- Calcium silicate injection (ADVACATE)
- Combined spray drying and electrostatic precipitator (E-SO_x)
- Combined SO₂/NO_x removal processes

6.13.1 Wet Scrubber (Lime and Limestone FGD)

This method was introduced in 1970 for flue gas desulfurization [628–630]. Wet scrubbers are the most widely used technology for SO₂ control throughout the world. Generally, a slurry mixture of lime and limestone is used in a scrubber to remove the sulfur dioxide. These are favored because of their availability and relative low costs. However, sodium- and ammonium-based sorbents have also been used in a slurry mixture. The slurry is injected into a specially designed vessel where it reacts with the SO₂ in the flue gas. The preferred sorbent in operating wet scrubbers is limestone followed by lime. The chemical reaction that takes place with limestone or lime sorbent is shown below.



Calcium sulfite (CaSO₃) produced in the reaction is further oxidized to calcium sulfate (gypsum). The excess oxygen (from excess air) in the flue gas can initiate the oxidation reaction. In some design, a forced oxidation step, in situ or ex situ (in the scrubber or in a separate reaction chamber), involving the injection of air is carried out. The chemical reaction is shown below.



A variety of scrubbers have been designed to carry out the above two reactions and a brief description of their operating principle is given below.

Spray tower: Spray nozzles atomize the pressurized scrubbing liquid into the reaction chamber providing large particle surface area for efficient contact and subsequent reaction.

Plate tower: The scrubber consists of a number of plates stacked at a certain interval. The flue gas is dispersed through several opening or slots in the plate holding the scrubbing liquid, which also provides large sorbent surface area.

Impingement scrubber: In this design, a vertical chamber incorporates perforated plates with openings that are partially covered by target plates. The plates are flooded with the sorbent slurry and the flue gas is accelerated upwards through the perforations. The flue gas and sorbent liquid make contact around the target plate, creating a turbulent frothing zone to provide the desired reaction contact.

Packed tower: A tower is packed with inert packings. The flue gas flows upward through the packing material in the counter-current direction to the liquid sorbent flow which is introduced at the top of the packing through a distributor.

Commercial wet scrubbing systems are available in many variations and proprietary designs. Systems currently in operation include:

- Lime/limestone/sludge wet scrubbers
- Lime/limestone/gypsum wet scrubbers
- Wet lime, fly ash scrubbers, and
- Other wet scrubbers that utilize seawater, ammonia, caustic soda, sodium carbonate, potassium and magnesium hydroxide based scrubbing solution

Wet scrubbers can achieve removal efficiencies as high as 99%. It is expected that wet scrubbers, where the end product is gypsum, will become a more popular FGD technology, since disposal of waste faces increasingly stricter governmental regulations. However, wet scrubbing technology still needs to treat the waste water before disposal. A flow diagram of the process is shown in Fig. 6.19.

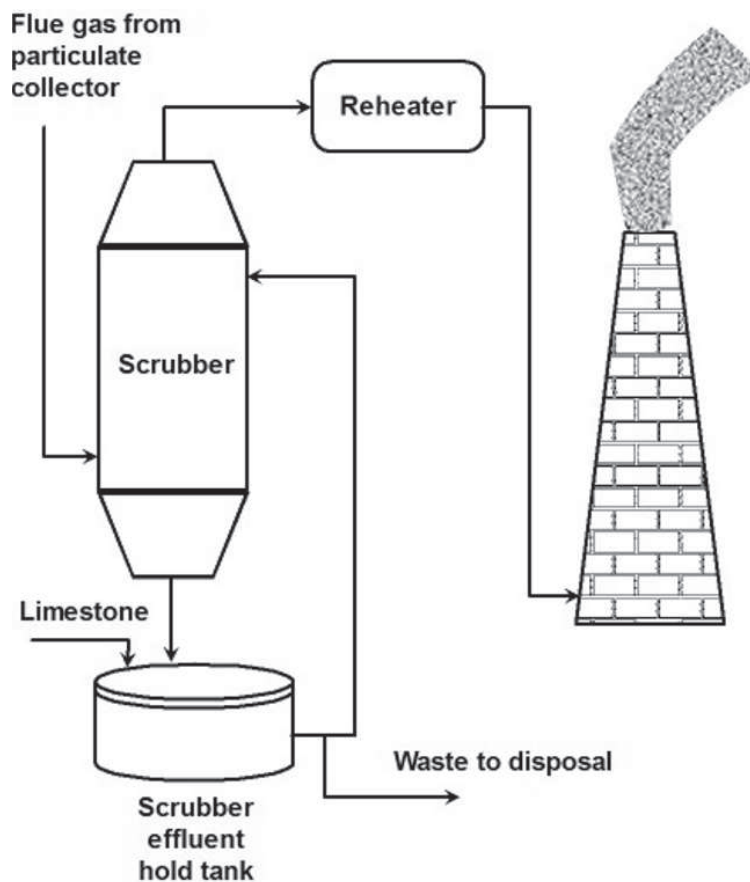


Fig. 6.19. A schematic diagram of wet scrubbing system for flue gas desulfurization.

Generally a high liquid to gas ratio is used to avoid scaling. In some units forced oxidation was also tried to avoid scaling. A thiosulfate-forming additive is mixed with the slurry to facilitate the removal of scales that might deposit on the wall. It was also noted that by maintaining a certain pH, using an organic acid buffer, SO₂ removal could be enhanced.

6.13.2 Dry Sorbent Injection Method

This method for flue gas desulfurization evolved from spray drying technology. This method of SO₂ emission control relies on the atomization of a sorbent – most commonly an aqueous lime slurry – in a reaction chamber upstream of a particulate collection device. A basic schematic diagram of the process is shown in Fig. 6.20. Two processes are currently practiced commercially for capture of SO₂ from the flue gas: Furnace injection and Duct injection.

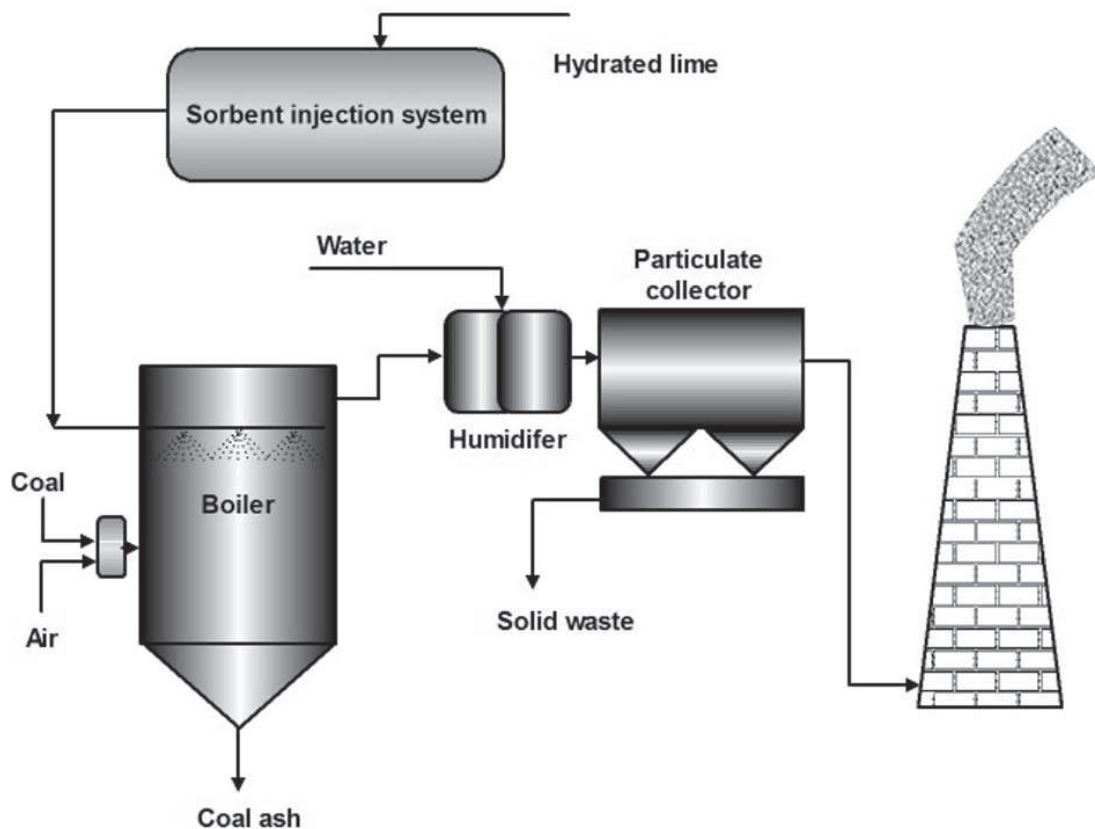


Fig. 6.20. Dry sorbent injection system.

6.13.2.1 Furnace Injection

Furnace injection systems are typically designed to operate at 15–25°C (27–45°F) approach to the adiabatic saturation temperature of the flue gas. Dry sorbent is

injected directly into the section of the furnace where temperature ranges between 950°C and 1,000°C. The fine droplets absorb SO₂ and form the product calcium sulfite and sulfate as the water evaporates. A downstream electrostatic precipitator (ESP) or baghouse collects the dry salts along with fly ash present in the flue gas. Use of a baghouse enhances the performance of the dry scrubber because additional SO₂ absorption occurs as the flue gas passes through the accumulation.

The reactions taking place in the furnace are as follows:



To avoid CO₂ release, dry powder of calcium oxide is mainly used as the sorbent. However, a lime slurry, also called lime milk, can be atomized/sprayed into the reactor vessel in a cloud of fine droplets. Water is evaporated by the heat of the flue gas, thus does not require any waste water treatment facility. About 10 s of residence time in the reactor is sufficient to allow for the SO₂ and the other acid gases such as SO₃ and HCl to react simultaneously with the hydrated lime to form a dry mixture of calcium sulfate/sulfite. The unreacted lime is recycled and mixed with fresh lime slurry to enhance sorbent utilization. Other factors that may affect the performance include flue gas temperature, SO₂ concentration in the flue gas and the size of the atomized or sprayed slurry droplets. The absorber construction material is usually carbon steel making the process less expensive in capital costs compared with wet scrubbers. However, the necessary use of lime in the process increases its operational costs.

Spray dry scrubbers are the second most widely used FGD technology. However, their application is limited to flue gas volume from about 200 MWe plants on average. Larger plants require the use of several modules to deal with the total flue gas flow. This is why in general the technology is used in small to medium sized coal-fired power plants. Spray dry scrubbers in commercial use have achieved a removal efficiency in excess of 90% with some suppliers claiming >95% SO₂ removal efficiency under certain conditions.

The Babcock & Wilcox Company (B&W) designed a limestone injection multistage burner (LIMB) system to improve the efficiency of the system [631–637]. The description of the system is shown in Fig. 6.21. Humidification of the flue gas before it enters an ESP is necessary to maintain normal ESP operation and to enhance SO₂ removal. The goal of LIMB process was to remove more than 50% SO₂ and NO_x from the flue gas. Combinations of three bituminous coals (1.6, 3.0, and 3.8% sulfur) and four sorbents were tested and overall removal efficiency in the range of 50–63% was reported when using limo lime. B&W further modified the design and called it the *coolside* process.

In the coolside process, dry sorbent is injected into the flue gas downstream of the air preheater, followed by flue gas humidification (see Fig. 6.22). Humidification enhances ESP performance and SO₂ absorption. SO₂ absorption is improved

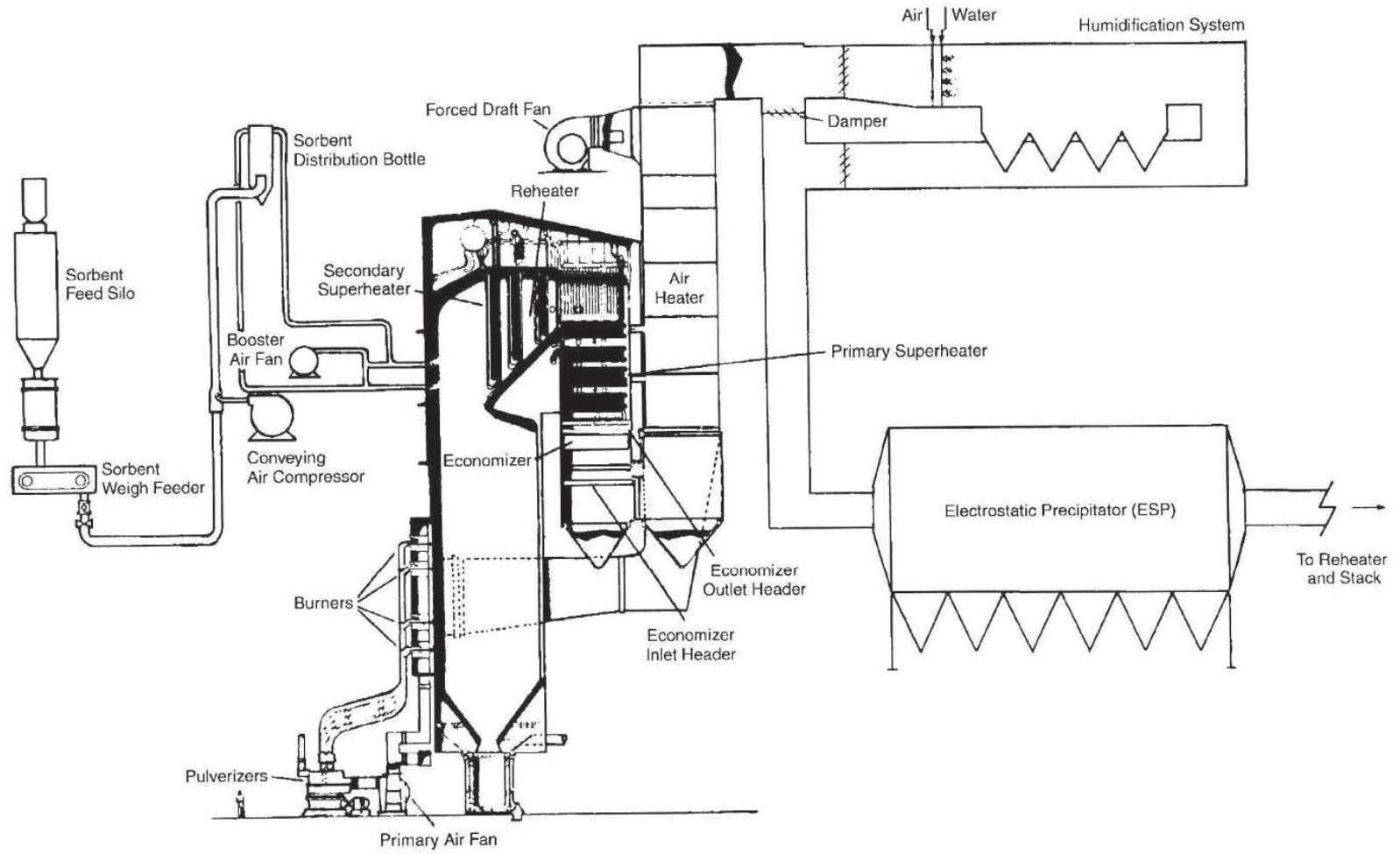


Fig. 6.21. A limestone injection multistage burner (LIMB) designed by Babcock & Wilcox Co. (Adapted from [638]).

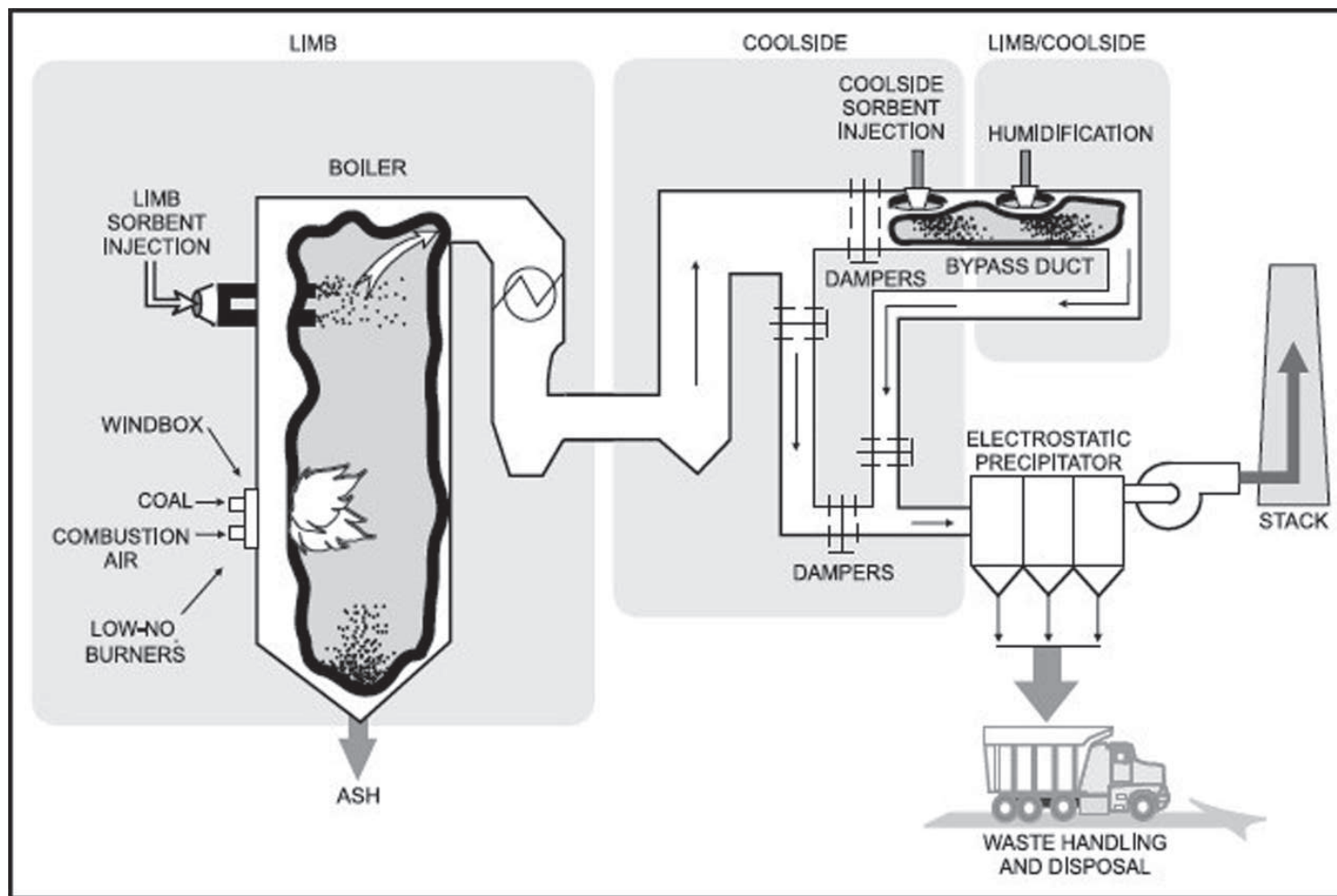
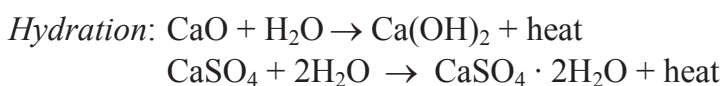
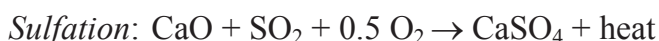
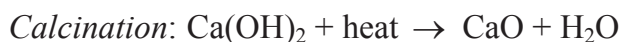
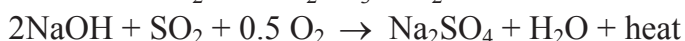


Fig. 6.22. The coolside process that couples flue gas humidification with hydrated lime injection into the duct. (Adapted from [639]).

by dissolving sodium hydroxide (NaOH) or sodium carbonate (Na₂CO₃) in the humidification water. The spent sorbent is collected with the fly ash, as in the LIMB process. Bituminous coal with 3.0% sulfur was used in testing, and SO₂ removal of 70% was reported. SO₂ capture takes place according to the following reactions:



The additional reactions involving NaOH are as follows:



6.13.2.2 Duct Injection

In this process, dry sorbent is injected in the flue gas duct between the air preheater and particulate collector. Most commonly used sorbent is hydrated lime, however, sodium bicarbonate has been also used. Approximately 50–60% SO₂ is captured with lime, and the capture efficiency may be increased to 80% by using sodium bicarbonate. It is primarily used for those applications where a moderate degree of desulfurization is required at low capital cost. However, sodium bicarbonate is relatively expensive [640].

6.13.2.3 Calcium Silicate Injection (ADVACATE)

An advanced version of duct spray injection is the ADVANCED siliCATE (ADVACATE) process [641]. ADVACATE uses an advanced silicate that is more absorbent than lime. This process removes 90–95% of the sulfur dioxide and other acidic gases from stacks of any coal-fired boiler. A schematic diagram of the process is given in Fig. 6.23.

This dry duct injection system utilizes a fly ash-based throwaway sorbent to remove sulfur dioxide. High surface area calcium silicate hydrates are made by slurring Ca(OH)₂ (calcium hydroxide) with fly ash and recycled sorbents in

water at elevated temperatures. The resulting sorbent has the handling properties of a dry powder while maintaining moisture levels of up to 50–76% by weight.

The dry powder is injected into the duct, where sulfur dioxide removal takes place. Some removal of SO_2 also takes place in the particulate collection device. Sulfur dioxide captured by dry powder is collected with the fly ash and is separated into waste and recycle streams.

The calcium silicate formed has a large surface area capable of adsorbing a large amount of water. Sulfur dioxide dissolves into the water to react with calcium ions. The final products are calcium sulfite and calcium sulfate. Calcium sulfite is the main product. The ADVACATE absorbent has been tested in a 10 MW pilot plant, and 89% of SO_2 removal and 61% of lime utilization were achieved [642].

The Electric Power Research Institute estimates that the new process will cost \$85 per kW versus \$215 per kW for conventional flue gas scrubbing.

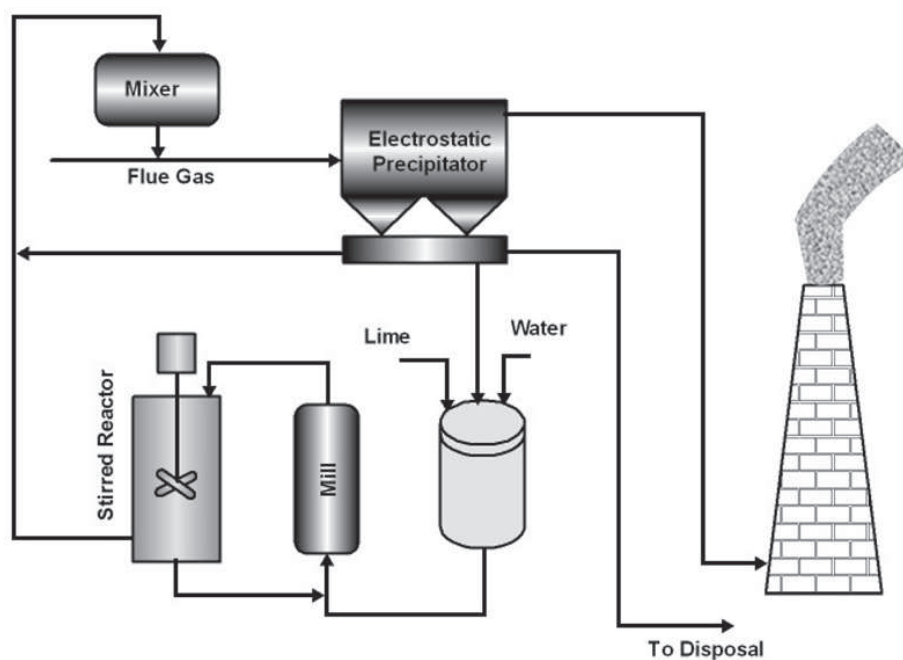


Fig. 6.23. A schematic representation of ADVANCED siliCATE (ADVACATE) process.

6.13.2.4 Combined Spray Drying and Electrostatic Precipitator (E-SOx)

The E-SOx technology combines improved electrostatic precipitation technology with conventional spray drying FGD techniques for better efficiency [643, 644]. A schematic diagram of the process is shown in Fig. 6.24.

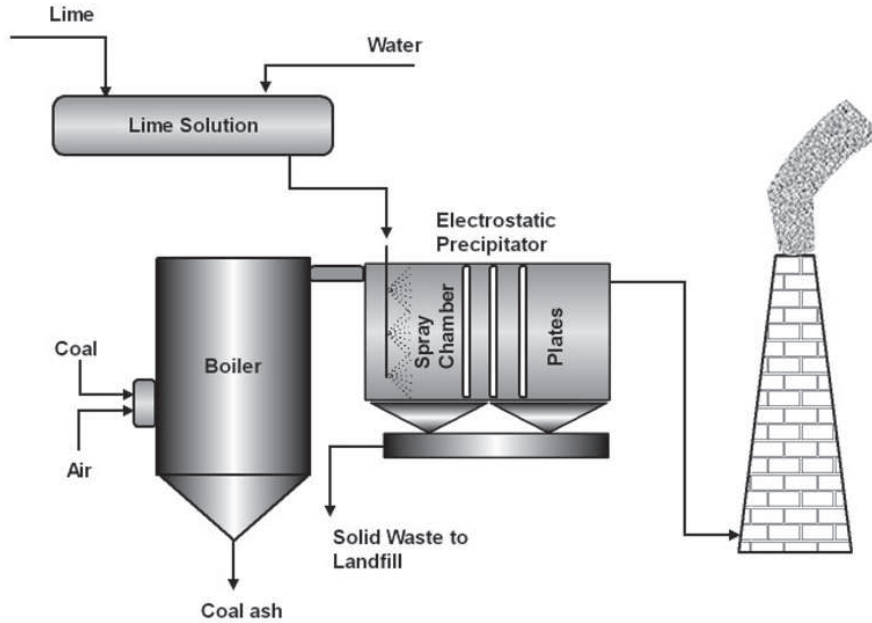


Fig. 6.24. The E-SO_x process for enhancing flue gas desulfurization.

6.13.2.5 SO_x -NO_x Rox Box (SNRB)

This process combines hydrated lime and ammonia injection upstream of a hot, catalytic baghouse (Box), where the solid products calcium sulfite and sulfate and particulate (Rox) are removed, and the NO_x is reduced to nitrogen and water. The design of the burner is shown in Fig. 6.25.

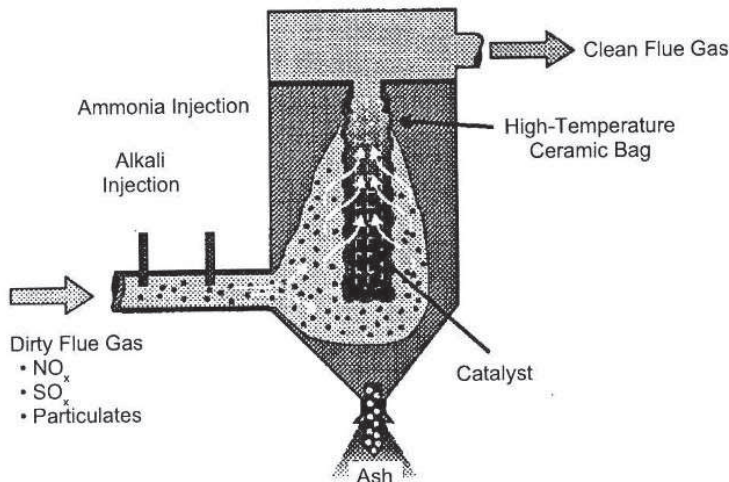


Fig. 6.25. The burner configuration for simultaneous removal of SO_x-NO_x-RO_x-BO_x. (Adapted from [638]).

A comparison of costs among various flue gas desulfurization methods is shown in Table 6.20

Table 6.20. A comparison of costs of various flue gas desulfurization processes.

Process	Plant capacity (MWe)	Sulfur content of coal (%)	Targeted SO₂ reduction (%)	Capital costs (\$/kW)	Annual levelized costs (\$/t of SO₂ removed)
Wet limestone scrubber					
Forced oxidation	300	1.7	90	209	540
Wallboard gypsum	300	2.6	90	243	476
Inhibited oxidation	300	2.6	90	234	476
Dibasic acid (additive)	300	2.6	90	211	463
Magnesium enhanced	300	2.6	90	189	477
Lime spray drying					
	300	1.7	90	160	490
	300	2.6	90	173	439
Dry sorbent injection					
Furnace injection	300	2.6	50	94	751
Duct injection	300	2.6	50	98	768
LIMB	100–500	1.5–3.5	60	31–102	392–791
Coolside	100–500	1.5–3.5	70	69–160	482–943
ADVACATE	300	2.6	90	84	327