

CLEANING OF FLUE GASES IN THERMAL POWER PLANTS

ČIŠČENJE DIMNIH PLINOV V TERMOENERGETSKIH POSTROJENJIH

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Keywords: FGD, desulphurization of flue gases, dry desulphurization process, CFB technology, semi-dry desulphurization process, SDA technology, wet calcite process.

Abstract

In the scope of this paper, all three processes for desulphurization of flue gases (FGD) are presented. These are a dry procedure, a semi-dry procedure, and a wet calcite procedure for desulphurization of flue gases. Each procedure is described, and the main chemical reactions between acid components in flue gases with reagent and schematic flow chart drawings of each desulphurization procedure are presented. The focus of this paper is to acquaint the reader with the technological possibilities for flue gas desulphurization processes.

Povzetek

V sklopu članka obravnavamo tri postrojenja za čiščenje dimnih plinov (razžvepljevanje dimnih plinov). To so suhi postopek, pol suhi postopek in mokri postopek za čiščenje dimnih plinov. Vsako postrojenje je opisano, predstavljene so osnovne kemijske reakcije procesa in shematska tehnološka risba postrojenja za odžvepljevanje dimnih plinov. Namen članka je seznaniti bralca z tehnološkimi možnostmi postrojenj za čiščenje dimnih plinov.

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1 INTRODUCTION

In the last decade, large thermal power plants were forced to build and improve their flue gas treatment systems, because many countries in the developed world had passed legislation dictating the level of emissions that a polluter must not exceed in order to be able to operate in the future, [1]. The systems for flue gas treatment in thermal power plants are intended to lower acid and dust components in order to maintain the health of the environment to the greatest extent possible, [2].

This paper will be focused on systems for reducing sulphur dioxide from flue gases in thermal power plants, [3]. All three currently commonly used desulphurization processes for flue gases (dry calcite process, semi-dry, and wet process for desulphurization of flue gases, commonly known as DeSO_x processes) will be presented, [4].

We will make a detailed review of the wet process for desulphurization of flue gases in thermal power plants because it is the most commonly chosen BAT, [5], (Best Available Technology). Its advantages are its favourable reagent and the harmlessness of cleaning the by-product, which can be further used in other parts of industry or disposed of in the environment, without any known side effects. With detailed engineering from the beginning of the desulphurization process to its execution, a very high level of scrubbing acid components from flue gases can be achieved by using a proper reagent; lime or limestone are often used. A by-product of this process is gypsum. It can be used for commercial purposes or further inside a thermal power plant as a medium in other industrial processes, such as the stabilization of electrostatic precipitator ash.

2 SULPHUR DIOXIDE

Sulphur is a chemical component and is present in every coal that is burnt in boilers to produce steam that drives turbines and generators to produce electricity. As the quality of coal can vary, so too can the amount of sulphur that is present in it. We can assume that the lower the coal quality is, the higher the amount of sulphur. As coal is burned in boilers, gaseous elements are formed: sulphur dioxides in a gaseous state. Other similarly formed components in boilers are sulphur trioxide (SO₃), hydrochloride (HCl), and hydrogen fluoride (HF), also in a gaseous state.

Sulphur dioxide is an irritant and a colourless gas with a characteristically sharp odour. It is a major pollutant, with large amounts produced in refineries, in old abandoned coal mines, and in the chemical and rubber industries. Especially large amounts of this gas are emitted through flue gases from thermal power plants, which use coal as their primary fuel.

When sulphur dioxide enters the atmosphere, it reacts with oxygen and water, and sulfuric acid is formed. This phenomenon is known as acid rain, and it affects human health and nature, especially forests. It also affects buildings and monuments, and real estate in general.

3 DRY DESULPHURIZATION PROCESS

The dry calcite process is also known as the circulating fluidized bed process or the CFB process. For the removal of acid components from flue gases, hydrated lime is used. Together with ash from the boiler, the hydrated lime is circulating inside the absorber and electrostatic

precipitator. In these two devices, the entire reaction of cleaning of flue gases occurs. The system for dry cleaning of flue gases consists of absorbent storage, reagent preparation, absorber (scrubber), particulate removal (ESP), recycling, and disposal devices for the reaction products.

The CFB technology dry flue gas cleaning is primarily intended for small and medium thermal power plants, which use coal with a high concentration of sulphur as their primary fuel. In comparison to the wet flue gas cleaning process, the CFB technology is relatively favourable, and its scrubber capacity and quality are very competitive. In addition, the CFB technology can also reduce the concentration of other environmentally harmful substances, such as SO₃, HCl, HF, mercury, and heavy metals, in flue gases, [6].

The CFB technology has been developed to the point that it can also be used in large thermal power plants intended for high-volume electricity production. The flue gas flow in such installations could easily exceed 1 million norm m³/h. At this level, the technology is capable of scrubbing 98% of all acid components from flue gases. The amount of sulphur in coal can be up to 2.5% in order to reach the mentioned scrubbing efficiency of the absorber. The estimated financial investment to implement a dry desulphurization unit in a thermal power plant block with a capacity of 150 MWe is approximately €49,500,000.

3.1 Working principle of dry calcite process

The basic working principle is based on technology used for more efficient coal burning in boilers: circulated fluidized bed boilers. Flue gases that come from the boiler are directed to the lower part of the CFB reactor (also called the “absorber”), into which process water and the reagent (hydrated lime) are delivered. As flue gases exit the CFB reactor chamber, they encounter the suspension of process water, hydrated lime, and ash. As the flue gases and suspension come into contact, a chemical reaction that eliminates the acid components from the gases occurs. The main efficiency parameter of the process of scrubbing of flue gases in the reactor is the ambient temperature.

Part of the by-product of this reaction is ash that accumulates on the bottom of the reactor. From there, it is discharged from the lower manhole of the reactor on the transportation belt, which transports ash to the final disposal place. However, it is essential to maintain the proper amount of ash in the reactor in order to ensure an optimal scrubbing process. All other particles that leave the reactor chamber in the flow of flue gases are captured inside the electrostatic precipitator. In the first fields of the precipitator, usable particles of hydrated lime and ash are collected. They are returned to the reactor in order to decrease the consumption of the reagent (hydrated lime) and to lower the costs of the consumed reagent. Parts of the ash and reagent that are too small to return to the reactor chamber pass through all the stages of the electrostatic precipitator and are deposited in the central by-product silo.

From the electrostatic precipitator, flue gases are forwarded through an ID fan into the stack. The fan is needed to balance the pressure drops that are present in the system, because of the reactor chamber and electrostatic precipitators. From there, sulphur-free flue gases enter the atmosphere.

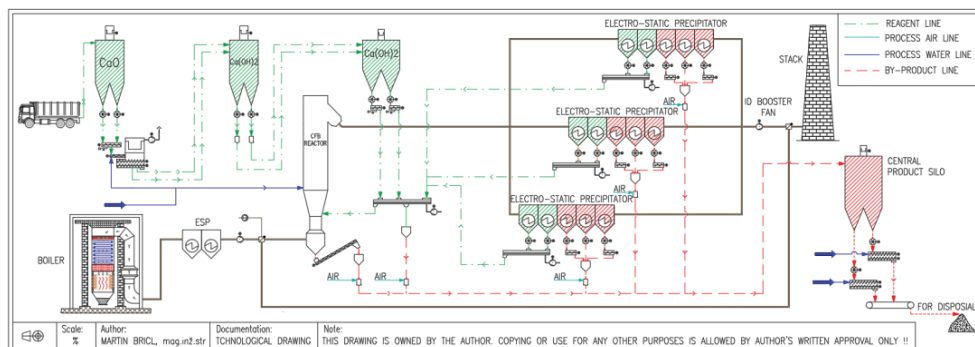


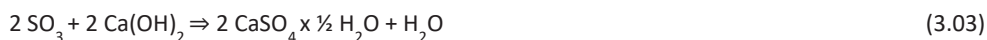
Figure 1: Schematic technological drawing of dry desulphurization unit

3.2 Chemical aspect of dry desulphurization process

The reaction of scrubbing acid components from flue gases happens in the reaction chamber. The reagent, which is hydrated lime $\text{Ca}(\text{OH})_2$, ties the acid components that flue gases contain to itself. The reagent is in a liquid state, and acid components are in a gaseous state. The reagent in a liquid state is obtained from the following reaction:



The reaction happens on the surface of hydrated lime, which has been in contact with the process water. Furthermore, flue gases need to be exposed to process water in order to achieve a high level of scrubbing process. Process water is delivered directly to the reactor chamber. The humidity of flue gases in the reactor chamber is critical. It is determined with the help of the temperature difference of flue gases before and in the reactor chamber. The optimal temperature difference is considered to be $\Delta T = 15^\circ\text{C}$. The main chemical reactions of the dry flue gas cleaning process are the following:



In the process of flue gases travelling through the reaction chamber or absorber, some other chemical reactions also take place.



As gaseous CO_2 is present in flue gases from the thermal power plant, the formation of limestone is also a part of the chemical process inside the absorber.



3.3 CFB Reactor

The CFB reactor is a steel structure consisting of five zones for flue gas cleaning, i.e. the desulphurization process. These zones are as follows:

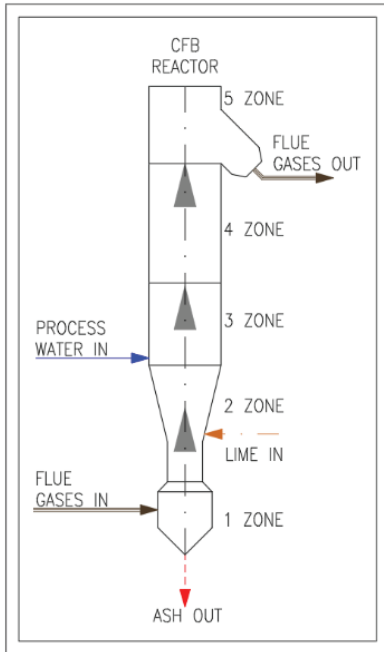


Figure 2: Section view of CFB reactor, where flue gases are cleaned

- **ZONE 1: ENTRY ZONE:** Here, it is important to regulate the proper amount of volumetric flow of flue gases. If the volumetric flow is too high, there can be damage to the electrostatic precipitator.
- **ZONE 2: VENTURI ZONE:** In this section, flue gases must be accelerated to reach suitable velocity to achieve the highest efficiency of the cleaning process.
- **ZONE 3: FLUIDIZED BED ZONE:** Zone with the highest turbulence, where the absorption of acidic components in gases and maintaining the stability of the reagent recirculation take place. In this zone, process water for flue gases is injected.
- **ZONE 4: RECIRCULATION ZONE:** This zone is located in the upper part of the CFB reactor. Here, the second phase of absorption of acid components from flue gases is executed.
- **ZONE 5: OUTLET ZONE:** Directing the flow of flue gases out of the CFB reactor and forwarding them towards the electrostatic precipitator.

The CFB reactor chamber does not need any particular cleaning process or maintenance to achieve a sufficient cleaning effect. The reactor chamber is made of stainless steel, as this material choice ensures its long operational life.

4 SEMI-DRY DESULPHURIZATION PROCESS

The semi-dry process for flue gas desulphurization is based on the injection of a dry reagent in the reactor chamber. Additionally, through spray levels process water is also added. This process is called semi-dry because the entry reagent is wetted with process water, but a by-product of the desulphurization process is entirely dry ash, which is concentrated in the dust filter.

The semi-dry desulphurization process consists of the following steps: preparation of the

semi-dry desulphurization unit in a thermal power plant block with a capacity of 150 MWe is approximately €51,500,000.

4.1 Working principle of semi-dry desulphurization process

This procedure of the desulphurization of flue gases is relatively simple. It consists of a reagent preparation module, an absorption chamber, and a fabric filter. Hot raw flue gases enter the absorption chamber through the flue gas disperser, where they come in contact with small drops of the previously prepared limestone suspension (average size of a suspension drop is just 50 μm). Acid components in flue gases are absorbed by alkaline components in suspension. The presence of water in the suspension drops is quickly eliminated because of the very high temperature in absorption chamber. The dynamic control of flue gas distribution, suspension production, and control of suspension drops size, ensures that there is no accumulation of water or parts of reagent inside the absorption chamber.

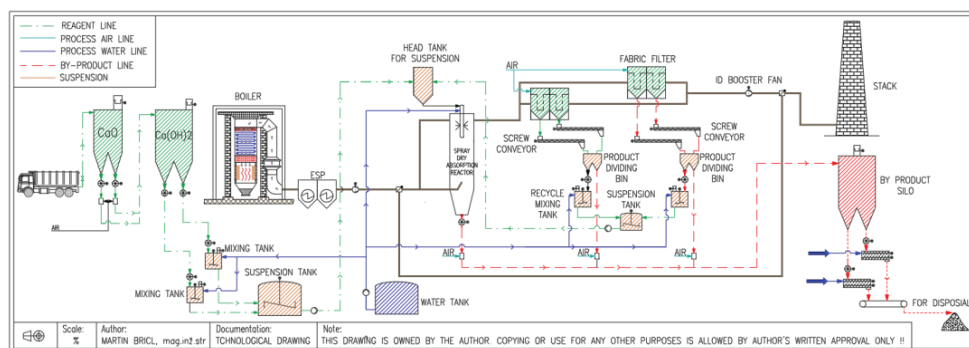


Figure 3: Schematic technological drawing of semi-dry desulphurization unit

A part of reagent and flue gas-ash is accumulated on the bottom of the absorption chamber, from where it is transported to the central by-product silo. Flue gases that pass through the absorption chamber are further directed to the fabric filter, where ash and dust particles are absorbed to prevent their entry into the atmosphere. Additionally, a part of unused reagent in dry form is returned to the first stage of reagent preparation in order to reduce reagent use. From fabric filter, flue gases directed to the stack, from where they enter the atmosphere, are cleaned. In order to eliminate pressure drops in the path of the flue gases, an additional ID fan needs to be integrated into flue gas ducts.

4.2 Chemical aspect of semi-dry desulphurization process

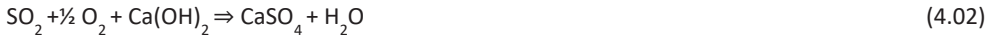
The two most important steps in the semi-dry desulphurization process are the following:

- Process of drop formation of sizes less or equal to 50 μm ;
- Effective dispersion of raw flue gases to exploit the biggest exposure of raw flue gases to the reagent suspension drops.

The chemical reactions take place inside the absorption chamber. Alkaline components in suspension drops absorb acid components from the flue gases (SO_2 , SO_3 , HCl , and HF). The reagent used for the semi-dry process is slaked lime or calcium hydroxide. The main chemical reactions of this process are the following:



A small part of SO_2 reacts with alkaline substances as follows:



Most of the sulphur dioxide reacts with suspension drops while they are still in the wet phase inside the absorption chamber. After the cleaning process of raw flue gases in the chamber, they are directed to the fabric filter, which has (as mentioned before) two main important tasks. These are:

- Separation of by-product, ash, and dust particles;
- Additional absorption of acid components in flue gases.

In addition, it should be mentioned that the absorption of CO_2 is part of the semi-dry desulphurization process. However, SO_2 is much more acidic than CO_2 and is, therefore, more strongly suppressed by alkaline suspension than CO_2 is. Part of it is, however, suppressed in the absorption chamber and is prevented from exiting the atmosphere. The amount of the suppressed CO_2 is very small in comparison with SO_2 . A specific feature of the semi-dry desulphurization process is the use of process water with the addition of chlorides. That positively affects the absorption process inside the absorption chamber. Instead of process water with added chlorides, seawater can be used, depending on the location of the power plant.

4.3 Description of absorption chamber

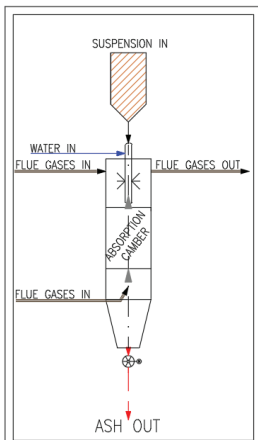


Figure 4: Absorption chamber of semi-dry unit

The main component of the absorption chamber is a device to minimize suspension drops to the size of $50 \mu\text{m}$. This is a rotary device with a corrosion- and abrasion-protected central core. The main task of this device is to distribute reagent suspension to the process. The main advantage of this device is a very quick adaptation of its operation to the changes in volumetric flue gas distribution, changes of the temperature of flue gases, or the composition of flue gases. The described unit can adapt to these changes quickly and easily; therefore, it is suitable for boilers that have changes in their operational regimes.

The chamber can process from $400,000 \text{ Nm}^3/\text{h}$ up to $1,600,000 \text{ Nm}^3/\text{h}$ of flue gases. In the case of a very large volumetric flow of flue gases, there can be two entrances for raw flue gases in the absorption chamber. The first entrance is on the chamber's side, where 60% of flue gases volumetric flow enters, 40% of the flue gases' volumetric flow enters through opening on the roof of the

absorption chamber. The chamber is made of stainless steel. Additional inner protection of all steel surfaces against acid components is made of rubber.

5 WET DESULPHURIZATION PROCESS

The wet desulphurization process is based on a wet limestone scrubber, [7]. This process is commonly used in big thermal power plants, primarily because of its very high efficiency of flue gas cleaning (95–99% efficiency of scrubbing SO₂ from raw flue gases), and its very affordable reagent. The main reagent is calcite [CaCO₃], which is much cheaper than the lime or hydrated lime that is used as a reagent in dry and semi-dry desulphurization processes.

The end product of wet flue gas cleaning is gypsum [CaSO₄ x 2 H₂O], which can be reused in the cement and mining industries, where gypsum can be used to fill in old closed mine shafts to stabilize the mining terrain.

The main element of the wet desulphurization process is the absorber. Other parts of the equipment needed include a limestone preparation plant, where calcite or limestone is crushed and prepared in suspension. Additionally, a gypsum dewatering plant to reduce moisture in the by-product is required. Auxiliary equipment including oxidation compressors, compressors for instrumental air, high voltage electrical equipment, and pumps. In the case of emergency in the absorber, there is usually also an emergency drainage tank to empty the limestone suspension, which is located in the bottom part of the absorber.

The estimated investment to implement a wet desulphurization unit in a thermal power plant block with a capacity of 150 MWe is approximately €73,000,000, [8]. Because of the extensive scope of equipment, the initial investment is higher than that for the dry or semi-dry desulphurization processes. However, it should be noted that the operational costs are significantly higher for dry and semi-dry processes.

5.1 Working principle of wet desulphurization process

Raw flue gases are directed through flue gas ducts to the absorber. Fresh process water and a fresh limestone suspension are also delivered to the absorber. Fresh process water can be supplied from a nearby river or lake. Furthermore, seawater, [9], is suitable for the wet desulphurization process because it contains a high amount of chlorides that improve the effect of desulphurization. The limestone suspension must be prepared in advance in the limestone preparation plant, which consists of a delivery bunker, a day silo for limestone, and wet ball mills with corresponding tanks. Limestone is crushed in the mills, particles of limestone are separated in a hydro cyclone, and suitably sized particles of limestone are passed for further suspension preparation in tanks. The suspension is delivered to the absorber from these tanks.

All chemical reactions occur in the absorber, which consists of the zones that are described in chapter 5.4 in detail. After a suitable amount of time of flue gas retention in the absorber, they exit cleansed of the SO₂ component. They enter the atmosphere through the wet stack on the absorber or through the existing stack in the thermal power plant.

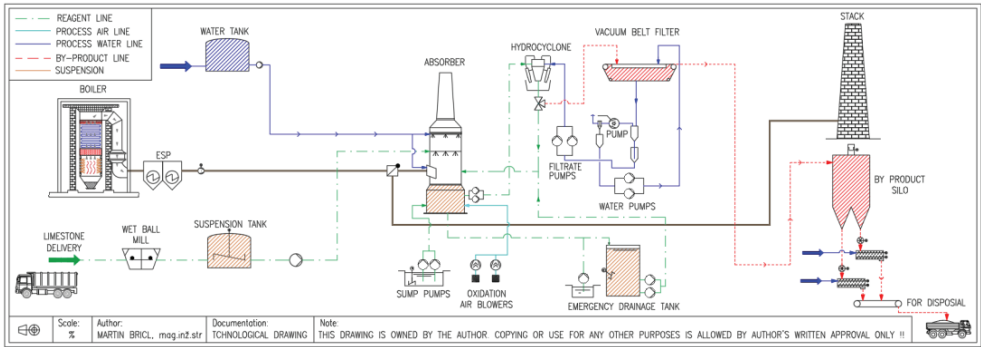


Figure 5: Schematic technological drawing of wet desulphurization unit

A by-product of the wet desulphurization process is, as mentioned before, gypsum. It is pumped from the bottom of the absorber to the vacuum belt filter, where the moisture in it is eliminated. Relatively dry gypsum is then forwarded to the by-product silo and from there to the final disposal landfill. Gypsum can also be used in the cement industry, as well as a building material.

5.2 Chemical aspect of the process

The chemical aspect of the wet desulphurization process is based on reactions between the acid components in flue gases and the freshly prepared limestone suspension. The wet desulphurization process removes SO_2 from the flue gases via the absorption of acid components into the limestone suspension. A by-product of this process is gypsum. The process removes acid components, such as SO_2 , SO_3 , HCl , and HF , from flue gases. Some of the chemical reactions during the wet desulphurization process are summarized below.

- Absorption of SO_2 into the liquid phase

First, we need to achieve the conversion of sulphur dioxide from a gaseous state into a liquid state. The chemical reactions are as follows:

The acid components in flue gases, specifically Sulphur oxides SO_2 , and SO_3 , HCl , and HF , dissolve in water or the limestone suspension as follows:

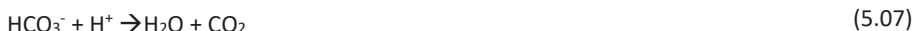


The next step of the wet desulphurization process is the dissociation of acid:



- Dissolution of limestone and neutralization reactions

Limestone dissolves in the water slurry and neutralizes acids from the flue gas absorption. A by-product of this dissolution is CO₂.



- Oxidation reactions

The oxidized air is delivered into the lower part of the absorber through absorber agitators. It is required to oxidize the sulphite to sulphate.



- Crystallization and precipitation reactions

Crystallization takes place in the lower part of the absorber. The finally produced sulphate ions will react with the calcium ions. The result is the formation of gypsum.



5.3 Absorber

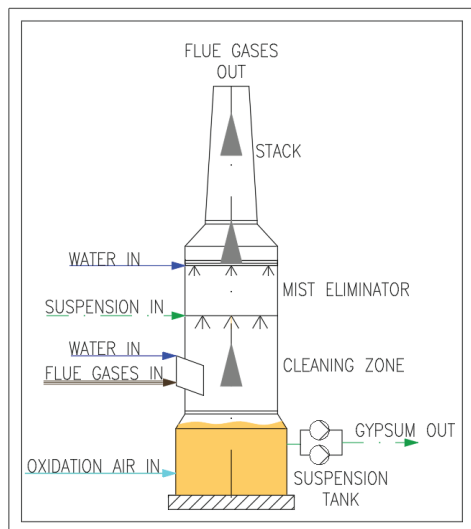


Figure 6: Absorber unit for wet desulfurization of raw flue gases

As mentioned before, the absorber is the most important part of equipment in the scope of the wet desulfurization process. The wet absorber has three zones for the cleaning process. In the first zone, there is a calcite suspension tank. This suspension is then pumped with the help of circulation pumps to the spray levels, where it comes into contact with flue gases. In the second zone, the reaction is started between harmful substances in flue gases (SO₂, HCl, HF, SO₃) and the reagent in a CaCO₃ water suspension. As the harmful substances react with the reagent, they fall back to the bottom of the absorber where they form a by-product of wet flue gas desulfurization and cleaning: gypsum. In zone three, water drop eliminators are installed in order to return water to the process and decrease the use of process water in the cleaning process. The path of flue gases

through the absorber is marked with grey arrows. The absorber must be properly technically maintained to ensure a high cleaning effect during its operational lifecycle.

6 CONCLUSION

The technology of flue gas desulphurization has its beginnings in the early 1970s. It has greatly improved the quality of living because it prevents SO₂ and other harmful substances from entering the atmosphere. Although this technology is not cheap, it has been widely implemented in almost every thermal power plant in the developed world to preserve the environment.

Further development of this technology can also be expected. All countries of the developed world have committed themselves to reducing their emissions of greenhouse gases, mainly CO₂. Pilot tests have been made on scrubbing flue gases in thermal power plants to simultaneously eliminate SO₂ and CO₂. The preliminary results have been positive, but further development of this technology and the related sorbents is required.

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Nomenclature

(Symbols)	(Symbol meaning)
<i>FGD</i>	Flue Gas Desulphurization
<i>BAT</i>	Best Available Technology
<i>CFB</i>	Centrifugal Fluidized Bed
<i>SDA</i>	Semi Dry Absorption
<i>ID fan</i>	Induced Draft fan
<i>SO₂</i>	Sulphur Dioxide
<i>SO₃</i>	Sulphur Trioxide
<i>CO₂</i>	Carbon Dioxide
<i>HF</i>	Hydrogen Fluoride
<i>HCl</i>	Hydrochloride
<i>CaCO₃</i>	Calcite
<i>Ca(OH)₂</i>	Hydrated Lime
<i>DeSO_x</i>	Desulphurization