Technologies for the Control of Sulphur Dioxide Emissions From Coal /Pet Coke Fired Boiler

Prof .Veena. A Shinde [a], Mr.Kushal V. Kadam [b]

[a] Professor of Chemical Engineering Department, Bharati Vidyapeeth College of Engineering, Pune, Maharashtra

[b] PG Student of Chemical Engineering Department, Bharati Vidyapeeth College of Engineering,Pune,Maharashtra

Abstract

Emissions of sulfur dioxide after burning the coal / pet coke in boiler causes serve damage not only to the environment, historical monuments like TajMahal but also to the human health. Because of the ecological and human health impacts of sulfur dioxide regulatory standards have been set to bring down the SO_2 emission into the atmosphere. This paper presents a review of methods of flue gas desulphurization (FGD) processes for the reduction of the emission of SO_2 with recovery of an economical by-product ,selection of flue gas desulphurization technology and provides a description of results of the limestone based flue gas desulphurization installed on the pet coke fired boiler . Among the various flue gas desulphurization processes the most widely used one is the limestone based flue gas desulphurization process because reagent limestone is easily available and cheap also which produces saleable by-product gypsum.

Keywords: - flue gas desulphurization, gypsum, limestone, SO_2.

"1. Introduction"

Sulphur dioxide is the major pollutant which causes air pollution in urban areas which in turn contribute to acid deposition that results in influencing climatic changes. Most of Asian sulphur emissions originate from coal combustion, which satisfies at present about 80% of the energy demand in the region[1]. flue gas desulphurization is widely applicable as means of controlling SO_2 emissions from power stations. The flue gas desulphurization together with measure to reduce SO_2 emissions from power stations will significantly reduce sulphur emissions to meet central pollution control board norms for SO_2 [2].Emissions of SO_2 can be controlled in several ways. It may be possible to switch to a fuel or ore that has lower sulphur content, or improve the efficiency of the industrial process so that less fuel is required. The sulphur in the fuel or ore can in principle be removed before use however, in practice it is uneconomic to remove more than a small percentage of the sulphur. The sulphur can also be removed during use. However, in many applications, the most efficient means of controlling SO_2 emissions is to remove the SO_2 from the flue gases before they are released to the atmosphere by using flue gas desulphurization technology[3].

1.1 Central pollution control board norms for SO_2

The Central Pollution Control Board of India has set three different standard for SO_2 in the ambient air 120 µg/ m^3 for industrial areas, 80 µg/ m^3 for residential areas and 30 µg/ m^3 for sensitive areas as an annual average (Annual Arithmetic mean of minimum 104 measurements in a year taken twice a week 24 hourly at uniform interval.) Annually the average of these areas should not exceed 80 µg/ m^3,60 µg/ m^3, and 15 µg/ Nm^3 as an 24 hrs.(24 hourly/8 hourly values should be met 98% of the time in a year. However, 2% of the time, it may exceed but not on two consecutive days) [4].

1.2 Fundamentals of FGD

All commercial FGD processes are based on the fact that SO_2 is acidic in nature and remove the SO_2 from flue gases by reaction with a suitable alkaline substance. The commonly used alkaline materials are limestone (calcium carbonate). Because of limestone is an abundant and relatively cheap material than other alkalis such as sodium carbonate, magnesium carbonate and ammonia which is expensive than limestone .The alkali used reacts with SO_2 in the flue gas to produce a mixture of sulphite and sulphate salts (of calcium, sodium, magnesium or ammonium, depending on the alkali used). The proportions of sulphite and sulphate are depending on the process conditions. The reaction between the SO_2 and the alkali can take place either in solution called wet flue gas desulphurization processes or at the wetted surface of the solid alkali called dry and semi-dry flue gas desulphurization processes)[3].

In wet flue gas desulphurization systems, the alkali usually in a solution or more slurry form and flue gas are contacted in a spray tower. The SO_2 in the flue gas dissolves in the water to form a dilute solution of acid that then reacts with alkali. The sulphite and sulphate salts produced precipitate out of solution, depending on the relative solubility of the different salts present. Calcium sulphate for example is relatively insoluble and readily precipitates out. Sodium and ammonium sulphates are very much more soluble[3].

In dry and semi-dry systems, the solid alkali is brought into contact with the flue gas, either by injecting or spraying the alkali into the gas stream or by passing the flue gas through a bed of alkali. In either case, the SO_2 reacts directly with the solid to form the corresponding sulphite and sulphate. The solid produce quite porous and finely divided. In semi-dry systems, water is added to the flue gas to form a liquid film on the particles in which the SO_2 dissolves, promoting the reaction with the solid. [3]

1.3 Selection of FGD Process

The selection of FGD processes by differentiating the parameter as sorbent used, by-products produced, removal efficiency and capital cost. Selection of the most appropriate FGD process for a particular application will normally be made on economic grounds, i.e. the process with the lowest overall through-life cost. However, there are many different factors that affect the overall cost.

These include:

- Technical Consideration.
- Economic Issues
    - Operating costs
    - Capital costs.
- Commercial Consideration

Technical considerations include the efficiency of desulphurisation process that can offer the flexibility of the process, the space availability that the FGD plant requires and the technical risks.

Economic issues include the capital and operating costs, including the cost of the plant, the costs of the sorbent used any revenues or expenses arising from disposal of the by-products and maintenance costs.

Commercial considerations include the commercial risk, the maturity of the technology, the number and size of units already in operation and performance of process and suppliers' guarantees. [2]

"2. Methods of Flue gas desulphurization"

2.1 Wet Flue gas desulphurization

2.1.1 Limestone Process

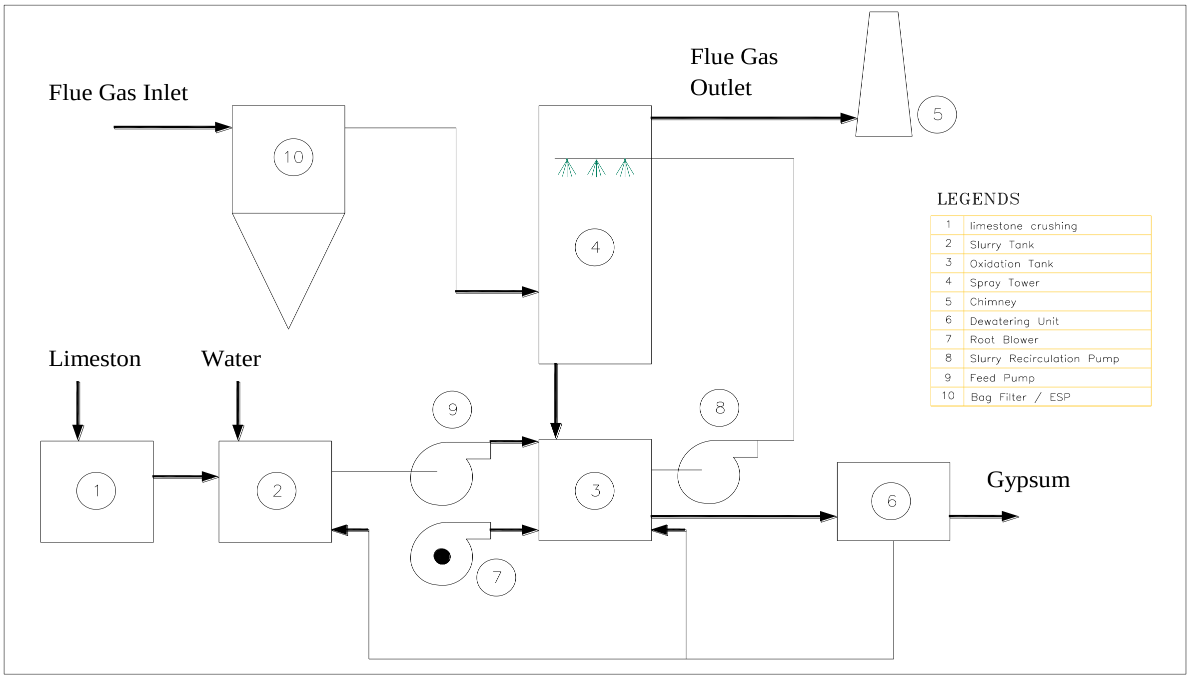
Process Description:-

In the wet limestone process, the incoming flue gas from boiler after ESP / Bag Filter is brought into contact with aqueous slurry of limestone in a scrubber tower. Sulphur dioxide in the gas reacts with the slurry to form sulphite of calcium and then oxidizes in oxidation tank to produce Gypsum, which is continuously removed from the oxidation tank in the form of slurry. This slurry is passed through hydro cyclones which separates heavier gypsum particles which are further sent to filtration plant where gypsum is removed in the form of flakes (10 -15 % moisture) and filtrate is recycled back to the process [5].

Chemical Reactions:-

$CaCO_3+SO_2+½ H_2O \rightarrow CaCO_3. ½ H_2O + CO_2$

$CaSO3.½H2O +3/2 H_2O + ½ O_2 \rightarrow CaSO_4.2H_2O$



"Figure 1. Limestone process"

2.1.2 Sodium Process

Process Description:-

In the Sodium process, the incoming flue gas from is brought into contact with an aqueous slurry of NaOH / NA_2CO_3 in tower. Sulphur dioxide in the gas reacts with the slurry to form Sodium Bisulphite which is continuously removed from the tank. In large scale systems, the by-product is often sent directly to evaporation ponds. In smaller industrial plants, the by-product is frequently sent to a wastewater treatment plant or discharge after neutralization and oxidation [7].

Chemical Reactions:-

$Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$

OR

$2NaOH + SO_2 \longrightarrow Na2SO_3 + H_2O$

$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3$

2.1.3 Ammonia Process

Process Description:-

The ammonia/ammonium sulphate or ammonium scrubbing process works in a similar way to the limestone gypsum process except that aqueous ammonia is used as the scrubbing agent. SO_2 is removed from the flue gas by reaction with ammonia, and the final product is ammonium sulfate[8].

Chemical Reactions:-

$2NH_3 + SO_2 + H_2O \longrightarrow (NH_4)_2SO_3$

$(NH_4)_2SO_3 + ½\, O_2 \longrightarrow (NH)_2SO_4$

2.1.4 Seawater Process

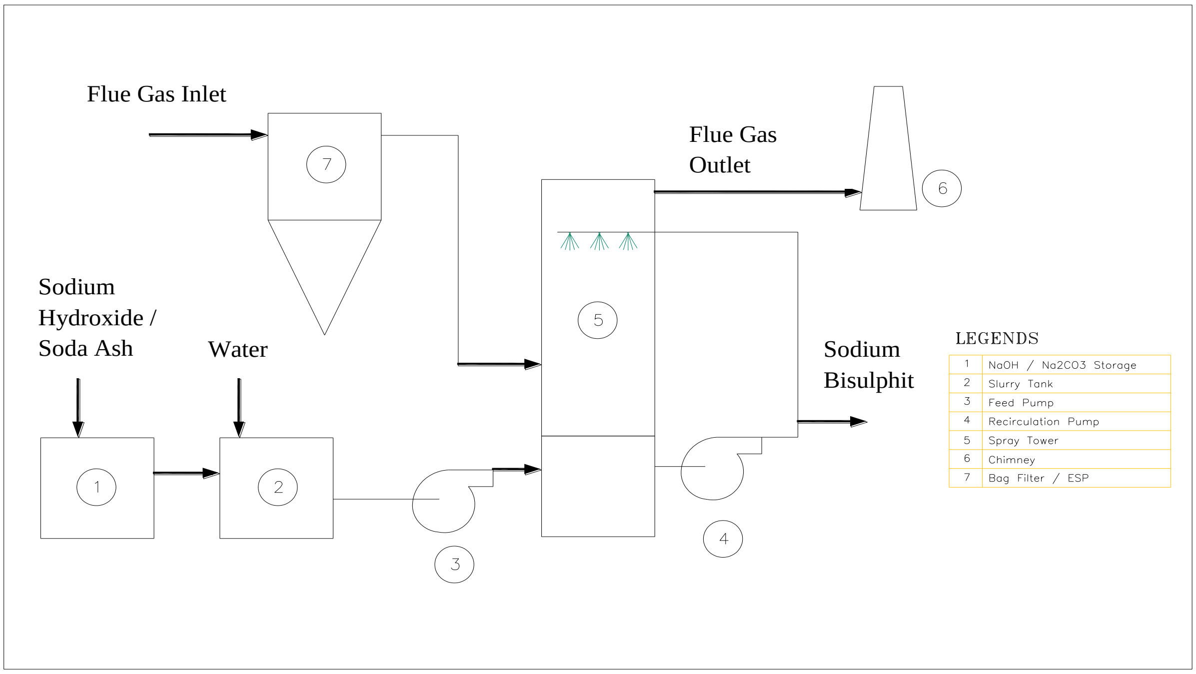
Process Description:-

There are two basic seawater FGD process concepts: one uses the natural alkalinity of the sea water to neutralize absorbed SO_2 and other uses added lime. All Commercial Sea Water FGD processes rely on the alkalinity on the bicarbonate in sea water to neutralize the SO_2 there by producing sulfite or sulfate [2], [10].

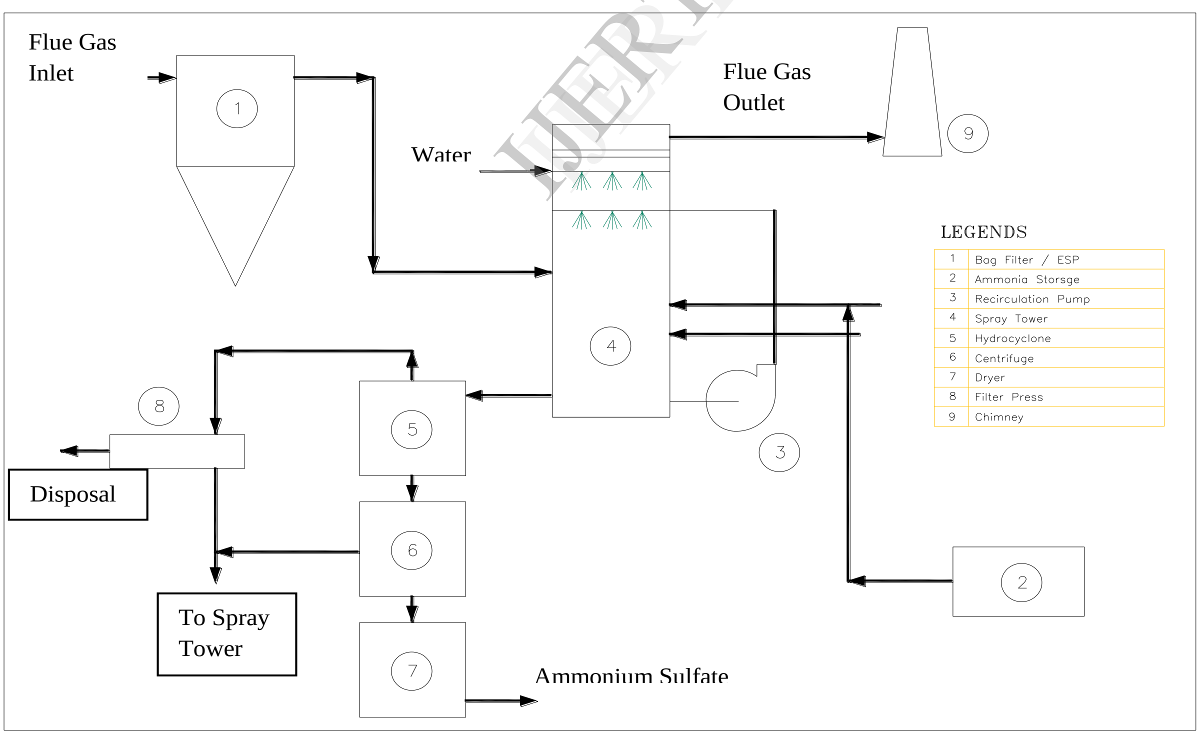
Chemical Reactions:-

$SO_2 + H_2O \longrightarrow HSO_3^- + H^+$

$HSO_3^- + ½\, O_2 \longrightarrow SO_4^{2-} + H^+$



“Figure 2. Sodium process”



“Figure 3. Ammonia process”

2.2 Semi Dry Flue Gas Desulphurization

2.2.1 Spray Dryer Process Description

In spray dryer processes, sulfur dioxide is removed from the flue gas by contact with an Atomized spray of reactive absorbent such as lime slurry or sodium carbonate solution. The Sulfur dioxide reacts with the absorbent while the thermal energy of the flue gas vaporizes The water in the droplets without saturating the flue gas to produce a fine powder of spent Absorbent. The dry product, consisting of sulfite and sulfate salts, unreacted absorbent, and fly ash, is collected in a fabric filter or electrostatic precipitator (ESP)[6],[2].

Chemical Reactions:-

$CaO + H_2O \rightarrow Ca(OH)_2$

$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$

2.3 Dry Flue Gas Desulphurization

2.3.1 Furnace Sorbent Injection

Process Description:-

In the furnace sorbent injection is a technique in which lime or limestone is injected directly into the section of the furnace where temperature ranges between 950 ^oC to 1000^oC.Hydrated lime or limestone decomposes when exposed to furnace temperature and becomes porous solid with high surface area. The reactive sorbent captures SO2 in suspension to form calcium sulfate and remaining unreacted sorbent are Aeration oxidizes all the calcium sulfite to calcium sulfate and forces precipitation to occur on existing gypsum crystals in the reaction tank. This minimizes tendency for gypsum to precipitate on surfaces in the absorber and cause plugging of pipes and nozzles by maintaining gypsum concentration in absorber. carried out of the furnace by the flue gas and collected in a fabric filter or electrostatic precipitator (ESP) [6], [5].

Chemical Reactions:-

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + SO_2 + ½\ O_2 \rightarrow CaSO_4$

"3.Experimentation"

Wet Limestone Flue Gas Desulphurization Process

The wet limestone flu gas desulphurization process as demonstrated at Shree Cement 44 MW power plant A simplified explanation of the SO2 absorbed in there circulated slurry reacts with dissolved limestone ($CaCO_3$) in the slurry to form calcium sulfite hemihydrate ($CaSO_3 \cdot ½H_2O$) according to the following reaction:

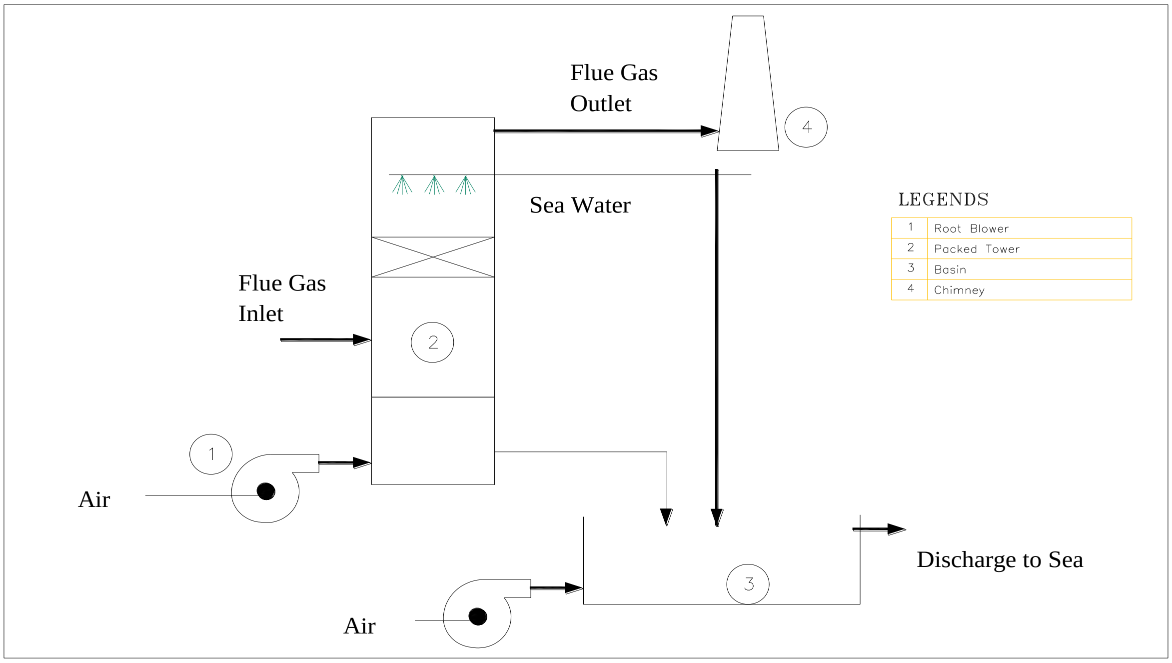
$SO_2 + CaCO_3 + ½\ H_2O \rightarrow CaSO_3 \cdot ½H_2O + CO_2$

Carbon dioxide formed from reaction of limestone with SO2 is released into the flue

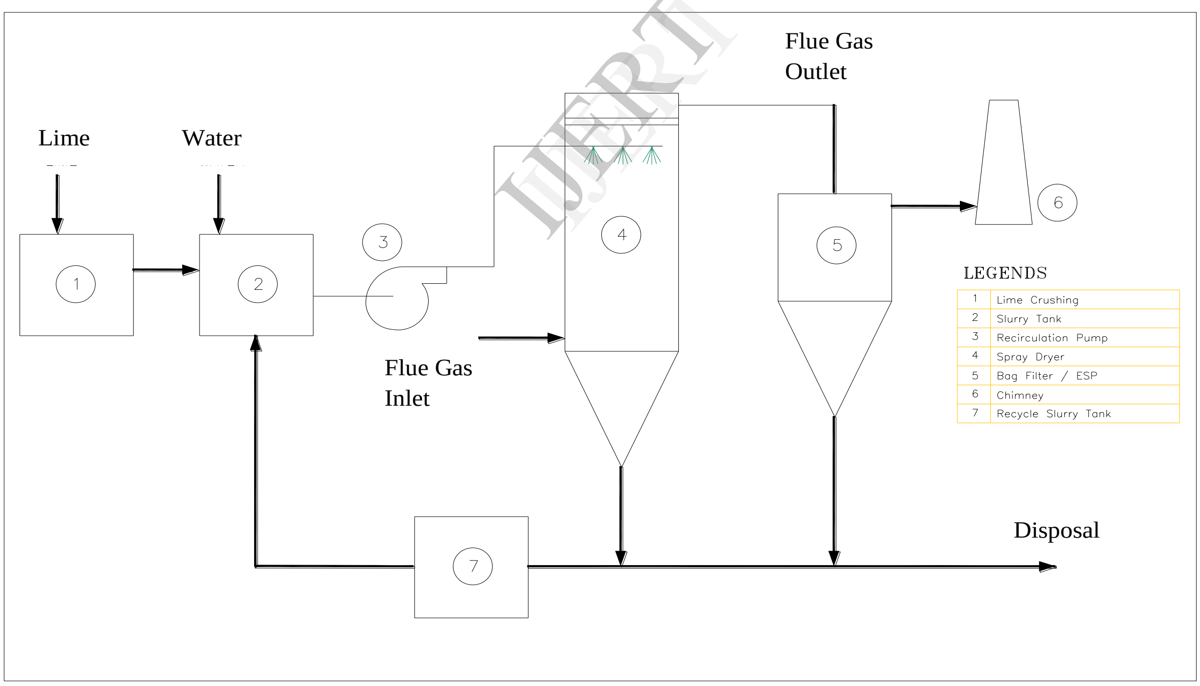
gas. Oxidation air is bubbled through the slurry to convert $CaSO_3 \cdot ½H_2O$ to gypsum

($CaSO_4 \cdot 2H_2O$) according to the following reaction:

$CaSO_3 \cdot ½H_2O + ½O_2 + 3/2\ H_2O \rightarrow CaSO_4 \cdot 2H_2O$



"Figure 4 . Seawater process"



"Figure 5. Spray dryer process"

3.1 The individual steps involved in the removal of SO_2 from gas streams by the limestone process may be summarized as follows:[2].

1) Transfer of SO_2 in the gas phase to the gas liquid interface.
2) Dissolving SO_2 into water at the interface.
3) Ionization of dissolved SO_2.
4) Transfer of H^+, $HS0_3^-$, and SO_3^{2-} ions from the interface into the liquid interior.
5) Dissolving and ionization of $Ca(OH)_2$ or $CaCO_3$ to form Ca^{2+}.
6) Reaction of Ca^{2+} with SO_3^{2-} and HSO_3^- to form $CaSO_3$ in solution.
7) Precipitation of $CaSO3_. 4H_2O$.
8) Dissolving O_2 in water at the interface.
9) Transfer of dissolved O_2 from the interface into the liquid interior.
10) Oxidation of sulfite ions to sulfate ions.
11) Reaction of Ca^{2+} with $SO^{2\ -}$ to form $CaSO_4$ in solution.
12) Precipitation of $CaSO_4.2H_2O$.

3.2 Operating Parameters

Parameter	Unit	Value	
		Inlet	Outlet
Flue Gas			
Gas Flow	kg / hr	258357	273257
	Am^3/hr	280000	244812
Gas Temp	DegC	130	47
Gas Composition			
CO_2	Vol%	15.70	14.58
H_2O	Vol%	2.56	11.56
N_2	Vol%	78.03	70.86
O_2	Vol%	3.24	2.95
SO_2	ppm	4000	400
Fuel			
Fuel		Pet Coke	
Carbon	Wt %	84.34	
Hydrogen	Wt %	2.66	
Nitrogen	Wt %	0.39	
Sulphur	Wt %	7.93	
Moisture	Wt %	2.00	
Ash	Wt %	0.77	
Oxygen	Wt %	1.91	
GCV	kCal/kg	7936	

Limestone Specifications		
Purity	%	80
Particle Size	90% below 325 mesh & 100% below 200mesh.	
Composition		
$CaCO_3$	Wt%	79%
SiO_2	Wt%	9.2%
Al_2O_3	Wt%	3.2%
Fe_2O_3	Wt%	2.12%
$MgCO_3$	Wt%	2.3%
Na_2O	Wt%	0.3%
K_2O	Wt%	0.81%
Liquid to gas ratio		
L/G ratio	gal / 1000a cf	96-110

“Table 1. Operating parameters ”

3.3 Material of Construction Major Equipments

Sr. No	Part Description	MOC
A]	**Slurry preparation and transfer circuit**	
1	Lime Stone slurry preparation tank	Carbon Steel + Chlorobutyl Rubber (Thickness 5 mm)
2	Lime Stone slurry transfer Pump	Alloy Steel
B]	**Flue gas circuit**	
1	Diverter Valve	Carbon Steel
2	Booster Fan	Carbon Steel
C]	**Desulphurisation circuit**	
1	Spray Tower	Carbon Steel + Chlorobutyl Rubber (Thickness 3 mm)
2	External Structural Supported Chimney tower	Carbon Steel + Natural Hard Rubber (Thickness 3mm)
4	Spray Headers	Carbon Steel + Chlorobutyl Rubber (Thickness 5 mm)
5	Slurry Spray Nozzles	Silicon Carbide
6	Mist Eliminator	PP
7	Mist Eliminator Washing System	Carbon Steel + Natural Rubber (Thickness 3mm)
8	Slurry recirculation Pump	High Chromium Alloy
9	Oxidation Tank	RCC + Chlorobutyl Rubber (Thickness 10 mm)
10	Oxidation Pipe	Carbon Steel + Chlorobutyl Rubber (Thickness 5 mm)

Sr. No	Part Description	MOC
D]	**By product discharge system**	
1	Gypsum Slurry pump	Alloy steel
2	Hydro Cyclone	Carbon Steel + Chlorobutyl Rubber (Thickness 5 mm)
3	Rotary Vacuum Drum Filter	Carbon Steel/ GRP

"Table 2. Material of Construction Major Equipments"

3.4 Running Cost

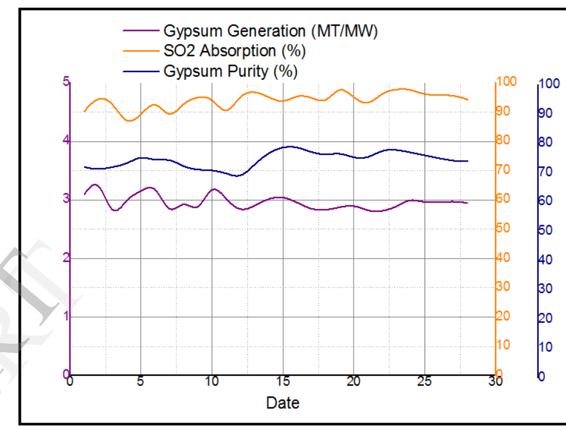
Sr. No.	Description	Unit	Value
1	**Limestone**		
i	Limestone Consumption	kg/hr	4245
ii	Cost of Limestone	Rs/kg	0.25
iii	Cost of Limestone	Rs/hr	1061
2	**Fresh water**		
i	Fresh Water consumption	m^3/hr	18
ii	Cost of Fresh Water	Rs/m^3	25
iii	Cost of Fresh Water	Rs/hr	450
3	**Electricity consumption**		
i	Power Consumption	kW	1078
ii	Cost of Electricity	Rs/kWh	2.84
iii	Cost of Electricity	Rs/hr	3062
4	**Running Cost for FGD Plant [1(iii)+2(iii)+3(iii)]**	**Rs/hr**	**4573**
5	**Gypsum production**		
i	Wet Gypsum (15 % Moisture & 78 % purity)	kg/hr	7576
ii	Dry Gypsum (78% Purity)	kg/hr	6440
iii	Cost of Gypsum production from FGD Plant (78% purity)	Rs /ton	710
6	Landed Cost of Mined Gypsum (78% Purity)	Rs/ton	1908
7	Savings to due to Gypsum Production	Rs/ ton	1198

"Table 3. Running Cost"

"4. Results and Discussions"

We had got the following result after successful trial on limestone based flue gas desulphurization plant :-

- SO_2 Absorption Efficiency -90 %
- Limestone Consumption- 4245 kg/hr
- Gypsum Generation -7576 kg/hr
- Gypsum Purity (Min) – 78 %



"Graph 1.One of the Result of month Nov 2012 shows the relation between gypsum generation, SO_2 absorption and gypsum purity "

"5. Future market"

In India rely heavily on thermal power plant for power supply. India has large number of coal or pet coke fired units burning pet coke or indigenous coal. These coals or pet coke content sulphur and the emphasis on environment. There will be a larger market for flue gas desulphurisation new plant. The massive increase in electrical generating capacity required to keep place with increasing power demand means that the emphasis for flue gas desulphurization units.

"6. Conclusion"

The wet limestone flu gas desulphurization process as at Shree Cement 44 MW power plant uses a counter current scrubbing process with in force oxidation to produce gypsum and achieving a high degree of SO_2 emissions reduction when burning high-sulfur coals (pet coke) because of easy availability of limestone at low cost .

The consumption of gypsum in cement making so therefore saving due to in house gypsum production and achieve less payback period for limestone based flue gas desulphurization system.

The cost of installing a flue gas desulphurization unit depends on various factors such as scale of process, sulphur content in the coal or pet coke, availability and cost of reagents. In India it has large natural reservoirs of limestone and hence limestone process is better than other processes.

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