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COMPREHENSIVE INDUSTRY DOCUMENT ON SULPHURIC ACID PLANT

cpcb
CENTRAL POLLUTION CONTROL BOARD
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FOREWORD

Sulphuric acid (H_2SO_4) is one of the most important chemical having a wide variety of industrial usage. Fertilizer industry is the main consumer of H_2SO_4, at present. Besides, steel, rayon & staple fiber, alum, petroleum refining and inorganic chemicals are other important sectors, which consume H_2SO_4. In India, there are around 140 Sulphuric Acid Plants with an estimated annual Installed Capacity of about 12 Million MT. Most of these plants use elemental sulphur as raw material while a few plants use gasses from copper and zinc smelters to produce H_2SO_4.

Sulphuric Acid manufacturing process leads to emission of oxides of sulphur & acid mist as gaseous pollutants for which emission standards had been developed almost 20 years back. Since then, many improvement have taken place in the process of manufacturing of sulphuric acid and also the pollution control technologies. Improvements in the conversion and absorption stages are being introduced from time to time to increase conversion and absorption efficiencies. Further, large capacity plants have also come up. In view of these developments, CPCB took up a project to revisit the earlier emission standards. Necessary studies were carried out through M/S Siel Projects Engineering & Consultancy Services, New Delhi.

Dr. Prashant Gargava, Environmental Engineer; Shri B. K. Jena, JSA; and Ms. Sakshi Batra, SRF have co-coordinated the project activities and finalized the present Report under guidance of Shri N. K. Verma, Ex-Additional Director; Shri P. M. Ansari, Additional Director; and Dr. B. Sengupta, Member Secretary of Central Pollution Control Board.

I trust that this Report would be useful to all those interested in pollution control in sulphuric acid manufacturing industry.

April 12, 2007 **(J. M. Mauskar)**

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1.0 INTRODUCTION

Sulphuric Acid is an important chemical, which has large-scale industrial uses. Its major user is the phosphate fertilizer industry. Other important applications are in petroleum refining, steel pickling, rayon & staple fiber, alum, explosives, detergents, plastics and fibers etc. Sulphuric Acid Industry is very old and has been continuously adopting the technological developments. It started with Lead Chamber process followed by contact process with Single Conversion Single Absorption (SCSA) and now Double Conversion Double Absorption Process (DCDA) process.

In India, there are about 140 Sulphuric Acid Plants (130 Sulphur based & 10 Smelter Gas based) with Annual Installed Capacity of about 12 Million MT. As in some places, there are more than one stream/unit with some common facilities these plants are situated in 131 locations. It may be observed that about 25% of the installed capacity is located in Paradeep (Orissa) only consisting of 2 plants (4 streams/units). Capacity-wise number of plants can be categorised as below and also given in figure 1.1:

Installed Capacity (MT/Day)	Number of Plants	%
upto 50	18	12.9
51-100	45	32.1
101-200	40	28.6
201-300	17	12.1
301-500	5	3.6
501-1000	9	6.4
1001- 2000	4	2.9
above 2000	2	1.4
Total	140	100.0

The current annual production of Sulphuric Acid is about 5.5 Million MT, against the installed capacity of 12 Million MT/Annum from Sulphur based as well as Smelter Gas based plants. Some of the plants have been closed down due to various reasons. It is learnt that many captive plants have been closed down due to non-viability of the main plant, viz. Single Super Phosphate etc., while merchant plants have closed down due to poor demand. The demand of Sulphuric Acid is fully met by the current production, as the installed capacity is more than double the demand.

CAPACITY-WISE DISTRIBUTION OF SULPHURIC ACID PLANTS

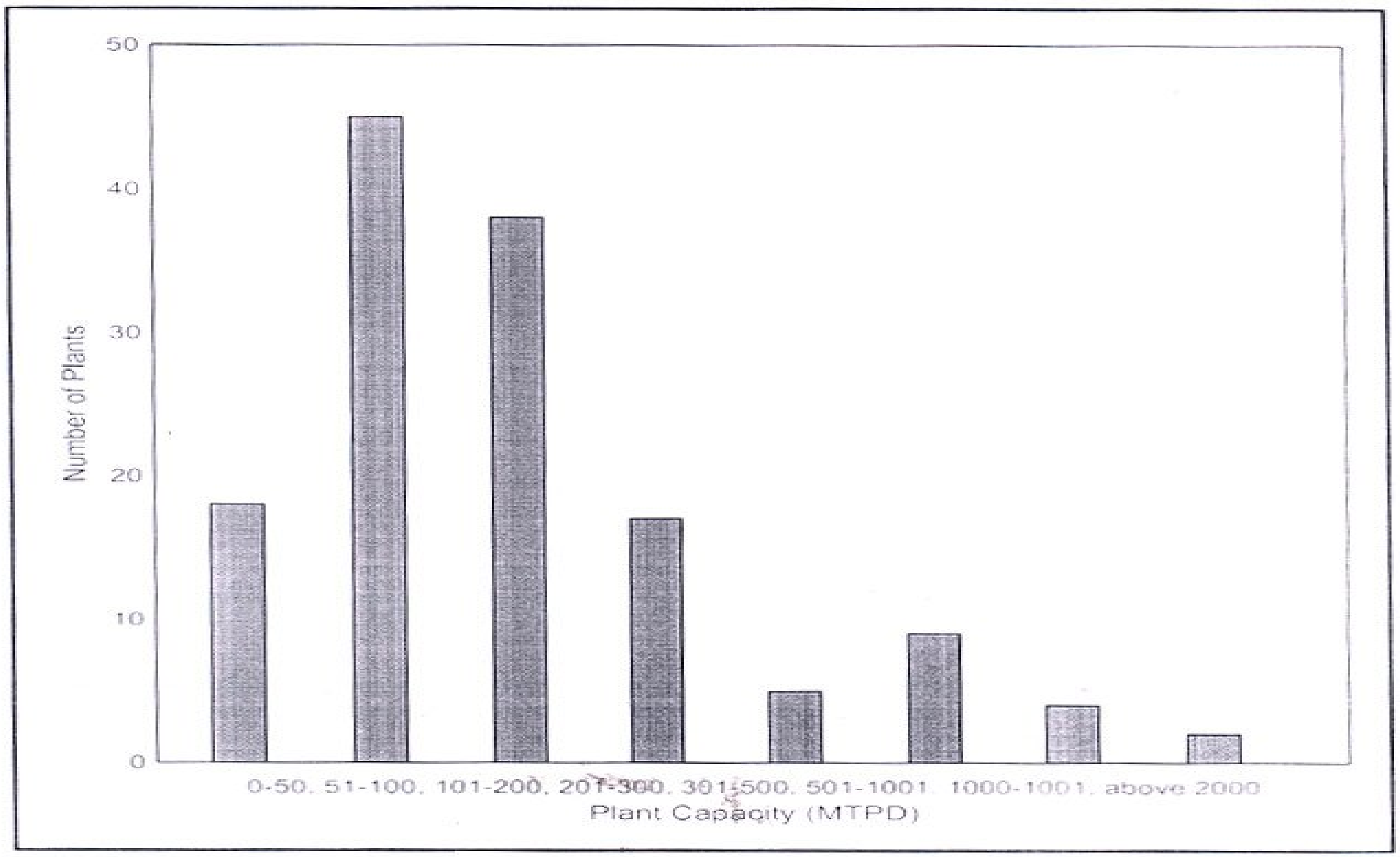


Fig 1.1

The Sulphuric Acid production through Contact Process is very mature. However, improvement in conversion and absorption stages are being introduced from time to time to increase conversion and absorption efficiencies, which also result in reduction in emissions. Most of the plants use elemental sulphur as raw material and in few cases Copper/ Zinc Smelters gases are being used to produce Sulphuric Acid.

The environmental problems arising due to Sulphuric Acid manufacture include:

- Off gases from absorption tower containing oxides of Sulphur (SO_x) and acid mist.
- Liquid effluent generated through waste heat boiler blow-down, spillage & leakage from equipment, washing of equipment, cooling tower bleeding etc.
- Generation of Solid Waste viz. Sulphur muck & spent catalyst.

Presently, Gaseous emission limits prescribed by CPCB for Sulphuric Acid Plants are as under:

SO_2	:	4.0 Kg/MT of Sulphuric Acid produced (Conc. 100%)
Acid Mist	:	50 mg/Nm^3

However, due to advancement in process and pollution control technologies, it may be possible to further reduce & control the emissions of SO_x and acid mist. Besides, large capacity plants have also come up at single location requiring better control. In view of this, CPCB took up a project to revisit the emission standards. Necessary studies were carried out through M/S Siel Projects Engineering & Consultancy Services, New Delhi.

2.0 STATUS OF EXISTING SULPHURIC ACID PLANTS

2.1 Process Technology

Technical features of manufacturing process technology of Sulphuric Acid Plants with regard to pollution control aspects are discussed below:

The primary raw material for producing intermediate product of sulphur dioxide is elemental sulphur. Nonferrous metals industry is also a large producer of sulphur dioxide where the roasting and smelting processes generate off-gases with a sufficiently high concentration of sulphur dioxide that could be converted to sulphuric acid as a byproduct. Significant number of sulphuric acid manufacturing facilities has been installed in metallurgical plants for the recovery of SO_2, mainly for environmental reasons. Pyrite is also used as a raw material for sulphuric acid production.

The theoretical requirement of Sulphur is 0.3265 MT/MT of 100% Sulphuric Acid. However, the actual consumption in DCDA Sulphuric Acid Plants generally varies from 0.330 MT to 0.340 MT/MT of 100% Sulphuric Acid depending on the SO_3, and acid mist escaping with the stack gases. The sulphur loss in fugitive emission is generally negligible.

Sulphuric Acid Plants vary in a number of respects depending on the raw material used to produce the gas containing sulphur dioxide. The broadest division is into hot gas and cold gas plants. In hot gas plants, which are usually based on the combustion of elemental sulphur, the hot gas from the sulphur furnace is cooled just to the required converter inlet temperature. Typical process flow sheet for Sulphur burning DCDA Plant is given in figure 2.1.

Cold gas plants, based on metallurgical or decomposition gases, are so designed that the crude sulphur dioxide containing gas must be cooled to low temperatures in the de-dusting and cleaning systems before being introduced into the sulphuric acid plant. It is therefore, necessary to reheat the cold feed gas to the requisite converter inlet temperature with reaction heat from the converter system. Typical process flow sheet for Metallurgical gas based plant is given in figure 2.2.

These traditional contact plants can be further subdivided into the double absorption process, which is the type of process now most commonly used in new plants with intermediate absorption and the older, without intermediate absorption also referred to as the single absorption or single contact process.

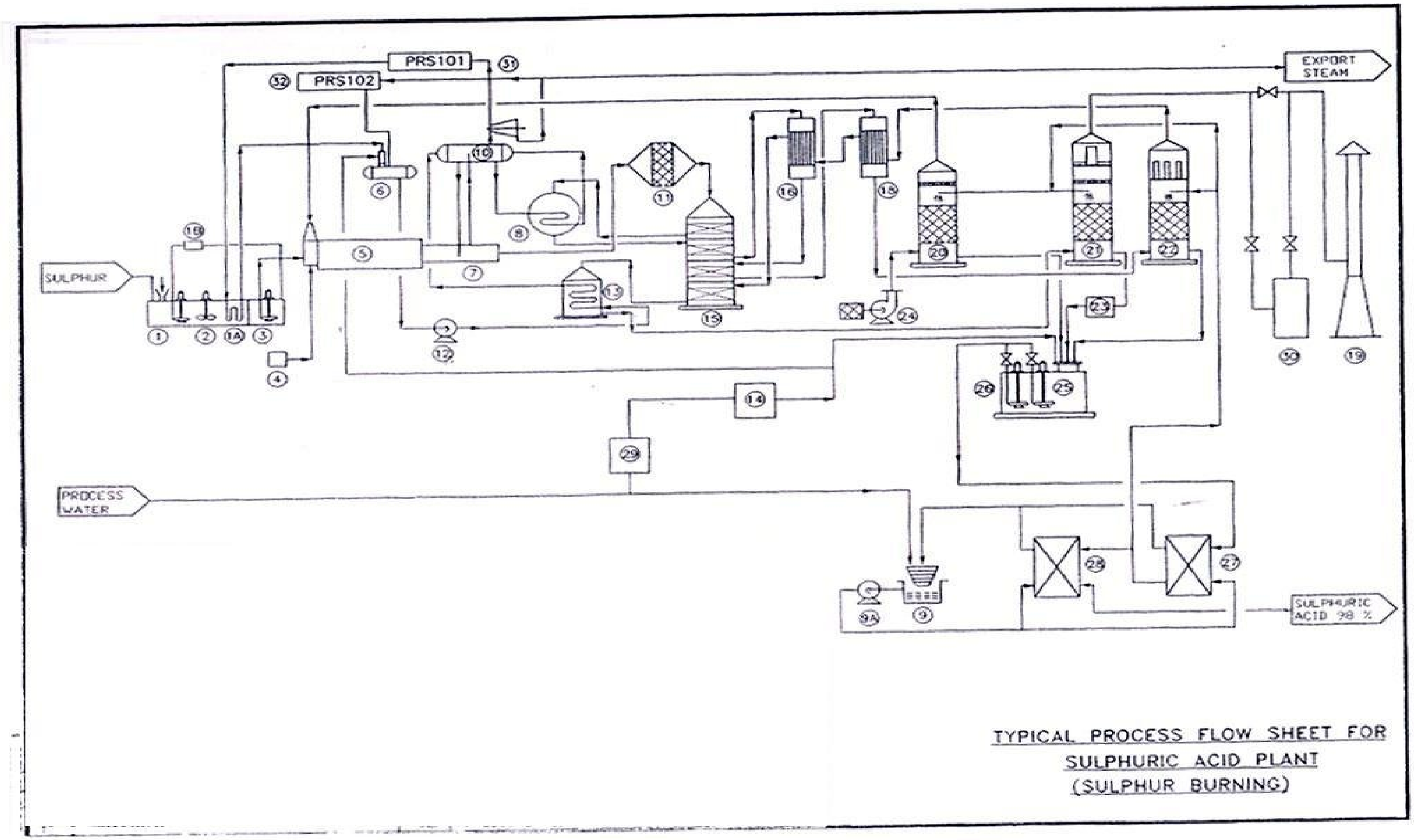

PRS101
PRS102
EXPORT STEAM
SULPHUR
PROCESS WATER
SULPHURIC ACID 98 %
TYPICAL PROCESS FLOW SHEET FOR
SULPHURIC ACID PLANT
(SULPHUR BURNING)

Fig: 2.1

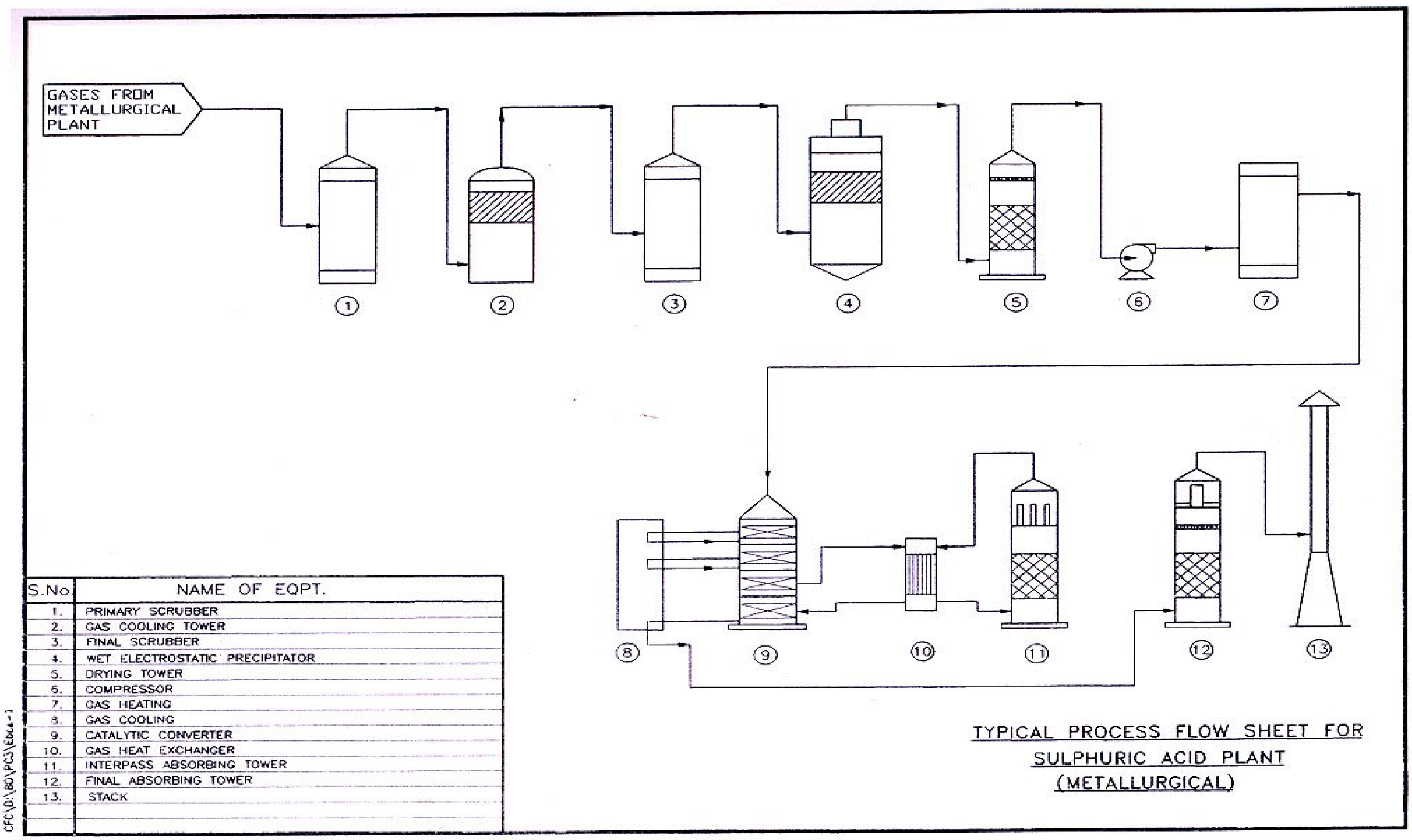

GASES FROM METALLURGICAL PLANT
S.No.
NAME OF EQPT.
1. PRIMARY SCRUBBER
2. GAS COOLING TOWER
3. FINAL SCRUBBER
4. WET ELECTROSTATIC PRECIPITATOR
5. DRYING TOWER
6. COMPRESSOR
7. GAS HEATING
8. GAS COOLING
9. CATALYTIC CONVERTER
10. GAS HEAT EXCHANGER
11. INTERPASS ABSORBING TOWER
12. FINAL ABSORBING TOWER
13. STACK
TYPICAL PROCESS FLOW SHEET FOR
SULPHURIC ACID PLANT
(METALLURGICAL)

Fig: 2.2

The contact process for the production of Sulphuric Acid is based on the catalytic oxidation of SO_2 to SO_3. Since the oxidation reaction of SO_2 to SO_3 is exothermic, the temperature of the gases after catalytic conversion rises. As the forward reaction progresses, the state of equilibrium is approached and the forward reaction comes to halt. In DCDA Plant, SO_3 is removed from the gas stream after 2nd and 3rd bed, which shifts the equilibrium and increases the rate of the forward SO_2 to SO_3 reaction resulting in higher overall conversion.

Double Conversion Double Absorption (DCDA) Process

The main steps involved in DCDA process are as below:

- Melting solid Sulphur with steam coils, followed by filtration or settling of impurities to obtain clean sulphur containing less than 10 mg/l of ash.

- Burning the molten Sulphur with air to produce gas-containing SO_2.

- Cooling the hot gas in Waste Heat Boiler System to produce superheated or saturated steam at conditions fixed, as per requirements.

- Catalytic oxidation of SO_2 to SO_3 in three consecutive passes of converter containing V_2O_5 catalyst with intercooling of gas in between. The exothermic heat of reaction is utilized to produce steam in Waste Heat Boiler system and to reheat the gases going to IVth pass from the intermediate absorber.

- Absorption of SO_3 (formed in IVth pass) in the final absorption tower.

The sulphur-burning DCDA process is considered to be the standard sulphuric acid production process based on approximately 10-12% SO_2 in sulphur furnace.

All reactions in the production of sulphuric acid from elemental sulphur are exothermic. The liberated heat must be dissipated under controlled conditions in such a way so as to maintain optimum gas temperatures in the converter system and optimum acid temperatures in the absorber circuits. The systems for gas and acid cooling are, therefore, essential components of a sulphuric acid plant. In most of the plants the high-pressure steam is generated with high-temperature heat recovered by indirect exchange with gases from the sulphur furnace and converter system.

Single Conversion Single Absorption (SCSA) Process

Before introduction of the DCDA process, SCSA was the standard sulphuric acid production process.

In principle, the SCSA process retains more gas heat than DCDA process, because there is no intermediate absorption stage with its associated heat losses. In a roaster-based plant the surplus heat is simply discharged, for instance by indirect air-cooling in an air cooler after the third bed. The reaction heat in a plant based on sulphur combustion is recovered by steam generation in economizers and evaporators. About 10% more steam is, therefore, produced per MT of sulphuric acid in a sulphur-burning SCSA plant than in a DCDA plant of the same capacity. Due to favorable energy balance, an SCSA contact plant can also process gases with lower sulphur dioxide content.

Present Status

At present most of the Sulphur based Sulphuric Acid Plants are based on Double Conversion Double Absorption (DCDA) process except for a few Smelter based plants, which are working on Single Conversion Single Absorption (SCSA) process.

Most of the plants from whom the information has been received or the plants visited for in-depth studies are based on DCDA process. Plants are coming up with 5-stage converter. Two Plants are equipped with 5 stages Converter.

The sulphur-based plants are using heat of combustion and conversion for producing superheated steam. In metallurgical plants the steam produced is of low pressure and is used for heating boiler water or for other process purposes. In high capacity plants and upcoming plants, heat of absorption is also utilized for producing low-pressure steam. One plant is also utilizing heat of absorption in producing low-pressure steam. Viability of Heat Recovery System shall improve with continuous increase in cost of energy.

2.2 Gaseous Emission

Gaseous emissions in Sulphuric Acid Industry consist unabsorbed SO_2/SO_3 gases and acid mist after final absorption tower. These are let off from the main stack (Chimney). Emissions are being dealt with development in equipment, catalyst and process modifications. Gaseous emission is in the form of SO_2, which is discharged due to low conversion efficiency or due to sudden failure of system in absorbing SO_3 and acid mist. Catalytic oxidation takes place from SO_2 to SO_3 and finally SO_3 is absorbed in 1 or 2 stages to produce Sulphuric Acid. Scrubbing system is also provided to scrub gases coming out during abnormal operations or at the start-up/shutdown operations.

Existing norms for SO_2 & Acid Mist emissions notified under the Environment (Protection) Act, 1986 are as under:

SO_2	:	4 Kg/MT of 100% Sulphuric Acid product
Acid Mist	:	50 mg/Nm^3

However, State Pollution Control Boards have also fixed industry specific norms based on the location and size of industry.

Kerala, Gujarat and Andhra Pradesh State Pollution Control Boards have fixed industry specific SO_2 emission norms of 3 Kg/MT , 2 Kg/MT and 1Kg/MT of 100% Acid produced respectively.

In advance countries, the gaseous emission norms for SO_2 are generally as under:-

Country	SO_2 (Kg/MT of 100% Sulphuric Acid)
Japan	1.0
U.S.A	2.0
U.K.	3.3

However, these are subject to variation as per the plant size & location.

For Acid Mist, Gujarat has fixed norm of 25 mg/Nm^3 while in Andhra Pradesh it is 34 mg/Nm^3.

For SO_3 emission, there is no norm from CPCB. However, in Maharashtra there is norm of 50 mg/Nm^3 of SO_3.

The main motivation for the process development is to achieve highest resource conservation resulting in lower SO_2 emission from Sulphuric Acid Plants. In recent years there has been a trend towards better conversion efficiency. Some plants have come up with upto 99.9% efficiency, resulting in SO_2 emission level of about 0.5 Kg/MT of Sulphuric Acid. Some technologies like tail gas scrubbing or triple absorption have the drawback of increased capital/operating costs. New plants may be designed with five bed converters but this layout is less attractive for existing plants equipped with four bed converters. Emphasis is towards minimising emissions in existing plants by doing changes in catalyst or mist eliminator, etc.

Details of Emissions of the eight Sulphuric Acid Plants monitored during In-depth Study are as under:-

Plants	SO_2 Emissions (Kg/Ton of Acid)	Acid Mist (Mg/Nm^3)	SO_3 (mg/Nm^3)
1	6.85 - 10.19	42 - 46	193 - 210
2	2.50 - 3.52	54 - 129	6 - 7
3	2.76 - 3.09	4 - 6	89 - 109
4	1.36 - 1.48	4 - 5	102 - 142
5	2.91 - 3.35	20 - 24	71 - 101
6	1.74 - 2.58	2 - 3	79 - 167
7.	2.00 - 2.14	Not Detected	54 - 71
8	1.65 - 3.45	12 - 16	8 - 12

The average emission levels from stack of some Sulphuric Acid Plants in India as per the information received through questionnaires/in-depth monitoring of 8 Sulphuric Acid Plants are given below and details are provided at Annexure-I

S.No.	Capacity of Plants (MTPD)	Avg. SO_2 (Kg/MT of Acid)	Avg. Acid Mist (mg/Nm^3)	Avg. SO_3 (mg/Nm^3) *
1.	upto 100	1.7 - 3.1	25 - 30	N.A.
2.	101-500	1.8 - 2.8	19 - 26	124-140
3.	above 500	1.9 - 2.6	11 - 19	85 - 130

While calculating the average emission levels, the data appearing unreliable/extreme-isolated data have been ignored. Data on SO_3 were available only for a few Sulphuric Acid Plants.

2.3 Scrubbing System

In DCDA Sulphuric Acid plants, emission levels of SO_2 are higher during start-up or shutdown when SO_2 to SO_3 conversion is not proper. Also in SCSA Plant, the emission levels of SO_2 are normally high. While in first case, the start-up scrubbers are required to take care of extra SO_2 load during unstabilized conditions, start-up & shutdown, in second case, a continuous scrubbing unit is required to take care of tail gases going out for the stack. Salient features for these scrubbers are as follow:

- Scrubbing during Start-up & Shutdown

When Sulphuric Acid Plant is started after a long shut down, proper conversion of SO_2 to SO_3 gases does not take place, i.e., conversion efficiency is low. Hence, scrubbing unit is run for controlling the emissions. The unit scrubs the gases in a tower through an absorbent chemical, viz., dilute Caustic Soda solution, ammonia, lime solution, etc. The system is chosen on the basis of maximum SO_2 and maximum SO_3 concentration in the gases. In some of the plants, systems are designed for as low as 1 Kg/MT of Sulphuric Acid for SO_2 and 25 mg/Nm^3 for Acid Mist. Most of the plants are equipped with Caustic/Lime Scrubbers.

During in-depth studies, it was found that out of 8 plants, 7 plants had Scrubbing units. One plant was running its Scrubbing plant continuously as per the directive of State Pollution Control Board.

It was reported that during start-up/shut down all plants are generally meeting the required emission norms with the help of Caustic Scrubbing system provided the same is operated. Typical Gas Scrubbing System is given in fig 2.3

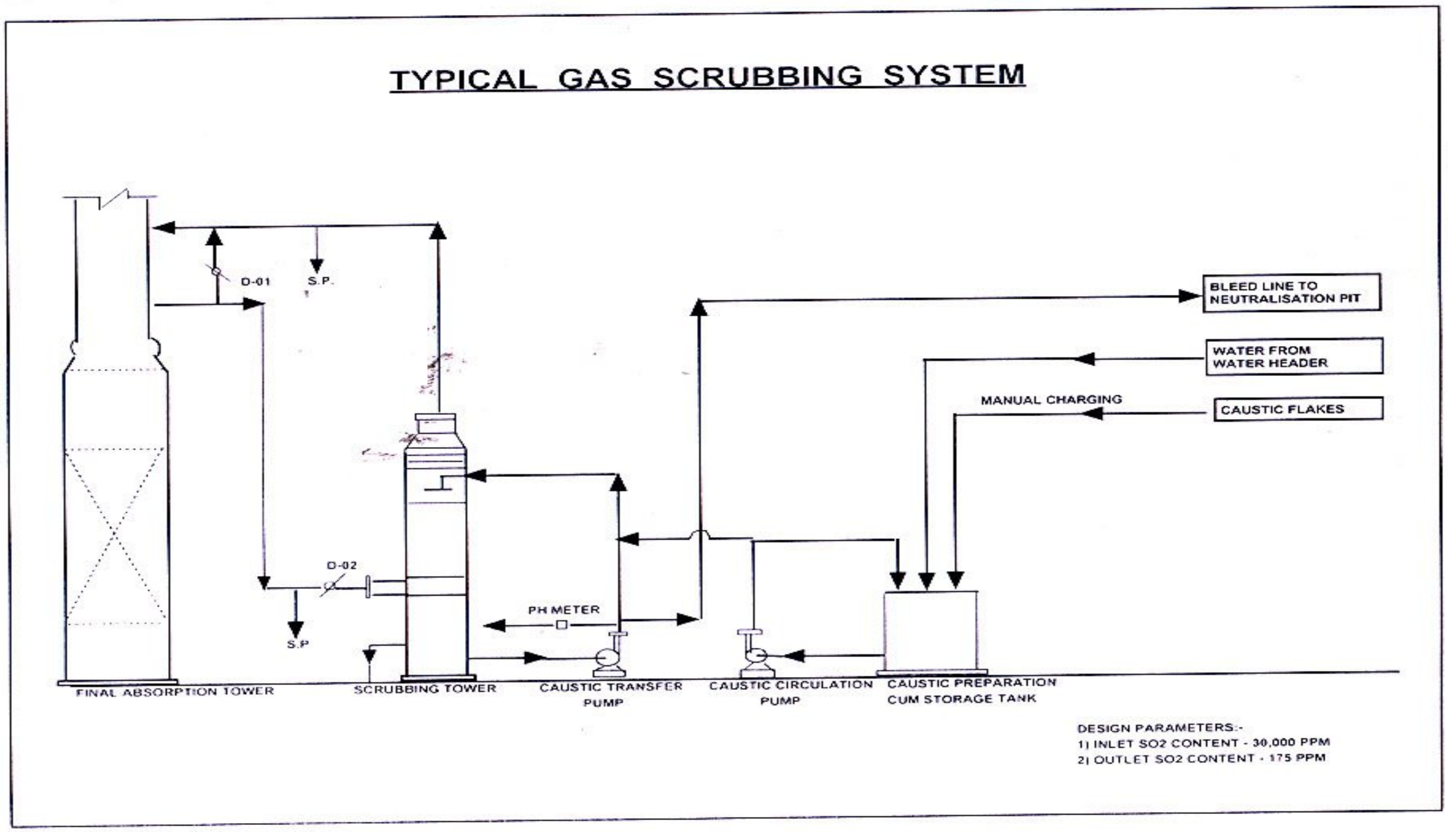

TYPICAL GAS SCRUBBING SYSTEM
D-01
S.P.
BLEED LINE TO NEUTRALISATION PIT
WATER FROM WATER HEADER
MANUAL CHARGING
CAUSTIC FLAKES
D-02
PH METER
S.P
FINAL ABSORPTION TOWER
SCRUBBING TOWER
CAUSTIC TRANSFER PUMP
CAUSTIC CIRCULATION PUMP
CAUSTIC PREPARATION CUM STORAGE TANK
DESIGN PARAMETERS:-
1) INLET SO2 CONTENT - 30,000 PPM
2) OUTLET SO2 CONTENT - 175 PPM

Fig: 2.3

- Continuous Scrubbing for Tail Gas Treatment

In India, the tail gas treatment plants have been installed for single absorption Sulphuric Acid Plants based on metallurgical gases where due to thermal imbalances caused by variation in concentration of the gases, DCDA process is not considered feasible.

The tail gas from Sulphuric Acid plant contains Sulphur Dioxide, concentration of which depends on the conversion efficiency attained in the conversion stages. The content of gaseous sulphur trioxide and sulphuric acid mist is essentially a function of the temperature and concentration of sulphuric acid in the absorbtion tower. Under unfavorable operating conditions (e.g. when the sulphur dioxide-containing converter feed gases are inadequately dried, or contain hydrocarbons) sulphuric acid mist is formed, which is not removed in the absorption system. This is true even when the concentration and temperature of the absorber acid are at their optimum values. The safest way to remove the acid mist is with a candle filter. However, this is not very effective for removing excess sulphur trioxide, which may result from poor absorption efficiency of tower.

One plant having capacity of 220 TPD with SCSA process has installed tail gas treatment plant based on technology from MESCO, Japan. The process is based on scrubbing of stack gases by calcine (Zinc Oxide) slurry. SO_2 is recovered from Zinc Sulphite Solution and cycled back to Sulphuric Acid Plant. Thus, Zinc Oxide also gets regenerated and fed back into the circuit. Sulphur Dioxide content in the exit gases reduced from about 16 Kg/MT to less than 1 kg/MT of acid. It can be reduced further to less than 0.3 Kg/MT of acid in second stage by installing an additional Absorption Tower.

One of the plants is having continuous Lime Scrubbing Plant. Lime Scrubbing is leading to Sludge handling problem. Due to low cost of lime, lime scrubbing has generally been adopted.

2.4 Liquid Effluents

In Sulphuric Acid Plants the wastewater is produced in the form of high TDS, highly acidic water coming out through spillage of leakages of acid in the system. The plant involves exothermic reactions so the heat generated is utilized for producing steam. Water used for high-pressure boilers is de-mineralized. The plant set up for producing DM water involves ion exchange and so the wastewater is generated in regeneration through injection and rinsing process. The water is acidic or alkaline with high TDS.

The alkaline water is used for scrubbing and the balance quantity is led to the effluent pit for neutralization. The Blow-down water is used for making brine solutions or making other chemical solutions as per requirement. Cooling tower blow-down water is of TDS around 2000 mg/lit, which is used for domestic service by some plants. Any acidic washings resulting from spillage or leakage are treated with alkaline solution before disposal to the pit or for domestic usage.

Raw water is generally available in industry from ground or surface water source. Water used for the different purposes in Sulphuric Acid Industry is depicted in figure 2.4.

- Water used in Waste Heat Boiler

Raw water is subjected to preliminary treatment, which includes clarification. After filtration, raw water is subjected to softening process where the hardness is removed for rendering water fit for use in cooling towers and also in low-pressure boilers. The water softening is carried out by use of chemical precipitation process plus cation exchange process or simply by cation exchange process. Chemical precipitation system using hotlime soda process followed by base exchangers to take care of residual hardness has been considered to protect the interior surfaces of boilers and also cooling towers due to safeguards against corrosion. This is cheapest process but due to handling of lime and soda, many plants do not use this process but prefer only cation exchange system where the resins after exhaustion are regenerated with brine solution.

Demineralisation of water is used when Waste Heat Boiler (WHB) pressure and temperature are high. This result in less lowdown from the boiler to maintain appropriate dissolved solids concentration in boiler drum avoiding foaming and priming effects. DM water also helps in maintaining better steam quality but the process is quite expensive and releases double the high TDS wastewater, which emanates out of the injection/ rinsing and regeneration.

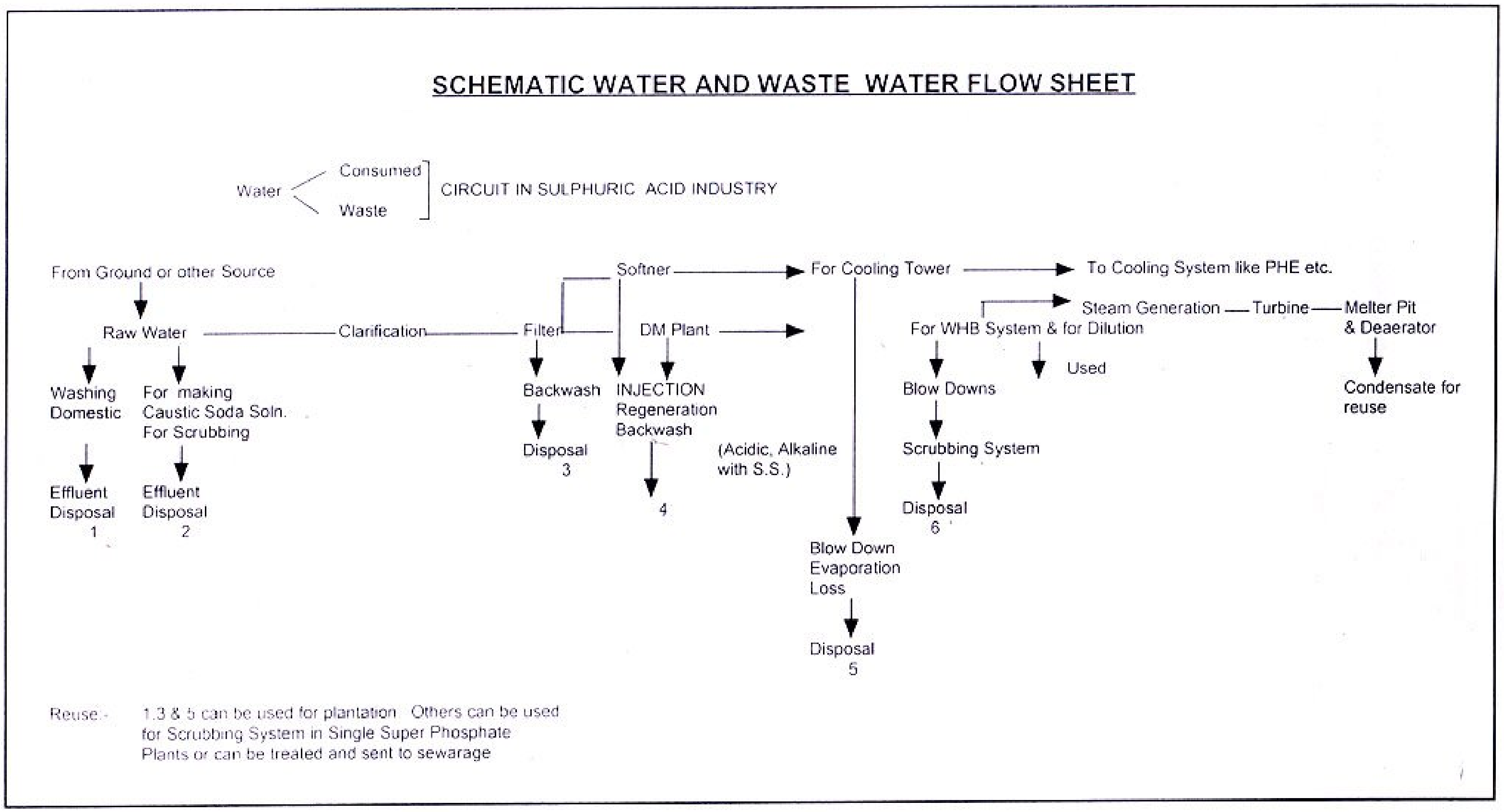

SCHEMATIC WATER AND WASTE WATER FLOW SHEET
Water
Consumed
Waste
CIRCUIT IN SULPHURIC ACID INDUSTRY
From Ground or other Source
Raw Water
Clarification
Filter
Softner
DM Plant
For Cooling Tower
To Cooling System like PHE etc.
Steam Generation
Turbine
Melter Pit & Deaerator
For WHB System & for Dilution
Used
Washing Domestic
For making Caustic Soda Soln. For Scrubbing
Effluent Disposal 1
Effluent Disposal 2
Backwash
Disposal 3
INJECTION Regeneration Backwash
(Acidic, Alkaline with S.S.)
4
Blow Downs
Scrubbing System
Disposal 6
Blow Down Evaporation Loss
Disposal 5
Condensate for reuse
Reuse:- 1,3 & 5 can be used for plantation. Others can be used for Scrubbing System in Single Super Phosphate Plants or can be treated and sent to sewarage

Fig: 2.4

- Water used in Cooling Tower

Cooling tower in Sulphuric Acid Plant is used for systems like Plate Heat Exchangers, etc. to maintain suitable temperature of acid. The water used in Waste Heat Boiler and cooling tower are functions of quality of water and efficiency of cooling system. Generally 1 to 1.5% evaporation and windage losses occur in cooling towers which are to be regularly replenished to maintain optimum TDS to avoid precipitation/ scale formation due to dissolved solid concentration.

- Water for Dilution of Sulphuric Acid

Water used in dilution of Sulphuric Acid is about of 15-17% of the production and does not generate wastewater. This also depends on the dryness factor in local ambient conditions.

- Water used in Scrubbing System

Generally Scrubbing System is operated continuously in manufacture of Sulphuric Acid from hot gases or in SCSA plants. In sulphur based DCDA plants it is used only at the time of start up of plant, any upset condition with regard to temperature or as a precautionary measure to avoid any spurt in emissions at the time of stoppage of plant. Hence, in conventional sulphur based plant, use of water in the scrubber depends on frequency and duration of operation of scrubber. The scrubber water is reused number of times after pH correction by using lime or caustic soda solution. pH is normally maintained at 7.5. It is discharged for final treatment only after precipitation of dissolved solids commences. Since the temperature of scrubbing water is not high as compared to ambient water conditions, dissolved solids contents after proper neutralisation for reuse can be raised upto 2000 mg/l.

Generation and disposal of liquid effluent vary from plant to plant. However, for a typical sulphur based DCDA plant of 1000 MTPD capacity, the total liquid effluent generation is about 300-400 KL/day. The major sources of effluent and approximate quantities of effluent for a 1000 MTPD capacity plant are as under:

- Regeneration from DM Plant	30-40 KL/day
- Boiler Blow down	50-100 KL/day
- Cooling Tower Blow Down	100-250 KL/day
- Miscellaneous (Scrubbing, floor washing etc)	100 KL/day

Water balance in a typical Sulphuric Acid Plant is given in fig 2.5

2.5 Solid Waste

The solid wastes generated in Sulphuric Acid industry are as follows:

- Sulphur Sludge:

Sulphur raw material is generally 99.8-99.9% pure and it contains impurities in the form of hydrocarbons, ash etc. which need to be separated before sulphur is burnt. These impurities are separated either by filtration process or by settling process. The sulphur sludge containing these impurities is removed mechanically or manually. Depending on the purity of sulphur, sulphur sludge is generated in the range of 2-5 kg/MT of sulphur used.

Manufacturers of Single Super Phosphate having captive Sulphuric Acid plant are using sulphur sludge for mixing with Single Super Phosphate. Others are selling it for extracting sulphur, manufacture of fire crackers, match etc.

- Catalyst Waste:

Activity of catalyst in the converter comes-down with time. Hence, it needs to be replaced periodically. Also during the operation some of the catalyst gets converted into dust. During shutdown, while sieving catalyst, the dust is removed. The catalyst waste contains Vanadium Pentaoxide, which is poisonous in nature. About 5% of the catalyst needs replacement every year. Catalyst waste generated from Sulphuric Acid Plant varies from 0.01 Kg/MT to 0.20 Kg/MT of Sulphuric Acid, produced.

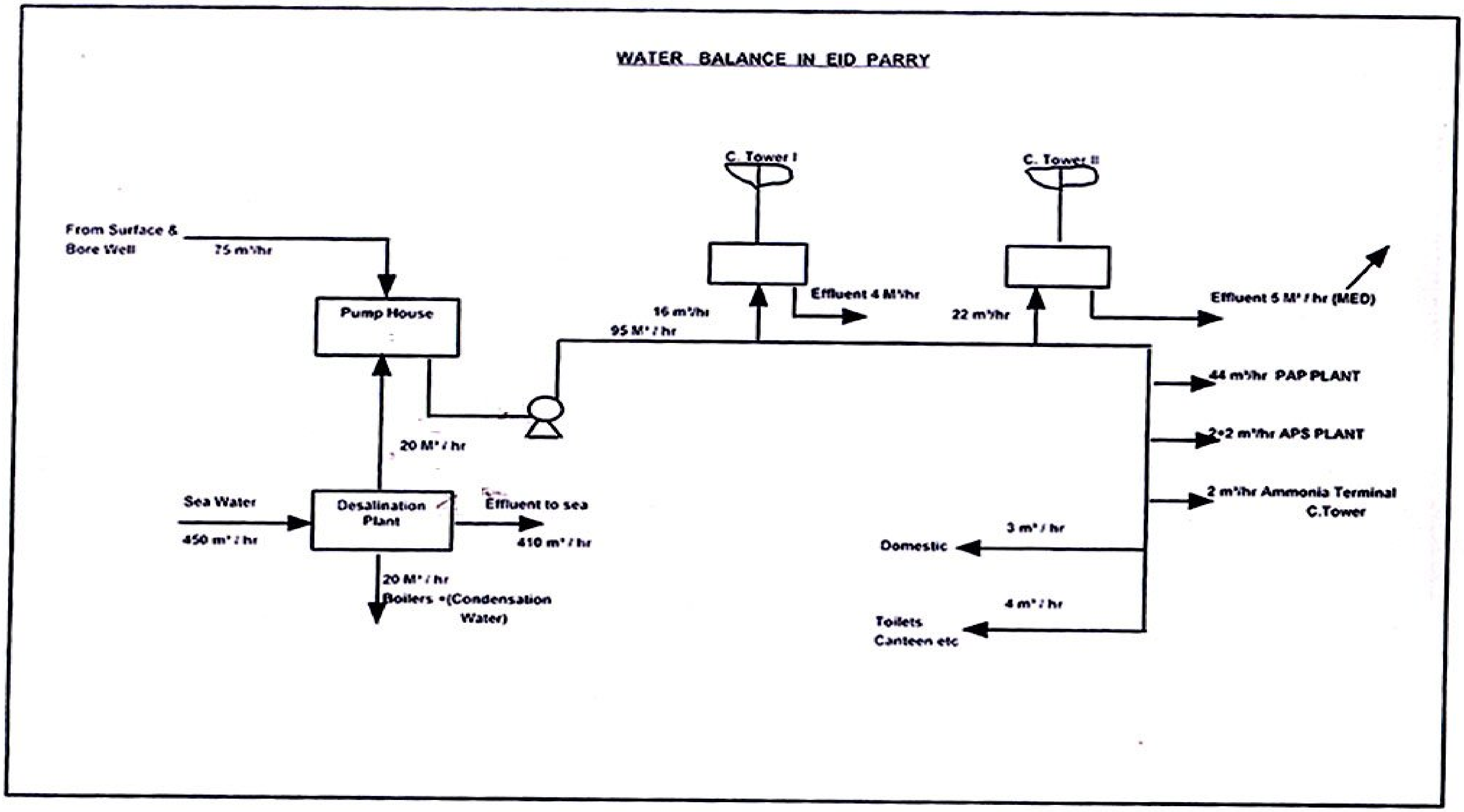

WATER BALANCE IN EID PARRY
C. Tower I
C. Tower II
From Surface &
Bore Well
75 m³/hr
Pump House
16 m³/hr
95 M³ / hr
Effluent 4 M³/hr
22 m³/hr
Effluent 5 M³ / hr (MED)
44 m³/hr PAP PLANT
2+2 m³/hr APS PLANT
2 m³/hr Ammonia Terminal
C.Tower
20 M³ / hr
Sea Water
450 m³ / hr
Desalination
Plant
Effluent to sea
410 m³ / hr
3 m³ / hr
Domestic
20 M³ / hr
Boilers +(Condensation
Water)
4 m³ / hr
Toilets
Canteen etc

Fig: 2.5

2.6 Noise Pollution

In Sulphuric Acid industry the main noise producing equipment are air blowers, steam turbines and some pumps. In some of the plants, these equipment are either placed in closed rooms or provided with accoustic insulation to reduce the noise level. As per the available data, Noise level in the industry is generally in the range of 85-95 db at a distance of 1 meter from the equipment. Noise levels at some Sulphuric Acid Plants as per the monitored data/ information received through questionnaires are given under:-

S.No.	Capacity of Plants (MTPD)	Plants for which data analysed (Nos.)	Average/ Maximum Noise Levels at a distance of 1 meter from Blower (dba)	Average/ Maximum Noise Levels at other places (dba)
1.	upto 100	6	82/100	68/90
2.	101-200	3	78/93	76/85
3.	201-300	2	88/91	79/80
4.	301-500	1	91/91	78/78
5.	501-1000	4	84/95	75/75
6.	above 1000	3	88/91	71/82

2.7 Waste Heat Recovery

All steps in the production of Sulphuric Acid from elemental Sulphur are exothermic. The liberated heat is dissipated under controlled conditions in such a way so as to maintain optimum gas temperatures in the convertor system, drying and acid absorbing systems, thereby, minimising SO_2 at the stack outlet. In the typical flow diagram of energy balance (figure 2.6), it is observed that out of the total energy input, 97% is accounted for as energy released in the conversion of S to H_2SO_4 and 3% of energy is consumed in driving the gas through the plant. Upto about 70% of the available energy is normally utilised for generation of high-pressure steam and the remaining 30% is usually lost as waste heat.

The waste heat system is completely integrated in DCDA plants. In economisers that cool the gases from third & fourth bed of converter, heat is utilised for preheating feed water for WHB System. Heat generated in Sulphur furnac, heats up this feed water and steam is generated at about 250^0 C temperature. This steam is superheated to about 400^0 C for cooling the Ist stage out converter gases. This superheated steam can be used for generating power and saturated steam for process heating.

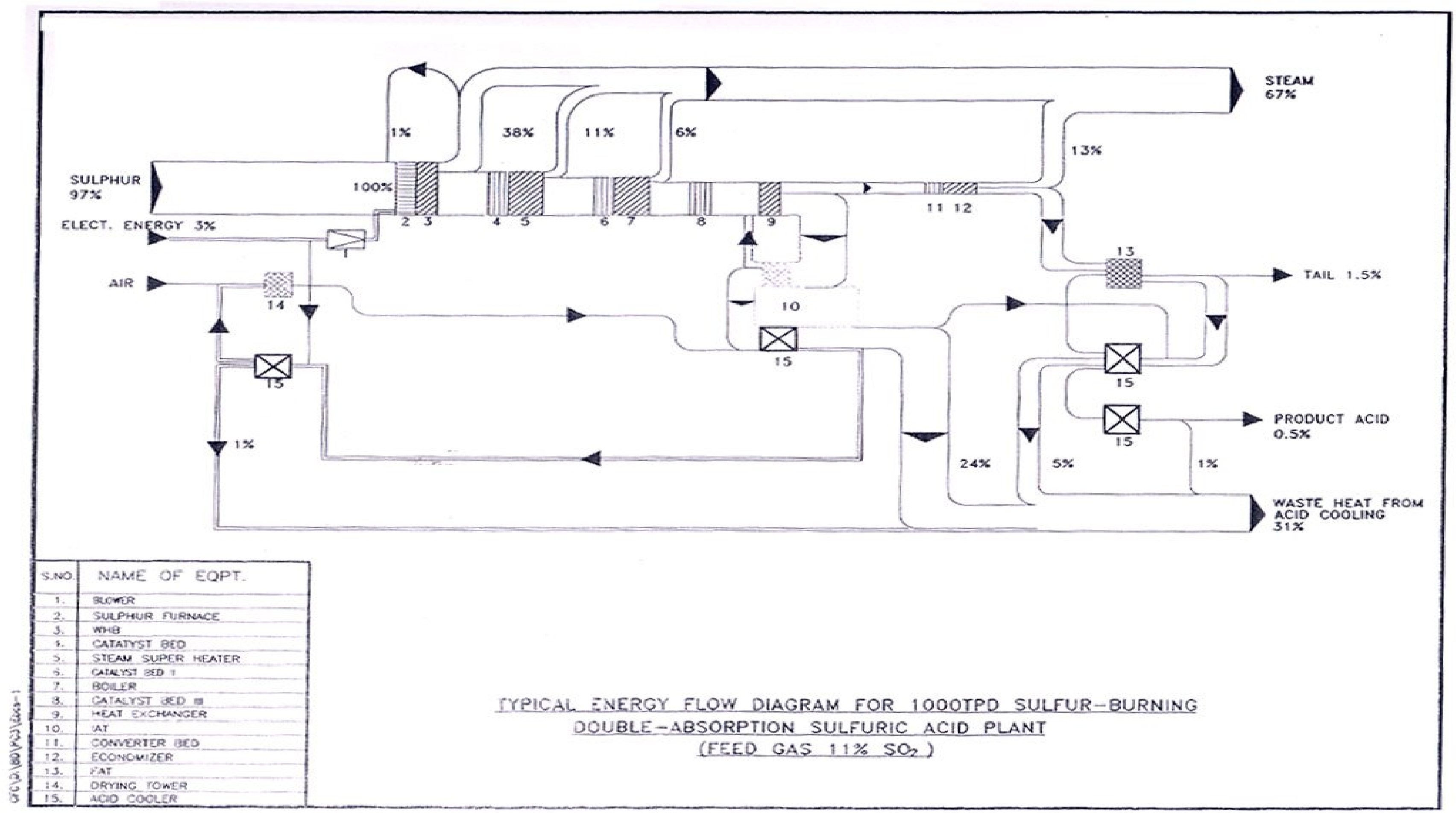

STEAM 67%
1%
38%
11%
6%
13%
SULPHUR 97%
100%
ELECT. ENERGY 3%
AIR
2 3
4 5
6 7
8
9
11 12
13
14
10
15
TAIL 1.5%
PRODUCT ACID 0.5%
1%
24%
5%
1%
WASTE HEAT FROM ACID COOLING 31%
S.NO. NAME OF EQPT.
1. BLOWER
2. SULPHUR FURNACE
3. WHB
4. CATATYST BED
5. STEAM SUPER HEATER
6. CATALYST BED II
7. BOILER
8. CATALYST BED III
9. HEAT EXCHANGER
10. IAT
11. CONVERTER BED
12. ECONOMIZER
13. FAT
14. DRYING TOWER
15. ACID COOLER
TYPICAL ENERGY FLOW DIAGRAM FOR 1000TPD SULFUR-BURNING
DOUBLE-ABSORPTION SULFURIC ACID PLANT
(FEED GAS 11% SO2)

Fig: 2.6

One industry is using the heat of absorption/drying for preheating the water for desalination unit.

Generally, in Sulphur based plants, total steam generation is 0.85-1.4 MT/MT of Acid Production depending upon the size & design of the plant. Around 0.1 kg of steam /MT of Acid is consumed for internal purposes.

One Fertiliser Industry in their Sulphuric Acid Plants is using Heat Recovery System (HRS) from M/s. Lurgi's Heat Recovery System (HEROS). The acceptance of this system is based on: -

a) Operation of Sulphuric Acid Plant should not become more complicated

b) Sulphuric Acid plant should be able to continue operation even if the energy recovery system does not work properly.

2.8 Housekeeping & Fugitive Emissions

In Sulphuric Acid industry, housekeeping is important. Sulphur being explosive in nature is stored in top open bins with boundary walls. The area of storage is generally equipped with water sprinklers or water hydrant system for fire extinguishing.

During in-depth studies, 4 monitoring stations were setup in all four directions & 4/8 hourly samples of ambient air were taken for analysing SO_2, SO_3 and Acid Mist. However, at all places, emission level of SO_2 in ambient air was found in the range of 40-80 $\mu g/m^3$ as against the standard of 120 $\mu g/m^3$.

SO_3 & Acid Mist Levels were found below detectable range at all stations.

3.0 REVIEW OF AVAILABLE PROCESS EQUIPMENT/ TECHNOLOGIES FOR POLLUTION CONTROL

The trends in Sulphuric Acid Plant design have changed considerably and several advancements have taken place in the various facets of sulphuric acid manufacturing technology over the past decades. Some of these are in the field of modified converter, catalyst, high efficiency mist eliminators, heat recovery from acid circuit (as Low Pressure steam), etc.

Pollution reduction commitments by the major corporations as well as Government regulatory requirements are responsible for the continuing trends to develop new and cost effective technologies to reduce the SO_2 emission level. Over the years, improvements in conventional sulphuric acid plant have enhanced the plant performance significantly.

3.1 Modified Converter

Existing plants are generally based on 4 stage Converter except for very few plants based on 5 stage Converter that have come up recently. 5-stage converter helps in increasing the conversion efficiency. This minimises the stack emissions level of SO_2. With conventional catalyst the conversion efficiency can be increased from 99.7% to 99.8%. (1 Kg SO_2 instead of 2 Kg SO_2 per MT of Acid)

3.2 Catalyst

In contact sulphuric acid process, there is often an interest in lowering the inlet temperature to the various catalyst beds in order to provide more favourable equilibrium conditions. The addition of Cesium Catalyst (CS) to the conventional Alkali-Vanadium Catalyst has long been known to enhance the low temperature properties of the catalyst.

The Cesium salt promoter stabilises the vanadium oxidation state of temperature below 420^0 and keeps the vanadium species solubilized in the melt and available for reaction. The stabilising effects of the Cesium appear at relatively low CS concentrations. At high temperatures (> 430^0 C), the activity of the conventional catalyst (Potassium - Vanadium) and the Cesium-promoted catalysts are fairly similar. However, near 410^0 C, the reaction rate of the conventional catalyst drops off dramatically due to the precipitation of vanadium compounds. As the temperature is further lowered the Cesium promoted catalyst maintains a higher reaction rate until the temperature drops well below 400^0 C when its activity finally begins to decline due to vanadium salts precipitation. Although the reaction rate of the Cesium-promoted catalyst drops off at relatively low temperatures, it is still sufficiently high to generate good conversion at acceptable catalyst loading.

Monsanto, BASF and Haldor -Topsoe are pioneer international companies manufacturing catalysts for Sulphuric Acid Plants. Monsanto has optimised Cesium promoted catalyst (CS-120 and CS-110). These products contain the optimum levels of alkali metal salts (potassium and cesium) to provide excellent low and high temperature performance in the converter. To cut SO_2 emissions, Topsoe introduced new Cesium promoted Catalyst VK 69. It has partly or fully replaced conventional catalysts in number of Sulphuric Acid Plants. Few plants in India also improved upon conversion efficiencies by using VK-69 catalyst in fourth stage. VK-69 was developed for operation under low SO_2 conditions following the inter-pass absorption tower in double absorption plant. It combines high vanadium content with a revised balance of its alkali-metal promoters.

VK-69 is manufactured in a unique 9-mm Daisy shape. This provides a very high surface area, which is important for efficient SO_2 conversion in the passes following the intermediate absorption tower. The high void fraction of the 9-mm Daisy shape ensures that this occurs without sacrificing a low-pressure drop.

Performance of DCDA Plant showing reduction in SO_2 emission by replacing VK 38 with VK 69 is given as under:-

Catalyst Type	VK-38	VK-69
Inlet Temp. (^{0} C) Overall Conversion(%) SO_2 in Stack (ppm)	420 99.70 375 (2.0 Kg/MT of acid)	400 99.88 150 (0.8 Kg/MT of acid)

Source: Sulphur No. 249, March-April, 1997
(What's new for Sulphuric Acid Services - by Lisa Connock).

Similarly, Cesium based Catalyst from Monsanto CS-120 & CS-110 results in higher conversion efficiency with low SO_2 emission rate.

It is a catalyst with an extremely high activity level and unlike traditional Cesium catalysts, the activity advantage exists in the entire temperature range. This translates into possibilities for strongly reduced SO_2 emissions and increased production rates. The low activation temperature makes Cesium based catalyst ideal as ignition layer in double-absorption plants in which the gas passes downstream of intermediate absorption tower often lack in preheat.

This extremely high activity of Cesium based Catalyst naturally provides a number of options for improved performance of existing double-absorption plants and in the design of new acid plants, namely;

- More than 50% reduction in SO_2 emission from existing double-absorption plants.

- The possibility of a significant increased production without increasing SO_2 emissions. This is possible by using higher strength SO_2 gas.

- Possibility of SO_2 emissions of 0.5 Kg/MT of acid or less from new or revamped plants.

Two plants in Europe, Boliden (Sweden) and Budelco (Netherlands), had to meet an SO_2 emission limit of 0.2 Kg/MT of Acid and 0.4 Kg/MT of Acid respectively, after a revamp. Installation of Cesium based catalyst in bed 4 and/or 5 appeared to be the only alternative to tail gas scrubbing. Both plants decided to install Cesium based catalyst and it is reported that both plants are operating with SO_2 emissions around 0.15 Kg/MT of Acid and 0.25 Kg/MT of Acid respectively.

Also at Serrana (Brazil) after installation of Cesium based catalyst in their 800 MTPD plant, emissions of SO_2 have been reduced from more than 1.0 Kg/MT of Acid to well below 0.5 Kg/MT of Acid.

Following is the data of Namhac Chemical Corporation (South Korea) when in 1997 they replaced conventional catalyst to VK-69 in fourth Pass.

S.No.	Process Details	Units	Catalyst	
			Before VK-69	After VK-69
1.	4th Pass Catalyst loading	Litre	97,000	90,600
2.	Acid Production	MTPD	1460	1490
3.	4th Pass Inlet Temp.	^0C	440	389
4.	Overall Conversion Efficiency	%	99.79	99.92
5.	SO_2 in Stack	Kg/MT	1.1	0.4

Catalyst loading is generally 170 to 200 liters per MTPD of Sulphuric Acid Plant capacity. However, it depends upon the type of Catalyst, percentage of SO_2 in Feed Gas, design of converter and manufacturers recommendations depending on the other process parameters.

With introduction of Cesium based catalyst, conversion level achieved is upto 99.9%. Also with Cesium based catalyst, conversion starts at 380^0 C as against $400\text{-}420^0$ C for conventional catalyst. As the Cesium based catalyst is almost 3 times costly, it is generally used in last bed of Converter only.

3.3 Mist Eliminators

Mist is inevitably formed at various points in Sulphuric Acid Plants. If mist is unchecked, carried through rest of the plant in the gas stream, causes corrosion inside the plant and environmental menace outside it.

Mist is distinct from acid spray, which is formed in the towers by purely physical process of aspiration into the gas stream of liquid droplets. Mist results, infact, not from the contact of SO_3 with water vapour but by the partial pressure of water vapour over the liquid absorption medium, and that is inversely proportional to the concentration of the sulphuric acid.

Well-engineered mist eliminators are critical to the cost-effective operations of every sulphuric acid plant. In the gas drying tower, as well as intermediate and final absorption towers, poorly performing mist eliminators contribute to corrosion of ducting, blowers, heat exchangers and vessels, and also to acid plant stack emissions. The fiber bed mist eliminators incorporate a specially wound fiber, computer controlled quality and a patented bi-component design.

Now a days, Mist eliminators that are designed to remove virtually any type of mist from any gas stream are available. Mist eliminators excell at collecting, the very difficult to remove, sub micron size mist particles from gas stream.

In the drying tower, combustion air for a sulphur burning plant or the gas feed in a metallurgical or spent acid plant is dried with sulphuric acid. The concentration and temperature of the circulating acid affect the amount of small acid mist formation. The higher concentration and temperature in sulphur burning plant increase the amount of small acid mist particles formed, thus requiring better mist collection equipment. In drying tower of spent acid and metallurgical plants, there is more potential for solids in the gases, and, as a result, coknit mesh pads or fiber bed mist eliminators are normally used.

Mist in the primary absorption tower is a combination of larger mechanically generated particles and smaller particles formed from the condensation reaction in the bottom of the tower. If the plant also produces Oleum, the overall mist loading will be approximately the same, but the size of the particles formed from condensation will be smaller. This is also the case with Heat Recovery Towers.

In final absorber also, the mist is formed in the same way as in the primary absorber, but the quantity of small mist from condensation is less. High efficiency Brownian diffusion type Brink fiber bed mist eliminators are normally specified for absorbing tower applications.

In plants with ammonia tail gas scrubbers, large amounts of submicron ammonium sulphate/sulphite salts are formed by chemical reaction with sulphur dioxide. Also plants with caustic scrubbers have weak acid mist created from residual SO_2 gas. High efficiency Borwnian, a diffusion type Brink fiber bed mist eliminators are necessary for these applications.

Koch Flexifiber Mist Eliminators

Utilizing the Brownian Diffusion collection mechanism, FLEXIFIBER Type BD, elements are able to achieve collection efficiencies of upto 99.95% on all submicron sulphuric acid mist. FLEXIFIBER Type IC fiber bed elements utilize the impaction mechanism to collect particles in 1 to 3 micron range.

Type/Collection Mechanism	Particle Size (micron)	Efficiency	Pressure Drop (mm water)
Brownian Diffusion	>3	100	50-500
BD	<3	99.95	
Impaction	>3	100	200
IC	1-3	95-99	
Impaction	>3	100	150
IP	1-3	85-97	
	0.5-1	50-85	
Impaction	>3	100	25-50
IS	<3	15-30	

Depending on the design, DEMISTER Mist Eliminators are able to remove 99.9% of acid mist having particles greater than 2 microns and 70% of the acid less than 2 microns. The DEMISTER Mist Eliminators are available in a wide array of materials, such as Alloy 66, which have a much greater corrosion resistance than alloy 20 or 316 L.

Monsanto Brink Mist Eliminators

These mist eliminators are designed to remove virtually any type of mist from any gas stream. Brink mist eliminators excel at collecting the very difficult to remove sub-micron size mist particle from gas stream.

The fibre bed eliminators incorporate a specially wound fiber, computer controlled quality and a patented bi-component design.

MEC Model	ES	HE	HE Plus	CS-ID	CS-IIP	HP	HV
Efficiency on Mist & Particle > 3 Micron	Approximately equal to 100%						
Efficiency on Mist & Particle <3 Micron	92-99.5%		50-95% 0.5μ-3μ	70-99% 0.5μ-3μ	70-99% 0.5μ-3μ	50-97% 0.5μ-3μ	
Pressure Drop (mm water)	100-500		100	200	250	200-300	

By choosing correct type of demister pads and candle mist, the acid mists can be brought down to 15 mg/Nm^3 against norm of 50 mg/Nm^3.

3.4 Tower Packing

Tower Packing Technology offers improved operation over dumped packing. This high performance structured tower packing with geometrically arranged corrugated sheets provides uniform gas distribution, resulting in intimate mixing and radial distribution of the liquid and gas streams. The increased efficiency offers improvements in moisture removal from the incoming air or minimizes the chance for SO_3 slip providing more effective contact with the down flowing acid stream.

The lower pressure drop offers savings in blower operating costs, increase in the unit's capacity or improvements to other ancillary equipment where the pressure drop savings may be applied.

3.5 Acid Distributors

Acid Distributors for Sulphuric Acid Towers require certain performance and physical characteristics for its smooth functioning. These include acid flow distribution, resistance to fouling or plugging, ease of cleaning and proper material selection for construction.

The purpose of a high efficiency acid distributor is to evenly distribute the acid across the towers cross section, thereby providing optimal acid/gas contact and reduce the possibility of poor performance due to acid and gas channeling.

High efficiency design, in alloy construction, provides a trough type design with up to 40 feed points per square meter. This design provides better distribution of the acid over lower feed point designs. The distributor is carefully designed to balance open area requirements for gas flow with adequate acid distribution. In general, open area is in excess of 50% ensuring that distributor does not restrict gas flow. Restricting gas flow by the distributor can cause distributor flooding or excessive pressure drop. Acid hydraulic within the distributor are designed to minimise their impact on point flow variation. The acid is directed onto the top of the bed via drip tubes, reducing entrained acid loading to the mist eliminators.

3.6 Packing Support

Acid Tower performance is directly affected by packing support design. Conventional packed tower supports consist brick arches supporting a ceramic grid in the flat bottom of the tower. Cross partition rings support the packing, keeping it from falling through the grid slots. An inherent problem with this support design is decreased open area. Where cross-partition rings and the packing support meet, open area for gas flow is reduced to about one third of the flow in a tower cross section, causing flooding and high pressure drop. Packing height requirements may also be affected by gas distribution at the packing support level.

In some instances, the limited production length of ceramic bars may necessitate more arch supports or walls, blocking gas flow even further. Bar loss frequently occurs due to rapid temperature changes, causing loss of the packing support alongwith the packed bed.

Compared to the conventional arch support, the Self-supporting Dome Packing Support offers twice as much open area for gas flow. Constructed of chemical stoneware ceramic, the dome increases the open area through the support, providing more even distribution and lower pressure drop than traditional arch supports. By eliminating brick arch supports, weight is removed from the floor of the tower and evenly distributed to the walls.

The unique dome configuration not only improves tower performance but is also economical. The dome requires much less material and labour to install on site and eliminates the time and expenses of constructing brick arch supports. Once keyed in place, the dome's durability is unsurpassed. As each piece fits into compression, it performs for the lift of the tower with little or no maintenance.

New construction is only one of the dome's applications. The design can easily be installed in existing towers in need of repair or retrofit to maximize efficiencies. This maintenance free and packing support can reduce installation costs and downtime as well as operating costs. That makes the dome support a viable solution to conventional packing support constraints.

3.7 Heat Recovery System

The objective of the Heat Recovery System (HRS) is to absorb SO_3 from the gas stream and recover the heat from the absorption process as low-pressure steam. The HRS consists of two-stage packed heat recovery tower, horizontal steam boiler and heater, diluter, acid circulating pump and acid drain pumps. Boilers feed water pumps are provided to supply the HRS boiler with deaerated water from deaerator as shown in the HRS flow scheme (figure 3.1).

The Heat Recovery System is basically an absorber that operates at about 200^0 C and uses a boiler to remove the absorption heat as steam (at upto 10 barg), instead of acid coolers (where heat is wasted). The hot gases leaving the first stage are then cooled in the second stage and the remainder of the SO_3 absorbed. Gases leaving the tower are essentially the same as gas leaving a conventional interpass tower.

3.8 Liquid Effluent

Sulphuric Acid plants do not face any problem with regard to wastewater treatment. The industry has set up systems for minimum use of fresh water and maximum reuse of treated water and has reached a stage where the discharges become negligible.

The possible discharges of Sulphuric Acid due to incidental leakages are collected through dyke systems (also statutory requirements) and then led to Neutralisation pit for making pH neutral.

- Water Softening or De-Mineralised Water Unit

De-mineralised water unit for Sulphuric Acid Plant can be designed to ensure that the regeneration/ rinse water is alkaline and can be used for scrubbing of gases. In case it is not alkaline, it may require pH correction .

- Boiler Blow-down

Due to conditioning of boiler feed water for maintaining proper alkalinity, blow-down is alkaline in nature and is also at higher temperature than ambient temperature. It can be used during operation of scrubbers for preparation of alkaline solutions. Therefore, in Sulphuric Acid Plants, blow-down water need not be discharged.

- Cooling Tower

Since cooling tower blow down is generally taken out at TDS of 2000 - 2100 mg/Nm^3, the water can be very well reused in domestic services and also for maintaining greenery in and around the process plants. This is useful resource and need not be drained.

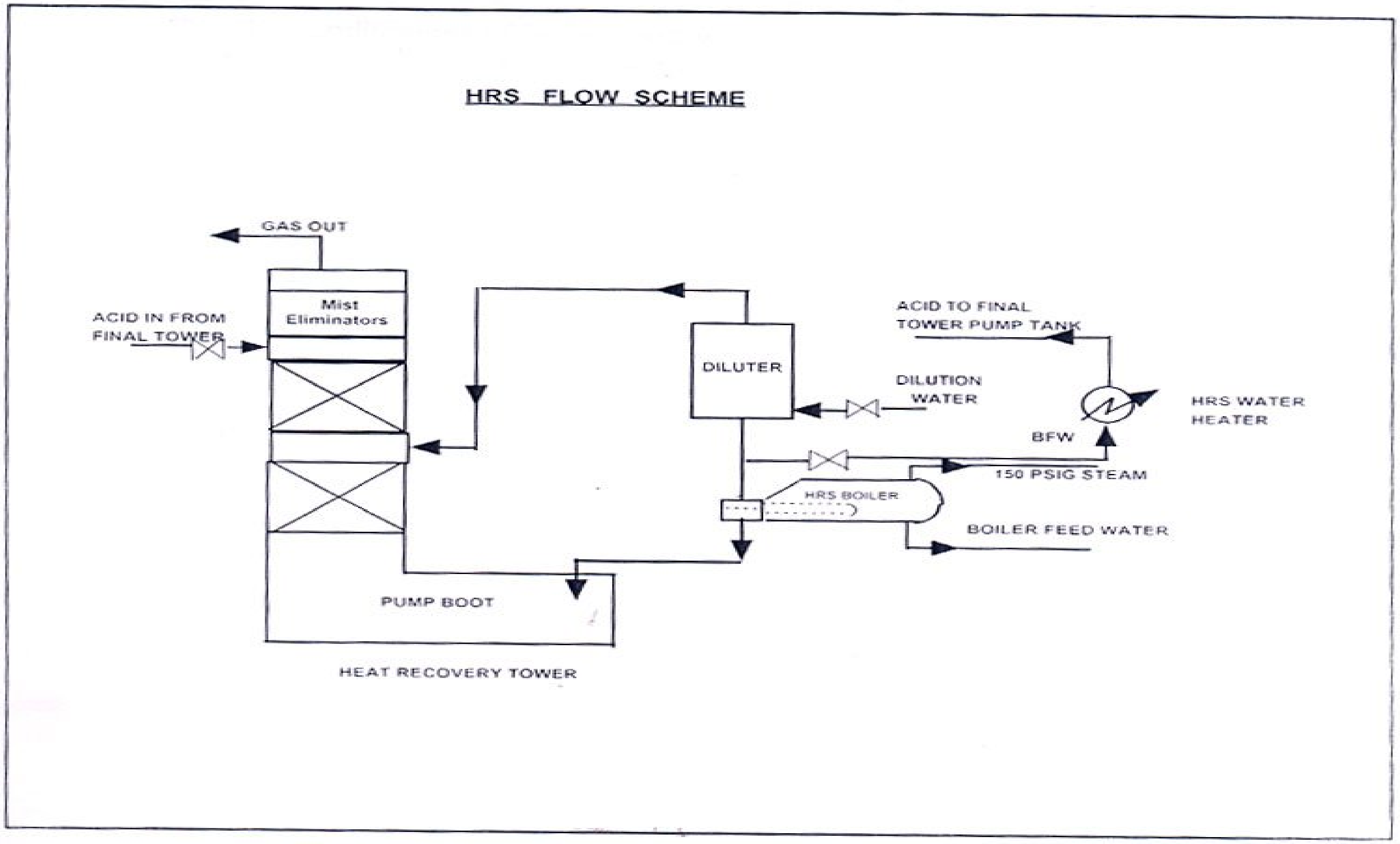

HRS FLOW SCHEME
GAS OUT
Mist
Eliminators
ACID IN FROM
FINAL TOWER
DILUTER
ACID TO FINAL
TOWER PUMP TANK
DILUTION
WATER
HRS WATER
HEATER
BFW
150 PSIG STEAM
HRS BOILER
BOILER FEED WATER
PUMP BOOT
HEAT RECOVERY TOWER

Fig: 3.1

4.0 FEASIBILITY OF ADOPTING MODERN PROCESS EQUIPMENT/ TECHNOLOGIES

Various technological options which may be considered for minimizing and control of pollution are given below:-

4.1 Process Technology

Advancements have taken place in the various phases of Sulphuric Acid manufacturing technology over the past decades. Main developments have been in the fields of catalyst, materials, mist eliminators, heat recovery from acid circuit, etc.

Modern technologies have played significant role in minimising gaseous emissions in the interest of environment. The main objective is to achieve more & more resource conservation resulting in lower SO_2 / SO_3 / acid mist emissions. In upcoming plants, following features are considered important:

- Selection of 5-stage converter for maximum conversion efficiency.
- Use of sulphur filter for minimising ash content.
- Use of Waste heat recovery from acid system.
- Use of Cesium based catalyst in last bed of Converter for maximum conversion efficiency.
- Selection of high efficiency mist eliminators ensuring minimum acid mist exhaust
- Use of suitable start-up scrubbing system.

The existing plants are generally on pattern of 4-stage converter. However, now trend is to provide 5-stage converter to have maximum conversion efficiency.

In existing plants, low temperature catalyst can be used in IVth bed to improve efficiency. New plants may be designed looking into all parameters so that the emission level is low. The results can be achieved after doing changes in Catalyst or in converter bed depending upon economical viability of the individual plant.

Sulphur burners which give complete combustion (with negligible carryover) can be used for above 500 MTPD capacity plants depending on economic viability. For getting maximum efficiency the process technology and use of Catalyst, mist eliminators, scrubbing system, acid distribution need to be taken care during selection of equipment/ machinery for new plants.

Even the smelter gas based plants may be converted to DCDA, on case-to-case basis, if feasible.

4.2 Gaseous Emissions

In Sulphuric Acid plants the concerned exhaust gases are SO_2, SO_3 and Acid Mist. These pollutants need to be controlled by selection of proper catalyst, mist eliminators, scrubbing system etc.

Catalyst

It is an important aspect of industry. Double absorption plants remove SO_3 from the gas stream after the third bed. The gas conditions in the 4th bed differ markedly from the conditions in first three beds (nearly entire SO_3 is removed and only little SO_2 remains, typically 0.6-0.8%). The low SO_2 concentration causes the rate of transportation of SO_2 by pore diffusion to the active interior of the catalyst to be impeded. Activity measurements on the crushed catalyst compared with measurements on whole catalyst pellets show that diffusional restrictions can reduce the rate of SO_2 oxidation by more than 50%.

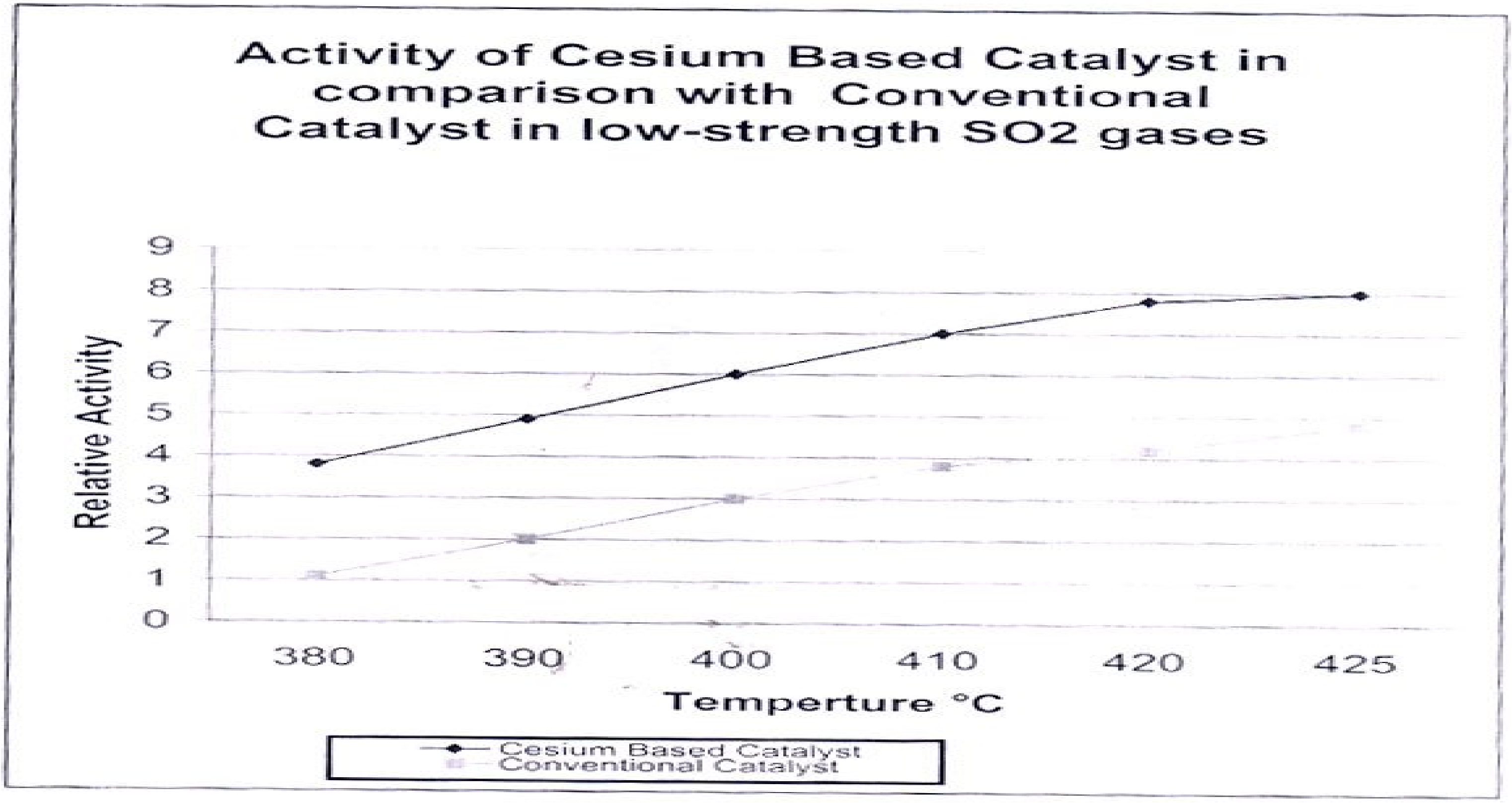
Typical economics of replacing conventional V_2O_5 catalyst by Cesium based Catalyst is given under:

- In a typical Sulphur Burning plant with flue gas of 10-10.5% SO_2, 60% reduction in SO_2 emission takes place after replacing Conventional Catalyst with Cesium based Catalyst.

- Activity of Conventional Catalyst drops off sharply at temperature below 400^0 C as against the activity of Cesium based catalyst, which is still active at temp. upto 380^0 C (Please refer figure 4.1).

Figure 4.2 shows improvement in overall conversion, which can be brought about by substituting Cesium based catalyst for Conventional catalyst in the fourth pass. For example a plant operating at 99.5% overall conversion with Conventional catalyst in IVth pass can achieve 99.75% conversion by loading the same volume of Cesium based catalyst.

Cesium based Catalyst offers high activity at low operating temperature. Emissions from existing plants can roughly be cut in half without increasing catalyst volume. The acid production capacity can be increased by using higher strength sulphur dioxide gas without increasing SO_2 emissions and plant pressure drop. New acid plants may be designed with low SO_2 emission by selecting different type of Catalysts for different stages.



Activity of Cesium Based Catalyst in comparison with Conventional Catalyst in low-strength SO2 gases
Relative Activity
9
8
7
6
5
4
3
2
1
0
380
390
400
410
420
425
Temperture °C
Cesium Based Catalyst
Conventional Catalyst

Fig: 4.1

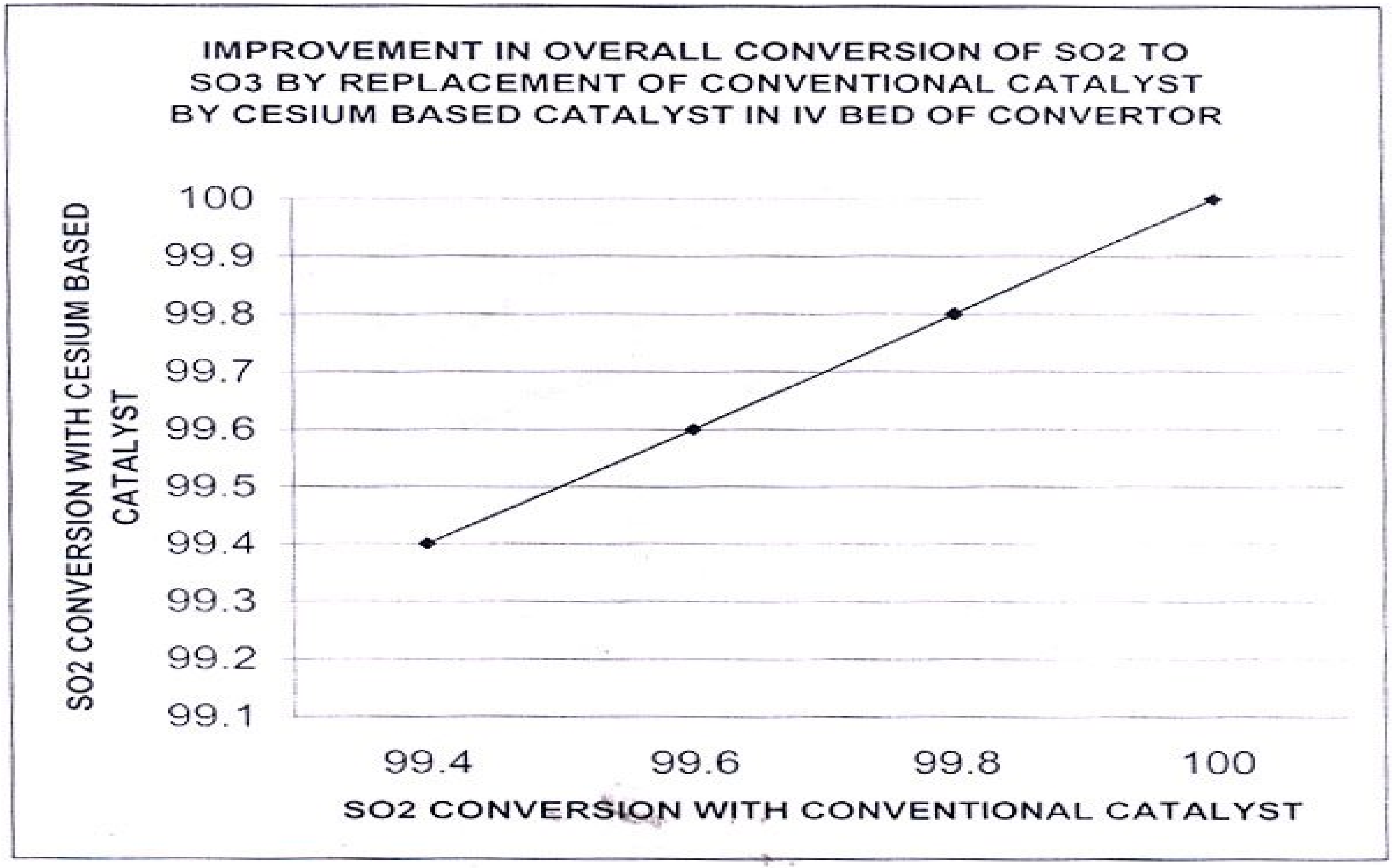

IMPROVEMENT IN OVERALL CONVERSION OF SO2 TO SO3 BY REPLACEMENT OF CONVENTIONAL CATALYST BY CESIUM BASED CATALYST IN IV BED OF CONVERTOR
SO2 CONVERSION WITH CESIUM BASED CATALYST
100
99.9
99.8
99.7
99.6
99.5
99.4
99.3
99.2
99.1
99.4
99.6
99.8
100
SO2 CONVERSION WITH CONVENTIONAL CATALYST

Fig: 4.2

Depending on the conditions of process and stack emission requirement, CS based Catalyst can be selected. Generally, it is used in 3rd /4th bed as entire bed or on top of 3rd and 4th bed. Some plants are using only on top of 4th bed for getting high conversion efficiency. Using CS Catalyst on top of Ist bed ensures improved start up and operations at low inlet temperature.

Cost variation (FOB Cost)

- Conventional Catalyst - Rs. 130 per litre
- Cesium based Catalyst - Rs. 325 per litre

The Comparative Cost Implication of replacing Ordinary Catalyst by Cesium based Catalyst in IV Bed is indicated below:-

Capacity of Plant (MTPD)	Incremental Cost of replacement of Conventional Catalyst with Cesium based Catalyst (Rs. Lac)	Savings/annum	
		Sulphur (MT)	Cost (Rs. lac)
100	14	16.5	0.50
400	56	66	2.00
1000	140	165	5.00

Mist Eliminators

Mist Eliminators are important part of Sulphuric Acid Plants. If proper mist eliminators are not provided and mist remains unchecked, it damages the downstream equipment by corrosion and also causes environmental pollution. Mist is formed at various different points of process. Fibre bed eliminators overcome this difficulty. Not only are they flexible, they also have the added advantage of being able to remove submicron particles.

The type of mist eliminator that is most suitable depends on the nature of the mist, especially its particle size. The severity of the mist formation in drying tower depends mainly on concentration of the drying acid. In plants operating on 98% acid concentration, mist formation is less as compared to plant running at 92% acid strength. The other factor, which plays an important role in selection, is low-pressure drop.

Upcoming new plants are normally selecting mist eliminators, which guarantee low acid mist in the exit.

There are different models of mist eliminators like Pad type, Candle type, etc. Pad type eliminators are generally used in drying tower. High Performance Tower Gard and High Performance Hi-Flow, tower Gard Captures, collects and returns acid mist to the tower with 99.9% collection efficiency on particles greater than 3 microns with 50 mm water column pressure drop. Hi-flow can handle upto 300% increased liquid load versus a conventional pad. In this, open-ended metal troughs are placed at the bottom of the pad. Within the pad, gas flow patterns are induced and push liquid out of pad to protected regions directly above each trough, discharging collected liquid near vessel walls.

For Absorption Tower, Candle type with fibre bed eliminators are used. High Efficiency (HE) and Cost Saver (CS) type candles are available.

- HE type consists fibers, which are packed between two concentric cylindrical screens.

- CS types are packed with a glass fiber mat collecting layer and a metal alloy mesh re-entrainment control layer on the downstream side (outside).

Cost difference of two is that CS are almost double the cost of HE. For a particular 100 MTPD plant if HE Candle Costs Rs. 1,60,000, CS Candle costs Rs. 3,00,000. These can be used as per requirement.

Cost implication as per level of acid mist removal is given as under:-

Capacity of Plant (MTPD)	Cost of Mist Eliminator (Rs./lac)		Additional Cost of Replacement (Rs.lac)
	50 mg/Nm^3 at Exit	25 mg/Nm^3 at Exit	
100	10	16	6
400	20	32	12
1000	35	53	18

Scrubbing System

Start-up Scrubber:

In DCDA Sulphuric Acid Plant start-up scrubber is provided to take care of high SO_x emission during starting of the plant or shut down due to unstable operating condition. As the plant is required to be operated only occasionally, Caustic Soda is preferred over lime due to sludge handling problem associated with the lime scrubbing.

The cost of start-up scrubbers for different capacity plants are expected to be as under:-

Capacity of Plant (MTPD)	Approx. Cost of Start-up Scrubber (Rs./Lac)
100	10
400	30
1000	60

Continuous Tail Gas Scrubber:

Generally in Smelter gas based plants, where SCSA Plants are installed due to low percentage of SO_2 in the feed gas, continuous tail gas scrubbing plant is required to be installed to meet the SO_x emission discharge norms.

As the tail gas scrubbing may further produce solid waste, its disposal has to be considered prior to selection of absorbant for scrubbing. Inspite of sludge handling problems lime scrubbing is preferred due to low cost of lime.

Cost of installation of Scrubbing System is about same for both DCDA and SCSA Plants. However, it has to be seen vis-a-vis operating cost for continuous scrubbing in SCSA plants & during disturbed conditions in DCDA plant. For cost comparison, specific study needs to be conducted to examine the feasibility on case-to-case basis.

Improved Procedure for adoption during starts up & shutdown of plants, when emission levels are generally high

- After stoppage of short duration (i.e. 6-8 hrs), SO_2 Scrubbing System should be taken in circuit before start-up of plant. This will take care of any unconverted SO_2 gas or unabsorbed SO_3.
- After longer period of shut down (i.e. when the temperature of catalyst bed in Ist pass is below 400^0 C), the heating of catalyst beds with burning of oil or natural gas be done to reduce emissions.
- The plant should run at low production in the beginning and production be raised in steps to have minimum emissions.
- Acid circulation to all towers (drying & absorption) are done before Sulphur burning.
- Adjustment of gas ducting valves be done in a way so as to achieve conversion temperature in minimum time i.e. Heat

Exchangers are to be bypassed till optimum temperature is achieved.

- At the time of stoppage of plant, blower should be run for atleast 3-4 minutes after stoppage of Sulphur Pump.

4.3 Liquid Effluent

In Sulphuric acid industry various source of liquid wastes are as under:-

i) Blow down from Waste Heat Boiler and Cooling Tower
ii) Scrubbed liquid from Scrubbing unit.
iii) Regeneration of DM Unit
iv) Plant Washings

Blow-Down

Blow-down of boilers and cooling towers are of high TDS. Boiler blow-down water is alkaline and at high temperature. It can be used for making chemical solutions or can be used in Scrubbers. Cooling tower blow-down is generally taken out at a higher TDS range of around 2000 ppm. This water can very well be reused in domestic services and also for maintaining greenery, subject to suitability.

Scrubbed Liquid

It is generally used at the time of start-up in sulphur based DCDA plants and used continuously in SCSA plants operating on gases from metallurgical plants. Use of water in scrubber depends on frequency and duration of operation of scrubber. The scrubber water can be reused after correction of pH. It also depends on the alkali used. In plants using dilute caustic soda for scrubbing, sodium sulphite and sodium bisulphite is produced on absorption of SO_2. Sodium Sulphite & bisulphite liquor can be sold to nearby tanneries. On further aeration sodium sulphate is formed which is a saleable product. The scrubbed liquid from scrubber can also be used for scrubbing gases in Single Superphosphate plants where such provision is provided. In plants that are using lime, the scrubbed liquid is filtered and the cake is used for earth filling. Water is reused.

Regeneration of DM Unit

The rinse and injection water of DM plant have very high TDS. The wastewater is treated for pH correction before putting for further use.

Plant Washings

Generally Sulphuric Acid plants do not face much problems with regard to, waste water through washings. Discharge due to incidental leakages is led to Neutralisation pits for making pH neutral. Neutralisation pits normally contain limestone beds where pH is corrected through perforation and neutral pH water is then reused. In some plants caustic soda is used for pH correction.

4.4 Noise Pollution

Main source of noise in Sulphuric Acid Plant are Blower Turbine and the Vent Steam.

Noise from Blower and turbine can be reduced by providing accoustic insulation around the equipment & keeping the equipment in closed rooms. For steam venting, silencers may be provided.

4.5 Waste Heat Recovery

The Sulphuric Acid plant is regarded as thermal energy plant. A lot of heat is evolved in sulphur burning, conversion of SO_2 to SO_3, air drying and absorption stages. Approximately 67% of this heat is recovered for production of high-pressure steam and about 31% of heat, which evolves in absorption and drying stages, is generally rejected. However, in large capacity plants where quantum of heat is significant this heat is recovered by Heat Recovery Systems(HRS) in which boiler is used to remove the acid heat as steam instead of cooling in acid coolers where heat is wasted by rejecting it to the Cooling Tower.

The heat evolved in plant can be used/-recovered by:

a. Providing adequate insulation on equipment, ducts and pipes.

b. Using condensate from all sources of feed steam.

c. Using Exhaust/Bleed steam of turbine for Melting/deaeration.

d. Using heat of acid in smaller units for heating DM Water for feeding to boilers and where feasible HRS can be put for recovery of energy.

e. Rectifying leakages of all kind where heat is lost.

Where Desalination units are working, heat of absorption/drying can be used for preheating the water for desalination unit. This increases the efficiency of the desalination unit.

The developments in utilisation of waste heat generated in Sulphuric Acid plant are significant in energy conservation and for improved overall efficiencies. The plant needs to be designed in such a way so as to maximise use of waste heat, to produce steam at high temperature and pressure for achieving maximum efficiency. The superheated steam so produced is used for generating power.

In steam system, it is possible to improve energy utilization not only by increasing the production of high-pressure steam but also by optimizing the steam quality. Use of specially designed waste-heat system makes it possible because of the high excess temperature of the gas to produce steam at upto 80 bar in a sulphuric acid plant instead of the normal 40-50 bar. The higher the quality of steam the more efficiently it can be converted into mechanical work or electrical energy. Production of high-grade steam is advantageous even if low-pressure steam for heating purposes is required in neighboring production plants. In this case, the high-pressure turbine drives a generator or other equipment for power generation.

A significant step towards more highly energy-efficient plants was taken with the introduction of heat recovery systems generating steam from the acid circuit. Thus, part of the heat formed in the absorption circuits (and normally dissipated with the cooling water) is transferred to a higher level and used for the production of low-pressure steam at 6-10 bar. Depending on the nature of the plant, upto 0.5 MT of steam per MT of acid can be produced in this way in addition to the high or medium pressure steam obtained from a sulphur burning plant.

Heat Recovery Systems are getting common in modern high capacity Sulphuric Acid Plants for recovering heat of absorption. The purpose of system is to absorb SO_3 from gas stream and recover the heat from the absorption process as low-pressure steam. HRS consists a two stage packed heat recovery tower, horizontal steam boiler, and heater, acid circulating pump and drain pumps.

The approximate cost of an HRS Unit for 1000 MTPD plant is around Rs. 14 crore. Considering steam cost as Rs. 400/MT, the total money realisation from this additional steam generation comes to Rs. 4.8 crore on 300 days production basis. Thus the investment of Rs. 14 crore can be paid back in about 3 years time.

4.6 House keeping & Fugitive Emissions

Like other chemical industries housekeeping in Sulphuric Acid Plants is an important aspect. In Sulphuric Acid industry sulphur is the major raw material, which needs to be stored properly with boundary walls. Sulphur dust present in the vicinity of sulphur storage forms an explosive mixture and can cause fire. So the area of solid as well as molten sulphur needs to be equipped with fire hydrant or other devices to take care of fire. No naked light is used in the area. Water showers are to be provided near acid storage and pumping areas. Steam and other hot vessels need to be insulated properly.

For fugitive emissions, areas like sulphur melter pit, equipment ducts etc. need to be completely tightened for any leakages of gases and other fumes. These fumes coming out are hazardous for operating persons as well as to the equipment. If any condensation of acid mist takes place in the plant, area becomes more prone to high corrosion due to low strength Sulphuric Acid formation. On this aspect inlet/outlet line of Cold Heat Exchanger require specific attention from design and maintenance considerations.

5.0 RECOMMENDATIONS

Based on the information received from the Industries & In-depth study at a few identified representative industries, on technologies for process and pollution control that are available and being followed in industries as well as available in the market, environmental management practices, etc., following standards are recommended after consultation with experts and representatives of industrial association:

EXISTING PLANTS:

Plant Capacity (MTPD)	SO_2		Acid Mist & SO_3 (mg/Nm[3])
	Load (Kg/MT of 100% conc. acid production)	Concentration (mg/Nm[3])	
Up to 300	2.5	1370	90
Above 300	2.0	1250	70

NOTE:

1. For plants having more than one stream/unit at the same location, combined capacity of all the streams/units shall be applicable on all the individual streams/units for compliance of the above norms.

2. The Stack Height of Sulphuric Acid Plant shall be 30 m or as per the formula given below, whichever is more:

   $H = 14 (Q)^{0.3}$

   Where "H" is the Height of Stack in meters; and "Q" is the maximum quantity of SO_2 expected to go out through the stack at 110% of the rated capacity of the plant as per the norms of gaseous emission. Whenever this formula is revised, the same will be applicable for determining the stack height in respect of the plants commissioned after notification of revised formula for stack height.

3. Scrubbing units shall have on-line pH meters with recording facility.

4. State Pollution Control Board may prescribe more stringent standard, if local conditions demand so.

NEW PLANTS:

Plant Capacity (MTPD)	SO_2		Acid Mist & SO_3 (mg/Nm[3])
	Load (Kg/MT of 100% conc. acid production)	Concentration (mg/Nm[3])	
Up to 300	2.0	1250	70

Above 300	1.5	950	50

NOTE:

1. For plants having more than one stream/unit at the same location, combined capacity of all the streams/units shall be applicable on all the individual streams/units for compliance of the above norms.

2. Scrubbing units shall have on-line pH meters with recording facility.

3. The Stack Height of Sulphuric Acid Plant shall be 30 m or as per the formula given below, whichever is more:

   $H = 14 (Q)^{0.3}$

   Where "H" is the Height of Stack in meters; and "Q" is the maximum quantity of SO_2 expected to go out through the stack at 110% of the rated capacity of the plant as per the norms of gaseous emission. Whenever this formula is revised, the same will be applicable for determining the stack height in respect of the plants commissioned after notification of revised formula for stack height.

4. For Sulphuric Acid Plants having more than one stream/unit at one location, the combined capacity of all the streams/units shall be considered for determining the Stack Height.

5. In Sulphuric Acid Plants, where there is separate stack for emission of gases from the Scrubbing Unit, the height of this stack shall also conform to the norm as for the Main Plant.

6. State Pollution Control Board may prescribe more stringent standard, if local conditions demand so.

Annexure-I

Status of Gaseous Emissions in Existing Plants

(INFORMATION RECEIVED THROUGH QUESTIONNAIRES & IN-DEPTH STUDY OF EIGHT SULPHURIC ACID PLANTS)

a) SO_2 EMISSION

UPTO 100 MTPD	101-500 MTPD	ABOVE 500 MTPD

(Kg/MT)	(Kg/MT)	(Kg/MT)
1.3 - 1.3 X	1.9 -2.6	1.9 -2.6
2.0 - 3.0	1.6 - 1.7 X	1.5 - 2.5
3.3 - 3.3 X	1.0 - 1.2 X	0.7 - 0.8 X
2.1 - 2.1 X	1.0 - 1.8 X	1.0 - 2.5
1.2 - 2.7	1.0 - 2.5	0.9 - 1.0 X
0.8 - 0.8 X	6.85 - 10.19* X	2.7 - 3.0
1.9 - 3.5	2.5 - 3.5 *	1.4 - 1.5 *
	2.0 - 2.1 *	2.9 - 3.3 *
	1.7 - 3.5 *	1.7 - 2.6 *
Avg. 1.7-3.1	Avg. 1.8 - 2.8	Avg. 1.9 - 2.6

b) ACID MIST EMISSION

UPTO 100 MTPD (mg/Nm^3)	101 - 500 MTPD (mg/Nm^3)	ABOVE 500 MTPD (mg/Nm^3)
45 - 45	10 - 14	15 – 25
25 - 25	15 - 20	15 – 40
21 - 33	5 - 10 X	15 – 30
12 - 16	18 - 28	15 – 20
9.3 - 9.3 X	15 - 30	4.3 - 5.11
	42 - 46*	4 - 5*
	54 - 129* X	20 - 24*
	12 - 16*	2 - 3 * X
		4 - 6*
Avg. 25 - 30	Avg. 19 - 26	Avg. 16 - 28

c) SO_3 EMISSION

UPTO 100 MTPD (mg/Nm^3)	101 - 500 MTPD (mg/Nm^3)	ABOVE 500 MTPD (mg/Nm^3)
8 - 12 X	8 - 12* X	79 - 167*
	193 - 210*	89 - 109*
	6 - 7* X	102 - 142*
	54 - 71*	71 - 101*
Avg.	Avg. 124 - 140	Avg. 85 - 130

* Monitored Data

X Not being considered for working out the average figures.

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