Navin G. Ashar · Kiran R. Golwalkar

A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents

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To the hundreds of scientists, engineers,
workers, and technocrats who have
contributed significantly towards
the development of knowledge and
technology for more efficient, safe,
and environment-friendly working
of these industries; and who will
continue to do so in future.

Preface

It gives us great pleasure to present this monograph for use and reference by design, development, production, and maintenance engineers, managements and all those associated with the industries manufacturing sulfuric acid and sulfonating agents.

This book attempts to update and compile the information and experience generated on the technology of manufacture of these chemicals over the last few decades, after earlier treatment of this subject by Andrew M. Fairlie in the 1940s and by Werner W. Duecker and James R. West in the 1960s.

These industries are vital for the technical and economic progress of any country—a fact which has been well acknowledged throughout the world. Even though the chemical reactions involved in production of these chemicals are well known and the technologies for their manufacture are well established, we have made an attempt to compile and *update* the information available.

This attempt is to compile the latest state-of-the-art on sulfuric acid and sulfonating agents based on our own experience for the design, erection, commissioning, operation, and maintenance of production plants as well as the experience of many well known industries and knowledgeable people in the field. In addition, we have attempted to highlight the important technical issues for future development, smooth and safe plant operation, and economic viability in view of the rising raw material and energy costs globally.

We have taken due note of standard works on the subject such as 'The Manufacture of Sulfuric Acid' by Werner W. Duecker and James R. West, 'Sulfuric Acid Manufacture' by Andrew M. Fairlie, 'Encyclopaedia of Chemical Technology' by Kirk and Othmer, 'Sulfuric Acid Manufacture' by King, Moats, and Davenport, 'Handbook of Sulfuric Acid Manufacture' by D.K. Louie as well as information available through websites of reputed manufacturers and technology suppliers for sulfuric acid plants and equipment required for the same.

It is hoped that the practising personnel and management will find the book useful for improving plant efficiency, safety, environment, diversification to value added products such as liquid SO_2 and SO_3, expansion of capacity, profitability, etc., and will be able to contribute significantly to the progress in the state-of-the-art in sulfuric acid industry.

We also hope that this monograph will stimulate creative thinking for further all-round development.

We welcome creative suggestions from knowledgeable experts for updating the improvements in this field and due acknowledgement of these will be incorporated in future editions.

The publication of this book has been made possible with very active and valuable help from the NEAT team.

Mumbai, India Navin G. Ashar
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Current Status of Manufacture of Sulfuric Acid

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1.1 Introduction

1.1.1 History of Sulfuric Acid

Sulfuric acid was known to medieval alchemists under a variety of names including *oil of vitriol* and *spirit of vitriol*. These substances were produced by the dry distillation of minerals including iron (bivalent) sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$ known as green vitriol and copper (bivalent) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$ known as blue vitriol. When heated, these compounds decompose into iron and copper oxides, respectively, giving off water and sulfur trioxide, the two of which combine to produce a dilute solution of sulfuric acid. Preparations like these have been ascribed to alchemists including the twelfth century Arab Abou Bekr al-Rhases and the thirteenth century German Albertus Magnus.

In the seventeenth century the German-Dutch chemist Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter (potassium nitrate, KNO_3) in the presence of steam. As the saltpeter decomposes, it oxidizes the sulfur to SO_3, which combines with water to produce sulfuric acid. In 1736, Joshua Ward, a London pharmacist, used this method to begin the first large-scale production of sulfuric acid.

In 1746 in Birmingham, John Roebuck began producing sulfuric acid this way in lead-lined chambers, which were stronger, less expensive, and could be made larger than the glass containers which had been used previously. This *lead chamber process* allowed the effective industrialization of sulfuric acid production, and with several refinements remained the standard method of production for almost 2 centuries.

John Roebuck's sulfuric acid was only about 35–40% sulfuric acid. Later refinements in the lead-chamber process by the French chemist Joseph-Louis Gay-Lussac and the British chemist John Glover improved this to 78%. However, the manufacture of some dyes and other chemical processes require a more concentrated

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product, and throughout the eighteenth century this could only be made by dry distilling minerals in a technique similar to the original alchemical processes. Pyrite (iron disulfide, FeS_2) was heated in air to yield iron (bivalent)sulfate, $FeSO_4$, which was oxidized by further heating in air to form iron (trivalent)sulfate, $Fe_2(SO_4)_3$, which when heated to 480 °C decomposed into iron (trivalent)oxide and sulfur trioxide, which could be passed through water to yield sulfuric acid in any concentration. The expense of this process prevented the large-scale use of concentrated sulfuric acid.

In 1831, the British vinegar merchant Peregrine Phillips patented a far more economical process for producing sulfur trioxide and concentrated sulfuric acid. In this process, sulfur dioxide, SO_2, produced by roasting either sulfur or pyrite in air, is combined with additional air and passed over a platinum catalyst at high temperatures, where it combines with oxygen from the air to produce nearly pure SO_3. Even so, there was little demand for highly concentrated sulfuric acid at the time, and the first sulfuric acid plant using this *Contact Process* was not built until 1875 in Freiburg, Germany.

The development of the less expensive and less easily contaminated vanadium pentoxide (V_2O_5) catalyst by BASF in Germany in 1915, combined with increasing demand for concentrated sulfuric acid by the chemical industry, has led to the gradual replacement of the lead-chamber process by the Contact Process. In 1930, sulfuric acid produced by the Contact Process accounted for only 25% of sulfuric acid production, while today nearly all sulfuric acid is manufactured in this way.

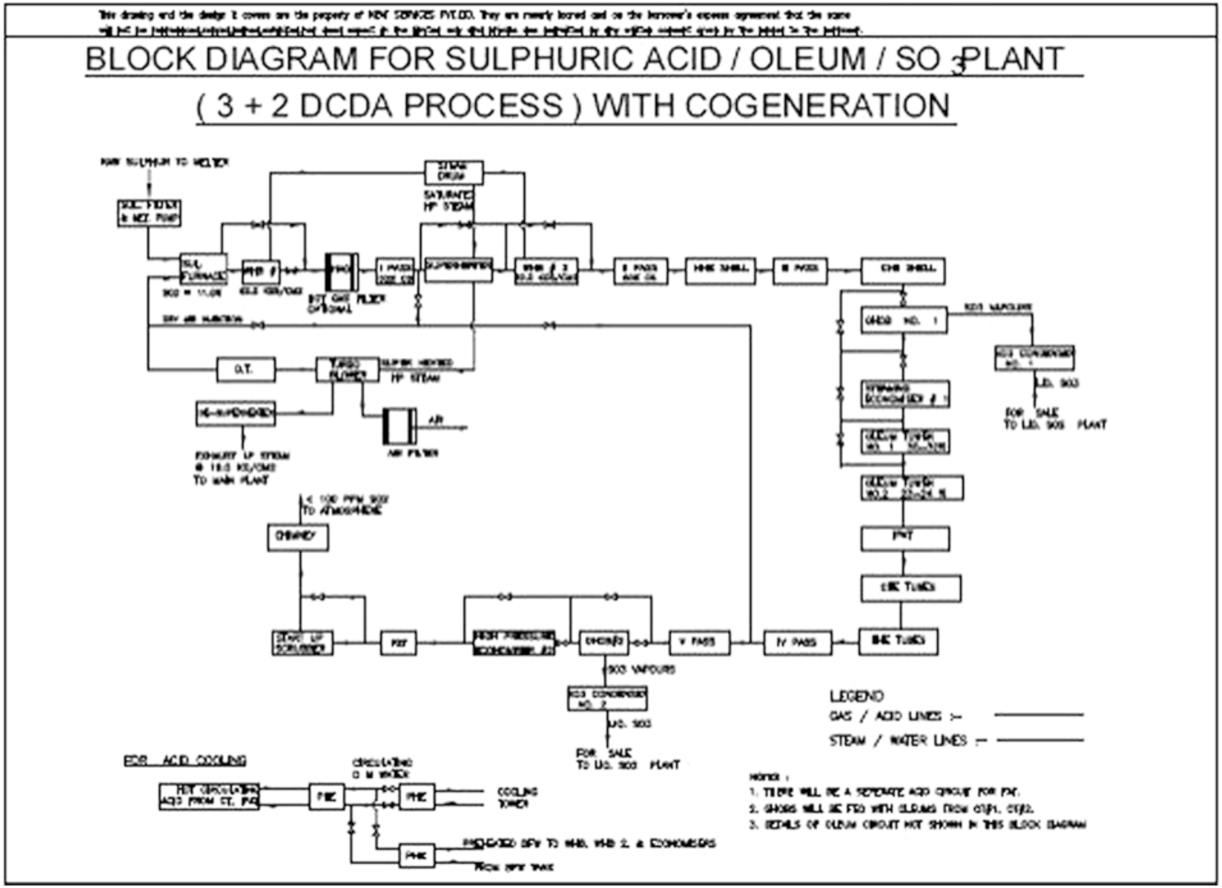
The conversion of SO_2 to SO_3 takes place by the reversible exothermic reaction

$$2\mathrm{SO}_2 + \mathrm{O}_2 \leftrightarrow 2\mathrm{SO}_3 \Delta\mathrm{H} = -22.93\,Kcal/\mathrm{gMole}$$

While the rate of the forward reaction increases with temperature, the equilibrium conversion decreases (thus reducing the yield of SO_3).

The Contact Process was further modified to the Double Contact Double Absorption process, which uses Le Chatelier's principle. According to this, when the SO_3 produced (as a result of conversion of SO_2 by the catalytic process) is absorbed by the intermediate absorption towers, the equilibrium conversion shifts to the right, i.e., more SO_2 is converted to SO_3. This is accomplished by reheating and then passing the reaction gases through an additional bed of catalyst. The SO_3 produced (additionally) is then absorbed in a second absorption tower.

[See Flow Diagram (3+2) DCDA process].


BLOCK DIAGRAM FOR SULPHURIC ACID / OLEUM / SO 3 PLANT
(3 + 2 DCDA PROCESS) WITH COGENERATION
RAW SULPHUR TO MELTER
SUL. FURNACE
STEAM DRUM
SATURATED HP STEAM
SUPERHEATER
I PASS
II PASS
III PASS
HHE SHELL
CHE SHELL
DRY AIR INJECTION
D.T.
TURBO BLOWER
SUPER HEATED HP STEAM
DE-SUPERHEATER
AIR
AIR FILTER
EXHAUST LP STEAM @ 18.0 KG/CM2 TO MAIN PLANT
< 100 PPM SO2 TO ATMOSPHERE
CHIMNEY
START UP SCRUBBER
FAT
HIGH PRESSURE ECONOMISER #2
GHOR/2
V PASS
IV PASS
IHE TUBES
CHE TUBES
PAT
OLEUM TOWER NO.2
OLEUM TOWER NO. 1
ECONOMISER # 1
GHOR NO. 1
SO3 VAPOURS
SO3 CONDENSER NO. 1
LIQ. SO3
FOR SALE TO LIQ. SO3 PLANT
SO3 VAPOURS
SO3 CONDENSER NO. 2
LIQ. SO3
FOR SALE TO LIQ. SO3 PLANT
LEGEND
GAS / ACID LINES :-
STEAM / WATER LINES :-
NOTES :
1. THERE WILL BE A SEPERATE ACID CIRCUIT FOR FAT.
3. DETAILS OF OLEUM CIRCUIT NOT SHOWN IN THIS BLOCK DIAGRAM
FOR ACID COOLING
HOT CIRCULATING ACID FROM ST. PAT
PHE
CIRCULATING D M WATER
PHE
COOLING TOWER
PHE
PREHEATED BFW TO WHB, WHB 2, & ECONOMISERS
FROM BFW TANK

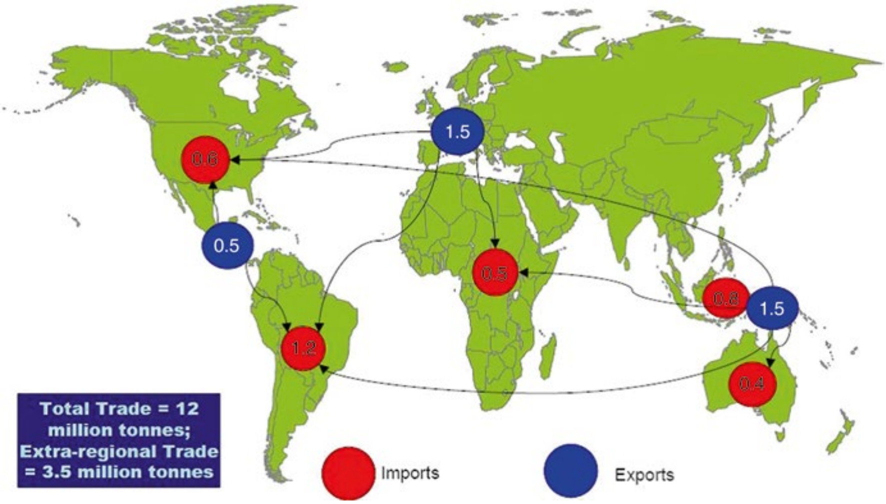


Fig. 1.1 Export/import of sulphur in the world during 2006

1.1.2 Current Status of Sulfuric Acid Production

Sulfuric acid is produced in almost all the countries of the world with the major producers being USA, Russia, China, Japan, Finland, Brazil, India, South Korea, Australia, Indonesia, Germany, Spain, France, and Belgium. The last four countries account for 70% of the total European production. USA and Canada account for nearly 40% of sulfuric acid production. The key importing and exporting regions are plotted in Fig. 1.1. Sulfuric acid is used directly or indirectly in nearly all manufacturing activities and is a vital commodity in any national economy. For this contribution, sulfuric acid is known as ‘King of Chemicals’.

Higher derivatives of sulfuric acid are 23–25% oleums, 65% oleums and pure SO_3, as well as liquid SO_2, which find applications in organic and petroleum processing.

Battery grade, pharmaceutical grade, laboratory (AR), as well as electronic grade sulfuric acids are purer and purer varieties of the acid and have specific uses.

1.1.3 Major Uses of Sulfuric Acid

1. It finds application as a dehydrating agent, catalyst, active reactant in chemical processes, solvent, and absorbent.
2. It is used in the process industries from very dilute concentrations for pH control of saline solutions to strong fuming acids used in the dye, explosives, and pharmaceutical industries.
3. It is produced and supplied in grades of exacting purity for the storage battery, rayon, alums, dye, and pharmaceutical industries, and in grades of less exacting

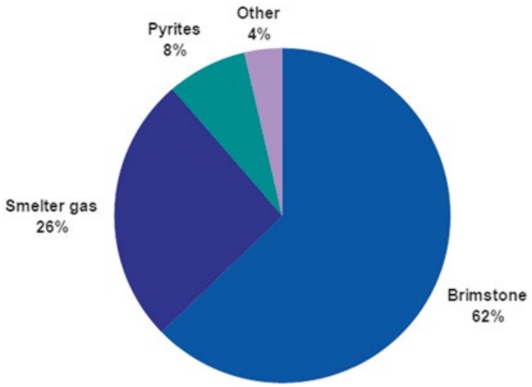


Fig. 1.2 World sulfuric acid supply totaled 200 million tonnes in 2006 of which smelter acid accounted for 26% of total production

specifications for use in the steel, heavy chemical, and super phosphate and phosphatic fertiliser industries.

4. Sulfuric acid is not a one-use product. Like a returnable steel drum, after initial use in some phases of the explosives, petroleum, and dye industries, the sulfuric acid is recovered in a form often unsuitable for use in the same process but of a strength and grade entirely suitable for use in other process industries.

Large amounts of sulfuric acid are consumed in the manufacture of phosphatic fertilizers, ammonium sulfate, etc.; for every tonne of P_2O_5, 3 tonnes of 100% sulfuric acid is required. The process for the manufacture of phosphoric acid by acid treatment of rock phosphate is complex and requires careful selection of the technology. The major processes for the manufacture of phosphoric acid are:

1. Prayon (Belgium) di- and hemihydrate
2. Single Tank Dor Oliver (USA)
3. Draft Tube GULF Process (Florida, USA)
4. Nissan (Japan)
5. Chemiebau (France)

The output of sulfuric acid at base metal smelters today represents about 26% (Fig. 1.2) of all acid production. Whereas in 1991 smelter acid production amounted to 27.98 millions tonnes, it is calculated that the output in the following decade will have grown to reach 44.97 millions tonnes in 2001. Smelter acid will be more than 25% of world sulfuric acid production compared to some 18% in 1991.

More sulfuric acid is produced than any other chemical in the world. In Western Europe in 1997 over 19 million tonnes were produced, the total production worldwide being estimated at around 150 million tonnes. About half of this output is produced in North America, Western Europe, and Japan. The world voluntary and involuntary sulfuric acid production from 2006 to 2015 is shown in Figs. 1.3 and 1.4.

Modern sulfuric acid plants are thus based almost entirely on the DCDA process and have replaced the chamber process completely.

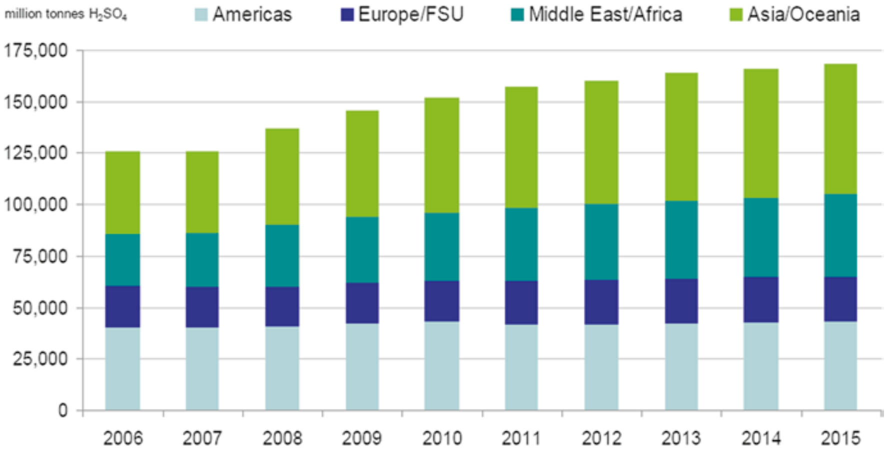


Fig. 1.3 World voluntary acid production 2006–2015 consuming an additional 14 million tonnes of sulfur

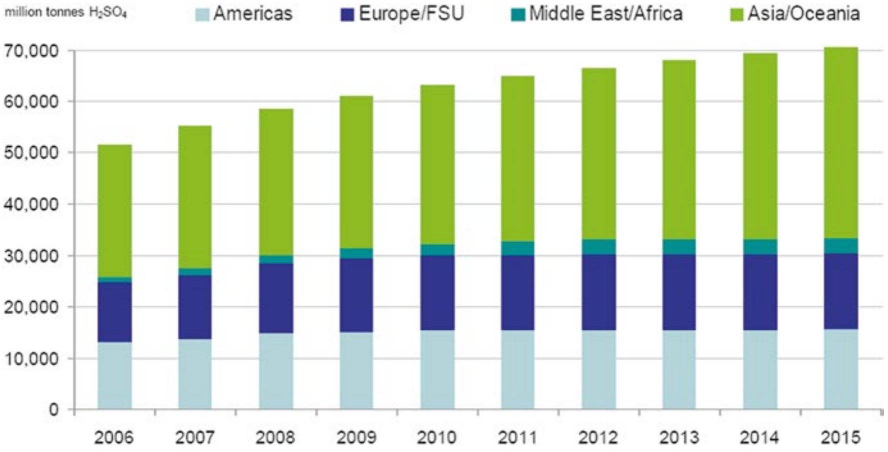


Fig. 1.4 World involuntary acid production 2006–2015 was almost 20 million tonnes new production

A few variants of the production processes are:

1. The wet gas plants wherein gases containing H_2S are used as source of SO_2. The burning of H_2S produces water vapor which affects the water balance in the plant, since moisture also enters the system through atmospheric air. The final strength of the product acid depends on this factor.
2. Spent acid recovery plants in the petroleum refining sector
3. Metallurgical plants which use copper, iron, and zinc pyrites as raw material.

The auto thermal operation of these plants (self-sustaining the reactions involving oxidation of SO_2 to SO_3) depends on the gas composition. Auxiliary gas cleaning and reheating equipment is provided in these plants for efficient and smooth working.

Some other processes:

Since considerable quantities of dilute waste acid are available from many industries, processes have been developed for recovery of the sulfuric acid in a concentrated form.

These have resulted into two major advantages:

Reduction in quantity of waste acid, which is an environmental problem and needs a considerable amount of neutralizing agents (e.g., lime).

Availability of concentrated sulfuric acid in-house, thus reducing the requirement for fresh acid to be purchased from outside sources.

In all cases, the materials of construction used have imposed severe limitations on design and, in some cases, plant efficiency.

Dilute sulfuric acid can also be heated under vacuum to increase its concentration. This process can recover concentrated acid from dilute acid.

Processes of Manufacture of Sulfuric Acid

2

2.1 Processes of Manufacture of Sulfuric Acid

The processes for the manufacture of sulfuric acid can be classified on the basis of raw materials used:

- Elemental sulfur
- Sulfide ores
- Spent acid
- Gases like H_2S

Many variants are available for each process utilizing the above-mentioned starting materials.

2.1.1 Elemental Sulfur

Process description for sulfuric acid 98.5% plant (commercial grade)

A typical sulfuric acid plant operating on sulfur as the main raw material consists of the following main sections:

1. Sulfur feeding section
2. Waste heat recovery section
3. SO_2 conversion section
4. Acid towers section
5. Acid cooling and storage/handling section
6. Plant infrastructure (electrical/civil/water treatment, etc.)

2.1.1.1 Sulfur Burning

Solid sulfur is dumped on the grids of the melter and is melted by means of the heat provided through steam coils in the melter. An agitator installed in the melter helps to melt the sulfur at a faster rate. Liquified sulfur is pumped to the pressure leaf filter and the purified sulfur stored in a separate compartment equipped with steam coils. Sulfur pumps are used to feed the liquid sulfur to the sulfur burner at a

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predetermined constant rate. The sulfur burner is preheated to a high temperature by an earlier oil firing and hence the sulfur being fed in ignites instantaneously, producing sulfur dioxide. Dried air is supplied to the burner by an air blower through a drying tower. The gases coming out from the burner are at temperature of 950–1,000 °C and contain 10.0–10.5% sulfur dioxide. They are passed through a waste heat recovery boiler where high pressure steam is produced while the gases are cooled to 390–410 °C depending on the plant design and gas duct layout.

The cooled gases are now passed through a multistage (four or five stage) conversion system (having three passes in the first converter and one/two passes in the second).

2.1.1.2 Conversion of SO_2 into SO_3

The design and operation of sulfuric acid plants are focused on the following catalytic gas phase chemical equilibrium reaction:

$$SO_2 + \tfrac{1}{2}O_2 \leftrightarrow SO_3 \Delta H = -99\,\text{kJ.mol}^{-1}$$

This reaction is characterized by the conversion, which is defined as follows:

$$\text{conversion achieved} = \frac{SO_2\,\text{in} - SO_2\,\text{out}}{SO_2\,\text{in}} \times 100(\%)$$

Both thermodynamic and stoichiometric considerations are taken into account in maximizing the formation of SO_3. The Le Chatelier-Braun principle is usually taken into account in deciding how to optimize the equilibrium. This states that when an equilibrium system is subjected to stress, the system will tend to adjust itself in such a way that part of the stress is relieved. These stresses are, for example, variations of temperature, pressure, or concentration of a reactant.

For SO_2/SO_3 systems, the following methods are available to maximize the formation of SO_3:

- Removal of heat—a decrease in temperature will favor the formation of SO_3 since this is an exothermic process.
- Increased oxygen concentration in the input side.
- Removal of SO_3 (double contact double absorption process) from the reaction zone.
- Raised system input pressure.
- Selection of the catalyst to reduce the working temperature (equilibrium).
- Increased reaction time.
- Increase in pressure of converter.

Optimum overall conversion of SO_2 in the system requires a balance between velocity of the forward and backward reactions (equilibrium achieved). However, this optimum also depends on the SO_2 concentration in the raw gas and on its variability with time. Consequently, each method is more or less specific for a particular SO_2 source.

Modern converter systems have cesium promoted ring type vanadium pentoxide as catalyst in the first and the last (fourth/fifth) passes and conventional vanadium pentoxide catalyst (also ring type) in the other two/three passes. A second waste heat boiler is provided to recover additional heat after the first pass of catalyst. A steam superheater can be provided in the waste heat recovery system, if required by the client in order to export the steam to nearby industry or to generate superheated steam for captive use.

Gases from the second pass of the catalyst are passed through a Hot Heat Exchanger (HHE) before entering the third pass of catalyst. Gases from the outlet of the third pass are passed through a Cold Heat Exchanger (CHE) and then through an economiser. The inter-pass absorption tower comes next and absorbs all the sulfur trioxide produced by the first three passes of the converter. Highly efficient **candle type demisters** in the IPAT completely remove all the acid mist generated in the tower so as to protect the catalyst in the later passes. Provision is made in the design of the gas ducting layout so that the economiser can be in commission or can be bypassed.

A dry air injection facility is occasionally provided at the outlet of the fourth pass to cool the gases before entering the fifth pass to about 380–390 °C. This is done with a view to maximize the overall conversion of SO_2 to SO_3 since the last pass can be operated at as low a temperature as possible.

Gases from the outlet of the fifth pass are taken through another economiser for preheating of boiler feed water before going into the final absorption tower. The circulating sulfuric acid in the DT (Drying Tower), IPAT (Inter Pass Absorption Tower), and FAT (Final Absorption Tower) is cooled by passing through plate heat exchangers where it exchanges heat with the cooling water. The water is then cooled by an adequately sized cooling tower.

2.1.1.3 Absorption of SO_3

Sulfuric acid is obtained by the absorption of SO_3 into H_2SO_4 (with an optimum concentration of at least 98%) with the addition of appropriate amounts of water to maintain the concentration.

The efficiency of the absorption depends on the following:

- H_2SO_4 concentration of the absorbing liquid (98.3–98.7%)
- Range of temperature of the liquid (normally 70 °C–120 °C)
- The heat of absorption being removed by Plate Heat Exchanger (PHEs) for anodically passivated sulfuric acid coolers
- Moisture content in the raw gas which can produce fine acid mist particles, which are very difficult to absorb
- An acid mist filter to arrest the mist of sulfuric acid in the system
- Temperature of incoming gas
- SO_3 emissions from the plant depend on:
- The construction and operation of the final absorber
- The acid mist formed upstream of the absorber through the presence of water vapor
- The device for separating H_2SO_4 aerosols

In modern plants, the strength of absorbing acid is automatically maintained at the optimum set point on the strength controller. This is done by controlling the addition of dilution water.

2.1.1.4 Tail Gas Scrubber

A two-stage alkali scrubber is provided for use during plant start-up to take care of any disturbed process conditions after any long stoppage. The concentration of alkali in the scrubbing liquor is maintained automatically.

However, the scrubber will not be required during steady running of the plant when a cesium promoted catalyst is used in adequate amounts in the last pass of the converter which is operated at 385–390 °C.

Process Description for Sulfuric Acid Plant (Battery Grade)

Gases from the outlet of the CHE/Economiser after CHE are taken to a 25% oleum tower before IPAT. The circulating oleum is boiled to produce SO_3 vapors which are absorbed in a glass/Teflon-lined steel (MS-PTFE) absorption tower. A glass acid cooling system is generally employed. The unabsorbed gases are led to IPAT.

In a variant to the above process, provision is made by means of a glass construction/MS-PTFE absorption tower (with glass internals—tower packing) parallel to the final absorption tower along with the glass acid cooling system.

Unabsorbed gases are led to a FAT/tail gas scrubber. It is advisable to provide a candle-type demister in FAT to prevent submicron mist particles in the exhaust gases.

Note:

- In both the above methods, demineralized water/cooled steam condensate should be used for maintaining the acid concentration.
- Separate acid strength indicator-recorder-controller systems are to be used for commercial grade and battery grade acid circuits in plants.

2.1.2 Available Techniques

Sources of SO_2

- Sulfur burning
- Pyrites roasting
- Metal sulfide roasting and smelting
- Sulfuric acid regeneration
- Metal sulfate roasting
- Combustion of H_2S or other sulfur-containing gases
- Other processes

Sulfuric acid production

Acid production is divided into two different groups depending on the strength/concentration of SO_2 in the gas stream.

Table 2.1 Principal metal sulfides producing SO_2

Metal sulfide	SO_2 percentage	Raw gases O_2 percentage	Process gases SO_2 percentage	Variability in time
ZnS-containing ores	6–10	6–11	6–10	Relatively low
CuS-containing ores	1–20	8–15	1–13	Can be very high
PbS-containing ores:				
– Sintering	2–6	~15	2–6	Relatively high
– Other lead smelters	7–20	~15	7–13	Low to very high (batch process)

Stronger gas processes have:
6–11 vol.% SO_2

- SCSA (6–8%)
- DCDA (8–11%)
- Weak gas processes are:
- Based on oxidation by H_2O_2
- Based on activated carbon
- Other processes

2.1.2.1 Combustion of Sulfur

The combustion of sulfur, which is obtained either from natural deposits or from desulfurization of natural gas or crude oil, is carried out in one-stage or two-stage sulfur combustion units at 900–1,050 °C. The combustion unit consists of a combustion chamber followed by a process gas cooler. The SO_2 content of the combustion gases is generally up to 11 vol.% and the O_2 content is low (but higher than 10%).

The gases are generally diluted to 10–11% before entering the conversion process. Sufficient concentration of oxygen is maintained in the process gas to ensure proper conversion of SO_2 to SO_3. Air may be injected at the inlet at the last pass of the converter if necessary.

2.1.2.2 Pyrites Roasting

Pyrite ores are roasted in fluidized beds. The gases from the roasters can contain dust, unburnt particles, etc., and hence are cleaned by using cyclones, bag filters, and electrostatic precipitators.

Temperature of the cleaned gas is brought up to the required temperature for conversion of SO_2 to SO_3 by means of auxiliary heaters or by exchanging heat with hot gases (produced after conversion).

Air is injected as needed to control the temperature of the process gas and to maintain the SO_2/O_2 ratio for satisfactory conversion.

2.1.2.3 Metal Sulfide Roasting/Smelting

Many metal sulfides (other than pyrites) produce gases containing SO_2 when roasted during metallurgical processes. It is necessary to distinguish the main ores as indicated in Table 2.1.

The concentration (vol.%) of SO_2 on the plant gases determines the total volume of gases handled. Any air injected into the system is additional—but this is generally a small amount.

Sizes of the plant units such as converter, heat exchangers, and absorption towers depend on the gas volume handled.

The exit gases from the IPAT need to be reheated before being admitted to the last stages (fourth generally) of the converter. The heat required for this purpose is taken from the hot gases coming out from the second and third passes of the catalyst. However, this amount of heat depends on the quantity of SO_2 converted to SO_3 and the gas temperatures depend on percentage SO_2. It is therefore seen that a certain minimum concentration of SO_2 is necessary to maintain autothermal operation of the plant, i.e., without having an additional external source of heat and increasing the number of catalyst passes.

Sulfuric Acid as a Byproduct from Copper Ore Smelters

When oxygen-rich air is blown through a copper matte a large amount of SO_2 is produced. This is contaminated with dust from the ores and hence it is cleaned by scrubbers and electrostatic precipitators and then fed to the (attached) sulfuric acid plant. This plant consumes all the SO_2 and produces sulfuric acid. However, due to copper converter operations, the percentage SO_2 and the gas flow vary considerably. External heating sources (oil fired burners) are provided if required and similar workings are used for zinc smelters and to use the SO_2 produced for sulfuric acid production.

Sulfuric Acid as a Byproduct from Lead Production

The gases produced from desulfurization of lead ores contain varying concentrations of SO_2 and dust, similar to gases produced during copper and zinc sulfide roasting.

Hence, the gases are cleaned by scrubbers and electrostatic precipitators and reheated to the temperature necessary for conversion of SO_2 to SO_3.

Auxiliary heating equipment (oil firing burners) is also used for this purpose, if required. The DCDA process is used in situations where percentage SO_2 in the gases is higher (9–10% approximately) and does not vary much, since autothermal operation is possible.

In the case of low/variable percentage SO_2 in the gases, a single absorption process with a good tail gas scrubbing system operating continuously is a better option.

Lead ores are contaminated with mercury which is poisonous to a vanadium catalyst. Hence, it is first removed by the patented Norwar process by scrubbing with mercuric chloride and recovering mercury by chlorination:

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2$$

$$2Hg_2Cl_2 + Cl_2 \rightarrow 2HgCl_2 + 2Hg$$

Mercury recovery is also possible by other processes.

2.1.2.4 Regeneration of Sulfuric Acid

Thermal decomposition of spent sulfuric acids to give sulfur dioxide is achieved in a furnace at temperatures around 1,000 °C. Spent acids come from processes where H_2SO_4 or oleum is used as a catalyst (alkylation, nitration, sulfonation, etc.) or from other processes where H_2SO_4 is used to clean, dry, and remove water.

Decomposition of sulfuric acid is represented by the overall equation

$$H_2SO_4 \rightarrow SO_2 + H_2O + \tfrac{1}{2}O_2 \qquad \Delta H = +202\,\text{kJ.mol}^{-1}$$

Spent acids are atomized in very small droplets to achieve good thermal decomposition. Energy is provided by the organics from the spent acids and by additional energy from natural gas, fuel oil, or coke. Preheating the combustion air reduces the amount of fuel needed. Furnaces can be horizontal (fixed or rotating) or vertical.

The SO_2 content in the gases mainly depends on the composition of the spent acids. The water and organics content affect the gas composition, which can vary from 2% to 15%. Sulfur, pure or waste, can generally be added to adjust the SO_2 content and to try to avoid large variations. Most of the energy from the combustion gases is recovered as steam in a waste heat boiler. Downstream, the gases are cleaned, demisted, and dried before going to the converter. The O_2/SO_2 ratio is important to get a conversion rate of SO_2 to SO_3 as high as possible. Upstream of the converter the gases are reheated to the ignition temperature through gas/gas heat exchangers using the conversion heat. A double absorption process can be more convenient if the SO_2 content of the gases is high enough (about 8%) at the converter inlet.

The conversion achievable is shown below.

- Single absorption:
  SO_2 content at the converter inlet **8%** with an O_2/SO_2 ratio of 1.1: **98%**.
  SO_2 content at the converter inlet **5–8 %** with O_2/SO_2 ratio of 1.1: **97–98%**.
  SO_2 content at the converter inlet below **5%** with O_2/SO_2 ratio of 1.1: **96–97%**.
- Double absorption:
  When achievable, double absorption leads to conversion up to **99.0–99.6%**.

Double absorption is considered as the BAT (Best Available Technique) for new plants. For existing plants, a single absorption can be advantageously combined with an ammonia scrubber, the by-product obtained being either sold on the market or recycled in the furnace.

2.1.2.5 Sulfate Roasting

Sulfates (e.g., iron sulfate) are decomposed in special furnaces with appropriate refractory linings. Operating temperatures often exceed 700 °C. Elemental sulfur coke, pyrites, fuel oil, etc., are also added to maintain the high temperature required for decomposition of sulfates.

Gases produced contain about 6% SO_2 but the composition is not constant. Hence, there is an additional sulfur burning furnace to maintain thermal stability in the converter passes.

The SO_2-containing gas leaving the furnace is cooled in a WHRB (waste heat recovery boiler), cleaned, and then admitted to the converter of the sulfuric acid plant.

Different types of sulfates are similarly decomposed for recovering SO_2 for subsequent conversion to sulfuric acid.

The sulfur dioxide-containing gas leaving the furnace is cooled in a waste heat boiler to about 350–400 °C and is subsequently passed to the gas cleaning system. The cleaned gases are fed to the sulfuric Acid plant.

2.1.2.6 Combustion of Sulfur-Containing Gases

Combustion of hydrogen sulfide (H_2S) or similar gases is achieved in a fixed furnace at about 1,000 °C. Combustion heat is higher than with sulfur combustion. Two different ways are used to process the gases to SO_3 and H_2SO_4:

- A dry process where the water is eliminated by condensation and then drying and the gases are processed as in the spent acid regeneration process.
- A wet process where the gases are processed with all the water and steam. At the end of the process, the absorption tower is replaced by a condenser where the control of temperature allows the production of 96% H_2SO_4, most of the water being discharged to the atmosphere.

The conversions achieved are comparable to those for sulfur burning plants.

2.1.2.7 Tail Gas Scrubbing

SO_2 abatement by scrubbing consists of a chemical reaction between SO_2 and a basic liquid solution. This operation is generally achieved in a gas/liquid contact packed tower or a scrubber. A liquid circulation loop is operated from the bottom to the top of the tower, where the liquid is distributed above the packing.

The gases enter the bottom part of the tower, and contact and react with the basic liquid solution on the packing. The SO_2 content in the outlet gases is achieved by controlling the pH of the solution and by adding more or less basic concentrated solution into the liquid circulation loop. One or two reaction steps may be needed depending on the inlet and outlet SO_2 content and the basic product used (ammonia, caustic soda, magnesium, or calcium hydroxides, etc.). The resulting by-products (ammonium-, sodium-, magnesium-, or calcium-, sulfate, sulfite, and bisulfite) can be sold or may have to be disposed of.

Various designs are used for the tail gas scrubbing system.

Venturi scrubbers followed by packed towers is the most common system used for sulfuric acid wherein the level of pH of the scrubbing liquor is automatically maintained at around 8.0–8.5 by addition of caustic soda solution at a controlled rate. An online pH meter is employed with a control valve for this purpose.

Lime solution is employed by some operators since caustic soda is costly.

However, the pipelines and spray nozzles tend to get choked due to formation of insoluble calcium salts. A variant of this method is the use of the dual alkali process wherein NaOH solution is circulated in the system and lime is used to regenerate NaOH from the spent scrubbing liquor. Other systems of proprietary design are also offered which are low in capital costs and utility consumption.

Table 2.2 Sulfuric acid production processes for new plants

New plants	SO_2 content in feed gas (vol.%)	Conversion achievable	With state of the art emission controller for new plants SO_3[a]
Single contact	6–10[b]	98.5%[c]	0.4 kg.ton^{-1}[d]
	3–6	97.5–98.5%	
Double contact	6–12[b]	99.6%	0.1 kg.ton^{-1}[d]
Wet contact process	0.05–7	98.0%	>10 ppmv SO_3
Process based on NOx[e]	0.05–8	nearly 100%	–
H_2O_2 Process		>99.0%	Very low

Note: with tail gas scrubbing there are practically no emissions of sulfur dioxide in modern plants

[a] $SO_3 + H_2SO_4$ expressed as SO_3

[b] When sulfur burning

[c] For existing plants the conversion achievable is 98%

[d] Per tonne of acid produced

[e] Possible emissions of NO_x

2.1.3 Overview of Techniques Applicable to Sulfuric Acid Production

This section refers to existing plants which may (or may not) be up-graded, although not reaching the specifications of new plants.

2.1.3.1 Overview

The six process routes are the principal process routes that are available. The following data on production processes have been presented in detail in the previous paragraphs and are summarized in Table 2.2 using an O_2/SO_2 ratio of about 1 ± 0.2 (possibly 0.8–3).

2.1.3.2 Single Contact Process

The SO_2-containing gases, which have been carefully cleaned and dried, are oxidized to sulfur trioxide in the presence of catalysts containing alkali and vanadium oxides. The sulfur trioxide is absorbed by concentrated sulfuric acid in absorbers, preceded if necessary by oleum absorbers. In the absorbers, the sulfur trioxide is converted to sulfuric acid by the existing water in the absorber acid.

The absorber acid is kept at the desired concentration of approximately 99 wt% by adding water or dilute sulfuric acid.

The single contact process is generally used with an SO_2 content of inlet gases of 6–10%; in new plants, the conversion efficiency is about 98.5% as a daily average and can be upgraded to 99.1% by good design and use of specially adapted doped Cs catalyst.

In existing single conversion single absorption plants, it is difficult to obtain better than 98.0% conversion; however, in some existing plants a conversion efficiency of 98.5% can be achieved with a large loading of catalyst in the last pass and operating at as low a temperature as possible (410–415 °C).

2.1.3.3 Double Contact Process (Double Absorption)

In the double contact process, the degree of conversion obtained is about 99.5%, depending on the arrangement of the contact beds and of contact time preceding the intermediate absorber. After cooling the gases to approximately 160–190 °C in a heat exchanger, the sulfur trioxide already formed is absorbed in the intermediate absorber in sulfuric acid with a concentration of 98.5–99.5 wt%. The intermediate absorber is preceded by an oleum absorber if required. The absorption of the sulfur trioxide brings about a considerable shift in the reaction equilibrium towards the formation of SO_3, resulting in considerably higher overall conversion efficiencies when the residual gas is passed through one or two secondary contact beds. The sulfur trioxide formed in the secondary stage is absorbed in the final absorber.

The double contact process including double absorption is shown in the block block diagram in Chapter 1 with the raw material—sulfur. In general, SO_2 feed gases containing up to 12 vol.% SO_2 are used for this process. The conversion efficiency in new plants can reach about 99.6% as a daily average in the case of sulfur burning.

In the DCDA process, the candle type demister developed by Monsanto (USA) was the major breakthrough. This prevents 99.99% of mist above 1 µm. Any mist carryover would hurt not only the heat exchangers but would also affect the catalyst activity in the converter passes 4 and 5.

Other Processes for Manufacture of Sulfuric Acid

2.1.3.4 Wet Contact Process (WCP)

This process is not sensitive to the water balance and has been used to treat off-gas from a molybdenum smelter as well as being installed in two desulfurization plants (one in a flue gas desulfurization system, the other on an industrial boiler) currently under construction. An earlier version of the WCP technology was used to treat lean hydrogen sulfide gases. For all gas feeds, sulfurous components in the gas are converted to sulfuric acid without the need to dry the gas first.

Roaster gases are cleaned by a combination of cyclones, bag filters, electrostatic precipitators, venture scrubber, etc.

An induced draft (ID) fan is provided at suitable point to convey the gases through the plant, and to overcome the pressure drop in the scrubbing system.

Cleaned gases (containing SO_2) are brought up to conversion temperature prior to admission to the converter. The SO_2 is converted to SO_3 by the catalyst and the hot gases from the converter exit are cooled by heat exchange with the incoming cold feed gas.

SO_3 combines with water vapor present in the gases and the sulfuric acid formed is condensed on specially designed condensers (where acid mist formation is minimized).

In addition to the usual utilities required for a sulfuric acid plant, there can be a need for an additional fuel (e.g., for oil/gas fired burners) for heating the process gas to conversion temperatures if the gas strength is low (less than 3.5–4.0% SO_2) since autothermal operation is difficult at such low strengths.

2.1.3.5 Pressure Process

The conversion of SO_2 to SO_3 increases as the operating pressure is increased since there is a reduction in volume during the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

The increase can be achieved by maintaining optimum temperatures in the catalyst bed. Increasing the process gas pressure can reduce the required size of the equipment, but the higher power consumption of the blower offsets the advantage gained. Hence most SA plants are built to operate at only a little above atmospheric pressure. Lately the *cold process* has become economically viable at high pressure; see Chap. 11.

Reduction in gas volumes can reduce both the required size of the equipment and the amount of catalyst required.

Hence, a capital saving is possible, but the blower consumes more power. As already said, this can offset the advantage gained.

The principal disadvantage of the pressure contact process compared with the conventional double-absorption process is that it consumes more power.

2.1.3.6 Other Processes

Other processes are defined as processes which yield sulfuric acid but which are not economically viable for large scale production for different reasons.

Unsteady State Oxidation Process

This new method of SO_2 oxidation is based on a periodic reversal of the direction of the reaction mixture flow over the catalyst bed. The process was developed by Dr. Matros[1] at the Institute of Catalysis of the former USSR. Basically, a large bed of catalyst is used both as a reversing, regenerating heat exchanger and as a catalytic reactor for the SO_2 oxidation reaction.

Cold SO_2 gas is fed into the catalyst bed and is heated to the catalyst ignition temperature by the heat stored in the bed. At this point the conversion reaction proceeds, producing heat. The heat is absorbed by the catalyst in the bed, increasing its temperature. When the front comes close to the exit side of the bed, the flow through the reactor is reversed. Flow reversals are made every 30–120 min. The main advantage of the unsteady state process is that the operating line for the first bed is almost vertical, giving first bed conversion of about 80–90% at a low exit temperature. The process is auto-thermal at low (0.5–3%) SO_2 gas concentrations.

The process is in operation in several plants in Russia and other Eastern European countries. (which the author has personally visited).

H_2O_2 Process

Use of H_2O_2 can oxidize the SO_2 to SO_3 which is then used to produce sulfuric acid. However, due to the high cost of H_2O_2 this process is not economical.

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[1] Currently Dr. Matros has emigrated to the USA and author has personal correspondence with him.

H_2O_2 is therefore used for oxidizing the remaining traces of (dissolved) SO_2 in the circulating acid in the plant. This minimizes the escape of SO_2 from tail gases from the final absorption tower.

2.1.4 Salient Features of the Modified (3+2) DCDA Process Developed by Neat

1. The first pass (as upper ignition layer) and fifth pass (entirely) of the catalyst bed will have a cesium promoted catalyst. This is to ensure faster pick-up of the conversion process after any stoppage and also to achieve closer approach to equilibrium conversion of SO_2 to SO_3. Instead of the conventional (3+1) DCDA Process, the (3+2) DCDA process can be used. In this innovation, after all the SO_3 produced in the first three passes has been absorbed in the oleum towers and the IPAT, the gases will be led through two more catalyst passes instead of the usual one. A dry air injection facility will be provided at the outlet of the fourth pass to increase the oxygen content of the gases which will help in shifting the equilibrium of the reversible reaction

   $$\mathbf{2SO_2 + O_2 \rightarrow 2SO_3 \Delta SH = -74.3\,Kcal/g\,Mole}$$

   further to the right. The fifth pass will contain cesium promoted catalyst which has a lower ignition temperature of 390.0–395.0 °C. As lower temperature favors higher overall conversion it is obvious that a higher yield of the above reaction will be obtained as compared to the conventional (3+1) DCDA process.

   The first pass of the converter will have as the upper half (approximately) cesium-based catalyst which has a low ignition point of 390.0–395.0 °C as compared to 410.0–420.0 °C for the conventional catalyst. This will allow the cooling of the WHB#1 outlet gases by a further 20.0–30.0 °C and thus produce some more steam. Another advantage is the faster pickup of conversion after any plant stoppage.
2. A higher (10.0–10.5%) SO_2 gas strength in the burner outlet gases will be possible due to use of a cesium promoted catalyst. This will also require lower volumes of gases to be handled, thus reducing power consumption.
3. Cesium activated catalyst is used to give stack emissions of 150 ppm SO_2 as against the 500–700 ppm permitted by the Environment Protection Agency of USA.
4. Air injections will be provided at appropriate places in the conversion system.
5. A separate acid circuit will be provided for the final absorption tower to minimize SO_2 content in the stack.
6. The drying tower and interpass absorption tower will have a common acid circuit.
7. Separate plate heat exchangers will be provided for FAT and (DT + IPAT).

8. A sulfur filter along with a standby filter can also be provided to ensure that only filtered sulfur is fed to the plant. This has the following advantages:
   - Fouling of heat transfer surfaces of boilers and heat exchangers is minimized.
   - Wear-and-tear of sulfur pumps is reduced.
   - Active surfaces of catalysts do not get masked by dust, and hence the conversion of SO_2 to SO_3 does not deteriorate with time.
   - Steady process conditions can be maintained leading to better quality product acid and oleum.
   - Finally, the rate of build-up of pressure drop over time is reduced. Hence power consumption does not increase.
9. Two centrifugal pumps are generally provided for filtering the raw sulfur. Metering pumps are provided to ensure steady sulfur feed to the burner. This helps in maintaining steady process conditions, very essential for efficient plant operations.
10. The sulfur burner is lined with insulating bricks, high alumina fire bricks, and very high alumina (60–65%), fire bricks to conserve heat inside and to enable operation of the plant at 10.0–10.5% SO_2 in the burner outlet gases. This will reduce the total volume of the gases handled and in turn will reduce the power consumption per MT of acid produced. For operating the plant at higher strengths (11–11.5%) of SO_2 the furnace shell is air-cooled by the incoming air, which is then sent to the burner. In certain designs the furnace shell is cooled by a separate air blower and the hot air generated is used elsewhere in the premises.
11. Teflon candle demisters will be provided in the DT to eliminate the possibility of acid mist carryover, which is a source of corrosion of the downstream equipment.
12. The heat exchangers will have disc and donut types of baffles instead of the usual segmental type. This will result in better gas distribution on the shell side and a lower pressure drop too.
13. Gas inlet and outlet nozzles of the equipment are designed to reduce pressure drop and to improve gas distribution.
14. Gas ducting from the first pass to the second WHB can be made of SS-304 to minimize the maintenance problems due to the high temperature at the outlet of the first pass.
15. MS-PTFE lined pipelines can be used (as optional) for acid for maintenance free service as compared to C.I. pipelines in conventional sulfuric acid plant design.
16. Sophisticated instrumentation with DCS will be provided for the automatic control of the process parameters and for monitoring the exit gas SO_2 concentration. Data loggers will be provided (as an optional facility) for automatic recording of all-important process data, which can be retrieved whenever required.
17. A very efficient two-stage scrubber with alkali circulation will be installed after the FAT. A pH meter with automatic control for fresh alkali addition to the scrubber liquid will also be provided. This scrubber will be used during plant

Table 2.3 Disposal and clean-up of metallurgical off-gases

SO_2 bearing gases produced from	Gas cleaning systems
Copper sulfide smelter	Gas scrubber, ESP
Lead sulfide smelter	Gas scrubber, ESP
Zinc sulfide smelter	Cyclones, gas scrubber, ESP

Note: the modern trend is to use WET ESP with special MOC like Hastelloy-variants for the wetted parts (electrodes). These have higher efficiency and less pressure drop

start-up/during upset process conditions only. It will **not** be required during steady plant operation.

18. A chimney in PP-FRP construction will be provided for the exit gases. The height of the chimney will be as per international standards. This chimney can be mounted on FAT or on a separate foundation.

2.1.5 Sulfuric Acid from Sulfides as Raw Materials

The gases produced during burning of metal sulfides contain varying amounts of SO_2 as well as considerable dust, which can reduce the activity of the catalyst. The dust is removed by water spray/dilute acid spray followed by electrostatic precipitators. This is to ensure a feed of clean gas to the converter.

Gases containing SO_2 from all metallurgical processes are also cleaned before the contact process to remove the following components:

- Fumes or aerosols formed by condensation of volatile metal components such as Zn, Pb, Sb, Bi, Cd and their chlorides, sulfates, and oxides.
- Volatile gaseous metals such as As, Se, Hg and their compounds.
- Gaseous non-metallic compounds such as HF, HCl, SO_3, and CO.

However, the heat evolved during combustion of the sulfides and conversion of SO_2 to SO_3 in the earlier passes may not be sufficient to reheat the return gases to the required temperatures, particularly when the percentage of SO_2 is below 3.5–4.0%

Double absorption processes based on metallurgical gases differ from hot-gas plants based on sulfur combustion in that cold feed gases must be heated to the converter-inlet temperature using the energy liberated in the oxidation of sulfur dioxide.

Auxiliary heaters operating on oil firing are also employed to heat the gases if required. In certain cases, additional sulfur is fed in to increase the SO_2 concentration (for evolution of more heat during conversion of SO_2).

Table 2.3 shows the different metallurgical off-gases, the main disposals, and the methods of cleanup.

2.1.6 Handling of Waste Gas/Stack Height

The height of the exhaust stack determines the maximum SO_2/SO_3 concentration in the ambient air surrounding a sulfuric acid plant. It is also well known that this concentration fluctuates widely in space and time due to the thermo-aerodynamic conditions of the low-level atmosphere (0–500 m). These conditions can vary due to the following factors:

- Vertical temperature and humidity content in air
- Wind speed and direction
- Turbulence of the atmosphere
- Sunshine intensity, etc.

Hence, a minimum stack height is generally prescribed by statutory authorities in all countries. In India it is the State Pollution Control Boards and the height is generally 30 m above ground level.

2.2 Process for Oleum Manufacture

2.2.1 Production of 25% Oleum

The gases exiting from the converter passes contain SO_3 and SO_2—*their relative quantities being dependent on the conversion of* SO_2 *that has taken place so far*. In the case of a four-pass converter of a sulfuric acid contact process plant, the typical extent of conversion of SO_2 are 60–65% in the first pass, 80–85% in second pass, 90–95% in the third pass, and up to 98–99.8% in the last pass, depending on the plant design, catalyst loading, operating conditions, etc.

It is essential that the gases contain as high a concentration of SO_3 as possible in order to have a good mass transfer rate for absorption in the circulating stream of oleum in the tower.

Generally, plant operators maintain the concentration of oleum at around 23–24% if only oleum is to be produced. However, higher concentrations of oleum of around 28–30% are used if it is desired to produce 65% oleum or liquid SO_3.

Higher strengths of oleum are not very corrosive to steel as compared to weaker 18–20% oleums. This property is taken into consideration when designing and constructing the oleum tower, piping, oleum boiler, heat exchangers, etc. (Readers should note that cast iron is unsuitable for use in an oleum environment.)

It is also found that, rather than a separate circulation tank for the oleum, an extension of the lower boot of the oleum tower with a submerged type circulation pump is safer and easier to operate. Appropriate sealing at the pump base frame prevents any escape of acidic vapors from the tank.

A single oleum tower can produce about 40–50% of the total output from the plant as 28–30% oleum. Two oleum towers in series are used (the second tower operating at a lower strength) if most of the plant output is to be produced as oleum. Part of the oleum from the second tower is transferred to the first higher strength tower to maintain the concentration—while appropriate amounts of sulfuric acid are added from acid towers to the second oleum tower.

The temperature of circulating oleum at the inlet of the tower plays a very important role in the proper absorption of the SO_3 from the gas phase. It is maintained as low as possible—and generally not allowed to exceed 52–53 °C. There is a considerable escape of acid mist from the oleum tower and hence it is almost always followed by an acid tower (the inter-pass absorption tower).

2.2.2 Production of 65% Oleum

It would seem logical to increase the strength of 20–25% oleum by absorption of SO_3 for production of 65% oleum. However, this route was found to present practical difficulties since the 40–42% oleums can solidify even at ambient temperatures at many locations.

In practice, the strength is therefore brought down from 100% (which is pure SO_3) to a level of 65% by adding 25–30% oleum in the required amount. This operation is carried out as follows.

Batch operation: A known amount of liquid SO_3 is taken in a tank equipped with outside cooling jacket and a circulation pump. A stream of 25–30% oleum is slowly added in a controlled manner while the circulation pump is running. Strength of the recirculation stream is monitored and the addition of oleum is stopped at the right time.

Continuous method: Liquid SO_3 is slowly added to the boot of the separate oleum tower wherein 65% oleum is being circulated. The strength and temperature increase as a result. A controlled stream of 25–30% oleum is added to maintain the strength at 65%.

An inline cooler is provided to control the temperature at 40–43 °C at the inlet of the tower. A product outlet valve is opened to take out the 65% oleum from the tower and transfer it to the storage tanks.

The cooling water stream is kept under negative pressure by running it using a siphon. This prevents ingress of water into the oleum tower in the case of a leak. Continuous monitoring of the conductivity/pH of the exit water stream from the cooler is carried out and a warning device is set to indicate a leaking tube.

Specially sealed level indicator tubes are provided on the boot of the tower. Either a transparent tube is attached to see the top of the indicator rod attached to a float or a magnet is attached to the top of the rod.

This magnet moves up and down in a stainless steel tube. An **external** follower magnet indicates the exact position of the **inner** magnet.

Pure Teflon (PTFE) gaskets are used as a precautionary measure in all flanged joints of pipeline and valves.

2.2.3 Production of Sulfur Trioxide

Though the multistage converters in the plant are generally able to convert more than 99.5% SO_2 to SO_3, it is practically difficult to condense it as such due to the low concentration of SO_3 in the process gas streams. Hence, the gases are passed through an oleum tower in the plant to absorb the SO_3 in a stream of circulating 25–30% oleum.

A controlled stream of the oleum is then heated (boiled) to release the vapors which contain almost 100% SO_3 with only traces of SO_2. The vapors are then condensed to obtain liquid SO_3 or are absorbed in oleum to produce 60–65% oleum.

For SO_3 condensers, the falling film type condenser (SO_3 vapors on the shell side and a trickling stream of water on the inside of tubes) is generally found to be safer as compared to a shell and tube type unit wherein water is circulated under pressure.

However, the latter has a higher heat transfer coefficient due to greater water velocities and needs a lower area for heat transfer. It should be fitted with a pressure release valve with a vent line connected to a scrubber.

Depleted oleum having a strength of about 20–22% is returned to the oleum tower to increase its strength again by absorption of SO_3.

2.2.3.1 Oleum Boilers (SO_3 Generators)

These are used for generating SO_3 vapors by boiling 28–32% oleums. The higher the strength of the oleum being boiled the lower the boiling point. Hence it is generally preferred to use higher strengths of oleum coming in to the boilers.

There are two distinct variants depending on the heating medium used for boiling oleum.

The heating medium is generally in the tubes and the oleum is on the shell side. An entrainment separator is built in or externally provided for separating droplets of oleum from the outgoing SO_3 vapors.

Steam Heated Oleum Boiler—SHOB

The heat transfer rates are high in SHOB due to condensing steam and hence these units are smaller in size. The hold-up of oleum on the shell is also less.

These units also need smaller support structures.

The plant designer has options available for locating these units since they do not need main process gas duct connections.

Safety issues: A dangerous situation can arise in the case of a tube leak as steam can react violently with oleum. Adequately sized safety valves and the provision of rupture discs is a must. The vent lines from these must be led away from the working area—they can be connected to the gas inlet of the final gas absorption tower or a suitable gas scrubber.

Regular replacement of the tubes every 2 years and pressure tests during annual shutdowns will be found useful.

Gas Heated Oleum Boiler—GHOB

Hot gases from the exit of one or more of the converter passes is used for boiling the oleum.

The heat transfer rates are low in GHOB due to process gas being the heating medium and hence these units are bigger in size. The hold-up of oleum on the shell is also greater.

These units need bigger and stronger support structures

The plant designer does not have many options available for locating these units since they need main process gas duct connections at inlet and exit.

2.2.4 Safety Issues

A dangerous situation can arise in the case of a sudden power failure or stoppage of the oleum feed pump as oleum can drain back into the tower boot and overflow from there. A non-return valve in the oleum feed line can prevent such incidents.

In the case of a tube leak, liquid oleum will enter gas ducts and can drain automatically and safely through a seal pot on the ground floor. A sudden increase of SO_3 mist in the stack gases can indicate such a leak, warning the plant operators.

Regular replacement of the tubes every 2 years, provision of stainless steel AISI-316 ferrules at the gas entries of the tubes, and pressure tests during annual shutdowns will be found useful.

The SO_3 vapors generated by the oleum boiler should be condensed or absorbed into a suitable medium. Apart from well designed, fabricated, tested, and maintained storage and condenser plant, operators will find the following practical suggestions useful for safe operation:

1. Use only pure Teflon PTFE gaskets in SO_3 vapor and liquid lines. Conventional acid resistant gaskets may not be able to withstand attack by SO_3.
2. Provide steam tracing lines, i.e., another steam line in contact with or in the near vicinity of the liquid SO_3 pipeline instead of a steam jacket.
3. Maintain a temperature of between 28 and 33 °C in the storage tanks for SO_3.
4. Provide a dual pressure gauge on the SO_3 condenser, which can indicate pressures below and above atmospheric.
5. Use a falling film condenser instead of a shell and tube type condenser wherein cooling water flows under pressure in the tubes.

   In the case of a tube leak, no water should enter the SO_3 side. The tubes in the falling film condenser are open to the sky and, in the case of a leak, the pressure gets released to the top opening.
6. Safety vents, rupture discs, and air vents will form standard mountings on the condenser and storages. Scrubbers will be connected to the vents and irrigated by 98% sulfuric acid for absorbing any SO_3 vapors released from the vents.

The general presentation of the technique of production of sulfuric acid from gases from metallurgical and other sources is divided into two parts as the techniques for the conversion of SO_2 to SO_3 and of absorption of SO_3 depend on the concentration of SO_2 in the feed gas entering the installation and on the variability of SO_2 concentration.

2.3 Environmental Considerations

The main pollutants emitted are:

- SO_2 resulting from incomplete oxidation.
- SO_3 resulting from incomplete absorption of SO_3.
- Droplets of H_2SO_4 resulting from absorption. H_2SO_4 mist emission due to inefficient absorption and inefficient demister provided in the final absorption tower. Modern plants also install specially designed candle type demisters in the FAT exit.

Many other pollutants may be emitted in trace amounts depending on the source of SO_2 and the H_2SO_4 production process, e.g., heavy metals (for example, mercury) when certain ores are treated

2.3.1 Monitoring of Pollution

Two approaches are used to monitor emissions:

- Monitoring the process: for example, the temperature of the contact beds or the SO_2 content entering the contact section and behind the intermediate absorption.
- Monitoring the emissions.

2.3.1.1 Monitoring of SO_2 Emissions

Continuous emission monitoring equipment for SO_2 is available and suitable for sulfuric acid plants and should be installed on all plants. Dual range instruments are available so that the much higher SO_2 emission concentration during start-up can be monitored as well as the relatively low concentration in the emission during steady operation. Emission monitor records should be retained and the competent authorities should consider the appropriate statistical analysis or reporting which is required.

2.3.1.2 Monitoring of Mist Emissions in the Stack

Emissions from S.A. plants generally consist of some unconverted SO_2, unabsorbed SO_3, and acid mist escaping from demisters installed in final absorption tower.

These are minimized by the following techniques:

- Providing a continuously operating alkali scrubber for SCSA plants.
- Using a DCDA process instead of SCSA and cesium promoted catalyst in the last pass of the converter.
- Strict control of process temperatures and SO_2 percentages in gases at the inlet to the converter.
- Use of efficient hot gas filters and sulfur filters to minimize the deposition of ash on the catalyst surfaces.
- Automatic adjustment of dilution water addition to control the strength of the circulating acid at optimum level (98.0–98.5%).
- Control of temperatures of acid and gas at the inlet to the absorption towers.
- Sufficient flow of acid in all towers.

- Efficient candle type demisters in all acid towers (drying, intermediate absorption, and final absorption).
- Provision of alkali scrubber for tail gases for plants (to minimize emission during plant startup and to take care of any process upsets).

2.3.2 General Techniques

2.3.2.1 Process Control Optimization

Operational controls should include means for:

- Warning of absorber acid feed failure.
- Warning of absorber acid feed over-temperature and control of temperature along the conversion tower.
- Indication of sulfur feed rate and air flow rate.
- Detection of acid leaks in acid coolers (pH-meter) and controlling the level of the acid reservoir.
- Ensuring acid concentration >98.5%.
- Emergency plant trips.
- pH-control on cooling water systems.
- To aid start-up the following will be necessary:
- Efficient catalyst preheating facilities, vented to the chimney. At least two catalyst stages must be above "strike" temperature before sulfur dioxide is admitted to contact the catalyst.
- Optimization of absorber acid strength and temperature before sulfur is admitted to the burner.
- Use of additional controls to ensure that sulfur cannot enter the system during shutdown.
- Before a long shutdown period the catalyst bed should be efficiently purged of SO_2/SO_3.

2.3.2.2 Fuels and Raw Materials Selection

Sulfur

Sulfur with low contents of ash, water, and sulfuric acid must be preferred.

Energy for Heating Systems

For the start-up of sulfuric-acid plants, heating systems are necessary. Where direct combustion is applied, low sulfur fuels are preferable.

2.3.3 Techniques to Control Emissions of SO_2

Table 2.4 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of SO_2 for the manufacturing of sulfuric acid. Most sulfuric plants have taken general primary optimization measures like process control.

Table 2.4 Techniques for reduction of sulphur dioxide emissions

Techniques	Applicability in processes	Emission level for plants operating at 9.5–10.5% SO_2 with a rated capacity up to 1,000 TPD mg SO_2/m^3 tail gas	 Kg SO_2/ton H_2SO_4 100 %
Contact process			
Single absorption + fifth bed	All SCSA	<2,000	<6
Double absorption + fifth bed	All DCDA	<1,000	<2.5
Single absorption + cesium catalyst in the last bed	All SCSA	<2,000	<5
Double absorption + cesium catalyst in the last bed	All DCDA	<250	<2.3
Single to double absorption	s.a.	<1,000	2.6
Tail gas scrubbing by			
Sodium hydroxide	All	<200	<2
Ammonium hydroxide	All	<200	<2
Calcium hydroxide	All	<200	<2
Activated carbon	All	<1,000	<2
Hydrogen peroxide treatment after and absorption	All	<200	<2

There are many other processes available for SO_2 removal from stack gases. Some of them are listed below:

1. *By absorption in liquid medium* such as
   (a) Sodium hydroxide solution
   (b) Sodium carbonate solution
   (c) Alkali fly ash
   (d) Ammonium hydroxide solution
2. *By treatment with active carbon*
   SO_2 bearing gases are passed through active carbon beds, which are periodically washed with water. The dilute acid produced can be used in the plant itself (instead of dilution water).
3. *By treatment with limestone slurry/lime water*
   Though this method uses cheap alkali, there are practical difficulties due to choking by calcium sulfite, etc.
4. *Use of turbulent contact absorber*
   This uses light spheres of plastic material in the absorber column instead of the conventional tower packings. The spheres are retained between suitably designed retainer plates and are self-cleaning.

2.3.4 Techniques to Control Emissions of SO_3 and H_2SO_4

Table 2.5 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of H_2SO_4 (taken as the sum of SO_3 and H_2SO_4) during the manufacture of sulfuric acid. Most sulfuric acid plants have taken general primary optimization measures like process control measures.

Table 2.5 Techniques for reduction of sulphur trioxide and sulphuric acid mist

		Emission level		
Techniques	Applicability in processes	mg H_2SO_4/ Nm^3 tail gas	kg/ton H_2SO_4 100%	Remarks
Wire-mesh	Large droplets (1–20 µm)	<100		Not efficient on mists
High efficiency candle type filter after absorbers	0.1–2 µm droplets	<50	<0.03	– Increased energy consumption – Production loss – Capacity loss – Plume suppression
Scrubbing	All	<10	<0.015	– Waste generation as in Sect. 4.2.3 – Plume reduction

Sulfuric Acid Plant with Cogeneration of Power

3

3.1 History

Earlier designs of sulfuric acid plants preferred minimizing initial capital cost and hence heat recovery equipment was not common. For example, these designs had atmospheric cooling ducts, air cooled heat exchangers, or air injection facilities instead of waste heat recovery boilers and economisers.

Later on, with rising energy costs, heat recovery equipment was incorporated in the designs. Efforts were also made to minimize energy consumption. Initially air preheaters (for recovering heat from hot gases between converter passes) were provided. The preheated air was fed to a furnace and the heat was recovered by a waste heat boiler installed after the furnace. However, it was found to have the following disadvantages:

1. A high furnace temperature requiring greater thickness of refractory lining and causing difficulty in operating at higher than 8% SO_2.
2. Higher pressure drops on the gas side causing higher power consumption by the blower.

Hence, improvements in waste heat recovery designs were made by installing additional waste heat recovery equipment like an additional boiler after the first pass of the converter and an economiser after the last pass.

The earlier designs of boilers (smoke tube type) generated steam at a lower pressure which was primarily used for process heating. Later designs of boilers were of the *water tube* type for generating steam at high pressure. This high-pressure steam was superheated in suitably designed superheaters generally installed after the first pass of the converter where the gases are available at 595–610 °C. It was then used for running a turbo generator set.

Since the early 1990s sulfur has been recognized as a source of energy due to the phenomenal rise in the price of crude oil and rise in demand for electric power. Monsanto of USA has developed the HRS process for maximizing steam generation (by recovering the heat from hot acid). Along with use of highly efficient steam turbines it will become possible to generate more than 10 MW power from a 1,000-TPD plant.

N.G. Ashar and K.R. Golwalkar, *A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents*, DOI 10.1007/978-3-319-02042-6_3,

3.2 Selection of Steam Turbo Generator Set

Some of the options available for selecting a steam turbine are as follows. These could be in single stage or multi stage construction. Further details can be discussed/obtained from the vendors concerned to suit the specific requirements on site

- Backpressure turbine
- Extraction turbine
- Reheat turbine
- Condensing type turbine

Some of the options to be considered for selecting an electrical generator at the sulfuric acid plant are:

- Induction type
- Synchronous type

The final selection of the turbine and generator will depend on the site conditions.

3.2.1 Selection Criteria for Steam Turbines

1. Steam consumption of the turbine for the steam available at site.
2. Speed (RPM) at normal operation.
3. Gearbox and common base plate design for the steam TG set.
4. Speed governor provided (mechanical/electronic).
5. Whether emergency trips are provided.
6. Instrumentation provided by vendor.
7. Generator speed and type of generator.
8. In the case of a condensing turbine, the supplier will quote for the complete package for steam condensation and system for recycling of the condensate.
9. Load on the cooling tower.

3.2.2 Technical and Economic Considerations

Some of the important considerations for cogeneration system are as follows:

1. Capital cost of steam turbo generator set consisting of
   (a) Turbine
   (b) Gearbox
   (c) Instrumentation
   (d) Other accessories for lubrication, bearing cooling, etc.
2. Infrastructure required:
   (a) Water treatment plant for producing DM water especially for silica removal (which can deposit on the turbine blades and cause damage)
   (b) Facilities for condensation and recycle of exhaust steam (condenser, cooling tower, water pumps, piping, and condensate extraction pump)
   (c) Raw water storage, de-aerator, boiler feed water storage and pumps

3. Cost of steam:
   (a) Whether the steam is generated by waste heat recovery system alone or whether any additional system is also involved (e.g., coal fired boiler running in parallel).
   (b) Whether the exhaust steam from the turbine can be used for process heating elsewhere in the premises, or exported to nearby units.
   (c) If there is no such possibility as above, then the steam will have to be condensed and a condensing-type turbo generator set may have to be installed.
   (d) Cost of steam lines, regulating valves, insulation and support structure, etc.
4. Steam generation equipment installed in the plant:
   (a) Waste heat boilers
   (b) Economisers
   (c) Steam superheaters
   (d) Steam de-superheaters
5. Type of electrical generator (synchronous or induction type)
6. Electrical switchgear and arrangement to use the power generated
7. Load characteristics: the sequence of operation of various drives/electrical loads, and their individual starting currents and running currents. A sudden heavy load can result in tripping of the TG set. This needs to be considered when some other units at the site are also supplied with the power generated.
8. Local regulations for power generation and use: whether privately operated power generation plants are allowed and whether the excess power (after meeting internal requirements) can be fed into the state grid. A totally dedicated system for internally utilizing the entire power generated has its own advantages and disadvantages depending upon site conditions.
9. Cost of DM water if all the condensate cannot be recovered.
10. Cost of accessories: capital and running cost for cooling tower water pumps, water treatment plant, etc.
11. Typical factors related to sulfuric acid oleum plants which affect cogeneration of power:
    - Waste heat recovery units installed and design of individual units.
    - Plant production rate and plant operating conditions.
    - Catalyst activity in individual passes.
    - Performance of all heat exchangers.
    - Design of existing electrical system.
    - Electrical motors connected to each drive and their operating loads.
    - Ducting design and insulation.
    - Climatic conditions on site.
    - Provision of instrumentation for waste heat recovery system.
    - Availability of skilled manpower round-the-clock.
    - Availability of maintenance facilities and requisite spares.

Due to the high cost of energy prevalent almost everywhere, it will be found that cogeneration facilities installed in a sulfuric acid plant will pay for themselves in a short period of time.

Large sulfuric acid plants can feed the surplus power (after meeting their own internal requirements) to the external grid, or to nearby consumers (smaller industries, etc.) and earn considerable revenue too.

It is thus clear that cogeneration improves the economic profitability of a sulfuric acid plant, and by contributing power to the main grid can reduce the load on local generating stations. In the case of thermal power plants operating on sulfur-containing fuels, this can reduce atmospheric pollution since the quantity of pollutants released per MWH generation is less in the case of a sulfuric acid plant than a thermal power plant.

The process steps – burning sulfur, roasting sulfide ores, SO_2 conversion, and SO_3 absorption – are exothermic processes. This means that, from a technical point of view, installations for removing energy are of great importance for the production of sulfuric acid. This is coupled most effectively with energy winning in different levels and forms. Energy winning is dependent on the process strategy for the target products, for the local conditions, and for a possible relationship to other production processes. The age of the production units is more important than energy generation/consumption because materials of construction and specific buildings fix the technical possibilities for energy optimization. A sulfur-burning process in conjunction with double absorption is the most energy efficient.

The different energy-winning techniques are:

- All techniques of steam generation as used in electric power generation with special apparatus such as super-heater, economiser, or steam boiler for sulfur burning.
- Steam generation by the inter-pass absorption with temperatures of 110–180 °C and steam pressures of 1.5–11 bar(ab).
- Steam turbines with power generation up to 15 MWh (1,250 tonnes day^{-1} 100% H_2SO_4 plant).
- Water preheating in the end absorption from 40 to 80 °C.

4

Sulfonating Agents and Derivatives Based on Sulfuric Acid

4.1 Summary

Sulfuric acid is called the king of chemicals. The first step to produce a useful product is sulfonation. Since the direct use of sulfuric acid is not feasible in all applications, the following auxiliary agents do play an important role. These are:

1. 25% oleum
2. 65% oleum
3. Liquid SO_3
4. Chlorosulfonic acid
5. Diethyl sulfate
6. Dimethyl sulfate
7. Chloro-oleums
8. Liquid sulfur dioxide
9. Sulfamic acid
10. Methane sulfonic acid

Outotec from Germany are suppliers of technology for large size (5,000 tonnes per day (TPD)) sulfuric acid plants and have innovated processes for sulfonation. See Appendix. Outotec have developed the Hero process which should also be considered for sulfonations.

4.2 Detailed Account of Sulfonating Agents

4.2.1 25% Oleum

4.2.1.1 Introduction

Until the mid-1950s all sulfonations were carried out using sulfuric acid of different strengths. The reactions carried out by sulfuric acid were unable to give the conversion efficiencies that were economical, especially in the manufacture of detergents.

N.G. Ashar and K.R. Golwalkar, *A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents*, DOI 10.1007/978-3-319-02042-6_4,

In certain dye intermediates the higher strength sulfuric acid was found to be essential part of the chemical reaction. This led many of the sulfuric acid plants to manufacture "fuming sulfuric acid," popularly known as oleum.

The initial product was in the range 20–25% oleum which meant 20–25% free SO_3 dissolved in sulfuric acid.

4.2.1.2 Technical Considerations

The basic reaction carried out in the oleum tower is absorption of SO_3 in sulfuric acid to form an adduct – $H_2SO_4 + SO_3 = H_2S_2O_7$.

This would correspond to 45% free SO_3 dissolved in sulfuric acid. Since the freezing point of 40–45% oleum is in the range 90–95 °F there is always a possibility of solidification and consequent choking of equipment and pipelines at ambient temperatures, especially in the cold season.

Hence, the industrial preference for manufacturing fuming sulfuric acid was in the range 20–25% free SO_3. This needs removal of exothermic heat of heat of dilution together with heat of absorption of SO_3 by specially designed coolers. Some plants have a gas heated oleum boiler for boiling the 25% oleum to produce pure SO_3 vapor.

4.2.1.3 Manufacturing

The manufacture of oleum is usually carried out in accordance with the block diagram in Chap. 1. The plant gases from the contact sulfuric acid plant (based on sulfur) having an SO_3 strength of 10–12% are first cooled by counter current heat in the cold heat exchanger (CHE) after pass 3. The temperature of gases leaving the CHE will be in the range 270–280 °C and this is further cooled by an economiser for pre-heating the boiler feed water. The cold gases in the range 140–160 °C from the economiser outlet are fed to the oleum tower.

The strength of the oleum is automatically controlled by an indicator-cum-controller to control the flow of sulfuric acid for dilution. This addition is done through an absorption tower so as to prevent any escape of SO_3 fumes from the oleum tower system. The level is controlled through a level controller allowing oleum to be pumped to the storage for cooling.

Besides exothermic heat being generated in the oleum tower, there is a sizeable sensible heat from the plant gases transferred to the oleum since the equilibrium demands the operation of the oleum tower in the range 50–60 °C. Earlier, this cooling was done by trombone coolers with an external water spray made from Shcdule-80M.S pipes. However, the compact plate-type heat exchangers now available are widely used by the industry. Since absorption of the SO_3 in the oleum requires very close temperature control, it is important that cooling of the oleum is done by cooling water supplied from a dedicated cooling tower for the 25% oleum section. Alternatively, for cooling of oleums, special coolers in SS-Alloy construction are available with anodic protection. These are selected purely from economic considerations.

The cold oleum is then dispatched to consumers in tankers with capacities varying from 10 to 20 MT. For special customers, SS-316 tankers are used instead of MS tankers.

4.2.2 65% Oleum

4.2.2.1 Introduction

The demand for higher strength oleums has made it imperative to go for those strengths of oleum which are commercially viable and transportable. As can be observed in Fig. 4.1, the strengths between 30% and 50% are not practical in view of the high freezing points. Hence, it was considered advisable to manufacture oleum having a free SO_3 content of 60–65%.

4.2.2.2 Manufacturing

Initially, 65% oleum was manufactured by addition of 1 tonne of liquid SO_3 to 1 tonne of 28–30% oleum in a mixer with a cooling coil arrangement. This was made in a batch manner and the product was then transferred to storage for sale.

Unlike 25% oleum, 65% oleum can be manufactured only by use of pure SO_3 gas evaporated out of 25% oleum in a boiler heated by energy available in the hot gases of the contact sulfuric acid plant – refer to the block diagram in Chap. 1. The pure SO_3 vapors are sent to the 65% oleum tower with facilities for cooling the heat generated due to exothermic absorption as well as dilution by addition of 25% oleum. A level controller is provided to maintain the tank level in the circulation boot.

The product from the continuous plant manufacturing 65% oleum is sent to storage for dispatch to the consumers in tankers of capacity 10–20 tonnes.

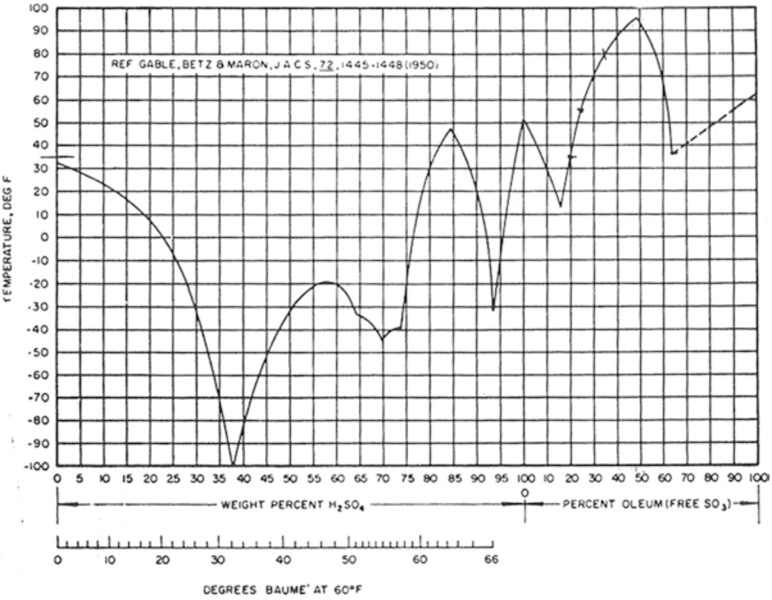


Fig. 4.1 Freezing point of H_2SO_4, oleum, and SO_3

The 65% oleum is transported in SS-316L tankers instead of MS when the iron content in the product is to be kept low.

4.2.2.3 Uses

The demand for 65% oleum is primarily for the manufacture of special dyes and intermediates such as H-acid. As a rule of thumb, 1 tonne of H-acid requires 3 tonnes of 65% oleum.

The 65% oleum is also used directly in other sulfonation reactions.

It is used as a raw material for generating pure SO_3 gas for sulfonation since the handling of liquid SO_3 was considered hazardous and difficult.

4.2.3 Sulfur Trioxide (Liquid or Gas)

4.2.3.1 Introduction

Both 25% and 65% oleum were introduced into chemical processing in search of stronger sulfonating agents. However, with the sulfonation process SO_3 was used and the weak sulfuric acid by-product required disposal as a waste product. Environmental consideration led to large effluent treatment plants (ETPs) with consumption of *lime* in large quantities. As a result, heaps of waste gypsum were formed and posed solid waste disposal problem.

Due to environmental and economic considerations, the use of pure sulfur trioxide in gaseous or liquid form was investigated. The main consideration was to tame the exothermic reaction and avoid unwanted co-products.

In 1960 in India, the production of liquid sulfur trioxide was less than 100 tonnes per annum (TPA). Today there are plants in India which produce more than 100 TPD of liquid or gaseous sulfur trioxide with purity of 99–99.5%. The total production of pure sulfur trioxide in India can be estimated as about 300,000 MTs in the year 2003; 60% of the production is for captive use.

4.2.3.2 Manufacture

The manufacture of liquid or gaseous SO_3 is carried out by boiling 25–32% oleum as in the case of manufacturing 65% oleum. The sulfur trioxide can be liquefied by condensing at 43–45 °C. Care should be taken to prevent any moisture ingress in the plant as it may cause serious operating problems.

The liquefied SO_3 is then taken to a product storage tank from which tankers are filled using intermediate lorry filling tanks.

For any sulfuric acid plant the production of liquid SO_3 is more profitable and hence the objective is to maximize the production of SO_3. Two important considerations for this are as follows:

1. *Mass transfer efficiency*
   Absorption of SO_3 from converter gases in the oleum tower—higher efficiency can be obtained when the strength of the circulating oleum is lower. However, this can lead to lower production rates of SO_3 vapors from the Gas Heat Oleum Boiler (GHOB)/Steam Heated Oleum Boiler (SHOB). Hence, a late innovation to maximize the production of SO_3 is to adopt a twin tower system wherein two oleum

towers operate in series with lean and strong oleum. This is found to be cost effective and enhances overall efficiency above 40%.

2. *Evaporation efficiency*

   The circulating oleum is boiled by the heating medium (plant gases for steam) to produce SO_3 vapors. If the boiling is continued for longer the amount of SO_3 vapor produced per tonne of oleum (fed to the boiler) will be more. However, this can result in a lower strength of the oleum leaving the boiler. Since oleums of strengths below 20% are very corrosive, this situation is to be avoided. Hence, from the practical point of view, the strengths of the oleums are 28–32% at the inlet to the boiler and 22–23% at exit.

The lean oleum from the exit exchanges heat with the incoming strong oleum for preheating before entry into the boiler. It is then further cooled in separate lean oleum coolers before putting it back into the oleum tower for fortification by plant gases.

In a twin-tower system, the first oleum tower operates at 30–35% oleum strength while the second oleum tower, which is in series with the first, operates at 21–24% for further absorption of SO_3 (from the exit gases of the first oleum tower).

4.2.4 Chlorosulfonic Acid

Chlorosulfonic acid [CSA] can be manufactured by using hydrochloric acid and sulfur trioxide and the process varies depending on the mode of raw material available—whether liquid or gaseous. The reaction involved is $SO_3 + HCl = ClSO_2OH$

Depending on the form in which the raw material is available, there are basically three known processes:

1. Monsanto, USA
2. Nissan, Japan
3. DMCC-NEAT, India

4.2.4.1 Monsanto Process

Monsanto developed this process for making chlorosulfonic acid using hydrochloric acid and sulfur trioxide in gaseous form. The gaseous HCl is initially absorbed into chloro-oleum containing 3–4% free SO_3. This is sent to the product tank from which it is dispatched after cooling. The unreacted HCl gases are then absorbed in another tower wherein HCl gas is sucked by a steam ejection system and absorbed in a large body of chloro-oleum containing chlorosulfonic acid and small percentages of SO_3. The exothermic heat of reaction is removed by a heat exchanger. The tail gases and unreacted SO_3 are then scrubbed with water and sent to the effluent treatment plant.

The entire system is under suction. The basic limitation of this process is high sulfate in the product (the general strength available is 98–99%) and a large quantity of effluent containing sulfuric as well as hydrochloric acids.

4.2.4.2 Nissan Process

Nissan independently developed this process using HCl gas obtained from reaction of sulfuric acid with chloride salts and SO_3 gas by boiling oleum.

The basic feature of this process is that the entire construction is in glass lined steel towers providing sufficiently high volume and height. There are a number of towers which ultimately give product CSA produced at a high temperature of 150 °C. The product is then cooled by a glass lined heat exchanger and sent for storage. The unreacted HCl gas is sent to a scrubber which produces a large quantity of liquid effluent. Due to maintaining the temperature of reaction close to the boiling point of chloro, it is claimed that the product has a purity of 99 %.

The entire system is under pressure. The limitation of this process is that the HCl and SO_3 gases are required to be fed at high temperature of about 90–100 °C. Another limitation of this process is that this cannot take gases directly from electrolytic cells producing HCl gas due to the danger of explosion (since a mixture of hydrogen and oxygen is formed after HCl is absorbed). In view of the large volume required, the basic drawback in this process is that the equipment can produce only small tonnage—around 20–30 TPD. For larger capacity, multiple units are required. This would require high capital cost, especially since all the equipment is glass lined or graphite.

4.2.4.3 DMCC-NEAT Process

The DMCC-NEAT process is able to handle HCl gas/liquid and can produce chlorosulfonic acid of 99.9% purity. The basic feature of this process is carrying out the reaction in three steps:

1. Generation of HCl gas, if liquid HCl is available as raw material.
2. Absorption of HCl in chloro-oleum in a polishing tower at very low temperature to produce high strength CSA.
3. Absorption of liquid sulfur trioxide in chloro-oleum to produce high strength chloro-oleum where the latent heat of evaporation of sulfur trioxide is used to control the temperature.

The entire reaction takes place at low temperature and at a controlled rate. The cooling of chloro-oleum is by liquid SO_3. The unreacted HCl gas is scrubbed and recycled to the system, eliminating any liquid effluent. The twin section system for scrubbing the SO_3 gas produces no gaseous effluent. Due to the excess of HCl in the polishing tower, the product is free from any sulfate impurity. Since the solubility of HCl in CSA is very low, the product is of high grade. The advantage of this process is that it is carried out at atmospheric pressure and all the equipment is in Mild Steel (MS) construction and corrosion is minimum due to lower temperatures. A large plant of up to 200 TPD capacity is feasible with this process. It may be of interest to the reader that India is today producing the maximum output of Chloro Sulphonic Acid in the world.

Usages of Chloro Sulphonic Acid

The major consumption of Chloro Sulphonic Acid is for the following:
Detergents
Pharmaceuticals
Dyes and pigments
Ion exchange resins
Miscellaneous

In India the first commercial production started with a 100 TPY plant in the early 1960s. Nevertheless, the production rapidly increased to 1,500 TPY by the late 1960s. During the 1970s the production and consumption kept up with an annual growth rate of 10%. In 1979 the production reached a level of 15,000 TPY. However, the phenomenal growth in consumption during the 1980s has reached a monthly demand level of 4,000 TPM and, with the production being erratic, scarcity conditions prevailed.

Major Producers in India

Sr. No.	Organization
1.	Dharamsi Morarji Chemical Co., Ambarnath, Roha, and Amreli
2.	Andhra Sugar, Hyderabad
3.	Delhi Cloth Mills, Delhi
4.	Shree Sulphurics Limited, Ankleshwar
5.	Udaipur Phosphates, Udaipur
6.	Grasim Industries, Nagda
7.	Rama, Vapi
8.	Aarti, Vapi—Gujarat
9.	Atul Ltd, Valsad—Gujarat

Major producers of CSA out of India have been MONSANTO in USA, BASF in Germany, Akshochem in Netherlands, Nissan in Japan, and Chemiebau in France.

Note that the total active production is about 300 TPD. Hence the total chloro production which can be marketed is only 275–325 TPD and at best can give 80,000–1,00,000 TPY. The major cost factor in production and marketing of CSA is the transport costs. Hence the location of plants situated away from a supply of hydrochloric acid or the consumption market of CSA will be uneconomical. It is, therefore, quite logical that the leading manufacturer of CSA would consider generating additional production capacity in remote areas, unless it is for captive use.

As regards India, the CSA production and supply was a near monopoly of M/s. Dharamsi Morarji Chemical Co. Ltd. situated at Ambernath for over 25 years since 1961. Being a hazardous chemical, CSA was not imported and hence the demand pattern in Indian can be linked with production by DMCC in the 1980s.

However, CSA being a corrosive chemical, production for only 310 days per annum can be expected, despite best maintenance, and hence the gap between the actual production and the capacity will always prevail.

Consumption Pattern – Present Market Assessment

There has been an upsurge of demand for CSA during the last 5 years in India. The consumption pattern has also undergone considerable change since the early 1980s.

A recent survey indicated that world demand of CSA is distributed as follows:

Detergents	40%
Pharmaceuticals	20%
Dyes	15%
Crop protection	10%
Ion exchange resins, plasticizers, and others	15%

Against the above backdrop, **the Consumption Pattern as estimated in India is as follows**:

Consumption pattern		MTs	%
	Shampoos and detergents	20,000	23.3
	Sulfa drugs and saccharin	20,000	23.3
	Vinyl sulphone and its Intermediates	22,000	35.6
	ASC and other derivatives	12,750	14.9
	Pesticides and other uses	11,000	12.9
		85,750	100.0

Based on the above pattern of consumption and capacities already installed, NEAT recommends new CSA plants only on the basis of in-house availability of raw materials, viz., SO_3 and HCl. Hence the recovered HCl or by-product HCl from caustic cells offer a good opportunity to produce value-added chemicals such as CSA.

As regards present consumers, the market is based on export oriented products such as *vinyl sulfones* (VS), *acetyle sulfonyl chloride* (ASC), *para toluene sulfonyl amide* (PTSA), etc.

Growth in Demand of CSA in India

As regards the CSA demand in India, a continuous rise in demand of approximately 5,000 TPY is observed. This is likely to continue in view of liberalization of the Indian economy and export demand for value-added products manufactured using CSA.

It is interesting to note that, apart from the increase in demand, the capacity utilization of CSA will depend on its location, materials of construction, and technology. Hence, the existing plant may not be running with full capacity utilization. It is interesting to note that on 70% utilization there is a gap of almost 8,000 tonnes of CSA. This has resulted in the price rising from Rs. 3,500/tonne to Rs. 5,000/tonne during shortage.

4.2.5 Diethyl Sulfate

Diethyl sulfate (DES) is a highly toxic chemical compound with formula $(C_2H_5)_2SO_4$. It occurs as a colorless liquid with a peppermint odor.

Diethyl sulfate is used as an alkylating agent to prepare ethyl derivatives of phenols, amines, and thiols.

4.2.5.1 Physical and Chemical Properties

Molecular formula	$C_4H_{10}O_4S$
Molecular weight	154.19
Physical state	Viscous liquid
Color	Colorless
Odor	Ethereal odor, peppermint odor
Vapor pressure	2 mmHg at 55 °C
Boiling point	208 °C
Freezing/melting point	−25 °C
Auto ignition temperature(1,502.60 °F)	817 °C
Flash point	104 °C (219.20 °F)
Explosion limits, lower	4.1 vol.%
Solubility in water	Decomposes
Specific gravity/density	1.2000 g/cm^3

Manufacture of DES

DES is best manufactured by using chlorosulfonic acid as sulfonating agent:

$$2C_2H_5OH + ClSO_3OH \rightarrow (C_2H_5)_2SO_4$$

It is important that commercial alcohol 95–96% is first distilled in a packed column to 99.5% and passed through a molecular sieve to make the alcohol bone dry. The reacted mass is then distilled under vacuum in glass lined well stirred vessels to produce DES of international grade.

A modification of the above with lower purity and yield can be achieved with sulfur trioxide being injected in the suction of the circulating pump.

4.2.6 Dimethyl Sulfate

Molecular weight 126.13, $C_2H_6O_4S$

4.2.6.1 Properties

- Colorless, oily liquid
- Boiling point 188 °C (with decomposition)
- Solubility in water: g/100 g = 2.8 at 18 °C
- Density of vapor (air = 1): 4.35
- Flash point °C: 83
- Ignition temperatures °C: 470
- Explosive limits vol.%:
  - Lower 3.6
  - Upper 23.2
- Heat of vaporization at 25 °C: = 92.1 kcal/kg
- Specific gravity at 15 °C: 1.33 (liquid)

- Heat of combustion at constant pressure = 2,863.6 kcal/kg
- Toxicity: a very poisonous and carcinogenic substance:
  - Handling
  - Detection
  - Cleaning/treating the spillage
- Precaution: large quantities of water and dimethyl sulfate (DMS) must not be allowed to come into contact in an uncontrolled manner: the acid and heat produced during hydrolysis may result in a *continuously increasing speed of reaction*. In addition, the acid attacks iron containers, and a substantial build-up of hydrogen pressure may result.

4.2.6.2 Manufacture of DMS

Dimethyl sulfate is manufactured by sulfonation of dimethyl ether. Liquid sulfur trioxide is fed by a metering pump to a reactor to which methanol is added through a catalytic converter as dimethyl ether.

Crude DMS is further treated in a converter wherein the reaction is completed. This is then fed to a series of distillation kettles operating under vacuum. The vapors are condensed and the product DMS is transferred to day tanks wherein the quality is checked and sent to storage by gravity. The product is then filled into drums for dispatch to the consumers.

It is important to note that DMS is a very poisonous chemical and has a threshold limit value (TLV) of 1 ppm. The manufacturing process (though seemingly very simple) requires expertise and knowledge of handling DMS, especially during unforeseen breakdowns.

In India there are two major manufacturers of DMS producing about 80–100 TPD. A substantial quantity of this product is exported to various countries of the world.

4.2.6.3 Typical Values for Raw Materials and Utilities Consumption per MT of DMS

Sulfur when supplied as liquid SO_3	0.30–0.35 MT
Methanol (100% basis)	600–650 kg
Power	150–200 kWh
Steam at 14 kg/cm^2	1,500–2,000 kg
Fuel oil (if adequate steam is not available)	150–200 L

4.2.7 Chloro-Oleum

4.2.7.1 Introduction

It has been generally observed that for chlorosulfonation, excess chlorosulfonic acid is generally used to obtain better yields. HCl gas is evolved during the first phase of the reaction, which needs to be scrubbed. It can then be recycled as dilute HCl into the CSA plant. However, many of the consumers of CSA are far away from the CSA manufacturing plants. In view of this, in-situ conversion of HCl gas back to CSA has been considered economically viable. Chloro-oleum is a mixture of CSA and liquid SO_3. Since the reaction is exothermic, adequate cooling facility will be provided whenever chloro-oleum is used.

4.2.7.2 Manufacture of Chloro-Oleum

Chloro-oleum is manufactured by absorption of SO_3 in chlorosulfonic acid with intermediate cooling between the absorption towers. The chloro-oleum is marketed in various grades depending on the specific requirement by the consumer. The most popular strengths are 20–25% free SO_3 and 15–20% free SO_3.

4.2.7.3 Grades of Chloro-Oleum Marketed Generally

- Grades:
  - 15–20% free SO_3
  - 20–25% free SO_3
- Uses:
  - Chlorosulfonation of fatty alcohols, toluene, etc.
  - Manufacture of detergents
  - Saccharine
  - Pharmaceuticals
  - Dye intermediates etc.
- Consumptions per MT of chloro-oleum:
  - HCl (as 100% dry HCl gas): 0.313 MT
  - Liquid SO_3: 0.687 MT
  - Makeup water consumption for cooling towers: will depend on site conditions

4.2.7.4 Comparison Between CSA and Chloro-Oleum

	CSA	Chloro-Oleum
Rates of reaction	Slow	Fast
Cooling facilities required	Less	More
MOC of major equipment	MS/MS-GL/SS-316L	MS/MS-GL
Advantages	HCl is evolved which can be recycled to CSA Plant	Reduced CSA consumption Reduced effluent generation
Disadvantages	See “Effluent treatment required” below	Higher cooling capacity required
Safety in use	Easy to control	Temperature can rise quickly during reactions, and hence, more careful control required
By-products/side reaction	Better orientation of sulfonation reactions	More amount of sulfones (which are undesirable) are produced as by-products
Purity of products obtained	Better purity in one-step reaction	Further purification required
Effluent treatment required	If there is no CSA plant nearby, facilities for HCl scrubbing and disposal will have to be provided	No effluent is generated

4.2.8 Liquid Sulfur Dioxide

4.2.8.1 Introduction

Sulfur dioxide is one of the most extensively produced sulfur compound. Irrespective of the source of the sulfur, the first oxidation is in form of sulfur dioxide. Hence it can be called the key chemical for the heavy chemical industry.

Liquid sulfur dioxide expands by about 10% when warmed from 20 °C to 60 °C under pressure. Pure liquid sulfur dioxide is a poor conductor of electricity, but high conductivity solutions of some salts in sulfur dioxide can be made. Liquid sulfur dioxide is only slightly miscible with water.

Sulfur dioxide is extremely stable to heat, even up to 2,000 °C. It is not explosive or flammable in admixture with air. The oxidation of sulfur dioxide by air or pure oxygen is a reaction of great commercial importance and is commonly conducted at 400–700 °C in the presence of a catalyst, e.g., vanadium oxide.

Manufacture of Liquid Sulfur Dioxide

The conventional method of producing sulfur dioxide is by combustion of sulfur followed by absorption–desorption, drying, and cryogenic condensation. This process is capital intensive, hazardous, saddled with corrosion, and involves high utility consumption:

$$S + O_2 \rightarrow SO_2 \qquad \Delta H = -297\,\text{kJ/mol}$$

Molten sulfur at 140 °C is fired in an 8–10 m long furnace using preheated (80 °C) air. The theoretical temperature achieved by the exit gases will depend on percent sulphur dioxide of the exit gases is given in Fig. 4.1. For the production of liquid SO_2 at a high concentration of 16–18%, since the adiabatic temperature in single stage combustion will be high (1,600–1,800 °C), a two-stage combustion system can be used.

Subsequently pure sulfur dioxide is produced by chemical reduction of sulfur trioxide with sulfur. This route is more direct and attractive due to the fact that sulfur trioxide is produced in a sulfuric acid plant. However, hitherto the process used by IG Farben Industrie of Germany under US patents 3,432,263 and 3,455,652 (1966) adds solid or molten sulfur to 25% oleum at 110 °C giving 98.5% SO_2 and 1.5% SO_3. The excess sulfur trioxide is further reacted with solid sulfur in a tower and then traces of sulfur trioxide are removed by absorbing in 98% sulfuric acid prior to compression and condensation.

This process deals with use of liquid sulfur and liquid sulfur trioxide under pressure (8–10 kg/cm^2) to produce pure sulfur dioxide at relatively low temperature without the need for compression or refrigeration.

Thermodynamic and Kinetic Consideration of the Process

It is interesting to note that the highly exothermic sulfur oxidation in a furnace at about 1,000 °C can be carried out at reasonably low temperatures of 50–110 °C in a pressurized reactor. This takes place by the following reaction:

$$\mathrm{S(Liq)} + 2\mathrm{SO_3(Liq)} \rightarrow 3\mathrm{SO_2(Gas)}$$

$$\Delta\mathrm{H} = -7\,\mathrm{kcal/g\ mol}$$

$$\Delta\mathrm{F} = -36.71\,\mathrm{kcal/g\ mol}$$

Since the free energy change is large and negative, the reaction is almost instantaneous. In addition, the reaction generates one additional mole in gaseous form. Thus the pressure of the reactor builds up.

In stoichiometric addition of liquid sulfur trioxide (30–40 °C) to molten sulfur (135–140 °C) under a pressure of 8–10 kg/cm^2, the sulfur dioxide (after cleaning) formed (98–99%) can be liquefied at room temperature. The exothermic heat removal of about 15,625 kcal/tonne of sulfur dioxide produced is achieved by circulating cold water through the jacket.

Since the reaction is instantaneous and complete, the reactor volume is very small. However, 25% oleum is used as a carrier to provide uniform mixing of liquid sulfur trioxide and liquid sulfur. Agitation with a proper mechanical seal is provided to ensure complete reaction.

The increase in molecules of SO_2 by 50% enables a build-up of pressure without use of a compressor. Figure 4.2 gives the condensation temperatures of pure sulfur dioxide at different pressures. This indicates that, if a pressure of 7–8 kg/cm^2 is maintained in the system, the liquefaction can be achieved at ambient temperature using water at 35–40 °C; cooling is required at the rate of 1.12 million kcal/tonne of product.

International Scenario

Fifty years ago the world production of liquid sulfur dioxide was less than 1,00,000 tonnes. Over the past 5 decades the use of sulfur dioxide in petroleum refining as solvent, in the manufacture of paper pulp, in textiles as sulfites, bisulfites, and hydrosulfites, in effective control of fermentation in wine making, and as preservative for fresh fruits and vegetable has increased the demand many fold.

The traditional method of manufacturing liquid sulfur dioxide involved a sulfur burner, SO_2/nitrogen separation, SO_2 compression, and condensation. The process is highly capital intensive and generates a significant amount of by-product that requires disposal.

END USES… Sulfur dioxide, sulfurous acid anhydride, is a non-flammable, colorless gas at normal ambient temperature with a characteristic pungent odor. It is supplied as a water clear liquid-compressed gas with a purity of 99.98%. The commercial grade containing not more than 0.05% moisture is suitable for most applications. It has a boiling point of 14 °F.

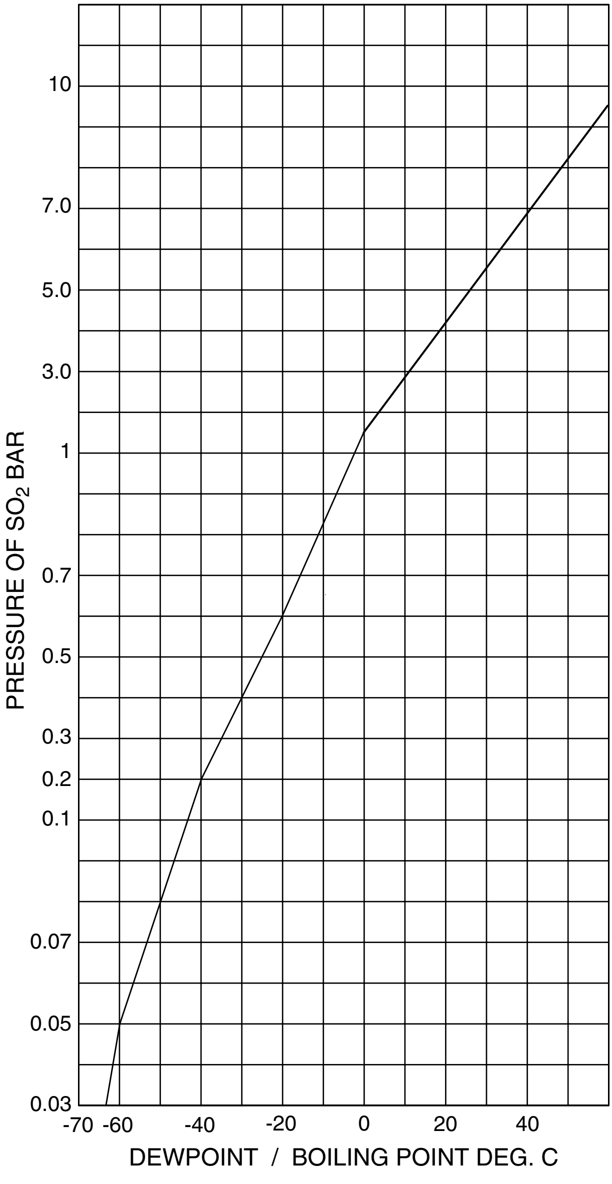


Fig. 4.2 Condensation Temperature of Pure Sulfur Dioxide at Different Pressure

Applications of sulfur dioxide are diverse. It is used:

- To make other chemicals such as bisulfides, metabisulfites, thiosulfides, sulfites, hydrosulfites, and sulfonates.
- To produce dimethyl sulfoxide or thionyl chloride.
- Directly in sulfite pulping in the paper industry.
- In the production of in situ sodium hydrosulfite.

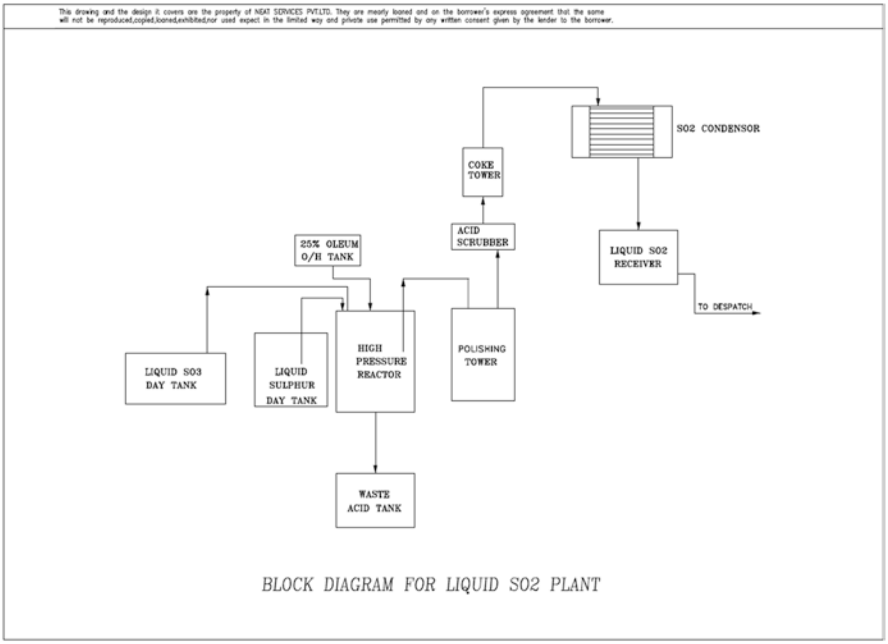
Table 4.1 End use pattern—1999 estimate—merchant market only

Derivative	Percent	Derivative	Percent
Chemical manufacture	40	Agriculture and food	15
Sodium hydrosulfite	20	Water treatment	10
Other chemicals	20	Miscellaneous	10
Pulp and paper	25		

- As a redundant in the production of chlorine dioxide from sodium chlorate.
- To remove excess hydrogen peroxide in the bleaching process.
- In food and agriculture.
- In corn processing to remove the kernel hull for making high fructose corn syrup and ethanol.
- As a sterilant, preservative, and bleach in certain food and beverage products. In water treatment it is used as a chlorine scavenger, reducing free chlorine.
- In waste-water treatment plant discharges.
- In metallurgical processing in the purification of certain elements from their ores, for the recovery of certain elements from mixtures of other materials, and increasingly in the reduction of cyanides in leachate from gold mining.
- In pollution control.
- To reduce hexavalent chromium ions to be more innocent trivalent form for easier disposal (see Table 4.1).

Process Description

Continuous production of liquid sulfur dioxide using liquid sulfur and liquid sulfur trioxide is economically feasible when it is attached to an existing sulfuric acid plant producing oleums and liquid SO_3. A block diagram is given below:



Sulfur trioxide gas is available from the main sulfuric acid plant by boiling oleum. Hot sulfur trioxide is cooled and condensed in an SO_3 condenser and stored in an SO_3 storage tank. Likewise, liquid sulfur is received in a day tank. Molten sulfur and liquid SO_3 are pumped into the reactor at regulated rates using metering pumps. The reactor is initially charged with 25% oleum from the overhead tank.

The temperature of the reaction is maintained by circulation of hot/cold water using vessels and pumps, respectively. The sulfur dioxide gases are then directed to polishing towers in which lumps of solid sulfur react with the unreacted sulfur trioxide. The gases then subsequently pass through a sparger containing sulfuric acid for removal of trace sulfur trioxide. The gases then pass through a demister and a coke tower to remove the acid mist.

Pure sulfur dioxide is then transferred via condensers to receivers. These are then sent to loading tankers from which one-tonne cylinders or road tankers are filled for sale.

Operational Considerations

Condensation and Filling Section

It is important that all the SO_3 gas is absorbed in the sulfuric acid sparger and the sulfuric acid mist is removed by cyclone separator as well as mist eliminator and traces are trapped in the coke tower.

Care should be taken to handle liquid SO_2 under pressure and protective gear must be available for handling liquid SO_2 leakage or SO_2 vapors.

The clean SO_2 gas under a pressure of 7–8 kg/cm^2 enters the condenser through a non-return valve and is condensed by water from the cooling tower. The quantity being condensed can be seen through a look glass and can be stored in liquid SO_2 receivers from whence it will go to the filling tank for filling the cylinders and generally a weighing machine, as per the normal practice of handling liquefied chemical gases under pressure. A scrubbing system for purging is provided which uses alkali.

Simple Precautions to Ensure Safe Operation of the Liquid SO_2 Plant

- Do not allow accumulation of sulfur in the reactor at any time.
- Do not allow the temperature of the reactor go beyond 70 °C at any time.
- The purge system must be tested at least once a day.
- Do not allow ingress of water in any section of the plant that could give any contact with SO_2/SO_3.
- Keep an eye on the pressures, temperatures, and amperes of the electric drives.

Economics

Hitherto, liquid SO_2 has been manufactured by compression and refrigeration using furnace gases by burning sulfur with air in a furnace or by using oleum and sulfur.

Economically, both of the above technologies have inherent handicaps. The capital cost per tonne of liquid SO_2 in the above technologies will be at least two to three times higher than the capital cost required for the process recommended here.

As regards raw material and utilities in both processes, one-third of the cost is common by using sulfur. In the process using 25% oleum there is continuous bleed of oleum producing 99.5% sulfuric acid which may have a low resale value because of its color, and it can be utilized in the manufacture of phosphatic fertilizers only. Whereas, in the process recommended here, the liquid SO_3 will be completely reacted and only occasionally will the reactor have to be drained for removal of unreacted impurities in the sulfur. The cost of sulfur trioxide which will be higher than that of oleum is to be balanced against the saving on interest, depreciation, and maintenance of capital equipment as well as savings on utilities (Fig. 4.3). This cost can be reduced to the cost of sulfur by a novel process under development by NEAT.

Environmental Considerations

Most sulfuric acid plants the world over have the problem of disposal of settled sulfur sludge. Modern plants have a sulfur filter and the filter cake containing 50–70% sulfur is a sludge disposal problem. This can be converted to SO_2 and subsequently converted to 98% sulfuric acid by the process described with minor modifications. NEAT has applied for an international patent for the same.

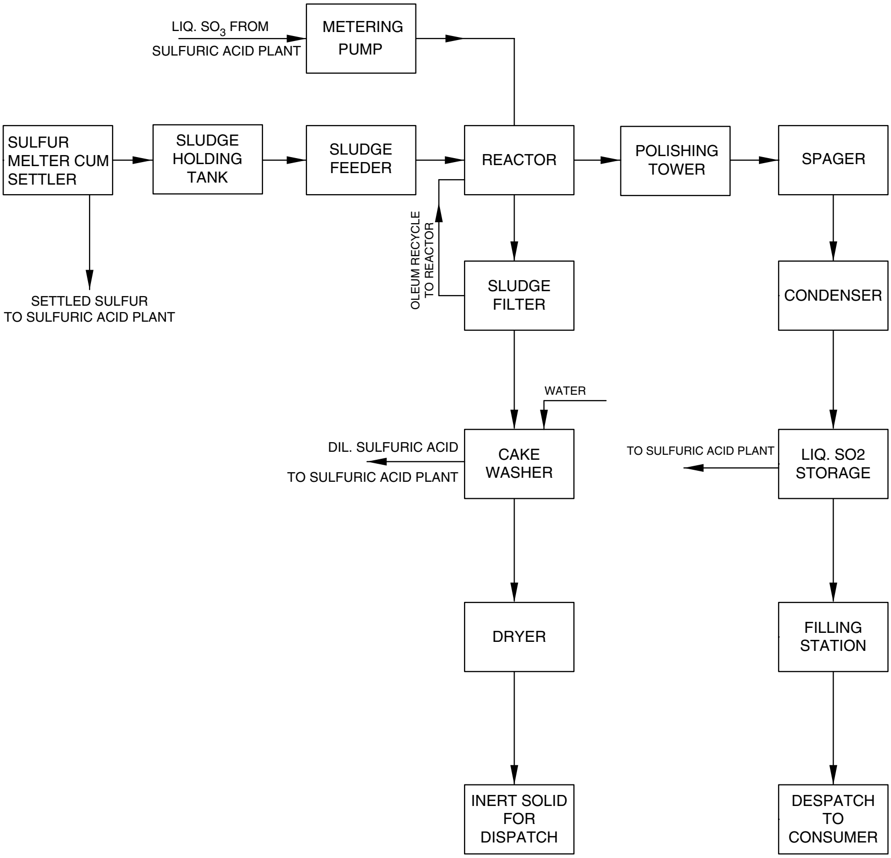


Fig. 4.3 Liq. So_2 from Molten Sulfur Sludge

From environmental considerations the storage of sulfur cake is a fire hazard and a solid waste disposal problem. The *leachate* being acidic creates liquid effluent problems.

It is suggested that the sulfur sludge in a slurry/molten form can be pumped into the reactor and be converted to sulfur dioxide. If there is no market for liquid sulfur dioxide the reactor can operate at moderate pressures and recycle the sulfur dioxide thus produced back to the sulfuric acid plant for conversion to SO_3 and sulfuric acid.

Conclusion

In conclusion, the above is a process using liquid sulfur and liquid SO_3 under pressure for production of liquid SO_2 for merchant sale. We have also attempted to present the solution to the disposal of sulfur cake/sulfur sludge generated in the manufacture of sulfuric acid.

Properties of Sulfur Dioxide

Name	Sulfur dioxide			
Molecular weight	64			
Chemical formula	SO_2			
Appearance	Colorless gas			
Specific gravity	2.264 w.r.t. air			
Solubility (water) (g/L)	185 at 0 °C: 43 at 50 °C			
Melting point (°C)	–75.5			
Boiling point (°C)	–10.0			
Heat of reaction to SO_2 (kJ/kg s) $S + O_2 \rightarrow SO_{2-}$ 9,230 kJ/kg s	–9,230 (base 25 °C)			
Viscosity (Ns/m^2)	20×10^{-6}		28×10^{-6}	
At temperature (°C)	200		400	
Thermal conductivity (W/m °C)	1.16×10^{-2}	1.45×10^{-2}	1.74×10^{-2}	2.33×10^{-2}
At Temperature (°C)	225	350	450	650
Latent heat of fusion (at m.p.)	27.65 kcal/kg			
Density at –10 °C	1.46 g/cm^3			
Latent heat of vaporization (at b.p.)	96.17 kcal/kg			
Standard density at 0 °C (1,013 mb)	2.93 kg/m^3			
Density relative to air (0 °C, 1,013 mb)	2.263			
Specific heat, C_p (1,013 mb):				
0 °C	140.2 kcal/kg			
100 °C	158.37 kcal/kg			
300 °C	180.38 kcal/kg			
500 °C	195.21 kcal/kg			

Innovations/Modifications in the Technology for the Manufacture of Sulphuric Acid

5

5.1 Introduction

As the manufacture of sulfuric acid has increased over the years, plant designers, operators, and maintenance engineers have developed and improved the technology for its manufacture, leading to more efficient plants. These developments are briefly presented as improvements/innovations in process, catalyst, plant equipment, etc.

5.1.1 Improvements in Process

The old chamber process used oxides of nitrogen to oxidize SO_2 to SO_3. This process could not produce higher strengths of the product acid. It was replaced by the contact process where the SO_2 was converted to SO_3 by the platinized asbestos catalyst. The plants running on this process could produce sulfuric acid of 98.5% strength.

The earlier version of this contact process was known as the single contact single absorption process as the SO_2 was passed through the converter to produce SO_3 which was then absorbed in a single absorption tower.

Some of the innovations in this process were as follows. These were aimed at improving the degree of conversion and heat recovery while reducing the initial capital cost and the cost of production:

1. Use of atmospheric cooling ducts for hot gases.
2. Control of gas temperatures by air injections at appropriate places.
3. Control of gas temperatures by use of air pre-heaters (hot gas/air heat exchangers) with simultaneous recovery of heat as hot air.
4. Heat recovery as low pressure steam with use of
   (a) One boiler—only after sulfur burner
   (b) Two boilers—after sulfur burner and after first pass of converter
   (c) Two boilers + economisers—adding an economiser for further heat recovery
   (d) Same as above, while producing high pressure steam

N.G. Ashar and K.R. Golwalkar, *A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents*, DOI 10.1007/978-3-319-02042-6_5,

   (e) HP steam—saturated
   (f) HP steam—superheated
5. Use of the HP steam for power generation directly **or** for steam driven equipment (air blower).

5.1.2 Double Contact Double Absorption DCDA Process with Variants

In the earlier variants of the DCDA process, the SO_2 was converted to SO_3 by catalyst passes and the SO_3 was then absorbed in the inter-pass absorption tower. The gases from the exit of the IPAT were again reheated to about 425–435 °C and subjected to more catalyst passes.

This was done in accordance with the Le Chatelier's principle for increasing the overall degree of conversion achieved.

The process was indicated by the number of catalyst passes preceding the IPAT and following it:

1. (2+2) DCDA two catalyst passes preceding the IPAT and two passes following it.
2. (3+1) DCDA three catalyst passes preceding the IPAT and one pass following it.
3. (3+2) DCDA three catalyst passes preceding the IPAT and two passes following it.

The DCDA process could be operated with a higher percentage SO_2 in the converter inlet gases and thus reduced the gas volumes to be handled. The equipment and gas duct sizes could be reduced, resulting in lower capital cost for the plant.

5.1.3 Use of Progressively Improved Catalysts

1. Nitrogen oxides … in the old chamber process
2. Platinised asbestos … contact process SCSA
3. Vanadium pentoxide based with potassium/sodium compounds as promoters … both SCSA and DCDA process
4. Vanadium pentoxide based with cesium compounds as promoters … both SCSA and DCDA process

   The equilibrium conversion of SO_2 to SO_3 is higher at lower temperatures while the catalyst had an ignition temperature of at least 400–405 °C practical operation. The earlier catalysts were able to achieve a maximum conversion of SO_2 up to 99.5–99.6%.

   Since the cesium promoted catalysts have a lower ignition temperature of 380–385 °C it became possible to achieve up to 99.85% conversion, thus reducing the escape of SO_2 from the stack gases further without use of alkali scrubbing system. It also enabled feeding higher concentrations of SO_2 in the converter inlet gases while still operating below an exit temperature of 610–615 °C for the first pass.

5. Improved shapes of catalyst pellets:
    - Pellets—with sizes of 6–8 mm diameters and 8–12 mm lengths
    - Rings—hollow pellets which had gas contact surfaces inside and on the outer surface for better catalytic action. It was also seen that the converter passes with these catalyst pellets were able to operate without increase in the resistance to the gas flow—thus without increase in the pressure drop on the gas side for a much longer duration.
    - Star/daisy shapes—these have even more surface area and hence better catalytic action.

5.2 Heat Recovery Equipment

Most of the developments in the SCSA process were followed for the DCDA process with provision of WHRB and economisers along with steam superheaters to generate the maximum amount of steam. It was possible to produce power or to run the blower with the turbine running on the HP superheated steam. The exhaust steam was used for process heating—melting of sulfur, evaporation of dilute alum/ phosphoric acid solutions/ for multiple effect evaporators, etc.:

- Waste heat boiler no. 1
- Waste heat boiler no. 2
- Steaming economisers
- Steam superheater

Recent variants have attempted steam generation (as LP steam) or getting hot water from the hot acid circulating in the IPAT and FAT. Generation of LP steam needs very careful process control for the acid concentration to minimize the corrosion of equipment and piping.

Hot water is obtained by cooling the acid by DM water in a closed circuit and the DM water is cooled by process water in another heat exchanger. The heated process water is then used as per need.

A cooling tower can also be provided to cool the process water if there is no continuous need in the plant for the hot water.

In another plant design, the air blower is arranged *downstream* of the drying tower to recover the heat of compression as pre-heated air to the sulfur burning furnace. This, however, required a very efficient acid mist demister in the DT to prevent corrosion of the blower internals.

Innovative heat recovery systems developed by Monsanto known as HRS and by Outotec known as Hero Process or Alfa can be considered.

5.2.1 Use of Alonised Tubes and Candle Demisters

The return gases from IPAT are heated again to ignition temperature of the catalyst in the subsequent pass. The heat required for this was generally obtained from the gases leaving the third pass and entering the IPAT. The heat exchangers were provided with steel tubes which were subject to attack by the acid mist coming from IPAT.

This often reduced the rate of heat transfer or even punctured the tubes, causing process upsets. Hence the tubes were alloyed with aluminum to minimize corrosion which could overcome the process difficulties to a considerable extent.

Stainless steel demister pads were installed after the IPAT in the path of the return gases to arrest the acidic mist particles, but these were not sufficiently efficient.

Later developments of very efficient candle type demisters installed in the IPAT itself enabled use of steel tubes again because the acid mist particles were separated with 99.5–99.9% efficiency.

These however increased the resistance to gas flow, resulting in somewhat more power consumption by the air blower. This disadvantage was offset by the higher sustained heat transfer in the gas-to-gas heat exchangers and the performance of the catalyst in the later passes which is very essential to achieve an overall higher degree of conversion.

5.2.2 Separate Acid Circuits for IPAT, DT, and FAT

A common acid circulation tank (with an acid pump installed) is generally used to circulate acid through all the towers. The strength of the acid becomes lower while passing through the drying tower due to absorption of moisture in the air/wet gases. On the other hand, the concentration of acid increases while passing through the IPAT and FAT due to absorption of SO_3. In most cases, dilution water is added to maintain the acid strength.

It is to be noted that SO_2 is soluble in the acid to a certain extent. Since the conversion of SO_2 to SO_3 is only about 92–95% complete by the time the gases exit the third catalyst pass, the concentration of SO_2 in these gases is about 0.7–1.1% depending on the plant conditions.

A considerable amount of SO_2 therefore dissolves in the circulating acid in IPAT. The acid pump sends the same acid to the FAT.

The gases at the inlet of the FAT contain only about 0.05–0.12% SO_2 *and hence stripping of* SO_2 *can occur from the acid coming down in the FAT.*

The exit gases from the FAT can therefore contain a higher concentration of SO_2 *(0.20–0.25%) which is unacceptable due to the stringent air pollution control laws in all countries. This situation is taken care of by providing separate acid circulation tanks for the FAT (and for DT + IPAT) with appropriate instrumentation for addition of dilution water and level control in both tanks.*

5.3 Innovations/Modifications in Technology

These were made to improve the working of the plant and were based on the experience gained over many years by plant engineers and designers.

5.3.1 Sulfur Melter

Steam coils are installed in the sulfur melting units. Low pressure steam – about 5–6 kg/cm^2 – is supplied to the coils through a pressure regulating valve on the main steam line. It also has a safety valve set to release steam at 6.5–7.0 kg/cm^2. A condensate recovery header is generally provided for all the coils in the melting, settling, and pumping sections of the facility. Condensate from the steam jacketed sulfur feed line to the burner, feed pumps, and sulfur filtration system (wherever provided) is also recovered along with the above. It is then sent to the boiler feed water tank.

Earlier designs used a circular shape for the submerged coils. It was difficult to take out these coils for maintenance or for complete cleaning of the pit during annual shutdowns due to the settled sludge.

Improvements in sulphur melter design:

- Circular coil type design: changed to two vertical pipe headers connected by horizontal pipes.
- Provision of paddle type submerged agitator for faster melting.
- Installing the melter above ground level. This arrangement was found to be better as it minimized exposure of workers to vapors from the melter. An exhaust fan with a collection hood is also provided on the grid where raw sulfur is generally dumped.
- Acid resistant brick lining for sulfur pit walls for increasing the life.
- Provision of steam nozzles for fire fighting in addition to water spray nozzles.

5.3.2 Sulfur Filter

The earlier method for removal of settled muck in the melter involved manual scooping of sludge. Provision of an on-line strainer was not very efficient. Hence it was replaced by filtration of liquid sulfur by pumping it through steam jacketed filters:

1. *Cartridge type*: These were simple on—line strainers having stainless steel screens positioned in a vessel provided in the sulfur feed line to the burner. A bypass line or a parallel standby unit was also arranged. These could become quickly filled up due to their small capacity to hold the sludge, and frequent changeover was necessary.
2. *Pressure leaf type*: These units had a much larger filtration area and capacity to hold sludge. The units had a number of stainless steel filter leaves arranged vertically. These had exit nozzles at the bottoms fixed on a manifold which carried the filtered sulfur outside the vessel.

Safety features like a steam pressure control valve, air vent, side bottom drain, and arrangement to open the unit (for cleaning) either manually or through hydraulic system were provided in later versions.

5.3.3 Sulfur Burning Furnace

Earlier design: Vertical mild steel vessel lined with refractory bricks and having a checker work construction over which the stream of burning liquid sulfur would trickle down. There was always a chance of hot spots due to improper sulfur distribution as well as incomplete combustion. This could cause particles of unburnt sulfur getting carried over to downstream units.

This design was then modified to the horizontal burner with refractory partition walls (with gas passages below and above the walls). The burning of sulfur was considerably better in this.

Provision of tangential air injection from one/more nozzles to the burner further improved the combustion of the sulfur and minimized the formation of pools of liquid sulfur burning directly on the bricks.

Further modifications were the addition of checker work to the horizontal burner with partition walls and use of fire bricks with higher alumina content (45 and 65%).

In order to control the shell temperature, two or more layers of insulating bricks were put between the shell and the fire bricks, especially in locations having high ambient temperatures.

Heat recovery as hot air from the burner shell was also tried successfully by provision of an air cooling jacket on the shell. This also served to limit the metal temperature.

5.3.4 Hot Gas Filter

Variants of the units are as follows:

- A horizontal filtration bed made by graded, screened pieces of fire bricks. The top layer consisted of bigger pieces to prevent disturbance of the lower bed of finer pieces—which is the real filter medium. The bottom layer again consisted of bigger pieces. A gas distributor plate at the gas inlet nozzle further ensured proper distribution of dirty gas over the bed. The beds were provided with cast iron or refractory brick supports and grids.
- A parallel unit was also provided in certain plants for use when the running unit is being cleaned.
- A vertical filtration bed of crushed, screened refractory bricks was held between two concentric screens of stainless steel. The entire bed material could be drained out in a short time in this quick discharge (cartridge type) design.
- The vertical filtration bed consisted of quartz pieces with louvre type supports—which could provide more surface area and use of finer material for higher efficiency dust particle removal.
- It may be noted that the hot gas filters not only minimized deposition of dust particles in the catalyst beds but also increased the heat capacity of the conversion system. In the case of a long plant stoppage, there could be more heat retention in the plant when blinds are inserted in the gas inlet line of the HGF. The unit would also protect the top layer of the first pass catalyst from any soot/unburnt carbon particles during plant start-up (during commissioning or after an annual shutdown.)

5.3.5 Converter

The SO_2 in the gases is converted to SO_3 by the catalytic converter which is then absorbed in a stream of sulfuric acid of optimum concentration and temperature.

Old plants had a three-pass converter which generally could not achieve an overall conversion of more than about 90–93%. This caused a lot of atmospheric pollution due to the escape of unconverted SO_2 as well as higher cost of production due to a greater consumption of sulfur. Besides, the energy efficiency was also low because little effort was made to recover the heat of the reaction:

$$SO_2 + 1/2\,O_2 \rightarrow SO_3$$

Later designs were based on a four-pass converter with inter-pass cooling of the gases. This was able to increase the overall conversion to 96.0–97.5% in the single contact single absorption process. Heat recovery equipment was installed between catalyst passes to improve the energy efficiency.

Modern designs of the DCDA process (*with five catalyst passes*) further improved the overall conversion to 99.0–99.5% with better heat recovery too.

The higher investment required for these plants was offset by reduced cost of production by operating the plants at higher percentage SO_2 to the converter from the current level of 7.5–8.0% to 9.5–11.0%.

The *modified converter designs* have the following features:

1. Loading of catalyst in five passes in an optimized schedule – 16–18% in the first pass, 20–23% in the second, etc. The quantity depends on gas velocity, percentage SO_2 in feed gas, position of IPAT after third or fourth pass, requirement to produce oleum or sulfuric acid or both, etc.
2. Covering the catalyst layers with screened fire brick pieces/quartz to prevent them from getting disturbed due to incoming gases
3. A removable perforated CI gas distribution plate at gas entry to distribute the gases uniformly over the converter cross section.
4. Provision of CI support grids, CI columns, and CI partition plates (with cover of a refractory layer) for the catalyst passes *for smaller capacity plants. Larger plants have dome shaped structures for catalyst supports.*
5. Internal lining of insulating bricks to the converter shell made from steel.
6. A layer of acid resistant bricks in addition to the insulating bricks.
7. Use of cesium promoted catalysts in first and fourth/fifth passes. This would enable the start of conversion at about 385–390 °C earlier than conventional catalysts having an ignition temperature of 410 °C, i.e., faster after any plant stoppage). This will improve the efficiency of conversion to as high as 99.9% instead of the 99.5% offered by DCDA (3 + 1) systems.

This enabled operation of the plant with an increased percentage SO_2 of 9.5–11.0% as the exit temperature of the first pass would still be below 610 °C—at which the catalyst or gas duct life would be reduced.

8. Use of special stainless steel shells instead of mild steel shells for the converter reduced the time required for erection of the plant as no brick lining was provided internally. The special quality stainless steel was considered to have adequate resistance to corrosion.
   The external insulation was done to minimize heat losses.

5.3.6 Heat Exchangers

- Shell and tube type—this was a conventional design. The performance could be affected by the formation of idle gas pockets and the orientation of the incoming and outgoing gas nozzles, which in turn reduced the plant efficiency.
- Disc and donut type—this design has inner tubes placed in baffles which are alternately shaped as disc and donut. The orientation of gas inlet and exit nozzles does not affect the gas distribution as a result (no idle pockets are possible). The pressure drop on both tube and the shell side is lower, thus saving on power consumption by the blower.
- Acid resistant lining is provided at the bottom plate with a suitable drain for the acid condensate, if any.
- Acid resistant ferrules are provided at the gas entry points of the tubes to minimize corrosion of welded joints with tube sheets. Provision was made of expansion bellows for the shell to minimize stress due to thermal expansion.
- Alternatively, gas to gas radial heat exchangers are also used in plant design to reduce overall pressure drop.

5.3.7 Acid Towers

The designs were modified progressively as follows:

- Flat bottomed towers with more than one layer of acid resistant bricks and two such layers on the side walls. The acid outlet nozzle at the bottom was lined with a cast iron pipe which was changed to lining with PTFE pipe.
- Concave bottomed towers were constructed to minimize the deformation of the flat bottoms taking place over years of operation due to the heavy weight of the acid resistant bricks.
- Since the job of brick lining took a long time for laying and curing, steel shells with Teflon PTFE lining is proposed. This can make the tower lighter in weight and reduce the cost of civil foundation.
- Specially shaped packings for tower internals were introduced to improve the gas–liquid contact while reducing the pressure drop in the towers. These were partition rings, raschig rings, intalox saddles, berl saddles, etc., made of ceramic materials.
- Only two or three layers of the partition rings are arranged as the lowest layers and the remaining rings/tower packing are randomly filled in. Care is taken while filling that the rings are not thrown from a height but are slowly introduced. This

is done by putting them in buckets/small containers which are lowered into the towers and then emptied after reaching the bottom.
- The distribution of acid is achieved by cast iron distributors. The latest trend is to use trouble free Saramet/Sx/Zecor acid distributors.
- The current trend is to avoid brick-lined tower and use special alloys such as Sx from Sandvik (Sweden). However, due to the high capital and maintenance costs, these are not yet popular.

5.3.8 Demisters

- Old designs of the plants were provided with quartz beds supported on suitable CI/AR brick grids in a separate vessel after the acid towers. The gases from the exit of DT or FAT would enter from the top and pass below the quartz bed. The exit nozzle was provided at the top of the vessel and hence the gases changed their direction and passed through the bed—which resulted in removal of the acidic mist.
- Stainless steel 316 mesh pads of 150 mm thickness were installed in DT and FAT as an improvement; but this too was not a perfectly efficient arrangement. It was unable to separate acid mists of less than 5 µm particle size from the gas streams.
- This could have damaged the heat exchangers and the catalyst in a DCDA plant and hence it was felt necessary to have very efficient demisters installed in the IPAT. Candle type demisters with specially treated glass fibers/Teflon fibers were developed for this purpose. The phenomenon of separation by Brownian motion as well as impaction is used.
- Modern candles are installed inside the IPAT on a tube sheet which can be fitted with a number of such candles (to reduce the pressure drop on the gas side). The gas flow is generally from the *outside of the candles towards the inside to make use of the larger surface area. An acid separation seal pot is provided below the candle bottom seal plate.*

5.3.9 Alkali Scrubbers

The stringent air pollution control laws in almost all countries have made it essential to provide alkali scrubbers after the FAT to remove the acid mist particles and unconverted SO_2 from the stack gases.

These scrubbers are found to be very useful during plant start-up after any long stoppage (during project commissioning, after annual overhaul, or after any long maintenance breakdown) or when the process is upset—due to excess sulfur feed, disturbed converter temperatures, or a steam leak in the gas stream

The following variants of the alkali scrubbers were used:
- Single stage with spray nozzles.
- Single stage with polypropylene packings.

- Two-stage packed tower (first stage with water as scrubbing liquor and second stage used alkali solution).
- First stage a venturi contactor and the second a packed tower in this design of the scrubber.
- The above [venturi + packed tower] design was preceded by a humidifier section. The packed tower was followed by a demister pad/candle type demister in a separate vessel or in a separate attachment above the packed tower.
- Scrubber exit connected to MS chimney with rubber lining.
- Scrubber exit connected to PP-FRP chimney with a separate MS chimney also. This arrangement had envisaged bypassing the scrubber during normal running of the plant.
- Dynawave (reverse jet) scrubber—designed by Monsanto Enviro Chem.
- Dual alkali process (caustic regeneration) was developed to regenerate the caustic soda content by treatment of the spent scrubbing liquor by lime. This was able to reduce the operating cost as the scrubbing was done by lime indirectly.
- Sulfacid process (active carbon based). The tail gases from FAT exit were treated by activated carbon and then washed with DM water. This was able to reduce the percentage SO_2 % in stack gases while generating a quite dilute (about 6–8%) solution of sulfuric acid. It could not be used fully as dilution water due to the high volumes produced; it also needed regeneration of the activated carbon bed which increased the investment. The pressure drop on gas side was also on the higher side.

5.3.10 Gas and Air Ducts, Bellows, and Butterfly Valves in Sulfuric Acid and Oleum Plants

Air ducts are provided to convey air from the air blower to the drying tower inlet and then from the drying tower to exit to the sulfur burning furnace (which is also used to burn the sulfide ores). The air ducts also convey dry air for injecting into the SO_2 conversion system—either in the gas ducts or through an air injection pipe installed inside the converter.

Operating pressures in the air lines are generally more than in the gas lines while temperatures in the air line are considerably lower (ambient to 65–70 °C). Temperature of the air is higher, say, 100–250 °C if it is preheated before admission to the burner. It could be more only when hot air is being generated with the specific purpose of using it as a drying medium in other process units.

The diameters of the air lines are therefore smaller than the hot ducts in most plants. They are provided with external insulation and cladding in the case of hot air lines. Air lines used for supplying cooling air injection do not need external insulation.

5.3.10.1 Gas Ducts

These are used to convey the SO_2- and SO_3-bearing—generally hot—gases from the waste heat recovery boiler to the converter system (including connections to the hot and cold exchangers, IPAT, and FAT) in a plant running on sulfur as raw material. For those plants which use metal sulfides as raw material, the gas cleaning sections of the plant operate at a lower temperatures. After the clean-up the gases are reheated to the necessary temperatures.

The operating pressures in the gas lines are considerably lower than in the air lines, while the temperatures are much higher (400–600 °C). The diameters of the gas ducts are therefore much larger and hence they need more space and elaborate support structures.

Modern plant designers suggest the use of castable refractories with suitable reinforcement by stainless steel fibers on the inside of the ducts for reducing the metal wall temperatures and to minimize the loss of heat. Layers of insulating material and heat resistant castable (made from high alumina compositions) are provided. Since this can considerably increase the weight of the ducts, the present trend is to use ceramic fiber paper nearest to the metal wall. It is a very light material but capable of substituting the castable insulation.

It is also suggested by certain designers to use stainless steel 316 as the material of construction for certain ducts—e.g., the exit from the first catalyst pass to WHRB # 2 as the temperature is about 600–620 °C and it conveys gases containing SO_2 and SO_3.

5.3.10.2 Flared Ducts

Volume of gases increases with temperature, the plant gases can be as high as 1050 ˚C after the burner and 600 ˚C after the first pass, this increases the volume considerably. These can increase the entrance and exit losses at the nozzles of the equipments at either end of the ducts, resulting in higher pressure drops on the gas side. It is the practice to use flared shapes (slowly expanding) at the connecting points of the nozzles. This reduces the gas velocity as well as improves the gas distribution in the equipment cross section.

5.3.10.3 Expansion Bellows

The high operating temperatures in the gas lines make it necessary to provide expansion bellows in the gas lines to minimize the mechanical stresses that can arise due to thermal expansion (during running of the plants) and contraction (when the plant is stopped). The bellows allow a certain degree of freedom for the expansion/contraction. There is a possibility of reduced life of the ducts, even developing cracks in welded portions, if the bellows are not provided.

Factors that should be considered in the design of expansion bellows are:

1. Diameter (and thickness of metal wall—after considering corrosion allowance) of the duct.
2. Material of construction and the maximum permissible stress.
3. Coefficient of thermal expansion of the material.
4. Operating temperatures—normal, minimum, and maximum.
5. Operating pressures—normal, minimum, and maximum.
6. Gas composition.
7. Length of the duct segment being considered—depends on the plant layout, nozzle orientation of the units at either end of the duct, and space available between units which are connected by the duct under consideration.

8. Expected thermal expansion of the duct (and the likely mechanical stresses).
9. Layout of the duct—whether horizontal, vertical, or inclined.

5.3.10.4 Butterfly Valves

Typical butterfly valves in the earlier designs were of the flanged end connections type. These required thick flanges and gaskets for making leakproof connections. However, gas leakages were observed from the glands due to corrosion of the gland packings by the hot gases. The gas leaks polluted the working areas and were a nuisance.

Improved designs of modern butterfly valves have the following features:

1. A continuous dry air injection in to the gland from the main dry air line coming from drying tower exit. The pressure of dry air is always more than the gas pressure and hence no gas can leak out. Ingress of a very small quantity of dry air cannot cause any process problems.
2. The use of cast iron flaps mounted on SS-316 shafts having square shaped end outside the duct. The operating key fits properly on the square end and does not slip during valve operation.
3. An outside indicator arrow which indicates the exact position of the inner flap.
4. The ends of the valves are welded to the ducts instead of having a flanged connection.

5.3.11 Acid and Oleum Cooling

The circulating streams of acid in the IPAT and FAT need to be cooled before admission to the towers since they get heated while passing through by heat of absorption of SO_3 and heat contained depending upon the specific heat which will be dependent upon its composition mainly on the percentage of SO_2, SO_3, N_2 and O_2 entering the towers.

In the case of the drying tower, the acid stream absorbs moisture from the air and this adds the heat of dilution. However, due to the flow of air at a temperature lower than that of the acid, the resultant temperature of the exit acid stream is only marginally more by about 3–5 °C. This depends on the relative humidity (moisture content in the air) and the air flow rate.

Generally the following are considered to be the optimum temperatures at the inlets of the respective towers.

Drying tower	65–70 °C (lower temp. of 60 °C is better)
IPAT tower	75–80 °C
FAT tower	70–75 °C

If the plant has only one acid circulation tank, then all the exit streams from the towers get mixed. Separate acid pumps or a common acid pump can supply acid to the towers through separate cooling arrangements. These are in the form of trombone coolers (rows and columns of CI pipes over which water spray trickles down) having more cooling area for DT than FAT.

IPAT coolers have more of pipes since more heat is to be removed.

This set-up needed a large area due to the number of pipes; besides, no heat recovery was possible. Part of the trickling water would evaporate and cause a haze in the vicinity on rainy days.

Modern cooling systems use plate heat exchangers which need a much smaller area than the above (only about one quarter). It is possible to get hot water of up to 65–70 °C from the PHE and thus recover heat from the hot acid. This hot water can be used for process work or for heating offices during winter, etc.

An alarm is provided to warn the plant operators of a leak in the PHE. It is based on a sensor which sends a signal if the water stream becomes acidic.

A dual cooling system is a modification of the above which maintains the cooling efficiency. The acid is first cooled by demineralized water in a closed circuit. It is in turn cooled by process water or water from a cooling tower. The heat transfer surfaces remain clean where DM water is being circulated.

In the case of an oleum system, initial cooling is done by process water or by cooling tower water. The oleum is cooled to 47–48 °C in this manner. Further cooling to 42–43 °C is carried out by chilled water. This method is followed at sites where ambient temperatures are high (cooling water not available below 30 °C).

Equipment Required for Manufacture of Sulfuric Acid, Oleum, and Liquid SO_3

6

6.1 Equipment and Facilities Required

The following discusses the major equipment and facilities required for producing commercial grade sulfuric acid from sulfur as the main raw material by the DCDA process. Additional equipment required for producing the acid from sulfide ores is also mentioned. *This list is not exhaustive*.

Some more units may be required depending on the site conditions or the requirements of the manufacturer:

1. **Sulfur receiving, feeding, and burning systems.** Weighbridge for receiving truck loads or liquid sulfur tankers, sulfur melting and settling pit equipped with steam coils, sulfur filter with accessories, sulfur feed pumps, refractory lined sulfur burning furnace equipped with sulfur spray guns.
2. **Waste heat recovery systems.** WHRB # 1 and WHRB # 2, economiser(s), boiler feed water tank and pumps, raw water storage and water treatment plant for soft water/DM water, level controllers for WHRB, etc.
3. **SO2 conversion systems.** Hot gas filter (optional—since sulfur filters will be used) and catalytic converters with internal supports for catalyst of the conventional (potassium promoted) and cesium promoted types.
4. **Hot and cold heat exchangers between the converter passes.** MS welded construction with ERW/seamless tubes having adequate heat transfer area to cool the gases between passes, counter-currently while reheating the gases returning from IPAT.
5. **Dry air supply and SO3 absorption system.** Air blower (s), drying, inter-pass and final absorption towers with internals (candle demisters, tower packings). The towers are of mild steel construction with an acid resistant lining of bricks. They are irrigated with a downward flow of acid. Modern plants use specially designed candle demisters in Teflon fibers or special glass fibers with stainless steel 316L cages having argon arc welding which give a long life compared to wire mesh pads. These candle filters can be the hanging or mounted type. In the hanging type the gas enters from the periphery and leaves from the center which

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provides more area and is more efficient, whereas the mounted type has gas entering from the centre and has less area but requires lower tower height.

6. **Acid circulating and cooling systems.** Acid circulation pumps and tanks, plate heat exchangers, connecting piping, cooling tower, water pumps, etc.
7. **Acid (98.5% technical grade) storage tanks with dyke walls all around. Acid delivery system for sale or for captive use is also installed.**
8. **Air and gas ducting**, with butterfly valves and expansion bellows at appropriate places and exit gas chimney with lightening arrester, aviation warning lamps, etc.
9. **Miscellaneous valves** for sulfur, water, acid, steam, etc.
10. **Sophisticated instrumentation with DCS** (optional) **system** consisting of temperature recorders for furnace, converter passes, heat exchangers, acid streams entering the DT, IPAT, and FAT, acid strength indicator-recorder-controller, level controllers, pressure indicators, air flow indicator.
11. **Alkali scrubbing system** consisting of alkali dissolving tank (if solid flakes are put in), water supply, pH indicator-controller; venturi and packed/spray tower, circulation pumps, demister candle, and fiberglass chimney.
12. **Electrical units.** Transformer (main incoming), metering panel and switch yard, electrical motors, motor control center, cables, starters with remote actuators, lighting systems, etc.
13. **Insulation materials.** Glass/mineral wool, aluminum cladding sheets for gas/hot air, steam lines, hot water, and sulfur lines, WHR systems, heat exchangers, converters, hot gas filters, etc.
14. **Cooling tower** and water pumps for acid cooling.
15. **Steel structurals**, railings, work platforms, ladders.
16. **Emergency power supply.** Diesel generator sets, fuel storage, automatic electrical change over switches, etc.).
17. **Oil/gas firing arrangement** for initial heating of plant units prior to starting sulfur feeding/commencing production.
18. **Process control laboratory apparatus** for gas, sulfur, acid, and water analysis, etc.
19. **Civil foundations** for various units, control room and laboratory, plant stores, and maintenance shed, etc.

6.2 Plant for Producing the Acid from Sulfide Ores – Additional Equipment

1. Ore weighing, feeding, crushing, and screening arrangements.
2. Dust control system for the crushers.
3. Wet electrostatic gas cleaning unit for removing the fine dust, auxiliary electricals.
4. Auxiliary heating system for the gases (for lean gas with low percentage SO_2).
5. Effluent treatment plant for any acidic liquid.

Equipment for handling pure sulfuric acid will be of glass construction/MS-PTFE construction along with glass piping with special supports and PTFE gaskets for the cooling systems. Acid circulation pumps will have Teflon coatings on the internals and will have mechanical shaft seals.

SO_3 vapors will be obtained preferably by heating 65% oleum instead of 25% oleum as it can contain some dissolved SO_2 from the process plant.

Double distilled DM water/steam condensate will be used as dilution water. The plant will be started with bought out battery grade acid for circulation

6.3 Equipment Required for Manufacture of 25% Oleum

The following equipment is also required in addition to the above:

1. Oleum tower with in-built circulation tank (boot) for oleum, and internals. This tower may not be fully lined with AR bricks as higher strength oleum is not very corrosive to steel. However, it is advisable to provide the lining up to the hot gas entry point.
2. Oleum circulation pumps (generally submerged and with mechanical shaft seals).
3. Cooling system for oleum—MS trombone type coolers with water spray falling down on the pipes or plate heat exchangers with special Viton gaskets.
4. Separate cooling tower and water pumps.
5. Oleum strength recorder—controller with feeding system for adding 98% sulfuric acid to the oleum tower boot at a controlled rate through a rotameter.
6. Storage tanks with special breather (irrigated with acid) for vapors.

6.4 Equipment Required for Manufacture of 65% Oleum

The following equipment is **separately** required in addition to the above:

1. Another oleum tower with in-built circulation tank (boot) for oleum, and internals. This tower may not be fully lined with AR bricks as higher strength oleum is not very corrosive to steel. However, it is advisable to provide the lining up to the hot gas entry point.
2. Another set of oleum circulation pumps (generally submerged and with mechanical shaft seals).
3. Another cooling system for oleum—MS trombone type coolers with water spray falling down on the pipes or plate heat exchangers with special Viton gaskets.
4. Separate cooling tower and water pumps.
5. Oleum strength sampling system with feeding system for adding 25–30% oleum to the oleum tower boot at a controlled rate through a rotameter.
6. Storage tanks with special breather (irrigated with acid) for minimizing the escape of SO_3 vapors.
7. A source of liquid SO_3 (SO_3 condenser) or pure SO_3 vapors (25% oleum boiler).

6.5 Equipment Required for Manufacture of Liquid SO_3

1. A 25% oleum boiler—heated either by steam or hot process gases.
2. Heat exchanger for pre-heating oleum feed to the boiler and for cooling the hot depleted oleum from the boiler.
3. Piping for hot oleum—stainless steel 316 is preferred. Sch 80 steel pipes can also be used.
4. SO_3 vapor lines.
5. SO_3 condenser with trickling water films to prevent ingress of water into the liquid SO_3 side as this is very dangerous.
6. Steam tracing arrangements for liquid SO_3 storage tank.
7. Separate cooling tower and water pumps.

7

Materials of Construction of Main Equipments

Glossary

C.I	Cast iron
IBR	Indian Boiler Regulations
CS	Cast steel
MSGL	Mild steel glass lined
MS	Mild steel plates
I.S	2002/2062

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Sr. No.	Equipment/Item	MOC	Remarks
1	*Sulfur pit*	RCC construction	
	AR lining	AR bricks IS:4860-1968 Class-II	To protect RCC due to free acidity in sulfur
2	*Furnace shell*	MS IS:2062 /IS:2002- GR 2A	
	Refractory lining	– Insulating bricks IS:2042-1972	One/two layers
		– Fire bricks IS:8-1983 Type-II or higher grade	High alumina bricks
	Hot gas filter		
A	*Horizontal filter bed*		
	Shell	MS IS:2062, top dome cladding SS321	
	Refractory lining on sides	Insulating bricks IS:2042-1972	
	AR lining at bottom	AR bricks IS:4860-1968 Class-II	
	Filter media	Graded fire bricks pieces **or** quartz pebbles	
	Support for filter media	Cast iron grids and columns	
b	*Cartridge type*		
	Shell	MS IS:2062, top dome cladding SS321	
	Filter media	Graded fire bricks or quartz pebbles	
	Support for filter media	SS-screen backed by MS framework	
3	Converter		
	shell	MS IS:2062, top dome cladding SS321	AR and fire brick arch structure and columns are also used in larger diameter converter
	Internal lining		
	On side	Insulating + acid resistant bricks	
	On partition plates	AR bricks	
	Catalyst support grids and columns	Cast iron	
	Partition plates	Cast iron	
4	Heat exchangers (HHE & CHE)		Modern designs of CHE incorporate and knock out pot for collection of the carried over acid mist. Modern designs of candle mist eliminators are very efficient and are installed in IPAT to minimize carry over of acid mist to down stream units . Thus, the problems due to corrosion are taken care of

	Tubes	A-179 MS seamless, Schedule-40	
	Shell	MS IS:2062	
	Expansion bellows	MS IS:2062	
	Tube sheets	MS IS:2002 Grade 'A'	
5	Acid towers (drying tower/interpass absorption tower) and acid circulation pump tank		
	Shell	MS IS:2062	
	Lining on shell	AR bricks 4860-1968 **Class-I**	One/two layers
	Lining at bottom	AR bricks 4860-1968 **Class-I**	Multiple layers
	Acid inlet and outlet pipes and acid distributor	Pearlitic/AR resistant C.I.	
	Tower packings	AR resistant	Raschig rings, Intalox Saddle, etc.
6	Piping and ducts		
	Air and gas ducts	MS IS:2062	Minimum thickness:
	Acid lines	CI (pearlitic type)/SS316	5 mm for air lines
	Oleum lines	MS Schedule-80/160 Seamless	6 mm for gas ducts
	Raw water	MS	
	Boiler feed water	MS seamless, Schedule-40/Schedule-80	Will be as per IBR or regulatory agencies of the country – corresponding to pressure
	Soft water	GI	
	Sulfur feed lines:		
	Inner pipe	MS seamless Schedule-40 pipes	
	Jacket	MS ERW pipes	
	Steam	MS seamless	As per IBR corresponding to pressure and temperature

(continued)

(continued)

Sr. No.	Equipment/Item	MOC		Remarks		
7	Valves	**Body**	**Plug/flap**	**Rating**		
	Air and gas ducts	MS	MS/SS-316*			*Optional SS-310, 321, 304
	Acid lines	CF8M	SS-316	10 kg/cm^2		Flanged type drilled to ASA150 tables. Wetted parts: Teflon lined
	Oleum lines	SS-316	SS-316	10 kg/cm^2		Flanged type drilled to ASA150 tables
	Raw water	C.I.	C.I.			
	Boiler feed water			As per IBR		
	Soft water	C.I.	C.I.			
	Liquid sulfur	C.I.	C.I.	10 kg/cm^2		With steam jacket
	Steam and boiler mountings					As per IBR
8	Pumps					
		Impeller	Volute	Shaft	Delivery pipe	
	Sulfur	C.I.	MS	MS	MS	
	98% acid	Alloy-20	Alloy-20	SS-316*	C.I.	*Optional Alloy-20
	25% oleum	Alloy-20	Alloy-20	Alloy-20	Alloy-20	
	65% oleum	SS-316	SS-316	SS-316	SS-316	Optional Alloy-20 for all
	Raw water	C.I.	C.I.	GM/MS	MS	
	Boiler feed water					
	Liquor circulation pump for scrubber					Optional Alloy-20. PP is more prone to maintenance problems
9	Heat recovery equipment					
	Waste heat boilers (#1, 2)	Complete construction as per Boiler Regulation Act				
	Economisers	Complete construction as per IBR			C.I. gills on tubes	
	Steam superheaters	Complete construction as per IBR			C.I. gills on tubes	
	Steam de-superheaters	Complete construction as per IBR				

* indicators optional MOC

Materials of Construction (MOC) of Equipment for CSA Plants

Equipments	MOC
Reaction tower	M.S. Acid resistant brick lines or M.S. glass/Teflon lined
Vent scrubber	MS rubber lined
Circulation pumps	SS-316L, Alloy 20 or M.S. Teflon lined
Pipelines	SS 316 L or M.S. glasslined or M.S. Teflon lined
Valves	Cast steel or Teflon sleeved
Gaskets	Teflon

Materials of Construction (MOC) of Equipment for Sulfamic Acid Plants

Equipment	MOC
Reactors	MS
Dissolver	MS glass lined
Crystallizer	SS-316L
Centrifuge	MS rubber lined or SS-316
Vent scrubber	MS rubber lined
Pipelines	MS Sch-80 for oleum
	GI for water
	PP for 70% mother liquor
Valves	Cast steel or Teflon sleeved
Gaskets	CAF for oleum and 70% mother liquor
	Rubber for water

Safety Precautions

8

8.1 Safety Precautions

Always remember that this is a chemical industry handling *corrosive and dangerous chemicals*.

Remain *alert on the job* and follow instructions carefully. If in doubt, always consult the plant manager.

Check that the following are always available:

- Personal safety devices, AR protective dress, gas masks, face shields.
- Fire fighting facilities, water hose pipes, sand and ash buckets.
- Emergency lighting, torches, DG sets, portable ladders, rope ladders.
- Safety showers, eye wash fountains.
- The general guidelines given below are for working in a particular area.
  Oil Firing/Gas Firing for Plant Heating
- Do not smoke near oil tanks or gas pipes.
- Check working of oil temperature thermostat every shift.
- Switch off any motor and remove fuses when carrying out maintenance.

8.2 Precautions

8.2.1 During Start-Up

The main steps involved in start-up of a sulfuric acid plant after a long stoppage are:

1. Boxing up of all equipment opened up for cleaning/maintenance/inspection, etc., testing for leaks, smooth running.
2. Establishing sufficient acid circulation in all the acid towers.
3. Heating up the various units of the plant so as to bring the temperatures of the furnace to a satisfactory level for the burning of sulfur, bringing the catalyst in the converter passes up to conversion temperature, removing moisture from

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various units, ensuring availability of sufficient steam for sulfur melters and pumps, etc.
4. Resuming sulfur feeding.
5. Stabilizing plant operating conditions (acid/oleum strength and temperatures).

After a short stoppage of a few hours, steps 1, 2, and 4 should be taken. Step 3 may not be required since the sulfur burning furnace does not generally cool down below ignition temperature.

8.2.2 During Oil Firing

- Ensure proper air flow first—and satisfactory working of valves in primary/secondary/tertiary airlines.
- Exit must be available for flue gases, air lines—else back firing/exploding of oil vapor may occur.
- Peepholes on furnaces must consist of clean transparent mica/toughened glass.
- Ensure manometer on air lines.
- Flue gases from furnace (after oil firing) should not enter drying tower.
- Oil heater to have proper thermostat (especially in cold ambient conditions) so that oil can be easily atomized on spraying through the oil burning gun.
- Ensure sufficient water level in BFW tank in boilers (after furnace).
- BFW pumps to be in proper working order + standby BFW pump should be available at a moment's notice in case of failure of the running pump.
- NRV in BFW line to boilers.

8.2.3 Sulfur Pit and Sulfur Feeding Section

- Do not walk on cover plates on liquid sulfur chambers.
- Do not smoke.
- Switch off motor and remove fuses when carrying out maintenance.
  On sulfur feed line; pumps, etc.
- Never exceed steam pressure beyond set values on safety valves.

8.2.4 Air Blower

- Do not remove guards from belt drives.
- Do not remove suction screen.
- Do not allow rain/wash water to enter the blower.
- Start with VFD only.
- Switch off motor and remove fuses when carrying out maintenance.

8.2.5 Hot Gas Filter and Converter System

- Always keep a watch if there are any gas leaks from the shell, gas ducts, or loose pressure points. The bypass valve mixing the cooled gases after WHB-I with hot (950–1,000 °C) burner gases causes major maintenance problems if location and operation are not correctly implemented.
- The external surfaces could be hot at some isolated spots if the insulation or cladding has come off. Hence take care while moving around these units.
- It may become necessary to repair/replace a thermocouple. Check whether the pocket for the same is intact or leaking. SO_2/SO_3-bearing gases can come out with pressure from a leaking thermocouple pocket; hence use a gas mask when this job is being done. It is better to stop the plant for a few minutes during this repair/replacement.
- Likewise, the plant may be stopped while attending to a pressure measurement nozzle.

8.2.6 Sulfuric Acid Towers, APTs, Acid Cooler Areas

- Always wear AR dress and face shield while operating in this area.
- Check the pH of cooling water physically (apart from pH meter) to detect any acid leak.
- Provide protective covers on all piping joint flanges—so that acid will not spray out in the case of any gasket damage.
- While testing acid pumps (after completing some maintenance work) always stand at a safe distance, and be ready to switch the pump off immediately if a leak is noticed.
- Switch off a motor and remove fuses when carrying out maintenance.
- Do not step directly on the APT covers when taking out samples of acid or doing any work. Use the cat-walk.
- Completely drain out acid from a pipe before opening. This can be done by loosening the lower bolts of a flanged joint and placing a drum below it. Acid collected in the drum can be transferred/put back in the APT by means of a small portable pump.
- Neutralize any acid spillage by soda ash and then wash with water. Prevent spreading of this water. Collect it and send to ETP.

Only filtered water should be used for acid cooling and it should not contain more than 50 ppm of dissolved solids. Regular blow downs of cooling tower basins are recommended to control the TDS level. Since the presence of chlorides in cooling water makes it corrosive, the acid coolers can be constructed using corrosion resistance materials like Hastelloy C-276.

In arid zones where water is scarce, the cooling towers can be replaced by thermal chilling systems and the chilled water can be retained in a closed cycle of DM water.

8.2.7 Oleum Tower, GHOB, Oleum/Oleum Heat Exchangers, and Oleum PHE

- The guidelines given for **sulfuric acid towers, APTs, and acid cooler areas** are also applicable here.
- Do not spray water directly onto any oleum leak. Absorb it in ash and prevent further spread.
- Collect the ash and neutralize small quantities at a time by taking it to ETP.
- Wash the area by dilute alkali *after all the ash* has been removed. Send the wash water to ETP.
- Do not overheat the oleum in GHOB beyond 135 °C.

8.2.8 Main Storage Areas for Sulfuric Acid, Oleum, and Liquid SO_3

- Always check the levels in all the tanks every shift.
- One tank should always be empty to collect any major leak of acid or oleum.
- Check dyke walls around the tanks every shift.
- Do not step directly on the tank covers for any work. Use the cat-walk.

8.2.9 Waste Heat Recovery Boilers, Economisers, and Boiler Feed Water Pump

This system operates with hot water under high pressure.

- Always open the valves in water lines slowly to avoid water hammer and likely damage to pipes and fittings.
- Boiler blow down valves are to be opened slowly while keeping watch on the water level in the boiler.
- The plant should trip in the case of a low water level in the boiler due to the electrical interconnection provided with air blower–sulfur feed pumps. This should be checked regularly.
- Safety vent valves for high steam pressure should never be tampered with.
- Keep a check on boiler water level and the working of the level controller.

8.2.10 Tail Gas Scrubber

- Make sure the circulation pumps and pH controller are always in working order.
- There should always be adequate stocks of 50% caustic solution available.
- Gas inlet/outlet valves must be in working order.

8.3 Electrical Equipment

- Always switch off the starters and remove the fuses before taking up maintenance work on motors, cables, relays, etc.
- Never enter the HT areas near main transformers or metering panels without proper permission.
- There should be sufficient lighting for boiler water level gauges and areas where acid, oleum, and liquid SO_3/liquid SO_2 are handled.
- See that no acid/oleum can fall on any electrical wires in the case of a leak.

8.3.1 General Precautions

- All railings, work platforms, and staircases should be periodically checked.
- Make sure all connecting pumps, blowers, etc., are switched off (connecting fluid lines for acid, gas, etc., should be blanked), their fuses removed, the vessels are thoroughly flushed, and proper work permits are issued before persons are assigned jobs inside closed vessels, tanks, acid towers, etc.
- All inlets and exits of such vessels must blanked off, cleaning manholes and vents to be opened, and air supply made available by fans or breathing apparatus before persons enter therein.
- Hang warning boards “Men Working Inside”.

8.4 Safety Interlocks

These safety interlocks are suggested to minimize consequences arising from human errors and damage to key/costly equipment.

These are to be provided for automatic tripping of the plant equipment/systems to protect the boilers, to prevent atmospheric pollution, to prevent damage to main air blower, etc. The detailed design of the interlocks should be made as per site conditions, actual plant design, etc.

The working of these safety interlocks should be checked at least once every week and recorded. Any non-functioning link/item should be immediately rectified and working of the interlock re-checked again to ensure plant and environmental safety.

Note: The technology to produce sulfuric acid, oleum, etc. using multi-stage catalytic converters has evolved over six decades and has been perfected for thermally and mechanically stable plants. It is therefore possible to consider digitally controlled systems (without human intervention) to run the plant. With this in view, the following safety interlocks may be considered as a step in that direction.

Safety interlocks for sulfuric acid, oleum, and liquid SO_3 plants:

Condition/situation which warrants a safety interlock	Likely consequences	Automatic interlock/sequence
1. FAT Acid pump failure	Release of unabsorbed SO_3 to the atmosphere	Air blower and sulfur feed pump should trip automatically (air blower first, followed by sulfur pump)
2. Low acid supply to FAT	Release of unabsorbed SO_3 to the atmosphere	Air blower and sulfur pump should trip automatically (air blower first, followed by sulfur pump)
3. FAT alkali scrubber circulation pump failure during plant start-up or after a long shutdown	Release of acid mist, unconverted SO_2 and unabsorbed SO_3 to the atmosphere	Air blower and sulfur pump should trip automatically
4. IPAT acid pump failure	• Loss of acid production • Exposure of demister candles to high temperature gases	Audio-visual alarm to be activated
5. Air blower tripping	Possibility of un-burnt sulfur carry over or explosion in furnace	Sulfur pump to trip automatically
6. Low air pressure at sulfur burner inlet	Possibility of un-burnt sulfur carry over or explosion in furnace	Sulfur pump to trip automatically
7. Very low water level in boilers	Damage to boilers	Air blower and sulfur pump to trip automatically
8. High steam pressure in boilers	Damage to boilers	Safety valves to blow off Air blower and sulfur pump to trip automatically
9. Over-speeding of steam turbine (for air blower/generator)	Damage to drive system	Steam supply to turbine to be cut-off followed by tripping of air blower and sulfur pump
10. A 25% oleum pump failure	• Loss of production of oleum • Likely corrosion of oleum boilers and unlined portion of oleum tower	Audio-visual alarm to be activated
11. Cooling water supply failure to SO_3 condenser	• Loss of production of SO_3 • Possibility of high-pressure in SO_3 condensation system • Release of SO_3 vapors from vent scrubber	Audio-visual alarm to be activated
12. Cooling water supply failure to 65% oleum cooler	• Possibility of high pressure in 65% oleum tower • Release of SO_3 vapors from vent scrubber	Audio-visual alarm to be activated

(continued)

(continued)

Condition/situation which warrants a safety interlock	Likely consequences	Automatic interlock/sequence
13. High pressure in SO_3 vapour line at SO_3 condenser inlet	• High pressure in SO_3 condenser and chance of release of uncondensed SO_3 vapors to atmosphere • Possibility of high pressure in oleum boiler, which can reduce flow rate of feed oleum to oleum boiler • Overheating of tubes, shell and consequent corrosion	Audio-visual alarm to be activated
14. High temperature of 25% oleum (more than 70 °C) at inlet to oleum tower	Damage to oleum piping, pumps, etc.	Audio-visual alarm to be activated
15. Failure of 98% sulfuric acid supply to vent scrubbers attached to 25% oleum system	Release of pure SO_3 vapors to atmosphere causing heavy pollution as well as loss of production	Audio-visual alarm to be activated
16. Failure of scrubbing liquid supply for vent scrubbers attached to 65% oleum system	Release of pure SO_3 vapors to atmosphere causing heavy pollution as well as loss of production	Audio-visual alarm to be activated
17. Failure of scrubbing liquid supply for vent scrubbers attached to SO_3 system	Release of pure SO_3 vapors to atmosphere causing heavy pollution as well as loss of production	Audio-visual alarm to be activated

Notes

- The various audio-visual alarms should be preferably located in the control room where plant personnel are generally present.
- Alternatively, corrective measures can be installed which can be automatically triggered by digitally controlled systems.
- The types of indication (color of light bulb, type of sound emitted by siren/hooters) should be distinguishable from each other.
- Separate panels will be provided for mounting these audio-visual alarms for a sulfuric acid plant, 25% oleum system, 65% oleum system, and liquid SO_3 system for drawing attention immediately to the system where a dangerous situation is likely to develop.

(continued)

Safety interlocks for liquid SO_2 plant:

Condition/situation which warrants a safety interlock	Likely consequences	Automatic interlock/sequence
1. High pressure in the reactor	• Damage to reactor • Possibility of release of pure SO_2 gas	Liquid SO_3 and sulfur pumps to trip simultaneously. Safety valves/rupture disc to be activated
2. High temperature in the reactor	• Possibility of runaway reaction	Liquid SO_3 and sulfur pumps to trip simultaneously. Safety valves/rupture disc to be activated
3. High pressure at inlet to SO_2 condenser	• Damage to condenser • Possibility of release of pure SO_2 gas	Liquid SO_3 and sulfur pumps to trip simultaneously. Safety valves/rupture disc to be activated
4. Failure of cooling water supply to reactor	• Possibility of runaway reaction	Liquid SO_3 and sulfur pumps to trip simultaneously. Safety valves/rupture disc to be activated.
5. Failure of cooling water supply to SO_2 condenser	• Damage to condenser • Possibility of release of pure SO_2 gas	Liquid SO_3 and sulfur pumps to trip simultaneously. Safety valves/rupture disc to be activated
6. High level in oleum or liquid SO_3 day tanks	• Possibility of spillage of these corrosive liquids	Audio-visual alarm to be activated
7. Failure of liquid SO_3 or liquid sulfur metering pumps	• Possibility of production loss • Jamming of reactor internals due to excess sulfur	Audio-visual alarm to be activated
8. Failure of alkali scrubber (either failure of scrubbing liquor circulation or complete consumption of alkali	• Possibility of release of dangerous amount of SO_2 to atmosphere	Audio-visual alarm to be activated
9. Blockage in purge header	• Possibility of plant personnel getting deprived of an important safety arrangement	The purge system must be checked at least once every day. One should not depend on alarms alone

Practical Guidelines/Safety Precautions for Operating a CSA Plant

1. Always keep a watch on pressures in dry HCl gas, SO_3 vapor pipelines. There should always be a slight negative pressure (vacuum).
2. Working of ejector/exhaust system at scrubbers must always be checked.
3. *Temperatures of following streams* should not exceed the values given:
   - Circulating CSA in primary and secondary tower 70 °C (max)
   - Weak sulfuric acid return to sulfuric acid plant 50 °C (max)

- Dry HCl gas …50 °C (max) at inlet to polishing tower
- CSA at outlet of product cooler: 50 °C

Safety Alarms for the Following Situations Should Be Provided

- Failure of supply of 98% sulfuric acid to HCl gas generator.
- High level in weak sulfuric acid tank.
- High pressure in dry HCl gas line to polishing tower.
- Low level in overhead HCl tank.
- Any leakage of trombone cooler for circulating CSA.
- Failure of steam ejector/exhauster for any reason.
- Failure of scrubber circulation pump (leading to SO_3 release).
- High temperature of circulating CSA at inlet of primary/secondary towers.
- High temperature of incoming SO_3 vapors.
- High/low level of CSA in intermediate (day tank).
- High level of CSA in main storage tanks.
- High level of CSA in the chloro-oleum circulation pump tank.

Sulfamic Acid

Alarms to be provided for following situation for safe working of the plant:

- High temperature of reactants.
- Failure of chilled brine supply to primary reactor.
- Failure of cooling water supply to secondary reactor and dilution tank.
- High temperature of hot air.
- Choking of centrifuge.
- Tripping of centrifuge motor.
- High electrical load on agitator motor in reactor.
- Failure of exhaust system/circulating liquor in vent scrubber (can lead to SO_3 release).
- High/low levels in mother liquor collection and recycle tanks.
- Failure of 25% oleum supply pump for overhead tank.
- Failure of urea feeder to overhead silo.
- Failure of star valve for reactor.
- Tripping of vibratory screen for sieving of sulfamic acid crystals.
- Failure of steam/water supply to plant.

Economic Considerations

9

9.1 Introduction

The manufacture of sulfuric acid has become very competitive all over the world due to the availability of large quantities of by-product sulfuric acid from metallurgical plants based on copper pyrites, zinc pyrites, iron pyrites, etc. Moreover, many consumers of sulfuric acid have started using waste sulfuric acid available at a much lower price instead of the fresh acid. The spread of sulfuric acid manufacturing plants has made it uneconomical to transport the acid safely over long distances. It has thus become imperative to explore markets for the acid in nearby areas only. In many countries the plants are located inland away from ports where sulfur is not available locally. The long distances from the ports involved in these countries increases the cost of transportation of sulfur to the plant site. It is customary to use tankers having capacities of 40–60 MT to reduce the cost of transportation. However this increases the risk of leakage during transport. Special regulations are imposed by each country in order to safeguard the surrounding environment.

The price of crude oil can materially affect the transportation/shipment costs of raw sulfur to the manufacturing plants which, in turn, increases the cost of manufacturing sulfuric acid from solid/molten sulfur compared to by-product acid from ferrous/non-ferrous metallurgical plants based on sulfide ores.

9.2 Options Available to Management for Improving Economic Viability

A sulfuric acid plant generally produces technical grade acid. However, plant management can explore the markets for the following products since they can realise much higher prices and they can be produced by "adding on" certain equipment as outlined below. This will improve the financial profitability of the organization.

N.G. Ashar and K.R. Golwalkar, *A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents*, DOI 10.1007/978-3-319-02042-6_9,

9.2.1 Product Mix

- Technical grade sulfuric acid.
- Battery grade/Analytical Reagent grade sulfuric acid: this will need PTFE lined/glass absorption towers, special PTFE lined pumps, glass heat exchangers, etc.
- Electronic grade for manufacture of electronic printed circuit boards.
- 23–25% oleum: an additional absorption tower with oleum circulation pump, trombone type or PHE type oleum coolers, dedicated cooling tower, etc.
- 65% oleum: in addition to the equipment required for the manufacture of 23–25% oleum, this will need a separate absorption tower, oleum circulation pump, cooling system, etc., and facilities for generation of pure SO_3 vapors (by boiling 25% oleum). Certain plants produce 65% oleum by mixing 30% oleum with liquid sulfur trioxide in a controlled manner.
- Liquid sulfur trioxide (SO_3): needs a specially designed water-cooled condenser, a dedicated cooling tower, storage tanks, etc.
- **Liquid sulfur dioxide (SO_2)**: conventional processes for manufacture of liquid sulfur dioxide are based on the burning of sulfur to produce gases with 16–18% SO_2, absorbing the SO_2 in water, stripping it to give moist SO_2 which is, in turn, dried, compressed, and subsequently liquefied by refrigeration. This needs a considerable amount of energy for compression and refrigeration. An innovative process developed and put into operation by NEAT Services Pvt. Ltd., India is based on the direct reaction of elemental sulfur with liquid sulfur trioxide in a specially designed reactor to produce pure dry sulfur dioxide, which can be liquefied by ordinary cooling tower water. This process does not need compression and refrigeration and hence the cost of production of liquid sulfur dioxide is considerably less than the conventional process. NEAT Services have applied for a patent for this process. Four plants based on this process have already been in operation in India for the last 5 years.
- **SO_3 bearing gases for sulfonation**: about 90–95% of the SO_2 fed to the converter is converted to SO_3 by the end of the third pass. The gases exiting from the third-pass thus contain upto 9.8–10% SO_3 and hence can be used for sulfonation of linear alkyl benzene (LAB) for the detergent industry by providing some additional equipments. The unconverted SO_2 can be scrubbed with alkali scrubber after the sulfonation plant.
- **Export of surplus power from the acid plant**: the sulfuric acid plant can generate electrical power by installation of steam turbo generator sets (which can run on the by-product steam produced by the plant itself). The quantity of electrical power generated is generally more than what is required to run the plant and hence the excess power can be used to run other units in the same premises or sold to nearby units.

Either dedicated power lines can be laid for supply of power or a wheeling arrangement can be made with the external grid for transfer of power.

9.2.2 Downstream Products

Some of the products which can be manufactured within the premises or at nearby locations (preferably on adjacent premises) in a profitable manner are listed below. The cost of manufacture of these products can be less because transportation costs for sulfuric acid, steam, etc. will be low. Direct pipelines can be laid from the sulfuric acid plant for conveying acid, steam, treated water, etc. There could also be considerable saving in capital investment due to common infrastructure facilities like the maintenance workshop, weighbridge, storage tanks, etc. Plant management will therefore carry out market surveys for these products:

- Alum (ferric and non-ferric)
- Single super phosphate
- Sodium sulfite and sodium metabisulfite
- Sodium sulfate/Glauber's salt
- Copper sulfate
- Manganese sulfate
- Zinc sulfate
- Ferrous sulfate
- Sodium thiosulfate
- Roll sulfur
- Powdered sulfur
- By-product steam (for sale to neighboring parties)
- Chlorosulfonic acid
- Diethyl sulfate
- Dimethyl sulfate
- Sulfamic acid
- Pulp and paper mill
- **Job work for evaporation of dilute solutions** (based on excess steam available in-house): dilute solutions of chemicals (e.g., from dye intermediate industries, sodium sulfate, etc., can be brought in tanker loads or by pipelines to the site. These can then be evaporated to the required extent in suitably designed evaporators (single- or multi-stage). This job can be done on contract wherein the cost of the evaporators can be shared by the sulfuric acid plant manufacturer and the outside party. It is also easy to determine the steam consumption by measuring the steam condensate produced by the evaporators. The terms and conditions for this type of job work can be negotiated with the outside party on a long-term basis.

9.3 Factors Affecting the Efficient Operation of the Plant

These are purely internal factors related to the operation of the sulfuric acid plant itself.

9.3.1 Conversion Efficiency

The conversion efficiency depends on the converter design, catalyst loading, type of catalyst, timely replacement of inactive catalysts and condition of heat exchangers, operation of absorption system, etc. The sulfur consumption norms per metric tonne of acid produced for different designs of the sulfuric acid plant are as follows:

- Single conversion with single absorption : 340–345 kg.
- Double conversion with double absorption : 330–332 kg.

Thus a significant saving in sulfur can be realized by the DCDA design as compared to the SCSA design. All new plants coming up are therefore of the DCDA design and old plants are being converted from SCSA to DCDA. This has also become mandatory for complying with the pollution control regulations in almost all countries.

9.3.2 Steam Generation, Internal Consumption, and Export of Excess Steam

9.3.2.1 Factors that Steam Generation Depends Upon

- Waste heat recovery system design (provision of waste heat recovery boilers and economisers).
- Quality of water fed to the boilers and working of instrumentation provided on the boilers for level control, etc.
- Collection and recycling of steam condensate to the boiler feed water tank.
- Condition of thermal insulation and cladding provided on gas ducts.
- Working of hot and cold heat exchangers.
- Activity of catalyst especially in the first and second passes.
- Certain modern plants have been designed for heat recovery system (HRS) based on heat recovery from acid coolers.
- Furnace shell temperature: there is more heat loss to the surroundings when the furnace shell temperature is high and this adversely affects the heat recovery by the waste heat boiler. Hence, modern furnaces are designed with optimum thicknesses of insulating and fire brick linings.

9.3.2.2 Internal Consumption of Steam

- This depends on ensuring use of dry powdered sulfur. A moisture content of about 1% in the sulfur increases the steam consumption by about 19%.
- Steam is also consumed in the plant for keeping the sulfur in the settling and pumping sections in a molten state, for heating the sulfur filter jacket, and for keeping the sulfur pumps and feed lines hot.
- Sulfuric acid plants having facilities for producing sulfur trioxide also consume some steam for keeping the liquid SO_3 lines and stores warm by means of steam tracing.

9.3.2.3 Export of Excess Steam

- A sulfuric acid plant generally produces more steam than it can consume internally. The excess steam can be used for generating power or for driving certain equipment like the main air blower, boiler feed water pump, etc., by steam turbines. The turbines could be *condensing, backpressure,* or *extraction* types.
- The steam from backpressure or extraction type turbines can be used in-house for process heating or for export to nearby industries.

9.4 Power Consumption

The power consumption norms are generally as follows:

- 45–50 KWH/MTPD of sulfuric acid (with cooling tower and water treatment).
- 60–65 KWH/MTPD of sulfuric acid (with oleum facility).
- However, the actual power consumption depends on factors such as:
- Percentage of SO_2 in sulfur burner outlet gases (since the overall gas volume depends on this).
- Type of catalyst (whether *ring* type or *pellet* type).
- Gas and air duct sizes.
- Overall pressure drop.
- Heat exchanger designs.
- Internal dimensions and packings used for acid and oleum towers.
- Plant layout.
- Use of steam for driving certain equipment like the main air blower, the boiler feed water pump, etc. Each of these factors needs to be closely looked into in order to minimize power consumption.
- Installation of capacitor banks for improving the power factor.
- Use of Variable Frequency Drives (VFD) for the air blower motor to adjust the blower speed as per the production rate desired.

In the present scenario there is a shortage of power. To circumvent this insufficiency, existing as well as new acid plants should have the provision of cogeneration of power.

9.5 Instrumentation

Accurately working instruments for indicating/recording/controlling the following parameters are essential for safe and efficient operation of sulfuric acid–oleum plants:

- Furnace temperature
- Sulfur dioxide percentage in furnace outlet gases
- Converter temperatures
- Acid concentration
- Oleum concentration
- Ammeters for all electrical drives

- Energy meters for different sections of the plants (for sulfuric acid, oleum, sulfur trioxide, etc.)
- Sulfur dioxide percentage in gases at exit of final absorption tower
- Steam pressure regulator for sulfur melter, sulfur pumps, and feeding system to furnace

All these instruments must have digital indicators and recorders in the control room.

In addition to the above instruments, the plant management may install sulfur flow meters, level indicators for acid and oleum storage tanks, a weighbridge for incoming sulfur supplies, and outgoing products, etc. *Regular monitoring of the instruments will be useful for efficient operation of the plant.*

A data logger for recording, retrieving, and analyzing the readings of the above instruments will be found very useful.

- **There should be a preventive maintenance program for all important equipment in the plant**: This will include:
  - A lubrication schedule for all pumps and motors.
  - Vibration analysis of air blower and pumps.
  - Temperatures and process conditions monitoring for furnace.
  - Heat exchangers and converters.
  - Thickness monitoring of various storage tanks, boiler water analysis.
  - A detailed study of all the breakdowns that have taken place in the past will indicate any changes in the plant operating conditions or the design to be carried out for minimizing breakdowns.
  - An inventory control of all necessary spares: a detailed analysis of the consumption of various spares in the last few years will assist procurement of essential spares in the right quantities. This will enable reduction in the funds blocked for inventory. Long-term relationships may be built with reliable local suppliers of various spares. Lead times (i.e., time required for procuring supplies) for spares to be obtained from outstation vendors may also be looked into and efforts made to minimize.
- **Immediate availability of maintenance crew** whenever the need arises (for an isolated sulfuric acid plant at a remote location it would be advantageous to provide living quarters for essential maintenance technicians at the site itself).
- **Proper safety and start-up procedures should be followed**, especially after annual plant shutdown. This will reduce the quantity of waste acid produced initially (since it is difficult to dispose of this waste blackish dilute acid).
- **Ensuring proper quality and quantity of the product before despatch**. This will minimize controversies arising out of improper quality or short supplies to the customers.
- **Good housekeeping** will ensure safe, accident-free working and better morale of the operating staff.

9.6 Other Important Factors Affecting Economic Viability

9.6.1 Interest on Capital Employed

The initial investment will cover plant and machinery, civil structures (including administration building, stores, and maintenance shed), infrastructure for water treatment, storage tanks for products, storage yard for raw sulfur, road for internal movement, storm water drains, effluent treatment plant, etc. The capital investment will thus depend both on the production capacity planned for each of the products for the present and the future and on the infrastructure required at present and in the future.

9.6.2 Factors Influencing the Cost of Sulfur

1. Quality of sulfur – whether bright yellow or brown sulfur.
2. Distance from the source.
3. Fluctuation of foreign exchange rate vis-à-vis local currency.
4. Transport requirements from the local port to the plant site (cost of unloading from the ship, cost of reloading on the rail/road containers, transport to site, unloading at site, etc.).
5. Cost of inventory at site depending on the time required for obtaining fresh supplies.

9.6.3 Factors Influencing the Cost of Feeding Sulfur to the Plant

- Issue of raw sulfur from the storage yard to the plant melter.
- Cost of melting.
- Cost of filtration: it is found more advantageous to filter the sulfur rather than filter the hot gases since this reduces wear and tear on the sulfur pumps, spray gun, etc.
- Cost of disposal of sulfur sludge.
- Maintenance cost of sulfur melter and steam coils.
- Maintenance cost of sulfur filter and accessories.
- *Note*: *these costs can be reduced if the raw sulfur is available from the supplier in molten form and is transported to the site in insulated tankers.*

9.6.4 Factors Influencing the Cost of Water Treatment

- Cost of raw water.
- Cost of producing soft water (if the heat recovery system consists of low-pressure boilers).

- Cost of producing DM water for boiler feed (if the heat recovery system consists of high-pressure boilers) and acid dilution.
- Cost of feed water treatment for cooling tower.
- Quantity of steam condensate recovered.

9.6.5 Cost of Initial Heating of the Plant Prior to Start-Up

1. *After freshly erected*: slow heating of all units is required to drive off the moisture in the system and to bring the catalyst beds up to ignition temperature. This generally takes 4–6 days.
2. *After annual shutdown*: same as above but generally is done over a shorter period of 36–48 h.
3. *After any long stoppage*: the plant heating by oil firing/gas firing is generally not required if the system temperatures have not fallen too much. The temperatures can be brought up by controlled feeding of sulfur (at low feed rate) while bypassing the heat recovery units as much as possible and circulating a stronger alkali solution in the tail gas scrubber. After the temperatures have come up the sulfur feeding rate is increased and the heat recovery units commissioned as per process conditions.
4. Sulfuric acid plants based on sulfur are auto-thermal in nature. However, if the plant is running on metallurgical ores like iron pyrites, copper and zinc sulfides etc., it occasionally needs additional fuel for maintaining the process conditions because the sulfur dioxide percentage in the gases from the burner is sometimes insufficient for auto-thermal operations.

   Note: *various methods for plant heating are available such as heating by firing of furnace oil, high-speed diesel, liquefied petroleum gas (LPG), natural gas, electrical heating,* etc. *Every effort should be made to minimize the time required for heating the catalyst beds and bringing the process conditions up to optimum.*

9.6.6 Factors Influencing the Cost of Power for Operating the Plant

1. The plant drives (motors) are running on power purchased from external sources.
2. The plant drives (motors) are running on power produced from internal sources, i.e., by installation of steam turbo generators.
3. Some of the plant drives are running on power purchased from external sources and some on steam turbines/power produced internally, e.g., the air blower, boiler feed water pumps, etc., can be run on steam turbines directly while other pumps are run on external power.
4. The type of steam turbine installed, i.e., whether backpressure type or condensing type. This will depend on the use of exhaust steam from the turbine at site.

5. The power supply from the local grid may be erratic, and if captive power generation facilities are not installed then it may become necessary to have a Diesel Generator Set (DG Set) available for emergency power. The operating and maintenance cost of the DG Set is, however, on the higher side.

9.6.7 Cost of Manpower

1. Permanently employed manpower for plant operations.
2. Contract personnel for issue of sulfur, water treatment, general housekeeping, and for annual shutdown jobs.

9.6.8 Cost of Maintenance

The following figures are based on the authors' experience and on information obtained from their clients:

1. About 5–7% of investment for plant and machinery for a new plant.
2. About 10–12% of investment for plant and machinery for an old plant.
3. Annual shutdown costs (for cleaning of sulfur pits, catalyst replacement, acid tower cleaning, etc.) depend on the run and the problems faced by the plant during the year and the need for replacement of any equipment.

9.6.9 Cost of Effluent Treatment

For operation of tail gas scrubbers.

For treatment of liquid effluents like acidic plant washings, disposal of sulfur sludge and acidic liquor from DM water plant, etc.

9.7 Cost of Sale of the Product

The product – sulfuric acid – is generally sold in Mild Steel (MS) tankers. However, certain grades of sulfuric acid (battery grade, analytical reagent grade, etc.) cannot be transported in MS tankers due to the possibility of iron pick-up. These are therefore sold in special containers of HDPE carboys, glass bottles (packed in special wooden crates), PTFE lined vessels, etc. These special methods of packing can increase the cost to the customer, and it is therefore usually agreed that, to reduce the cost, the empty containers will be returned to the manufacturer.

When the product acid/oleum is sold in tanker loads it will be found useful to install calibrated tanks of known capacity for filling the tankers. This will avoid controversy regarding short supplies. It is advisable to keep a sample of the product from each tanker lot and get it analyzed through an independent external agency.

Future Developments

10

10.1 Introduction

The technology for the manufacture of sulfuric acid is well established throughout the world. However, the following areas should continue to be addressed in order to improve the working and, hence, the profitability of these plants.

10.1.1 Design for Improved Plant Operation

- Design for more smooth and accurate plant operation with automatic process control: this will minimize inefficient operation and accidents which may take place due to any mistake on the part of the operating personnel.
- Use of higher concentrations of SO_2 in the sulfur burner exit gases in order to reduce the gas volumes handled (which can also reduce the overall pressure drop).
- Plant design with simplified equipment based on the experience of plant engineers for more than half a century in various plants.

10.1.2 Minimize Breakdowns and Maintenance Costs

The following areas should be addressed in order to minimize the breakdowns and maintenance costs (which maximizes the run time):
- Refractory lining failure
- Acid piping and cooler leakages
- Corrosion of demister pads/failure of candle demisters
- Heat exchanger tube leakages
- Loss of catalyst activity
- Waste heat boiler, economiser, and superheater tube leaks
- Breakdowns of the air blower and its drive system

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- Better materials of construction (MOC) for important equipment like acid towers (MS-PTFE towers and lines), heat exchangers, and converter internals
- Better designs for equipment

10.1.3 Minimizing Pollution

In view of the serious damage to the environment that can result due to acid rain, escape of unconverted SO_2/unabsorbed SO_3, and acid mist from sulfuric acid plants, every effort should be made to minimize pollution.

- Improving conversion of SO_2 with better converter design (fluidized bed converter, use of smaller catalyst particles).
- Better absorption of SO_3.
- Better scrubber designs, especially to take care of heavy pollution loads at start-up of the plant or after a long plant shut down.
- Marketable value added products from spent scrubbing liquor.
- Simpler and cheaper demister designs with reduced pressure drops.
- Unsteady state conversion to eliminate heat exchangers and associated costs.
- Separate acid circulation circuit for final absorption tower to avoid stripping of dissolved SO_2 from the inter-pass absorption tower acid circuit which can occur if a common acid circulation tank is used.

10.1.4 Use of Cheaper Raw Materials

The availability of bright yellow sulfur at low cost is declining all over the world and this is adversely affecting the economy of sulfuric acid plants. Hence, it has become imperative to explore the use of cheaper raw materials. Some of these are as follows:

- Brown sulfur, which can contain organic impurities
- Iron pyrites
- Other sulfur bearing materials—waste acidic sludge, gypsum, spent sulfuric acid itself from certain petroleum refineries

Use of these materials can cause operating problems like reduced life of heat exchanger tubes, masking of active surfaces of catalyst, agglomeration of catalyst particles, and escape of acid mist from the stack exit gases.

Pre-treatment of these materials or very efficient gas cleaning equipments (e.g., wet electrostatic precipitators) can be looked into and their designs improved further from present levels.

10.1.5 Disposal of Wastes Generated

Sulfuric acid plants and downstream units generate certain wastes as follows; these are difficult to reuse/dispose of:

- Sulfur sludge taken out from the melters and sulfur filters during cleaning. Efforts are made to use the sludge for agriculture, as a cheap fuel for brick kilns (this is now banned in most countries), and for recovery of sulfur as SO_2 by burning in metallurgical plants. **NEAT Services propose production of pure SO_2 from the sludge by their own process wherein it is reacted with liquid SO_3. The economics depend on site conditions.**
- Waste catalyst—especially with low residual vanadium pentoxide content.
- Spent scrubbing liquor containing a mixture of dilute solutions of sodium sulfite and sulfate.
- Dilute acid contaminated with various organics, other impurities, etc.
- Disposal of waste liquors containing sulfates of iron, sodium, etc.

10.1.6 Better Instrumentation

Efficient and safe operation of sulfuric acid plants depends on better instrumentation for indication and recording of the following:

- Sulfur feed—flow rate to burner and total amount fed in a given time.
- Air flow to sulfur burner and for injection into conversion system.
- Acid flow to each of the DT, IPAT, and FAT.
- Acid and oleum strength at inlet and exit from acid and oleum towers.
- Generation of HP superheated steam and use in various units in the plant such as turbo-blower/turbo-generator, sulfur melter, filter, and feeding section, as well as excess steam available and used in own premises or actually sold to external clients nearby.

10.1.7 Increased Heat Recovery/Utilization

Sulfuric acid plants are net exporters of energy. Since energy costs are rising worldwide it is imperative to maximize the heat recovery from the plants by addressing the following:

- More steam generation at higher pressure.
- Heat recovery from hot acid as LP steam or as hot water for captive use or for supply to other units in the same premises/nearby units.
- Power generation by use of own steam and sale of excess power after meeting own requirements.
- Better utilization of steam by better control of superheating and de-superheating.

10.1.8 Value Added Downstream Products to Improve Profitability

Since profits from sulfuric acid plants have reduced for a variety of factors, it is necessary to explore possibilities of diversifying the operations for value-added downstream products. Some of these have already been indicated in the chapter on economic considerations.

Efforts have been made to address some of the areas as outlined above in the technology available from the authors, which are as follows:

1. A sulfur filter and two centrifugal pumps are provided for filtering the raw sulfur. Metering pumps are provided to ensure a steady sulfur feed to the burner. This will help in maintaining steady process conditions, very essential for efficient plant operations.
2. The sulfur burner should be lined with insulating bricks and high alumina and very high alumina (60–65%) fire bricks to conserve heat inside and to enable operation of the plant at 10.5–11.0% SO_2 in the burner outlet gases. This will reduce the total volume of the gases handled and in turn will reduce the power consumption per MT of acid produced.
3. A higher (10.5–11.0%) SO_2 gas strength in the burner outlet gases will be possible by use of cesium promoted catalyst. This will also require lower volumes of gases to be handled, thus reducing power consumption.
4. Cesium activated catalyst is used to reduce SO_2 emissions below 200 ppm in the stack gases.
5. The first pass of the converter will have as the upper half (approximately) cesium-based catalyst, which has a low ignition point of 390.0–395.0 °C as compared to 410.0–420.0 °C for the conventional catalyst. This will allow the cooling of the WHB#1 outlet gases by a further 20.0–30.0 °C, thus producing some more steam. Another advantage is the faster pickup of conversion after any plant stoppage.
6. Air injections should be provided at appropriate places in the conversion system for increasing overall conversion.
7. The heat exchangers should have disc and donut types of baffles instead of the usual segmental type. This will result in better gas distribution on the shell side and a lower pressure drop.
8. Gas inlet and outlet nozzles of the equipment should be flared to reduce pressure drop and for better gas distribution.
9. Gas ducting from the first pass to the second WHB will be made of SS-304 to minimize the maintenance problems due to the high temperature at the outlet of the first pass.
10. MS-PTFE lined pipelines can be used (as optional) for acid for maintenance free service as compared to C.I. pipelines in conventional sulfuric acid plant design.
11. PHEs should be used for acid cooling duties to minimize maintenance.
12. A separate acid circuit should be provided for the final absorption tower to minimize SO_2 content in the stack.

13. Teflon candle demisters should be provided in the DT to eliminate the possibility of acid mist carryover, which is a source of corrosion of the downstream equipment.
14. Sophisticated instrumentation with DCS will be provided for the automatic control of the process parameters and for monitoring the exit gas SO_2 concentration. Data loggers should be provided (as an optional facility) for automatic recording of all-important process data, which can be retrieved whenever required.

Cold Process of Manufacturing Sulfuric Acid and Sulfonating Agents

11

[Patented by Navdeep Enviro and Technical Services (NEAT)]

11.1 Introduction

With the increase in cost of refractories, acid proof bricks, special quality mild steel, boiler tubes, alloy steels, etc., an innovative process is emerging in the manufacture of sulfuric acid and sulfonating agents.

This process is primarily aimed at sulfur as raw material. It consists of three steps:

1. Production of sulfur dioxide.
2. Conversion of sulfur dioxide to sulfuric acid by:
   (a) Conventional contact (3 + 2 DCDA) process
   (b) Use of pure oxygen under high pressure using an isothermal converter
3. Reaction of liquid sulfur trioxide under pressure with water to produce sulfuric acid.

If all three steps are successfully implemented on a plant scale, it is estimated that capital cost of the resulting sulfuric acid plant will be less than half compared to the current technology of a (3 + 2) DCDA plant of same capacity, will generate more steam at the rate of 1.4–1.5 tonnes per tonne of acid compared to 1.10–1.15 tonnes, the plant would require one-third area in comparison to conventional units, and finally it will have zero emission of sulfur dioxide.

These techniques are under development and plant scale production will be possible in the next 2–3 years.

11.2 Production of Liquid Sulfur Dioxide Without Compression or Refrigeration

The cold process for manufacturing sulfuric acid is, in turn, based on the cold process for sulfur dioxide. The cold process for sulfur dioxide is described in detail in the Appendix in a paper entitled "Ashar NG (1999) Liquid sulfur dioxide without compression or refrigeration" presented by one of the authors in Calgary (Canada) (1999) at a conference organized by British Sulphur.

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In short, liquid sulfur is reacted with liquid sulfur trioxide in a pressure vessel fed stoichiometrically by metering pumps. The reaction is

$$\mathrm{S} + 2SO_3 \rightarrow 3SO_2 \quad \Delta H = -7\,kcal\,/\,\mathrm{g}\,mol$$

The above reaction is carried out at 45–50 °C and conversion efficiency is 100%.

The sulfur dioxide produced at 5–6 K/cm^2 is then liquefied by water at cooling tower temperatures.

11.3 Conversion of Sulfur Dioxide to Sulfur Trioxide

11.3.1 Conventional Process

In the case that the conventional process of conversion of sulfur dioxide is adopted, the conversion of sulfur to sulfur trioxide as described in Sect. 11.2 can be carried out at a pressure slightly above atmospheric pressure to overcome a pressure drop in conversion and absorption. However, due to the availability of pure sulfur dioxide using a cesium activated catalyst, a higher strength of sulfur trioxide can be produced. This will reduce air flow and lower operating costs.

By-product sulfuric acid due to humidity in air will be in addition to the sulfuric acid produced using liquid sulfur trioxide. Conventional technology will be employed to produce liquid sulfur trioxide by boiling oleum.

Two moles of liquid sulfur trioxide will be recycled to produce sulfur dioxide.

11.3.2 Conversion of Sulfur Dioxide to Sulfur Trioxide with Pure Oxygen Using High Pressure Isothermal Catalytic Converter (Fixed or Fluid Bed)

Since pure sulfur dioxide is available by means of the *cold process*, pure oxygen is an attractive option to produce higher strength pure sulfur trioxide.

Pure sulfur dioxide is used as follows:

$$3SO_2 + 1\tfrac{1}{2}\mathrm{O}_2 \rightarrow 3SO_3$$

Two moles of liquid sulfur trioxide will be recycled to produce sulfur dioxide as described in Sect. 11.2.

If successful, this will be an innovative and impactful contribution that avoids the conventional converter, drying towers, interpass and final absorption towers, heat exchangers, acid coolers, etc.

11.3.2.1 Production of Sulfuric Acid Using Liquid Sulfur Trioxide

The cold process can be further extended to produce sulfuric acid as a cold process.

The overall cold process can be summarized as follows:

1. It uses previously proposed processes by one of the authors to convert liquid sulfur to liquid SO_2 and liquid SO_2 to liquid SO_3. Thereby, liquid SO_3 is produced without use of a sulfur furnace.
2. It uses a novel approach to combine SO_3 with water to produce sulfuric acid in which the mixing is done at a much higher pressure than in the conventional approach, leading to a much higher thermal efficiency (more efficient recovery of the energy of reaction) and steam production.
3. It uses the higher pressure steam for beneficial purposes more efficiently (for example for generating electricity using a steam turbine).
4. It uses various novel techniques to recycle residual energy, steam, and sulfuric acid to improve the efficiency of the reaction and the cost of the plant.

The highlight of the cold process proposed is the higher efficiency of recovering the energy of conversion of SO_3 to sulfuric acid with water. Conventional technology cannot fully recover the exothermic heat generated in this process.

Additional salient details of the overall cold process are as follows:

1. The mixing of SO_3 with water is performed at a higher pressure than in conventional plants. Advantage is taken of the lower latent heat of vaporization of water at a higher generating pressure to improve the utilization of the energy of the reaction of conversion of SO_3 to sulfuric acid as indicated in the reaction equation above. In the high pressure mixture, 98% sulfuric acid is kept under agitation and metered quantities of liquid SO_3 and water are injected to produce additional sulfuric acid with cogeneration of high pressure steam.
2. The steam is led to a mist eliminator which recycles sulfuric acid to the high pressure converter to improve further the concentration of the acid.
3. The steam is then led to process requirements or, for example, to generate electricity using a condensing turbine. Other uses of the steam can also be imagined.
4. The condensate is then recycled with makeup DM water for injecting to the high pressure reactor to recover further residual heat.
5. The sulfuric acid thus produced is under high pressure and is sent to a pressure reducer.
6. When 98% H_2SO_4 is sent to a pressure reducer, flash steam at atmospheric pressure is generated which is sent to a mist eliminator and then to deaerate and preheat the DM water in the storage tank. The acid mist is recycled into the pressure reducer tank.
7. The hot acid is then cooled and sent to storage for dispatch.

Apart from the benefits of the high pressure mixing of SO_3 with water to produce sulfuric acid, the proposed cold process for the manufacture of sulfuric acid has also been conceived to avoid the complexity of requiring a sulfur furnace and the related heat recovery system, the multipass static converter, counter current heat exchangers, the interpass absorption tower (IPAT), drying tower (DT), final absorption tower (FAT), mist eliminators, acid coolers, and alkali scrubber. The resulting plant is, as a result, of much lower cost in equipment and land use.

The overall cold process consists of the following stages:

1. Manufacture of liquid SO_2
2. Conversion of SO_2 to SO_3
3. Conversion of SO_3 to sulfuric acid

The third stage of converting liquid SO_3 to sulfuric acid, $SO_3 + H_2O \rightarrow H_2SO_4$, is carried out in a high pressure reactor of special material of construction. Alternatively a jacketed reactor using thermic fluid for cooling can be operated at atmospheric pressure. This stage provides the additional advantage of generating a larger amount of steam, about 1.4–1.5 tonnes per tonne of sulfuric acid produced, as against 1.1–1.15 tonnes per tonne of sulfuric acid produced by the conventional sulfur burning process.

The EPA of the USA has set a standard of 4 kg SO_2 emissions per tonne of sulfuric acid produced and mandated a stack height of 30–50 m from ground level. In urban areas local authorities even insist on a stack height of 100 m. The cold process proposed in this section has zero emission of SO_2 since liquid sulfur trioxide and DM water will be fed by metering pumps, and no exhaust stack needs to be provided.

11.4 Conclusion

As described in Chap. 1 of this book, the world production using sulfur is estimated at 150 million tonnes per year. The allowed emission of sulfur dioxide in the stack based on Environment Protection Agency (EPA) of USA standards, acid rain of about one million tonnes takes place every year. If future sulfuric acid plants are built using the cold process described here, not only will the cost of manufacture be reduced but also more cogeneration of steam as well as zero acid rain can be achieved.

Storage, Handling, and Properties of Sulfur, Sulfuric Acid, Oleum, and Liquid SO_3

12

12.1 Sulfur

12.1.1 Properties of Sulfur

Molecular weight	32.0
Chemical symbol	S
Appearance	
Solid	Rhombic or monoclinic crystals/fine yellow flakes
Available commercially as coarse/fine mixture of broken lumps **or** as granules (as produced after recovering from petroleum refineries)	
Solubility in water	Insoluble
Melting points for the different forms are:	
Rhombic	112.8 °C
Monoclinic	119.0 °C
Boiling point	444.6 °C
Flash point for pure sulfur	188 °C
Ignition point in the atmosphere	250 °C. *This can come down to 170* °C *due to the presence of hydrocarbon impurities*
Specific heat capacity	
Rhombic sulfur	3.63 + 0.0064T K **(range of temp. 273—368 K)**
Monoclinic sulfur	4.38 + 0.0044T K **(range of temp. 368–392 K)**

(continued)

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(continued)

Heat of fusion of sulfur	9.378 kcal/kg
Heat of combustion for the reaction $S + O_2 \dashrightarrow SO_2$	(−)70,900 kcal/kg mol
Ignition temperature for liquid sulfur	Approx. 250 °C
Dust cloud auto ignition temperature	Approx. 190 °C
Specific gravity	
Solid	
Rhombic	2.07
Monoclinic	1.96

12.1.1.1 Storage, Handling, and Safety

A large number of sulfuric acid and oleum plants use elemental sulfur as the main raw material. Liquid sulfur is taken out from the mines and is solidified. It is then made available as solid lumps or powder. Sulfur is also supplied as granules when recovered as elemental sulfur from petroleum refineries (by partial oxidation of H_2S).

It is transported by ships, railway wagons, or road trucks when solid. It is packed in bags of 500 kg or bigger capacity for ease of unloading at point of use and is dumped on grids of the melter (which are equipped with steam coils) either through small hand carts or by bucket loaders.

Care should be taken to avoid dust clouds during handling due to the possibility of fires or explosions. Metallic parts of conveyors and bucket elevators should generally be electrically bonded together and earthed to avoid build-up of static electricity.

Loaders and hand shovels should be of non-sparking materials.

12.1.1.2 Non-compatible Materials

Sulfur should not be stored with along with chlorates, nitrates, or other oxidizing materials, mineral acids, or metal powders.

No naked flames should be present in the sulfur storage area and all electrical wiring and motors should be flame proof. **Hot permits** should be issued by competent and experienced persons before undertaking any cutting or welding activities in such areas.

Solid Sulfur

Solid sulfur can be stored in open yards but it is better stored in covered sheds and protected from rain to avoid formation of acid. Rain water in the sulfur powder can increase steam consumption in the melter.

Solid elemental sulfur is non-toxic. However, persons working at the melters can inhale sulfur dust or vapor present and these can cause irritation to the eyes and mucous membranes of the respiratory tract.

The following exposure limits should not be exceeded.

In dusty condition	10 mg/m^3
If inhaled	5 mg/m^3

Sulfur has a low ignition point (250 °C) and in case of fire it burns with a barely visible blue flame in daylight. Burning sulfur produces SO_2 gas which is very irritating when inhaled, even in small quantities. Sulfur melters are either underground pits lined with AR bricks or above ground vessels. Both are provided with steam heating arrangements—steam coils in the underground melters and jackets for the vessels. The steam pressure maintained in the coils is about 6 kg/cm^2 which is sufficient to produce a satisfactory rate of melting when the sulfur is dry.

Agitators are provided in melters for faster melting of the sulfur if there are chances of the sulfur being damp.

Hydrocarbon impurities in sulfur can generate H_2S gas during melting of the sulfur and this can be very dangerous due to its highly toxic nature. It can also cause fires at the melters.

Hence adequate ventilation must be available at the melters. Vapors and gases should not be allowed to accumulate as there is a possibility of fire or danger to human life.

Exhaust hoods and fans should be provided to minimize such situations.

Fire extinguishers and steam hoses should always be available at the melters. Spraying of water should be minimized in the case of fire as it can produce acidic liquor and corrode steam coils and fittings as well as cause big lumps in the melter.

Liquid Sulfur

Appearance:

Liquid sulfur: light yellow liquid nearer to melting point, i.e., 125 °C.

It is seen to be dark brown and viscous if the temperature is more than 145 °C.

At a temperature greater than 160 °C *it is extremely viscous and cannot be pumped.*

Specific gravity of liquid sulfur:

The specific gravity of liquid sulfur ranges from 1.80 at 125 °C to 1.78 at 145 °C.

It can be stored in mild steel vessels with internal steam coils or with *provision of external jackets for day tanks in the plants.*

Liquid sulfur storage tanks should have filling lines which extend near to the tank bottom and should be vented to the atmosphere. It is better to have two steam-jacketed vent lines.

Tanks and pipes should be electrically earthed. It is necessary to equip storage tanks with steam blanketing to be used in case of fire and preferable to incorporate a high temperature alarm in the upper section of the tank to warn of fires.

Liquid sulfur is transported in insulated tankers with steam jacketing arrangements for the tanker and for the drain valves. Steam is supplied at the point of delivery if solidification has taken place.

The pumps and valves should also be steam jacketed (with separate steam connections for inlet and outlet). This can enable easier detection and repairs of any leakage of the jacketed pipe.

Mild steel can be used as MOC for pipes carrying liquid sulfur and for equipment used for handling sulfur. The inner pipes should be of SCH 80 and outer jacket can be of Class C

However, sulfur can corrode copper, silver, or their alloys and hence the electrical fittings should not be directly exposed to sulfur vapors or dust.

The normal handling temperatures for liquid sulfur are in the range of 125–145 °C which are below the flash point 188 °C of pure liquid sulfur. However the flash-point of relatively impure crude sulfur containing higher levels of hydrocarbons can be lower – up to 170 °C.

The viscosity of liquid sulfur increases rapidly with temperature. It is better to maintain the temperature of liquid sulfur between 125 and 130 °C for ease in pumping. The liquid can be easily sprayed through the nozzles of the spray guns installed in the burners for proper burning. At temperatures above 145–150 °C it becomes difficult to pump and spray. Hence, the steam pressure in the jackets of liquid sulfur lines, valves, pumps, etc., should be controlled at 3.5–4.0 kg/cm^2 by means of a pressure regulator. A safety valve should be provided on the steam supply line and set to blow off (release steam) at 4.8–5.0 kg/cm^2.

12.1.2 Safety

Liquid sulfur can cause severe burns in contact with skin. First aid treatment involves immediate cooling of the affected area from which the sulfur crust should not be removed. Removal of the crust can also peel off part of the skin. A qualified doctor should be consulted for further treatment (*own experience of the author*).

Spillages of liquid sulfur from pipelines can be arrested by spraying with water.

Fires at the melters are extinguished by a steam hose rather than by water spray as the latter can cause acidic liquor in the melter or big solid lumps.

Exhaust fans and a ventilator chimney at the melter can improve the working conditions.

12.1.3 Cleaning of Sulfur Tanks

The level should be brought down to as low as possible by consuming or transferring the molten sulfur inside. The remaining sulfur can then be drained out while spraying water over it to solidify it (whereupon it can be dug out later on).

The residual quantity in the tank/melter should be solidified by gradually putting small amounts of water in a corner and taking it out. Non-sparking tools and shovels must be used.

Fire extinguishers should be readily available and workers provided with gas masks to protect them from the SO_2 and H_2S which can be present.

12.2 Sulfuric Acid

12.2.1 Properties of Sulfuric Acid

Chemical formula	H_2SO_4
Molecular weight	98
Boiling point of …H_2SO_4, H_2O	290 °C
100% H_2SO_4	340 °C (decomposes)

12.2.1.1 Specific Gravities of Sulfuric Acid

Percent strength	Specific gravity
33.4 (battery acid 29° Be)	1.250
77.67 (Glover acid 60° Be)	1.706
93.19 (oil of vitriol 66° Be)	1.835
98.0–98.3 (commercial)	1.840

12.2.1.2 Viscosity of sulfuric Acid

It decreases slightly from 22 Cp to 19 Cp over the usual strengths 90–95% and then increases again to 25 Cp as the strength goes up to 99%.

12.2.2 Storage and Handling

- Sulfuric acid of 98% strength can be stored in mild steel storage tanks when the temperature is below 50 °C. Concentrated (98%) acid reacts with mild steel forming a layer of sulfate which prevents further attack. At temperatures greater than 55 °C the attack by acid increases and mild steel is not suitable.
- The storage tanks should have breather vents with drying agents so that the top layer of the acid does not get diluted.
- The degree of attack on iron and steel is greater with dilute than with concentrated acid. For strengths above 90%, carbon steel or stainless steel can be used for storage vessels.
- Dilute acid can be stored in HDPE carboys/tanks.
- The filling lines to the storage and lines from storage tanks to process should be kept as short as possible.
- Piping layout design should enable gravity flow of the acid to the reactors, to process vessels, etc., so that the pipes can be drained easily. This will be found useful while replacing any leaking pipe or gasket.
- Road tankers should be emptied out at the delivery point by gravity as far as possible.

- Vessels were used earlier to collect small amounts of the acid transferred by air pressure. These were known as acid eggs. An air compressor provided on the acid eggs can transfer acid to a height of 7.0–7.5 m at a pressure of 2.0–2.5 kg/cm^2.

This is not a very safe method due to the chance of acid spray in the case of a leak from the vessel.

12.2.3 Pipelines

- For 96–98% acids, seamless mild steel pipe may be used at temperatures lower than 50 °C. Mild steel PTFE-lined pipes is preferable as it will have a longer life.
- Such pipes can also be used for 77–78% acid.
- Sharp bends in the pipelines should be avoided as more erosion can occur.
- A radius of five times the pipe diameter should be chosen for bends.
- If acid is to be pumped continuously (acid inlet lines of absorption or drying towers) it is preferable to have a low linear velocity of 0.5 m/s in the pipes.
- Stainless steel is attacked by acid of lower strengths and hence is not suitable.
- Cast iron is not attacked by hot acid and hence trombone coolers (rows of CI pipes over which cooling water is sprayed for trickling down) are used for cooling sulfuric acid from 75–80 °C to 55–60 °C in the plants.
- Pipes with screwed connections should not be used due to the chances of leaks from threads. Flanged connections with PTFE or acid resistant compressed asbestos (where permitted) gaskets give better service life.

12.2.4 Pumps

- A standard centrifugal pump with a special mechanical seal is suitable. The mechanical seal should be enclosed.
- Alternatively a glandless pump may be used.
- Submerged pumps are also frequently used to avoid problems from leaks from shaft seals. They should be stored well supported at both ends and all openings should be kept closed when not in use.
- They should be handled very carefully when taking out from or while installing in the acid circulation tanks of the sulfuric acid plant.
- The area around the pumps should be surfaced with acid resistant tiles.

12.2.5 Safety

- Sulfuric acid is a very corrosive and dangerous chemical. The utmost care should be taken when handling it—pumping, filling in tanks, drawing samples, or emptying carboys, etc.
- All operating personnel must use face shields, safety goggles, acid resistant dress/aprons, gloves, and gum boots.

- Safety showers and eye wash fountains must be available at all times in areas where sulfuric acid is handled. These should have dedicated overhead water tanks which are always full of water.
- All flanged pipelines must be properly supported and the flanges should have covers. These pipes should not be installed at heights or directly above steam lines or electrical cables.
- There is a chance of hydrogen generation in the storage tanks due to reaction with the tanks. Purge out all gases from the tank before using a gas cutter or welding torch in order to avoid an explosion.
- An internal plug valve should be provided for the outlet nozzle. This should be remotely operable so that it can be closed if the nozzle leaks and acid starts coming out (*sometimes under pressure*).
- Storage tanks should be cleared every 2 years of the sludge accumulated inside. Wall thickness should be regularly tested by reliable ultrasonic thickness gauges.
- No one should walk on the roof of the storage tank at any time. The roofs should be of the slanting type to prevent accumulation of rain water.

12.3 Oleums

12.3.1 Properties of Oleums

20 % Oleum	
Melting point	(–) 10 °C
Boiling point	142 °C
Specific gravity	1.88 at 40 °C approx.
Specific heat	0.336
Viscosity	39 cp
30% Oleum	
Melting point	19 °C
Boiling point	118 °C
Specific gravity	1.92 at 40 °C approx.
Specific heat	0.337
Viscosity	48 cp
65% Oleum	
Melting point	2 °C
Boiling point	58 °C
Specific gravity	1.97 at 40 °C approx.
Specific heat	0.392
Viscosity	55 cp

12.3.1.1 Specific Gravities of Oleums at 60 °F

Percent strength	Specific gravity
20% Fuming acid (104.5% acid)	1.927
40% Oleum…(109.0% acid)	1.965
65% Oleum…(114.6% acid)	1.990

12.3.2 Storage and Handling

- Boiler quality carbon steel plate is a satisfactory material for construction of tanks, vessels, and pipelines.
- Stainless steels are also suitable and give better life but are more costly.
- Storage tanks for oleums of various strengths should be provided with vent scrubbers having continuous irrigation by sulfuric acid. The scrubbers should be fabricated from stainless steel 316 instead of mild steel or cast iron (*these can become corroded since both acid and oleum can be present*).
- Storage tanks should not be provided with large side manholes because of the risk of leakage. Cleaning nozzles should have full PTFE gaskets at least 6 mm thick and closed by at least 18 mm thick cover plates bolted securely.
- An internal plug valve which can close the outlet nozzle from inside will be found very useful in the event of a leak. This internal valve should have a long spindle which can be operated from the top of the storage tank.
- External ball valves (with flanged ends and PTFE gaskets) which are fitted directly onto the tank nozzles with the facility for remote operation from two different points can also be considered. These should be regularly operated to prevent them from becoming jammed.
- Oleum storage tanks should have magnetic level indicators and high level alarms. The tank should not normally be filled to more than 70% capacity.
- Steam tracing should be provided externally to prevent solidification inside the tanks. It should also be provided for the outlet nozzles and valves. The outer coils should not be in direct contact with the tank, nozzles, etc.
- External insulation and suitable cladding should also be provided. Care should be taken to prevent ingress of rain water in the insulation.
- Steam coils should not be provided internally as any steam leak can cause accidents due to violent reaction with oleum.
- Pressure in the steam line should not exceed 2.5–3.0 kg/cm^2. Pressure regulating and safety valves should be set accordingly.

12.3.3 Cleaning of Tanks

The sludge level building up in the storage tanks should be monitored regularly and the tank should be completely emptied once every 2 to 3 years. Sulfuric acid (98%) should be used for flushing tanks and vessels being used for oleums. No water should be put into the tanks.

If internal cleaning or maintenance work is to be carried out then all the remaining 98% sulfuric acid should also be removed first followed by blowing air into the tank. It should be confirmed that it is safe to enter the storage tank and that sufficient oxygen is available for breathing.

12.3.4 *Pipelines* for Oleums

Pipelines should be made from Mild Steel Schedule 80 pipes, tested to at least 8 kg/cm^2.

'A' or 'B' class pipelines are not suitable.

Flanges—as per ASA 150 Rating at least.

Gaskets for pipes—PTFE gaskets (3–6 mm thick) for handling oleums of strength 25, 30, and 65%.

Cast iron cannot be used in oleum service as it becomes brittle and the pipelines can leak suddenly.

Piping layouts should be simple and designed for liquid velocity not exceeding 0.6 m/s. The number of valves should be kept to a minimum. The lines should be self-draining.

Sharp bends increase turbulence and should be avoided wherever possible. Cast steel plug valves or ball valves with PTFE sleeves and flanged ends should be used.

Centrifugal pumps with special mechanical seals with either reinforced PTFE or ceramic seats are suitable for pumping oleum 25% and 65%.

Parts of instruments/thermowells likely to be in contact with *oleum* should normally be fabricated from stainless steel 316.

12.3.5 Safety

Vents should be provided on all vessels handling oleums.

The vent lines should be dipped into suitable seal pots with 98% sulfuric acid as sealing liquid or scrubbers (irrigated continuously with 98% sulfuric acid) should be connected to the vent lines.

The scrubbers should be of SS-316 construction, with acid resistant tower packings.

Operating temperatures—avoid temperatures lower than 35 °C for 25–30% oleum service.

Provide steam tracing and adequate insulation thereafter to the vessels, pipelines, valves, etc., to prevent solidification of oleums. Steam jackets should be avoided due to danger of steam leaking inside. The steam tracing lines should not directly touch the vessels or pipes as local hot spots can develop.

Concentration of oleum—avoid concentrations below 20% as it is very corrosive. Avoid concentrations in the range of 35–55% as the oleum may solidify at ambient temperature in the pipelines prevalent in many countries.

Spillage—do not spray water on the spilled oleum. Absorb spillage of oleum in fly ash, lime powder, or earth. Then remove the material and wash the area with dilute (5%) alkali and then plenty of water. Send wash water to ETP for neutralizing.

Do not use sawdust as it can be ignited. Always wear gas mask, shields, full length gum boots, and gloves while handling oleums.

Flushing of tanks, pipelines, etc. [for Maintenance purposes]:

Remove residual amounts of oleums as much as possible. Thereafter flush with 98% sulfuric acid followed by water, 5% alkali solution, and finally water again. Keep valves in the vent lines open during this operation.

12.4 Sulfur Trioxide

12.4.1 Properties of Sulfur Trioxide

Molecular weight	80				
Chemical formula	SO_3				
Appearance	Colorless gas/liquid				
Fumes on contact with atmospheric moisture					
Specific gravity	1.88				
Solubility in water	Reacts violently and forms sulfuric acid mist also				
Melting point	16.8 °**C**				
Boiling point	44.8 °**C**				
Specific heat capacity kcal/kg °C	0.646 at 20 °C				
Vapor pressure of liquid SO_3 at temp. °C	27	38	44	49	60
mmHg	300	600	760	1,100	750

Sulfur trioxide is normally kept in the liquid state at a temperature of about 35 °C and ambient pressure.
Commercially available SO3 has a boiling point of 44.5 °C.

12.4.2 Stablisers

Stabilizers in liquid SO_3 are patented inhibitors such as boron compounds, methane sulfonyl chloride, phosphorus oxychloride, and dimethyl sulfate.

12.4.3 Allotropic Forms of Sulfur Trioxide

There exist three solid forms of SO_3 called alpha, beta and gamma. The alpha form is stable while the beta and gamma forms are not stable. The melting point of the alpha form is 62.3 °C, at which temperature the vapor pressure of liquid SO_3 is 2.5 atm.

Forms of SO_3 melting points	°C
Alpha	62.3
Beta	32.5
Gamma	16.8

Liquid SO_3 is relatively stable between 32 and 44.5 °C at 1 atmosphere pressure.

Below 32 °C the beta form starts crystallizing and the danger then exists that the crystals might transform into the alpha form, which cannot be melted without increasing the pressure to 2.5 atm., as noted above.

The stabilizers which are used in liquid SO_3 only serve to prevent the crystallization of the beta form from liquid SO_3 below 32 °C. If the temperature drops further to 16.5 °C, the gamma form will crystallize, although there does not appear to be much danger of the gamma form transforming directly into the alpha form.

12.4.4 Storage and Handling

The following safety facilities should be readily available in all areas where sulfur trioxide is handled or stored:

- Safety showers with dedicated overhead water tanks. The shower should be copious an operate as soon as the affected person stands on the platform.
- Eye wash fountains or other means of washing the eyes with a gentle flow of tap water available from dedicated overhead water tanks.
- Mild steel storage tanks in which SO_3 is stored should be provided with steam tracing and insulation as well as cladding arrangements. The tank and all pipes/valves handling liquid SO_3 should be maintained at 34–38 °C.

Problems due to solidification of SO_3 in pipes and valves can be minimized by this precaution.

All pipelines should be of Sch 80 or stainless steel 316 and only PTFE gaskets of 4–6 mm thickness are to be used in the flanged joints. The flanges should be rated at least 10 kg/cm^2 and be of the welded type (not the screwed type).

Before using confirm that:

- Adequately sized vents are provided on liquid SO_3 storage tanks. These should be connected to scrubbers which are continuously irrigated by sulfuric acid.
- The tanks also have provision to add 98% sulfuric acid and nitrogen gas for flushing out any residual traces of SO_3 before taking up maintenance work.
- All SO_3 tanks are constructed from boiler quality steel and tested hydraulically at a pressure of at least twice the working pressure.
- All welded joints are radiographed.
- A magnetic level indicator, light glass, and sight glass should be provided.
- All nozzles have reinforcements as well as pad plates. Only SCH 80 pipes are used for nozzles.

12.4.5 Safety

Exposure to sulfur trioxide may occur due to leaks in pipes and process equipment. On escaping to the atmosphere, sulfur trioxide reacts with water to form sub-micron particles of sulfuric acid "smoke" which may be sufficiently dense to obscure the source of the leak.

12.4.5.1 Hazards of Sulfur Trioxide

Sulfur trioxide reacts violently with water to form sulfuric acid. Any inhaled SO_3 will react with moisture in the mucous membranes and intensely irritate them.

The eyes and respiratory tract lining can also be adversely affected by the sulfuric acid mist.

Very small concentrations (0.125–0.5 ppm) in the air, if inhaled, may be mildly annoying depending on individual sensitivity. Higher concentrations (2.0–2.5 ppm) are very unpleasant and still higher ones of more than10 ppm become unbearable.

Exposure to high concentrations of sulfuric acid mist (in excess of 100 mg/m^3) can be fatal.

Any leak from a filling or unloading pipeline attached to a road tanker can release SO_3 and form a v on the ground. It will then react violently with any water present, resulting in the production of a large cloud of dense sulfuric acid mist.

The gaseous sulfur trioxide leaking out will continue to produce dense fumes of sulfuric acid from reaction with moisture in the air.

If the local wind velocity is high or luckily not towards populated areas it will be diluted or may not cause a hazardous situation. However, if the air is still or close to an inhabited area, disaster can occur in the form of human casualties. This can happen up to 1 km from the leak spot.

Serious incidents have occurred with the spillage of oleum from tankers or from damaged sight glasses on pipelines carrying liquid SO_3.

Spillage should be contained/absorbed in ash or earth, then neutralized, and finally disposed of to land fill. No water should be sprayed on SO_3 spillage.

Annexures

1.1 Major Sulfuric Acid Plants in India and Abroad

List of sulfuric acid manufacturers in India:

Company	Location
1. Aarti Industries Ltd.	**Vapi, Gujarat**
2. Agro Chem Punjab Ltd.	Chandigarh
3. Albright & Wilson Chemicals (India) Ltd.	**Roha, Maharashtra**
4. Amal Rasayan Ltd.	Ankleshwar, Gujarat
5. Andhra Sugars Ltd.	Warangal, Andhra Pradesh
6. Arochem Silvassa Ltd.	Silvassa
7. Asian Fertiliser Ltd.	Gorakhpur, U.P.
8. Atul Ltd.	**Bulsar, Gujarat**
9. BEC Fertilizers	Bilaspur, Chhattisgarh
10. BEC Fertilizers	Pulgaon, Maharashtra
11. Bengal Chemicals & Pharmaceuticals Ltd.	Kolkata, West Bengal
12. Bharat Fertiliser Industries Ltd.	Wada, Maharashtra
13. Binani Zinc	Kochi, Kerala
14. Birla Cellulosic	**Surat, Gujarat**
15. Century Rayon	Kalyan, Maharashtra
16. Chemtech Acids & Chemicals (P) Ltd.	Kazipally, A.P.
17. Coimbatore Pioneer Fertilizers Ltd.	Coimbatore, Tamilnadu
18. Coromandel Fertilisers Ltd.	**Visakhapatnam, A.P.**
19. Dharamsi Morarji Chemicals Co. Ltd.	**Ambernath, Maharashtra**
20. Dharamsi Morarji Chemicals Co. Ltd.	Kumhari, Madhya Pradesh
21. E.I.D. Parry (India) Ltd.	Ennore, Tamilnadu
22. E.I.D. Parry (India) Ltd.	Ranipet, Tamilnadu
23. East Coast Fertilisers & Chemicals Ltd.	Ganjam, Orissa
24. Fertilisers & Chemicals Travancore Ltd.	**Aambalamedu, Kerala**
25. Fertilisers & Chemicals Travancore Ltd.	Udyogamandal, Kerala
26. Galaxy Surfactants Ltd.	Taloja, Maharashtra
27. Ganges Fertilisers & Chemicals Ltd.	Muzaffarpur, U.P.
28. Godrej Soaps Ltd.	Bharuch, Gujarat
29. Godrej Soaps Ltd.	Mumbai, Maharashtra

(continued)

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Company	Location
30. Gopalanand Rasayan	Tarapur, Maharashtra
31. Grasim Industries Ltd.	**Harihar, Karnataka**
32. Grasim Industries Ltd.	Nagda, Madhya Pradesh
33. Gujarat State Fertilisers Ltd.	**Sikka, Gujarat**
34. Gujarat State Fertilisers Ltd.	Vadodara, Gujarat
35. Guljag Industries Ltd.	**Jodhpur, Rajasthan**
36. Harshvardhan Chemicals & Minerals Ltd.	Indore, Madhya Pradesh
37. High Explosives Factory	Kirkee, Maharashtra
38. Hind Lever Chemicals Ltd.	Haldia, West Bengal
39. Hindustan Copper Ltd.	Ghatsila, Bihar
40. Hindustan Copper Ltd.	**Khetri, Rajasthan**
41. Hindustan Lever Ltd.	Chhindwara, Madhya Pradesh
42. Hindustan Organic Chemicals Ltd.	**Rasayani, Maharashtra**
43. Hindustan Zinc Ltd.	**Chanderiya, Rajasthan**
44. Hindustan Zinc Ltd.	Udaipur, Rajasthan
45. Hindustan Zinc Ltd.	Visakhapatnam, A.P.
46. Hindustan Heavy Chemicals Ltd.	Kolkata, West Bengal
47. Indian Electro Chemicals Ltd.	Ahmedabad, Gujarat
48. Indian Rayon & Industries Ltd.	Veraval, Gujarat
49. Indian Sulfacid Industries Ltd.	Panipat, Haryana
50. Indo Gulf Corporation Ltd. (Birla Copper)	**Bharuch, Gujarat**
51. Jay Shree Chemicals & Fertilisers	**Kolkata, West Bengal**
52. Jay Shree Chemicals & Fertilisers (Unit III)	Pataudi, Haryana
53. Kamar Chemicals & Industries Ltd.	Ranipet, Tamilnadu
54. Keerthi [Bangalore] Ltd.	Bangalore, Karnataka
55. Kesoram Rayon	Kolkata, West Bengal
56. Khaitan Fertilizers Ltd.	Rampur, Uttar Pradesh
57. Khaitan Chemicals & Fertilisers Ltd.	Indore, Madhya Pradesh
58. Kothari Industrial Corporation Ltd.	Ennore, Tamilnadu
59. Krishna Indchem	Visakhapatnam, Andhra Pradesh
60. Mardia Chemicals Ltd.	Surendranagar, Gujarat
61. Mittal Fertilisers Ltd.	Rae Bareli, U.P.
62. Nath Industrial Chemicals Ltd.	**Vapi, Gujarat**
63. Natraj Organics Ltd.	Muzaffarpur, U.P.
64. Navin Fluorine Industries	Surat, Gujarat
65. Nirma Ltd.	Ahmedabad, Gujarat
66. NRC Ltd.	**Kalyan, Maharashtra**
67. Ordnance Factories	Bhandara, Maharashtra
68. Ordnance Factories	Itarsi, M.P.
69. Oriental Carbon & Chemicals Ltd.	Dharuhera, Haryana
70. Oswal Chemicals & Fertilisers Ltd.	**Paradeep, Orissa**
71. Paradeep Phosphates Ltd.	**Paradeep, Orissa**
72. Phosphate Co. Ltd.	**Kolkata, West Bengal**
73. Pyrites, Phosphates & Chemicals Ltd.	Amjhore, Bihar
74. Rama Krishi Rasayan	Pune, Maharashtra
75. Rama Phosphates Ltd.	**Indore, M.P.**
76. Ranjan Chemicals Ltd.	Barauni, Bihar
77. Rashtriya Chemicals & Fertilisers Ltd.	Trombay, Maharashtra

(continued)

(continued)

Company	Location
78. Sahibabad Chemicals	Kanpur, U.P.
79. Sarada Fertilisers Ltd.	Udaipur, Rajasthan
80. SFL Industries Ltd.	Chandigarh
81. Shree Acids & Chemicals Ltd.	Gajraula, U.P.
82. Shree Sulphurics Ltd.	**Ankaleshwar, Gujarat**
83. Shriniwas Fertilisers Ltd.	Jhansi, U.P.
84. SIV Industries	Coimbatore, Tamilnadu
85. SMZS Chemicals Ltd.	Pune, Maharashtra
86. Southern Petrochemicals Industries Corp. Ltd	**Tuticorin, Tamilnadu**
87. SPL Pharma	Tamilnadu
88. Sree Rayalseema Hi-Strength Hypo Ltd.	Kurnool, A.P.
89. Sri Durga Bansal Fertilisers Ltd.	Lucknow, U.P.
90. Steel Authority Of India Ltd.	Bhilai, M.P.
91. Steel Authority Of India Ltd.	Bokaro, Bihar
92. Steel Authority Of India Ltd.	Rourkela, Orissa
93. Sterlite Industries India Ltd.	**Tuticorin, Tamilnadu**
94. Subhodaya Chemicals Ltd.	Rajahmundry, A.P.
95. Sundarbans Fertilisers Ltd.	Jalpaiguri, West Bengal
96. Tanfac Industries Ltd.	**Cuddalore, Tamilnadu**
97. Teesta Agro Industries Ltd.	Siliguri, West Bengal
98. Transpek Industry Ltd.	**Vadodara, Gujarat**
99. Travancore Titanium Products Ltd.	Thiruvananthapuram, Kerala
100. Tungabhadra Fertilisers & Chemicals Co. Ltd.	Bangalore, Karnataka
101. Ultramarine & Pigments Ltd.	Ranipet, Tamilnadu
102. Vam Organic Chemicals Ltd.	Bhartiagram, U.P.

List of Sulfuric Acid manufacturers abroad:

Company	Location
1. Mitsubishi Materials Corporation	Japan
2. Nissan Chemical Industries Ltd	Japan
3. Indo-Jordon Chemicals Co. Ltd	Jordan
4. Groupe OCP (Office Cherifien des Phosphates)	Morocco
5. ASARCO Inc	USA
6. Cargill Inc	USA
7. DuPont Environmental Solutions	USA
8. Mississippi Phosphates Corporation	USA
9. Rohm & Hass Company	USA
10. Citis S.A.S	France
11. Huntsman Tioxide	France
12. Rohm GmbH & Co KG	Germany
13. BASF N.V.	Belgium
14. Tessenderlo Chemie Ham	Belgium
15. Foskor Richards Bay	South Africa
16. Palabora Mining Company	South Africa

1.1.1 Rules of Thumb for Equipment Design for Sulfuric Acid Plant

1. **Gas velocity for converter, ducting, furnace, and absorption towers.**
   Linear gas velocity based on gas volume at NTP conditions is approximately as follows…

Through converter	0.30—0.40 m/s (depends on SO_2 % in feed gas)
Through ducts	5.0–6.0 m/s
Through furnace	0.40–0.50 m/s
Through absorption towers	0.65–0.75 m/s

These figures are for a sulfur-based DCDA plant.

A lower gas velocity can result in less pressure drop during in operation—hence lower power consumption, but the equipment is bigger. Initial capital costs will be higher. The design should be optimized on the basis of present and future plant capacity.

2. **Acid flow to each tower.**

Acid flow in DT and FAT	0.5 m^3/h/TPD acid production, i.e., 50 m^3/h for a 100 TPD Plant
Acid flow in IPAT	1.0 m^3/h/TPD acid production, i.e., 100 m^3/h for 100 TPD plant

3. **Water consumption.**
   For acid dilution about 18–20% of rate of production (if no oleum is produced).

   For steam generation—1.2–1.3 m^3/MT acid produced.

   For evaporation for cooling acid—about 1.5–1.6 m^3/MT acid produced if acid heat is not recovered as hot acid.

4. **Conversion of SO_2 achieved in the converter passes.**

First pass	60–65%
Second pass	80–85%
Third pass	90–95%
Fourth pass	96–98%
Fifth pass	99.0–99.8%

5. **Sulfur consumption—about 330–332 kg/MT of acid produced.**
6. **Power consumption—about 35–70 kWh/MT of acid produced depending on whether turbo blower is used, treated water is available at site, oleum towers are installed and run continuously or partially bypassed, etc.**
7. **Sulfur pit.**
   (a) 1% of moisture in sulfur increases the heat load by approximately 20%.
   (b) Capacity of settler should be sufficient to provide a retention time of 72 h, for example the capacity of settler of a 100-TPD sulfuric acid plant should be 100 tonnes since the sulfur consumption will be about 33 TPD.

   (c) Heat transfer area to be provided depends on whether the melter is provided with an agitator or not. Rate of melting for an **un-agitated** pit melter is 45–60 kg/h/m^2 of heating surface for a steam pressure of 4.0–6.0 kg/cm^2.
   (d) Rate of melting for an **agitated** pit melter is 110–115 kg/h/m^2 of heating surface for a steam pressure of 4.0–6.0 kg/cm^2.

8. **Sulfur burning furnace.**
   (a) **Temperature** of exit gases in °C = SO_2 % × 95 (assuming air at inlet to furnace is not preheated).
   (b) **Internal Volume** = 0.9–1.2 m^3/MT sulfur burned per day.
9. **Air volume** required per MTPD sulfuric acid.

Type of plant	Percentage SO_2 in furnace exit gas	Air volume (Nm^3/h)
DCDA plant	9.5–10%	95–100
SCSA plant	7.5–8%	120–125

10. **Catalyst Loading.**
   (a) **Total:** 160–190 L/MTPD sulfuric acid
   (b) **Catalyst distribution** for a typical 3 + 1 DCDA plant

Pass	I	II	III	IV
% Loading	16–18	21–24	24–27	30–34

11. **Surface area of heat recovery boilers:** as a first approximation these are as follows.

After furnace	1.3–1.5 m^2/MTPD sulfuric acid
After first-pass	0.8–1.0 m^2/MTPD sulfuric acid

12. **Surface area of heat exchangers** for a DCDA sulfuric acid plant.

Hot heat exchanger (after second pass)	1.5–2.5 m^2/MTPD acid
Cold heat exchanger (after third pass)	3.0–4.5 m^2/MTPD acid

13. **Pressure drops** across various units depend on the percentage SO_2 in furnace exit gases and design of individual equipment.

Drying tower	60–120 mm WG
FAT	60–120 mm WG
IPAT	80–150 mm WG
Demister candles in IPAT	150–450 mm WG
Overall pressure drop range	1,600–3,000 mm WG
Four pass converter with ring type catalyst	250–500 mm WG

14. **Steam generation** depends on heat recovery equipment installed, for example boilers, economisers, etc., and factors such as feed water temperature, boiler operating pressures, etc.

    As a rule of thumb, the steam generation is 1.05–1.25 MT/MT of sulfuric acid.

1.1.2 History cards for sulfuric acid plant

Plant management should initially record all information, design specifications, and recommended operating conditions. All relevant detailed information and operating as well as maintenance data for the equipment/process units in the plant should always be maintained thereafter. The records must be available for reference at any time.

These should include, but are limited to, the following main points.

It will prove to be very useful during analysis of plant operation, troubleshooting, maintenance work, annual overhauls, and when considering expansion of plant capacity.

Sulfur pit

- Overall dimensions.
- Total capacity.
- Calibration of different chambers.
- Details of all steam coils (nos., new, old, repaired, etc.).
- Fabrication drawings of melting, settling, and pumping chamber coils.
- Agitator (shaft and peddles, gearbox, bearings, speed, motor details).
- Total amount of sulfur issued in the last year (name of sulfur supplier, quantity obtained, average analysis) or in the period since the last plant shutdown/since the last time the pit was cleaned.
- Quantity of sludge removed from the sulfur pit every month, since last year/since last plant shutdown/since the last time the pit was cleaned.
- Repairs done to pit lining, cover plates, etc.

Sulfur burning furnace

- Overall dimensions.
- Assembly drawings of furnace – with details of expansion joints and types of refractory bricks used.
- External insulation or air jacket (if provided on the shell).
- Specifications of all types of bricks used for refractory lining.
- Repairs done in the last shutdown (position, cost of repair, etc.).
- Location of thermocouples and their calibration readings.
- Operating temperature (minimum, maximum).
- Arrangement for creating a whirling (rotating) zone of burning sulfur spray.
- Arrangement for removal of ash deposits during annual shutdown.

Sulfur spray guns

- Fabrication drawings, and details of matching nozzles on furnace shell.
- Specifications and spare sets of spray nozzles (minimum and maximum flow of liquid sulfur)
- Design pressure and test pressure
- Make (vendor)

Sulfur filter

- Overall dimensions
- Make

- Year of installation
- Assembly drawing—orientation of feed, discharge, and drain nozzles
- Operating pressure, test pressure
- Safety vents
- Filtration area provided
- Maximum limits of impurities permitted in raw sulfur
- Capacity in terms of filtered sulfur at exit with specification
- Specifications for filter leaves (MOC, area, and nos.)
- Filter aid used and total quantity of filtered sulfur obtained since last cleaning
- Dates of cleaning
- Quantity of cake removed during every cleaning
- Maintenance work done (repairs to shell, filter leaves, pipelines, cost incurred)

Waste heat boilers

- Make
- Serial no.
- Year of installation and commissioning
- Last inspection done on…
- Next inspection due on…
- Assembly drawing
- Working pressure permitted—as per latest inspection
- Test pressure
- Heat transfer area
- Shell volume
- Type-smoke tube type/water tube type
- Specifications of tubes (type, ID, OD, length, composition)
- Boiler shell (ID, OD, length, composition, volume)
- Boiler mountings (make, installation dates, specs)—all valves, level controllers
- Ferrules used for boiler tubes (nos. and specs)
- Repairs carried out to waste heat boiler
- Copy of boiler inspector’s reports
- Specifications of feed water as given by manufacturer—TDS, pH, silica content, conductivity, dissolved oxygen limits
- Maximum limits for water inside the boiler—TDS, pH, silica content, conductivity, dissolved oxygen limits
- External insulation and cladding
- Arrangement to bypass hot gases—internal/external

Hot gas filter

- Assembly drawings—nozzle orientations for gas inlet/exit/thermocouples/sampling points/bottom drain point
- Specifications of brick lining and filter mass
- Sample of filter mass used
- External insulation and cladding
- Quantity of dust removed during shutdown
- Operating pressure drop on gas side with corresponding rate of production
- Pressure drop build up during every month and corresponding rate of production

Converter

- Assembly drawings
- Overall dimensions

Pass no.	Catalyst type	Quantity	Pressure drop	Temperature rise as per design and operation	Dust removed during shutdown	Quantity replaced	Source of replaced catalyst
I							
II							
III							
IV							
V							

- Maintenance work done on shell, partition plates, grids, support columns, brick lining, insulation, and cladding, thermocouples
- Activity analysis, vanadium pentoxide contents, and attrition loss reports from catalyst manufacturer regarding the samples taken out during annual shutdown

Heat exchangers

- **Hot heat exchanger**
  - Location and nozzle orientation
  - Shell side (gas composition, inlet and outlet temperatures, pressure drops)
  - Tube side (gas composition, inlet and outlet temperatures, pressure drops)
  - Assembly drawing (heat transfer area, MOC of shell and tubes)
  - Specifications of tubes (MOC, ID, OD, length, composition)
  - Expansion bellows
  - Ferrules and brick lining
  - External insulation
  - Performance when unit is clean (heat exchanged, pressure drop on tube and shell sides)
  - Maintenance work done

- **Cold heat exchanger**
  - Assembly drawing (heat transfer area, MOC of shell and tubes, etc.)
  - Location
  - Shell side (gas composition, inlet and outlet temperatures, pressure drops)
  - Tube side (gas composition, inlet and outlet temperatures, pressure drops)
  - Specifications of tubes (MOC, ID, OD, length, composition)
  - Expansion bellows
  - Ferrules and brick lining
  - External insulation
  - Performance when unit is clean (heat exchanged, pressure drop on tube and shell sides)
  - Maintenance work done

Acid towers

Tower	Packing details (height, type, MOC)	Cleaning record	Damaged packings replaced	Pressure drop just before and after shutdown	Maintenance work done	Heights of U-seals at acid exit nozzle	Demister details (type, thickness, MOC, nos.)
Drying							
Inter Pass							
Final Absorption							

Design specifications/recommended operating conditions for different production rates—acid flow rates, temperatures, gas flow rates, compositions and pressure drops, demister pads/candles provided

Air blowers

- Make
- Serial nos. (if more than one blower is there)
- Year of installation
- Type—positive displacement/centrifugal
- Suction and discharge nozzle orientations
- Capacity curves—volume (Nm^3/h), delivery pressure, power required as per purchase order
- Capacity control systems provided
- Discharge pressure just before and after plant shutdown at full rated production
- Electrical load (kW)—*design and during operation*
- Operating speed—design and with controls (VFD, pulley drives, etc.)
- Specifications of steam turbine if used for running the blowers
- Maximum permissible speed
- Pulley sizes, belt specifications, and numbers
- Bearings: sizes, nos., specs
- Operating period (if there are more than one blower)
- Repairs/replacements of parts done

Acid pumps

- Make
- Serial no.
- Year of installation
- Type
- MOC of impeller, shaft, volute, discharge pipe, wearing ring, etc.
- Acid temperature specification and actual temperature at which the pump was used during the plant run
- Capacity curves—volume, discharge pressure, power required as per purchase order
- Depth of submergence—for submerged pumps
- Discharge pressure (rated)

- Electrical load (kW)
- Operating speed and speed control provided
- Maximum permissible speed
- Bearings: sizes, nos., specs.
- Operating period (for which the acid pump was run)
- Repairs done and parts replaced

Sulfur pumps

- Make
- Serial no.
- Year of installation
- Type
- MOC of impellor, shaft, volute, discharge pipe, wearing ring, etc.
- Sulfur temperature to which the pump was subjected
- Capacity curves—volume (m^3/h), discharge pressure (rated), power required
- Depth of submergence—for submerged pumps
- Electrical load (kW)
- Operating speed and speed control provided
- Maximum permissible speed
- Bearings: sizes, nos., specs.
- Operating period (for which the pump was run)
- Repairs done and parts replaced

Boiler feed water pumps

- Make
- Serial no.
- Year of installation
- Type
- MOC of impellor, shaft, volute, discharge pipe, wearing ring, etc.
- Water temperature to which the pump was subjected
- Capacity (Nm^3/h)
- Discharge pressure (rated)
- Electrical load (kW)
- Operating speed and speed control provided
- Maximum permissible speed
- Bearings: sizes, nos., specs.
- Operating period (for which the pump was run)
- Repairs done and parts replaced

Acid cooling system

- **Trombone coolers**
  - The following details should be separately recorded for each of the acid towers (drying tower, inter pass absorption tower, final absorption tower)
  - Year of installation
  - Type (welded flanges/screwed flanges), diameter, length
  - MOC of pipes

  - Acid temperature at inlet to coolers and outlet of coolers
  - Total number of pipes and bends, total cooling area
  - Repairs done (pipes clamped, pipes changed, bends clamped, and bends changed)
  - Cooling water temperatures at inlet and exit
  - Cooling water analysis

- **Plate heat exchangers/shell and tube heat exchanger**
  - The following details should be separately recorded for each of the acid towers (drying tower, inter pass absorption tower, final absorption tower)
  - Make
  - Serial no.
  - Year of Installation
  - Type
  - Heat transfer area
  - Maximum pressure permitted at inlet
  - Operating period (for which the heat exchanger was run)
  - MOC of plates (in case of PHE)
  - MOC of shell and tubes, thickness, ID, and OD
  - Maximum acid temperature permitted at inlet to coolers
  - Maximum acid temperature actually operated at inlet to coolers
  - Temperature of acid at inlet to each of the towers during plant run
  - Design and actual cooling water flow, temperature and analysis
  - Repairs done (tubes plugged/plates changed)
  - Corrosion protection (sacrificial electrode earthed) provided

1.1.2.1 History Cards

It is most essential that proper records of the performance and maintenance work done on key equipments in the plant are available at short notice to all concerned persons. Below is the format suggested for keeping the records on the key equipment.

Equipment	Year of installation and supplier	Original specifications	Material of construction of major components	Major maintenance problems experienced and details of repairs with costs	Life obtained after initial installation and after repairs	Whether any programme for replacement/modernization is being considered
1. Sulfur filter						
2. Sulfur pumps						
3. Sulfur burner						
4. Waste heat recovery boilers						
5. Water treatment plant						
6. Cogeneration system						
• Steam turbine						
• Generator						
• Gearbox						
• Steam superheater						
• Steam condenser						
• Steam piping and valves						
• Condensate extraction pump						
7. Electrical system						
• Main transformer						
• Metering pump						
• Bus bar						
• Main cables and starters (Ashar 1999)						
• Electrical motors						
• Plant lighting						
8. Converter						
9. Catalyst in each pass						

10. Hot and cold heat exchangers
11. Acid towers
12. Acid coolers
13. Air blowers and their drive system
14. Instrumentation
15. Storage tanks and product dispatch
16. 25% oleum system
17. 65% oleum system
18. Liquid SO_3 system
19. Effluent treatment plant
20. Alkali scrubber
21. Emergency power
22. Supply system
23. DG set and accessories
24. Changeover switchgear
25. Cooling towers for:
26. Cogeneration system
27. Acid coolers

1.1.3 Consumers of Sulfuric Acid and Related Products

In fact, sulfuric acid is so widely used that its consumption rate, like steel production or electric power, can be used to indicate a nation's prosperity.

Most of its uses are actually indirect in that the sulfuric acid is used as a reagent rather than an ingredient. The largest single sulfuric acid consumer by far is the fertilizer industry. Sulfuric acid is used with phosphate rock in the manufacture of phosphate fertilizers. Smaller amounts are used in the production of ammonium and potassium sulfate. Substantial quantities are used as an acidic dehydrating agent in organic chemical and petro-chemical processes, as well as in oil refining. In the metal processing industry, sulfuric acid is used for pickling and descaling steel; for the extraction of copper, uranium, and vanadium from ores, and in non-ferrous metal purification and plating. In the inorganic chemical industry it is used most notably in the production of titanium dioxide.

Certain wood pulping processes for paper also require sulfuric acid, as do some textile and fiber processes (such as rayon and cellulose manufacture) and leather tanning. Other end uses for sulfuric acid include effluent/water treatment, plasticizers, dyestuffs, explosives, silicates for toothpaste, adhesives, rubbers, edible oils, lubricants, and the manufacture of food acids such as citric acid and lactic acid.

Probably the largest use of sulfuric acid in which this chemical becomes incorporated into the final product is in organic sulfonation processes, particularly for the production of detergents. Many pharmaceuticals are also made by sulfonation processes.

Sr.	Item	Specifications	Consumed for
1.	98% technical grade sulfuric acid	Iron (Fe) content not to exceed 500 ppm	Fertilizers (superphosphate, ammonium sulfate), iron and steel pickling, manufacture of alum, petroleum refining, metal sulfates, viscose rayon, paints and pigments, explosives, etc.
2.	98% battery grade sulfuric acid	Iron (Fe) content not to exceed 20 ppm	Storage batteries
3.	98% reagent grade sulfuric acid	Iron (Fe) content not to exceed 1 ppm	Laboratory analysis and pharmaceutical industries
4.	98% electronic grade sulfuric acid	Iron (Fe) and other metals not to exceed 1–2 ppb	For manufacture of printed circuit boards
5.	25% oleum	Iron (Fe) and other metals not to exceed 100 ppm Strength not less than 20% free SO_3	Organic synthesis, detergents, dyes, etc.
6.	65% oleum	Iron (Fe) and other metals not to exceed 100 ppm Strength not less than 60% free SO_3	Organic synthesis, detergents, dyes, etc.
7.	Liquid sulfur trioxide (stabilized)	Purity not less than 99%	Organic synthesis, chlorosulfonic acid, etc.
8.	Liquid sulfur dioxide	Purity not less than 99% Moisture less than 100 ppm	Organic synthesis, refrigerant, textile, photographic chemicals, etc.

1.1.4 Pumps in Sulfuric Acid Plant

In sulfuric acid plants various types of centrifugal pumps are used and their constructional features depend on the type of application. The pumps for handling molten sulfur and sulfuric acid are vertical submerged type centrifugal pumps.

1.1.4.1 Pumps for Handling Molten Sulfur

The typical duty specification required for this service is of high delivery head and very low flow capacities. Sulfur has a melting point of 119 °C and a peculiar characteristic of a sharp rise in viscosity at a temperature above 150 °C. It becomes extremely difficult to pump liquid sulfur above this temperature. The practical range for operating a sulfur pump is 125–135 °C.

Plunger type pumps are positive displacement pumps that pump the liquid at a considerably higher pressure. The high pressure liquid is pumped through the spray nozzle and the higher the pressure the better is the atomization and burning of liquid sulfur. The plunger pump had limitations of capacity and, as bigger and bigger size plants started coming up, plunger pumps went on to become uneconomical, and hence obsolete. They were replaced by centrifugal pumps which are easy to maintain, simple to install, and occupy less space.

The vertical submerged type centrifugal pumps for handling molten sulfur have a jacketed construction for their column as well as discharge side pipes. They are available in various submergence lengths, i.e., from 1,000 mm onwards depending on the sulfur pit designs. In submerged type pumps the impeller and volute casing are submerged in the liquid, and hence priming of the pump is not required, making the operation of the pump extremely convenient. The impeller designs are of the non-clogging type. Depending on the delivery head specifications these pumps are supplied to operate on either two-pole or four-pole electric motors.

Molten sulfur is not considered to be a very corrosive liquid; hence the material of construction for pumps handling molten sulfur is carbon steel, cast iron and low grade alloy stainless steel.

Some users prefer to use carbon steel material with heat treatment for hardening of hydrodynamic bearings and suction wear plates so as to get improved life for these components.

In recent times cantilever type centrifugal pumps are becoming more and more popular for use in handling molten sulfur and contaminated molten sulfur applications. In these type of pumps the hydrodynamic bush bearings and wearing rings are avoided by using a more sturdy and heavy shaft. Two ball bearings are used at the coupling end which makes the shaft completely suspended from top. These pumps are usually used at lower speeds and give long and trouble free operation with virtually no maintenance.

1.1.4.2 Acid Circulation Pumps

The pumps for acid circulation are most important in the acid plant. It can also be said that this pump is the heart of the plant and hence any malfunction or failure in operation results in stopping the plant and hence is not acceptable. These pumps are used to circulate acid through the intermediate absorption tower, final absorption tower, and drying tower.

A typical design is described below.

The vertical submerged type centrifugal pumps for acid circulation are available in various submergence lengths, i.e., from 1,000 mm onwards depending on the acid circulation tank designs. Generally lower submergence lengths are preferred since the pump design becomes sturdier due to a single length column pipe and hence better concentricity of the shaft and impeller dynamic assembly with the column pipe and volute casing. The impeller designs are closed type. The closed impeller design reduces axial thrust on the pump bearings, thereby increasing bearing life. For pump flow capacities higher than at 200 m^3/h, a volute casing with double volute design gives a better and more balanced performance. The radial thrust is uniformly balanced when the volute design is of double volute type in high flow capacity pumps for getting a higher life of wearing rings and bushes in this case. Lower speeds are generally preferred.

Sulfuric acid is a typical media which behaves differently on different materials at various concentrations and temperatures of liquid. At any given concentration if there is a change in temperature the corrosion rate increases and the same applies in the case of change in concentration at the same temperature. The process design should be such that there is close control of the concentration and temperature of the acid since it is very corrosive.

As the pump is required to work continuously, a stand-by pump is kept ready installed to avoid stoppage of the plant in the event of any pump breakdown. Maintenance of a proper inventory of essential spares is also necessary in order to attend any breakdown with minimum downtime.

1.1.4.3 Pump Parts and Material of Construction

The important components of a centrifugal submerged type pump are volute casing, impeller, wearing rings, hydrodynamic bushes, shaft, bearing, bearing housing, impeller nuts, keys, couplings, column and discharge pipes, elbow, gaskets, packing, fasteners, gland packing, etc.

Hydrodynamic Bush Bearings/Intermediate Bearings

The pump shaft is suspended from the top ball bearing and has a guide at two locations, namely one at the stuffing box and one above the impeller. The guide above the impeller is a hydrodynamic type of bearing which is usually lubricated by the pumping liquid. This arrangement in turn consists of two components, namely volute journal (P. No. 27) and volute bearing (P. No. 28). The volute journal is fitted on the shaft and locked with a key. The journal rotates with the shaft in the stationary component, i.e., the volute bearing. The running clearance between these bearings is very important. In the course of operation the running clearance between these bearings may increase which results in a reduction in flow capacity as well as an increase in vibration.

The hardness of the rotating bush is usually kept higher than that of the stationary one by around 50 BHN.

The guide at stuffing box which is in the form of gland packing has dual purpose:

1. To provide an effective guide to the shaft.
2. To prevent ingress of hot corrosive fumes of acid going to the ball bearing at the top.

Sometimes for liquids which are extremely fuming, namely oleum, liquid SO_3 etc., a vapor sealing is provided at the stuffing box which can operate in two ways. One is an extra length stuffing box with labyrinth and seal cage arrangement through which clean air is passed to counter the fume pressure at the stuffing box. The other is a suitably designed mechanical seal which is a dry running type with an appropriate selection of mating faces, an effective alternative for sealing fumes.

Ball Bearings

Ball bearings are used at the drive end immediately next to the coupling as the power transmission takes place through these couplings. The full workload is exactly at the opposite end, i.e., impeller end, and the maximum torque takes place at this end. The bearings maintain proper alignment and take the axial as well as radial thrust generated in the pumping operation. The bearings are either grease or oil lubricated. Proper selection and fitment of the bearing on the shaft ensure good bearing life. The life of bearings used in process pumps is usually around 20,000 h.

It is vital to check bearing temperature and vibration at regular intervals as suggested by the manufacturers while planning the maintenance schedule of the pump.

Impellers

The impeller types depend upon the service required and are of open, semi-open, or closed types. Closed impellers with shrouds on both sides are most commonly used for handling clean acids as some manufacturers claim that this design of impeller gives a better pump efficiency. Proper hydraulic design of the impeller and minimum frictional resistance in the flow passage ensures better pump efficiency. The parameters, namely head and flow capacity, relate to the impeller diameter, vane height, and suction eye dimensions of the impeller. The impeller may have anywhere between five and seven vanes. The design of the closed type impeller also involves balancing holes on the back shroud of the impeller for balancing axial thrust. The closed type impeller usually has two wearing rings, namely impeller rings, which are press fitted onto the impeller.

The semi-open impellers have only one wearing ring. For liquids having comparatively high viscosity like molten sulfur a semi-open type impeller is usually preferred. These impellers are non-clogging and easy to clean whenever the pump is removed for maintenance. The frontal clearance, i.e., the distance between the suction plate/cover face and the impeller is very important when using a semi-open impeller. An increase in the frontal clearance drastically reduces the head or flow of the pump.

Casing/Volute

The casing/volute in which the impeller rotates is the main part of the centrifugal pump. It is where the kinetic energy converts into pressure energy. These are precision machined and bored. The locked fits enable maximum alignment. Proper hydraulic design of volute passages enhances the hydraulic efficiency of the pump. Volute casings for high flow capacity pumps are usually designed with a double volute which reduces the radial thrust on the impeller, thereby increasing the life of the hydrodynamic bushes and the wearing rings. The casings are also fitted with replaceable wearing rings, i.e., casing rings.

Column Pipe and Discharge Side Pipes

These are either in cast form or fabricated from seamless pipes and flanges welded at either end and machined. At the top end the column pipe is bolted onto the support plate and the bearing housing is fitted onto it. Likewise, at the lower end it is bolted to the head plate or volute wherein the hydrodynamic bushes are positioned. The column pipe may be in a single piece or in multiple pieces depending on the pump submersion length. So for submersion lengths more than 2,200 mm the pump is usually provided with intermediate bearing at appropriate locations for achieving a more stable and vibration free operation. All fabricated components require stress relief for longer pump life.

The discharge side components are elbow, pipe and spool. It is very important to maintain the two sides, namely column side and discharge side pipes, parallel. Care should be taken during installation of the pump at the site to ensure that the weight of delivery side piping is mounted independently of the pump so that it does not induce stress on the bottom bearings of the pump.

Support Plates

Mild steel support plates are generally offered as standard. Special construction is required for vapor sealing. Due to their heavy fabrication/welding the support plates need to be stress relieved before machining for top motor mounting. A flange recess is provided to accommodate the motor spigot in order to maintain the alignment. Stainless steel cladding or epoxy coating at the bottom is also provided for applications involving high amounts of corrosive fumes, i.e., oleum, liquid SO_3, etc.

Since sulfuric acid is extremely corrosive and the corrosion characteristic vary with change in temperature or concentration of the liquid, it is vital to know the correct operating conditions while selecting materials of construction for the various components.

1.1.5 Major Suppliers for Constructing Sulfuric Acid Plants

1.1.5.1 Introduction

Every year British Sulphur in collaboration with CRU situated at 31 Mount Pleasant London, WC1X 0AD, England arranges an annual conference on sulfur based industry, primarily dealing with sulfuric acid.

Most suppliers of technology, equipment, catalysts, and LSTK (Lumpsum Turnkey) contractors, as well as plant operators, engineers, and technocrats participate. We have broadly outlined the major internationally known suppliers under the following categories:

1. Know-how
2. Plant engineering and construction

3. Catalysts
4. Blowers, boilers, and turbines
5. Circulating pumps
6. Mist eliminators
7. General categories for tail gas scrubbing, special tower packings, alloy steels, etc.

Under the above categories some of the prominent organizations are as given below.

1. Know-how
    - Bayer, Germany
    - BASF, Germany
    - Ralph & Parsons, USA
    - Monsanto, USA
    - Mitsubishi, Japan
    - Nissan, Japan
    - NEAT, India
2. Plant engineering and construction
    - Lurgi, Germany
    - Chemitecs, Canada
    - Monsanto Enviro Chem, USA
    - Mitsubishi, Japan
    - Krebs & Chemie, France
    - Furnace Fabrica, India
    - Chemithon, Singapore
3. Catalysts
    - Monsanto, USA
    - Haldor Topsoe, Netherlands
    - BASF, Germany
    - Sud-Chemie, Germany/India
4. Blowers, boilers, and turbines
    - KKK, Germany
    - Elliot, USA
    - Foster Wheeler, USA
    - Thermal Systems, India
    - Thermax, India
    - Enmax, India
5. Circulating pumps
    - Chas-Lewis, USA
    - Reihne Hüte, Germany
    - Kishore Pumps, India
    - Chemlin Pumps, India
    - KSB, Germany
6. Mist eliminators
    - Monsanto Enviro Chem, USA
    - Koch Engineering, USA
    - Galiakotwala, India

7. General categories for tail gas scrubbing, special tower packings, alloy steels, etc.
    - Sandvik, Germany
    - Evergreen, India
    - Parry & Co., India
    - Burn & Co., India
    - ACC, India
    - Topac, India
    - Kimre Inc, USA

    Note: Addresses can be obtained from the internet.

Appendix: History of Manufacture of Sulfuric Acid (in India and Other Countries)

Sulfuric acid in India became the key for the manufacture of chemicals in the twentieth century.

In 1919 M/s. Dharamsi Morarji Chemical Co. Ltd. was pioneer in producing sulfuric acid in India. A Lead chamber process plant was imported on Turnkey basis from England. This produced weak sulfuric acid in the range of 50-60%.

Higher concentration was obtained by coal fired furnace using retorts in cascade format to produce 97–98% Acid. This was marked in glass carbouys or ceramic jars to consumers.

The intension of the company was to put this plant in Bombay city. The British Governor then (1919) asked M/s. Dharamsi Morarji Chemical Co. Ltd. to install the plant 60 km away to Ambernath in order to avoid pollution hazard.

M/s. Dharamsi Morarji Chemical Co. Ltd. is comparable to M/s. Monsanto of USA. In the year 1948 there were three sulfuric acid plants imported from Monsanto (USA) including nuts, bolts, and gaskets, each having a capacity of only 10 TPD.

The plants were imported by M/s. Dharamsi Morarji Chemical Co. (DMCC) Ltd at Ambarnath, M/s. Punjab Chemicals Ltd, and M/s. DCM at Delhi.

Subsequently three more plants of similar capacity were added by M/s. Eastern Chemicals at Chembur, M/s. Perry and Chemicals at Ranipet (Tamil Nadu), and M/s. Bengal Chemicals Ltd at Calcutta.

Due to a discouraging policy by the British government, the above-mentioned plants could not expand since imported chemicals from UK were cheaper than chemicals manufactured using sulfuric acid in India.

It was only after independence in 1947 that the expansion of the manufacturing capacities of sulfuric acid was deemed necessary and encouraged by the government of India.

Unlike the above scenario for India, sulfuric acid manufacture in Europe, UK, and USA have flourished since the mid-nineteenth century.

The sulfuric acid industry got a head start in the 1940s due to the invention of vanadium pentoxide as catalyst to convert sulfur dioxide to sulfur trioxide, popularly known as the "contact process." This enabled large sulfuric acid plants of high capacity to be built to produce phosphoric acid for the manufacture of phosphatic fertilizers.

In the 1960s the environment protection laws made it prohibitive to expand the single contact single absorption plants. The conversion efficiency of SCSA process giving 96–96.5% conversion produced SO_2 emission of 16–20 kg/tonne of sulfuric acid

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produced. This would lead to a large quantity of acid rain affecting the environment. Thus it became necessary to revise the manufacturing process by using double catalyst double absorption giving 99.5% efficiency conversion. This DCDA system became popular to produce, a single plant having an output of more than 1,000 TPD.

The energy costs due to formation of OPEC raising the crude oil price from US$ 8 to US$ 60 per barrel required further innovation in the 1970s to produce electricity by co-generation in the 1970s and 1980s. In view of this, the minimum capacity that is economically attractive is 500 tonnes per day and above. For example, the exothermic energy available per 100 tonnes of acid can give us a maximum of 1.8 MW of electricity with the 'HRS' system developed by Monsanto Chemicals of USA.

About the Authors

Navin G. Ashar has been Managing Director of Navdeep Enviro And Technical Services Pvt. Ltd., in India for 25 years. He is the author of more than 50 papers on sulfuric acid plant designs at ACHEMA (1964); recovery of sulfur from gypsum at British Sulphur, New Orleans; and DCDA processes at Delhi, India. More than half of Mr. Ashar's papers address environmental concerns connected to the sulfuric acid industry, including *Pollution Control with Profit*, N. G. Ashar, In the Proceedings of the Symposium on Environmental Pollution, Delhi, 1973, which described the change in the process (from SCSA to DCDA) to reduce sulfur dioxide pollution and stack emission from 5,000 to 500 ppm. The Research and Development work was based on first-hand knowledge gained by visiting various sulfuric acid plants throughout the world in the early 1970s. Mr. Ashar holds an MS Engineering degree from MIT. Mr. Ashar holds post graduate degree from MIT (Cambridge, USA) in 1958. He was faculty member of MIT (1958–61) in-charge of Solar Energy Research under Dr. Cabot's Fund.

Kiran Ramchandra Golwalkar is a consulting chemical engineer, based primarily in India, with decades of professional experience in the design, erection, planning, and operation of various facilities across the chemical industries. From 1968 through 1991, his work in India, Kenya, Thailand, and Indonesia influenced the manufacture of such critical products as sulfuric acid, 25% and 65% oleums, and impacted technical operations of liquid SO_3 plants, ferric and non-ferric alum units, and manganese dioxide reduction units. From 1992 to the present Mr. Golwalkar has worked and provided consultation for Navdeep Enviro and Technical Services Pvt. Ltd., in India.

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Works Consulted

Ashar NG (1999) Liquid sulphur dioxide without compression or refrigeration: a new technology already in operation. In: Proceedings of sulphur 99, Calgary, Alberta, Oct 1999, pp 173–182

Ashar NG (2012) Comparative study of techno-economic evaluation of the production of liquid sulphur dioxide. In: Proceedings of sulphur 2012, Berlin, Germany, Oct 2012, pp 165–172

Stefan B, Karl-Heinz D, Hannes S (2012) The mouse and the elephant—250 t/d skid-mounted vs. 5000 t/d mega acid plant. In: Proceedings of sulphur 2012, Berlin, Germany, Oct 2012, pp 183–192

Duecker WW, West JR (1959) The manufacture of sulfuric acid. Robert E Krieger Publishing Co., Inc., Huntington, NY, p 136

Perry’s chemical engineer’s handbook, 50th edn. McGraw Hill Publishing Co, pp 3–154

The chemical process industries, 2nd edn. McGraw Hill, p 149

Sander U, Rothe U, Kola R (1984) Sulphur-sulphur dioxide and sulfuric acid. British Sulphur Corp. Ltd and Verlag Chemie International, Inc.

Kohl A, Riesenfeld F (1984) Gas purification, 3rd edn. Gulf Publishing Co.

Herman de Groot W (1991) Sulphonation technology in the detergent industry. Kluwer Academic Press, Dordrecht

N.G. Ashar and K.R. Golwalkar, *A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents*, DOI 10.1007/978-3-319-02042-6,

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