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 H₂S

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. SO₂ 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
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 SO₂ into SO₃

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

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{SO}_3 \Delta H = -99 \text{kJ.mol}^{-1}
\]

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

\[
\text{conversion achieved} = \frac{\text{SO}_2 \text{in} - \text{SO}_2 \text{out}}{\text{SO}_2 \text{in}} \times 100(\%)
\]

Both thermodynamic and stoichiometric considerations are taken into account in maximizing the formation of SO₃. 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 SO₂/SO₃ systems, the following methods are available to maximize the formation of SO₃:

- Removal of heat—a decrease in temperature will favor the formation of SO₃ since this is an exothermic process.
- Increased oxygen concentration in the input side.
- Removal of SO₃ (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 SO₂ in the system requires a balance between velocity of the forward and backward reactions (equilibrium achieved). However, this optimum also depends on the SO₃ concentration in the raw gas and on its variability with time. Consequently, each method is more or less specific for a particular SO₂ 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 SO₂ to SO₃ 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 SO₃
Sulfuric acid is obtained by the absorption of SO₃ into H₂SO₄ (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:
• H₂SO₄ 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
• SO₃ 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 H₂SO₄ 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 SO₃ 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 SO₂**
- Sulfur burning
- Pyrites roasting
- Metal sulfide roasting and smelting
- Sulfuric acid regeneration
- Metal sulfate roasting
- Combustion of H₂S or other sulfur-containing gases
- Other processes

**Sulfuric acid production**
Acid production is divided into two different groups depending on the strength/concentration of SO₂ in the gas stream.
Stronger gas processes have:
6–11 vol.% SO₂
- SCSA (6–8%)  
- DCDA (8–11%)  
- Weak gas processes are:
  - Based on oxidation by H₂O₂  
  - 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 SO₂ content of the combustion gases is generally up to 11 vol.% and the O₂ 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 SO₂ to SO₃. 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 SO₂ to SO₃ 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 SO₂/O₂ ratio for satisfactory conversion.

2.1.2.3 Metal Sulfide Roasting/Smelting

Many metal sulfides (other than pyrites) produce gases containing SO₂ when roasted during metallurgical processes. It is necessary to distinguish the main ores as indicated in Table 2.1.

<table>
<thead>
<tr>
<th>Metal sulfide</th>
<th>SO₂ percentage</th>
<th>Raw gases O₂ percentage</th>
<th>Process gases SO₂ percentage</th>
<th>Variability in time</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS-containing ores</td>
<td>6–10</td>
<td>6–11</td>
<td>6–10</td>
<td>Relatively low</td>
</tr>
<tr>
<td>CuS-containing ores</td>
<td>1–20</td>
<td>8–15</td>
<td>1–13</td>
<td>Can be very high</td>
</tr>
<tr>
<td>PbS-containing ores:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Sintering</td>
<td>2–6</td>
<td>~15</td>
<td>2–6</td>
<td>Relatively high</td>
</tr>
<tr>
<td>- Other lead smelters</td>
<td>7–20</td>
<td>~15</td>
<td>7–13</td>
<td>Low to very high (batch process)</td>
</tr>
</tbody>
</table>
The concentration (vol.%) of SO\textsubscript{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\textsubscript{2} converted to SO\textsubscript{3} and the gas temperatures depend on percentage SO\textsubscript{2}. It is therefore seen that a certain minimum concentration of SO\textsubscript{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\textsubscript{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\textsubscript{2} and produces sulfuric acid. However, due to copper converter operations, the percentage SO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} to SO\textsubscript{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\textsubscript{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\textsubscript{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:

\[
\text{HgCl}_2 + \text{Hg} \rightarrow \text{Hg}_2\text{Cl}_2
\]

\[
2\text{Hg}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow 2\text{HgCl}_2 + 2\text{Hg} 
\]

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 H₂SO₄ or oleum is used as a catalyst (alkylation, nitration, sulfonation, etc.) or from other processes where H₂SO₄ is used to clean, dry, and remove water.

Decomposition of sulfuric acid is represented by the overall equation

\[ \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad \Delta H = +202 \text{ kJ.mol}^{-1} \]

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 SO₂ 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 SO₂ 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 O₂/SO₂ ratio is important to get a conversion rate of SO₂ to SO₃ 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 SO₂ content of the gases is high enough (about 8%) at the converter inlet.

The conversion achievable is shown below.

- Single absorption:
  - SO₂ content at the converter inlet 8% with an O₂/SO₂ ratio of 1.1: 98%.
  - SO₂ content at the converter inlet 5–8 % with O₂/SO₂ ratio of 1.1: 97–98%.
  - SO₂ content at the converter inlet below 5% with O₂/SO₂ 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% SO₂ but the composition is not constant. Hence, there is an additional sulfur burning furnace to maintain thermal stability in the converter passes.
The SO₂-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 SO₂ 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 (H₂S) 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 SO₃ and H₂SO₄:
- 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% H₂SO₄, 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
SO₂ abatement by scrubbing consists of a chemical reaction between SO₂ 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 SO₂ 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 SO₂ 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.
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 O₂/SO₂ ratio of about 1 ± 0.2 (possibly 0.8–3).

2.1.3.2 Single Contact Process

The SO₂-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 SO₂ 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).

Table 2.2  Sulfuric acid production processes for new plants

<table>
<thead>
<tr>
<th>New plants</th>
<th>SO₂ content in feed gas (vol.%)</th>
<th>Conversion achievable</th>
<th>With state of the art emission controller for new plants SO₃Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single contact</td>
<td>6–10Δ</td>
<td>98.5%c</td>
<td>0.4 kg.ton⁻¹d</td>
</tr>
<tr>
<td></td>
<td>3–6</td>
<td>97.5–98.5%</td>
<td></td>
</tr>
<tr>
<td>Double contact</td>
<td>6–12b</td>
<td>99.6%</td>
<td>0.1 kg.ton⁻¹d</td>
</tr>
<tr>
<td>Wet contact process</td>
<td>0.05–7</td>
<td>98.0%</td>
<td>&gt;10 ppmv SO₃</td>
</tr>
<tr>
<td>Process based on NOₓe</td>
<td>0.05–8</td>
<td>nearly 100%</td>
<td>–</td>
</tr>
<tr>
<td>H₂O₂ Process</td>
<td>&gt;99.0%</td>
<td>Very low</td>
<td></td>
</tr>
</tbody>
</table>

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

SO₃ + H₂SO₄ expressed as SO₃

When sulfur burning

For existing plants the conversion achievable is 98%

Per tonne of acid produced

Possible emissions of NOₓ
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 SO₃, 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, SO₂ feed gases containing up to 12 vol.% SO₂ 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 SO₂) are brought up to conversion temperature prior to admission to the converter. The SO₂ is converted to SO₃ by the catalyst and the hot gases from the converter exit are cooled by heat exchange with the incoming cold feed gas.

SO₃ 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% SO₂) since autothermal operation is difficult at such low strengths.
2.1.3.5 Pressure Process
The conversion of SO₂ to SO₃ increases as the operating pressure is increased since there is a reduction in volume during the reaction

\[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]

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 SO₂ 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. Matros¹ 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 SO₂ oxidation reaction.

Cold SO₂ 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%) SO₂ gas concentrations.

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

H₂O₂ Process
Use of H₂O₂ can oxidize the SO₂ to SO₃ which is then used to produce sulfuric acid. However, due to the high cost of H₂O₂ this process is not economical.

¹ Currently Dr. Matros has emigrated to the USA and author has personal correspondence with him.
H₂O₂ is therefore used for oxidizing the remaining traces of (dissolved) SO₂ in the circulating acid in the plant. This minimizes the escape of SO₂ 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 SO₂ to SO₃. Instead of the conventional (3+1) DCDA Process, the (3+2) DCDA process can be used. In this innovation, after all the SO₃ 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

\[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \Delta \text{H} = -74.3 \text{Kcal/g Mole} \]

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%) SO₂ 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 SO₂ 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 SO₂ 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 SO₂ to SO₃ 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% SO₂ 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 SO₂ 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 SO₂ 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
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 $\text{SO}_2/\text{SO}_3$ 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 $\text{SO}_3$ and $\text{SO}_2$—their relative quantities being dependent on the conversion of $\text{SO}_2$ 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 $\text{SO}_2$ 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 $\text{SO}_3$ 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 $\text{SO}_3$.

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 SO₃ 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 SO₃ 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 SO₃) 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 SO₃ 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 SO₃ 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% SO₂ to SO₃, 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 SO₃ 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 SO₃ 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 SO₃ vapor and liquid lines. Conventional acid resistant gaskets may not be able to withstand attack by SO₃.
2. Provide steam tracing lines, i.e., another steam line in contact with or in the near vicinity of the liquid SO₃ pipeline instead of a steam jacket.
3. Maintain a temperature of between 28 and 33 °C in the storage tanks for SO₃.
4. Provide a dual pressure gauge on the SO₃ 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 SO₃ 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 SO₃ 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 SO₂ to SO₃ and of absorption of SO₃ depend on the concentration of SO₂ in the feed gas entering the installation and on the variability of SO₂ 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$_2$SO$_4$ resulting from absorption. H$_2$SO$_4$ 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$_2$SO$_4$ 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 SO₂/SO₃.

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 SO₂

Table 2.4 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of SO₂ for the manufacturing of sulfuric acid. Most sulfuric plants have taken general primary optimization measures like process control.
There are many other processes available for SO\textsubscript{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\textsubscript{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.

### Techniques to Control Emissions of SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}

Table 2.5 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of H\textsubscript{2}SO\textsubscript{4} (taken as the sum of SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}) during the manufacture of sulfuric acid. Most sulfuric acid plants have taken general primary optimization measures like process control measures.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Applicability in processes</th>
<th>Emission level for plants operating at 9.5–10.5% SO\textsubscript{2} with a rated capacity up to 1,000 TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single absorption + fifth bed</td>
<td>All SCSA</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>Double absorption + fifth bed</td>
<td>All DCDA</td>
<td>&lt;1,000</td>
</tr>
<tr>
<td>Single absorption + cesium catalyst in the last bed</td>
<td>All SCSA</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>Double absorption + cesium catalyst in the last bed</td>
<td>All DCDA</td>
<td>&lt;250</td>
</tr>
<tr>
<td>Single to double absorption</td>
<td>s.a.</td>
<td>&lt;1,000</td>
</tr>
<tr>
<td>Tail gas scrubbing by</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>All</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>All</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>All</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>All</td>
<td>&lt;1,000</td>
</tr>
<tr>
<td>Hydrogen peroxide treatment after and absorption</td>
<td>All</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>
### Table 2.5  Techniques for reduction of sulphur trioxide and sulphuric acid mist

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Applicability in processes</th>
<th>Emission level</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire-mesh</td>
<td>Large droplets (1–20 μm)</td>
<td>&lt;100</td>
<td>Not efficient on mists</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High efficiency candle type filter after absorbers</td>
<td>0.1–2 μm droplets</td>
<td>&lt;50 &lt; 0.03</td>
<td>Increased energy consumption, Production loss, Capacity loss, Plume suppression</td>
</tr>
<tr>
<td>Scrubbing</td>
<td>All</td>
<td>&lt;10 &lt; 0.015</td>
<td>Waste generation as in Sect. 4.2.3, Plume reduction</td>
</tr>
</tbody>
</table>
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