FERTILIZERS TECHNOLOGY

CHEM 0905554

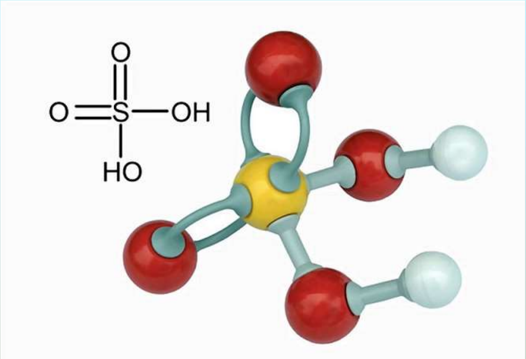
Spring Semester 22/23

CHAPTER 5

SULFURIC ACID MANUFACTURING

INTRODUCTION

- One of the oldest industrially applied processes.
- Discovered by a Persian physician and alchemist Ibn Zakariya Al-Razi in the 19th century.
- Saltpeter and sulfur were mixed in a glass container and burned in a moist atmosphere. Acid was collected from the condensed vapors.
- In England, 1746, the lead chamber reactor was invented. This invention allowed for higher production rates (<78%).



INTRODUCTION

- In England, 1831, a patent described the oxidation of sulfur dioxide over a platinum catalyst, the Contact Process.
- This process increased yields of reaction from 70 to above 95%.
- In 1913, BASF was granted a patent for the use of vanadium pentoxide (V_2O_5) as a catalyst for the Contact Process.
- By the 1930's, vanadium pentoxide was becoming the dominate catalyst used because of insensitivities to poisons and lower cost.
- In 1960 a patent application was filed by Bayer using the so-called double-catalyst process (double absorption).

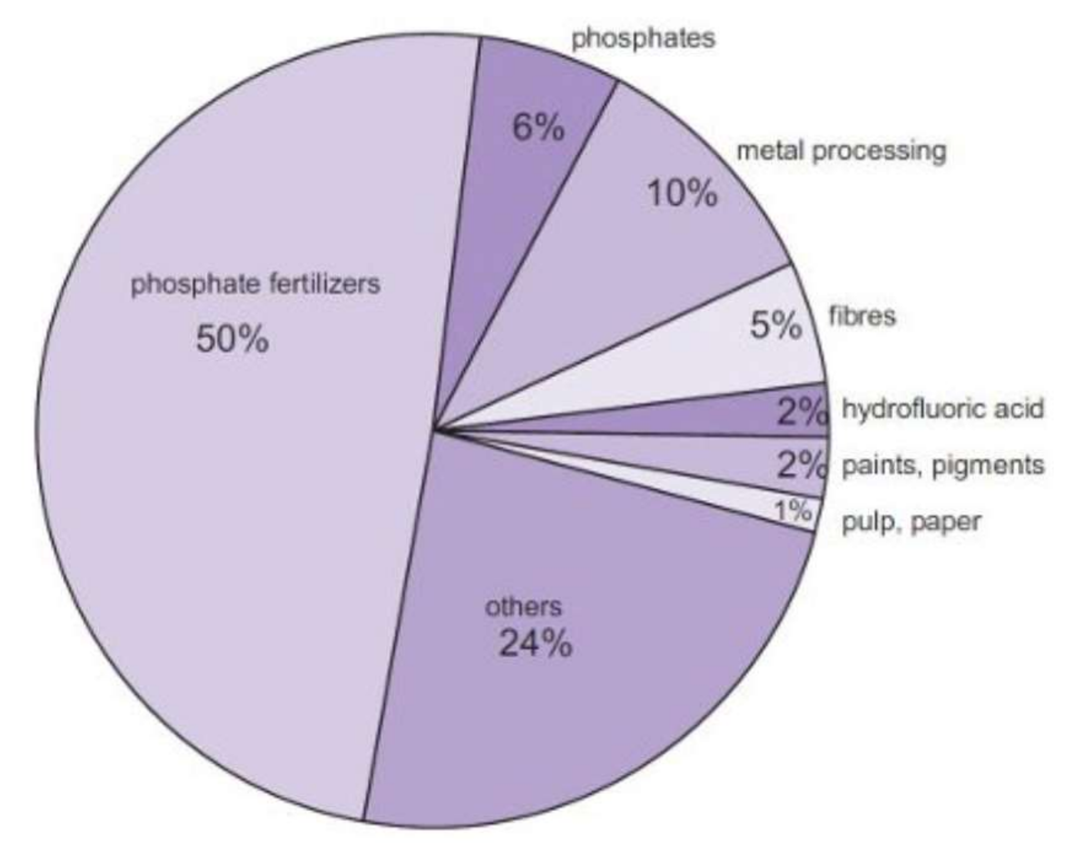
FORMS OF SULFURIC ACID

- Although 100% sulfuric acid can be made, this loses SO_3 at the boiling point to produce 98.3% acid.
- The 98% grade is also more stable for storage, making it the usual form for "concentrated" sulfuric acid.
- Other concentrations of sulfuric acid are used for different purposes:
  - ✓ 10%, dilute sulfuric acid for laboratory use (pH 1)
  - ✓ 33.5%, battery acid (used in lead-acid batteries) (pH 0.5)
  - ✓ 62.18%, chamber or fertilizer acid (pH about 0.4)
  - ✓ 77.67%, tower or Glover acid (pH about 0.25)
  - ✓ 98%, concentrated (pH about 0.1)

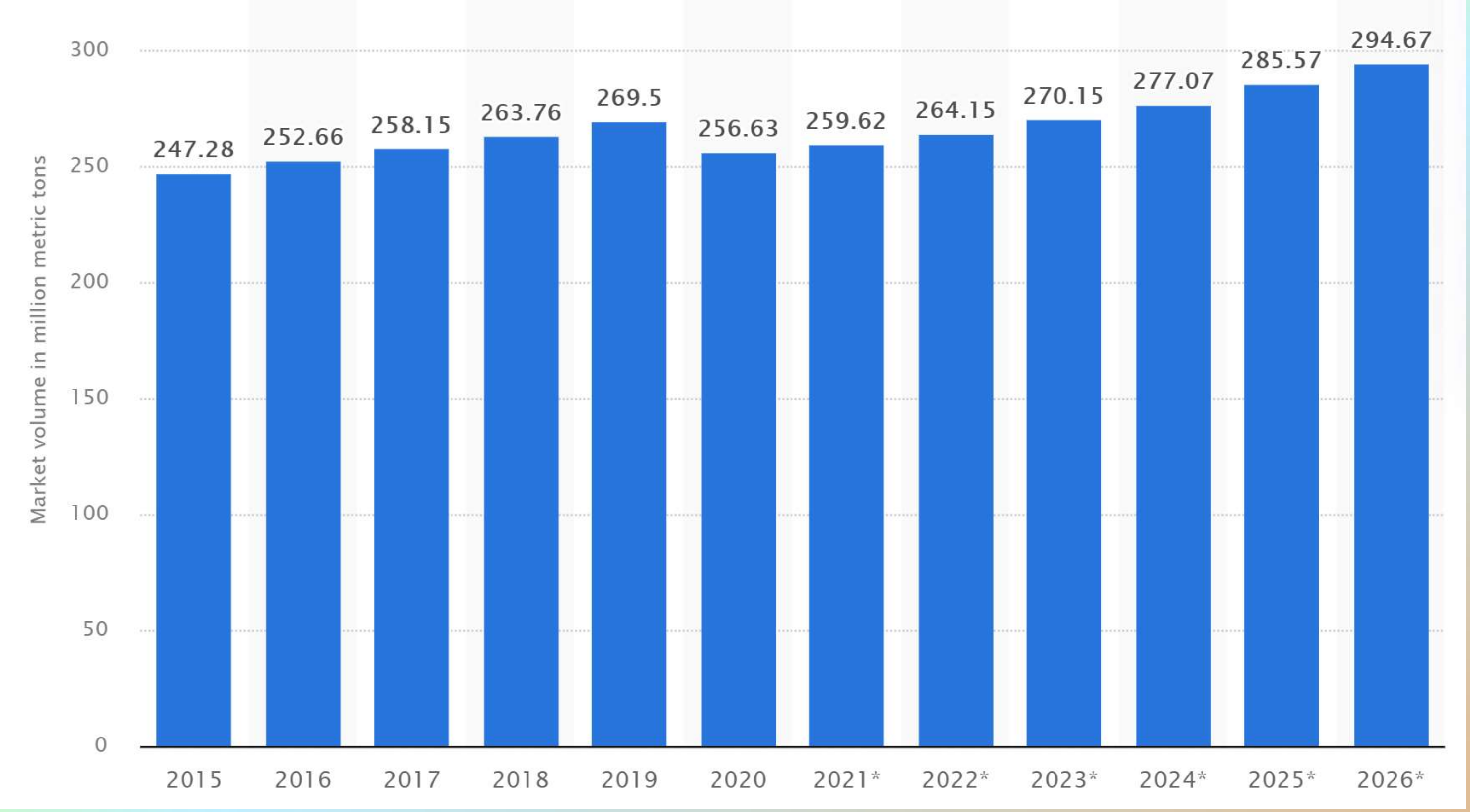
SULFURIC ACID USES

- Sulfuric acid is a dense clear liquid.
- It is used for:
  1. Making fertilizers.
  2. Organic chemical industry.
  3. Leaching metallic ores.
  4. Refining petroleum as a catalyst.
  5. Production of TiO_2 consumes large quantities.
- Worldwide, over 250 million tones of sulfuric acid are consumed per year.

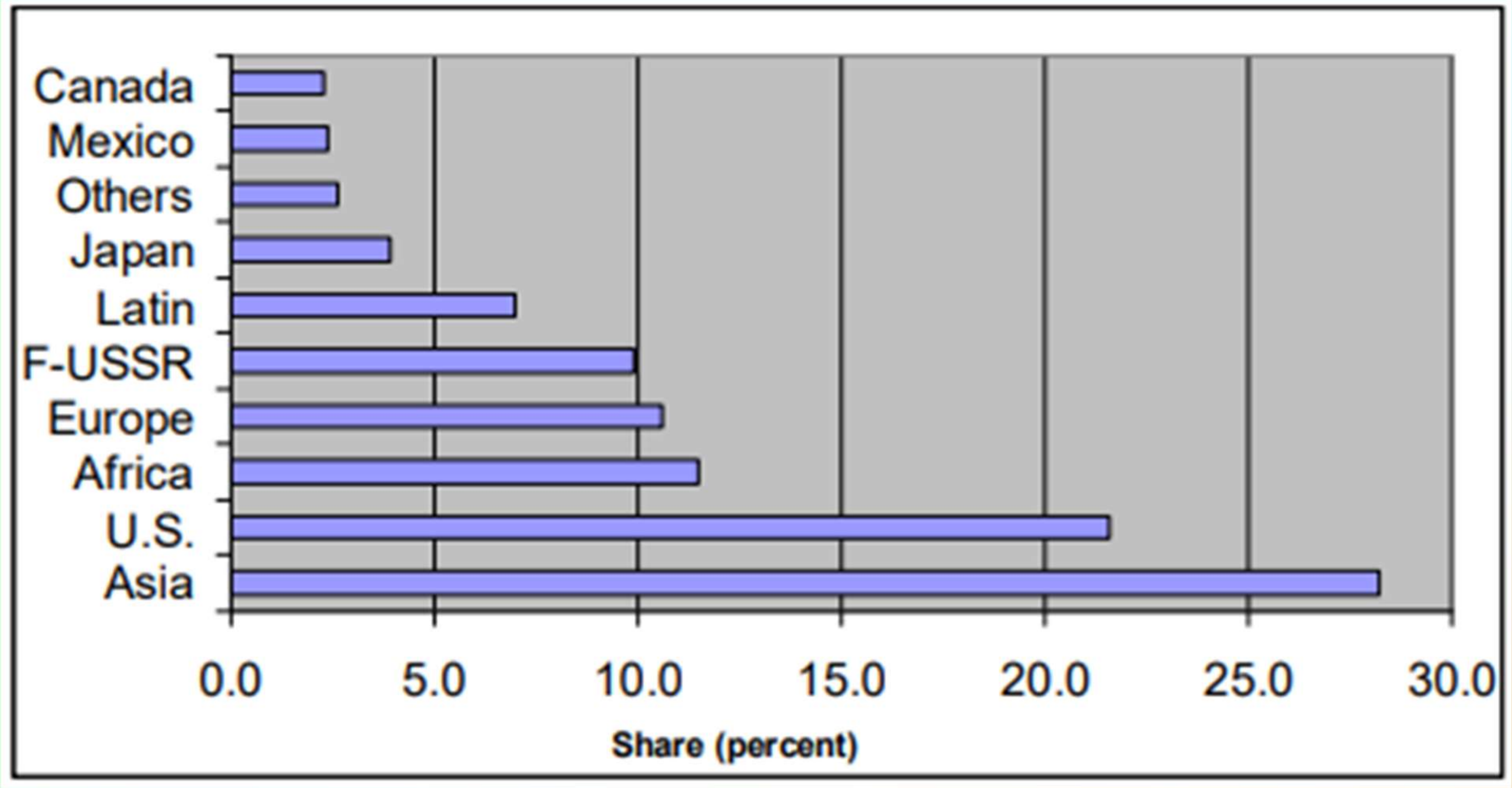
SULFURIC ACID USES



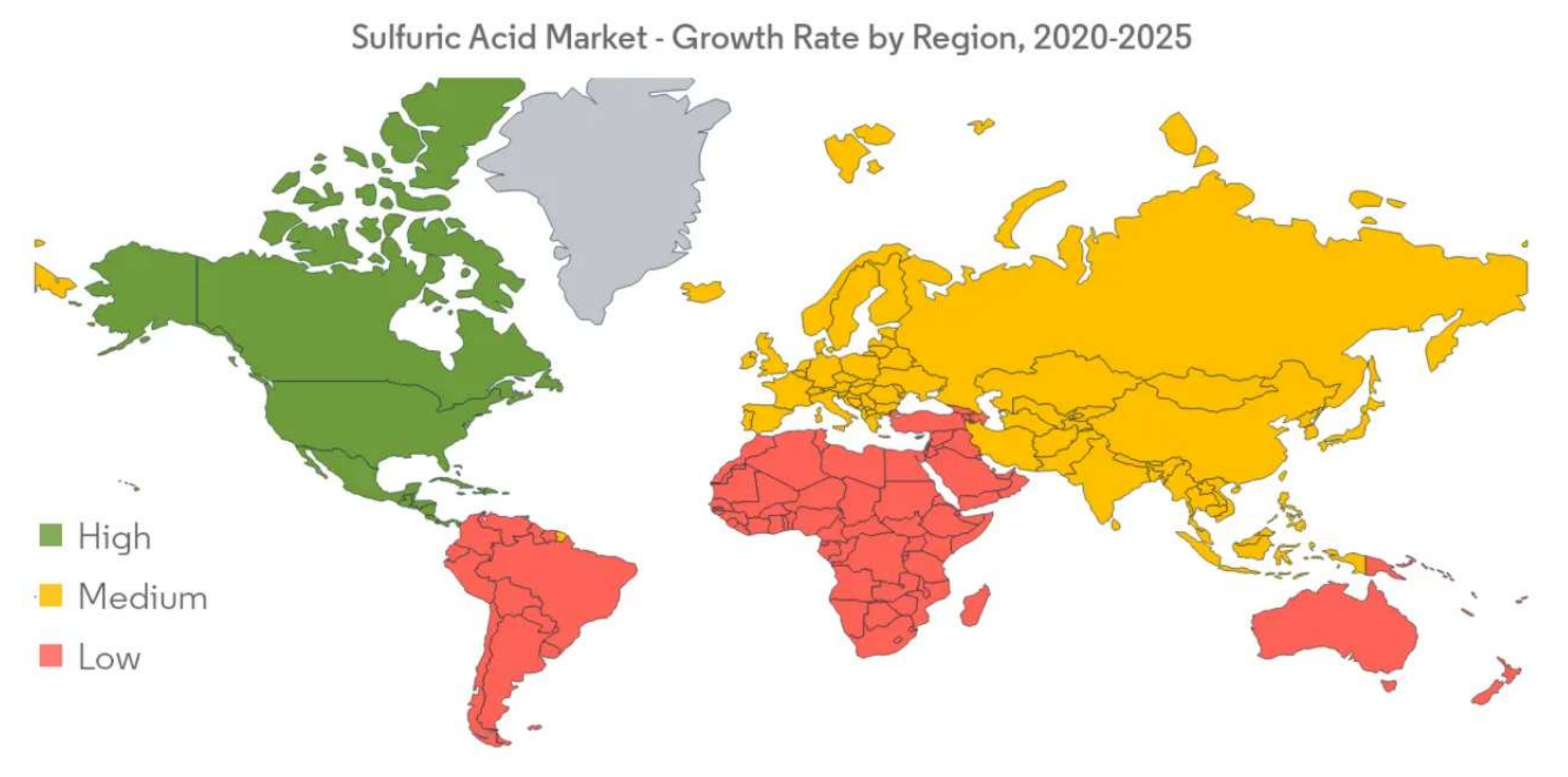
SULFURIC ACID WORLD PRODUCTION



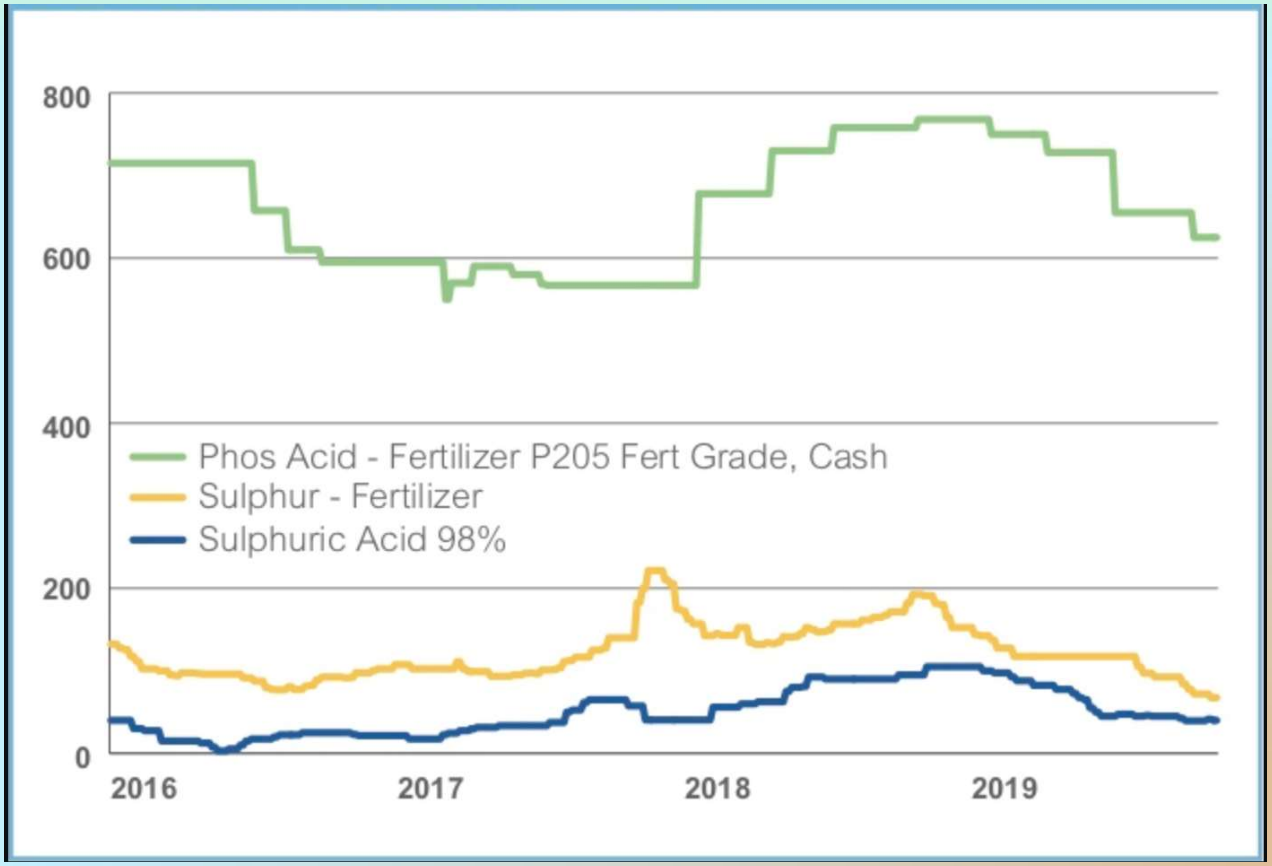
SULFURIC ACID PRODUCTION BY COUNTRY



SULFURIC ACID MARKET



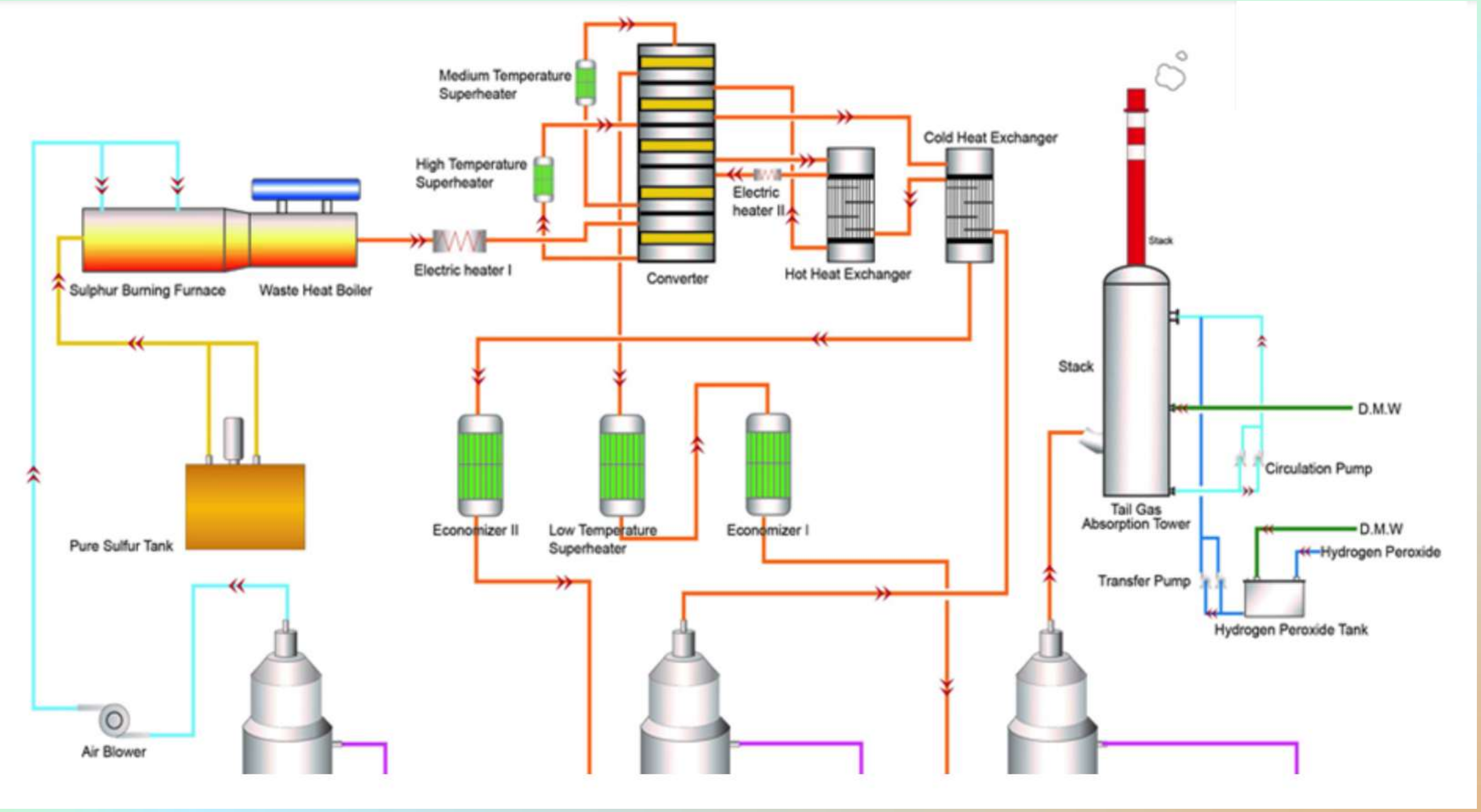
SULFURIC ACID PRICES



SULFURIC ACID PRODUCTION PROCESS

- The starting material for sulfuric acid manufacture is clean, dry SO_2 gas.
- This can be obtained by burning molten sulfur, from metallurgical off-gases or by decomposing spent sulfuric acid.
- Over the last decades the contact process has been used to produce sulfuric acid, replacing the traditional «Lead Chamber» process dating back to the 18th Century.
- In the contact process SO_2 is oxidized to sulfur trioxide (SO_3) at high temperature (about 450 ° C) in the presence of a vanadium catalyst.
- SO_3 then is dissolved in concentrated sulfuric acid forming fuming sulfuric acid (oleum). This can then be reacted safely with water to produce concentrated sulfuric acid.

SULFURIC ACID PRODUCTION PROCESS



RAW MATERIALS

- The main raw material for sulfuric acid production is SO_2 gas.
- It is obtained by:
  - (a) Burning elemental sulfur with air
  - (b) Smelting and roasting metal sulfide minerals (Cu_2S, ZnS).
  - (c) Decomposing contaminated (spent) sulfuric acid catalyst.
- Elemental sulfur is far and away the largest source.

CONVERTERS FEED COMPOSITION

- Compositions of acid plant feed gases entering SO_2 oxidation "converters" may also contain small amounts of CO_2 or SO_3.

	Sulfur burning furnace	Smelters and roasters	Decomposition furnace
Gas	Volume %		
SO_2	11	10	9
O_2	10	11	11
N_2	79	79	76

MAIN REACTIONS

Three Step Process:

- In the first stage of the contact process, sulfur is burned in air to make sulfur dioxide:

$$S_{(s)} + O_{2\,(g)} \xrightarrow{1150\,^{o}C} SO_{2\,(g)} \qquad \Delta H_R = -296{,}810\ Kj/kmol$$

- In the second stage, sulfur dioxide reacts with more oxygen to make sulfur trioxide:

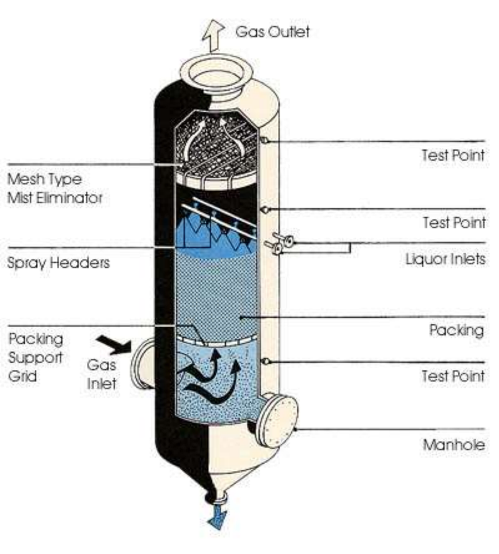
$$SO_{2\,(g)} + 0.5\ O_{2\,(g)} \overset{400-630\,^{o}\mathrm{C}}{\Longleftrightarrow} SO_{3\,(g)} \qquad \Delta H_R = -96{,}323\ Kj/kmol$$

- In the final stage, sulfur trioxide reacts with water to make sulfuric acid:

$$SO_{3\,(g)} + H_2O_l \xrightarrow{80-110\,^{o}C} H_2SO_{4\,(l)} \qquad \Delta H_R = -132{,}000\ Kj/kmol$$

MAIN STEPS

- Sulfuric acid is made from SO_2 and O_2 gases by:
  - (a) Catalytically reacting SO_2 and O_2 to form SO_3 (g)
  - (b) Reacting product $SO_{3(g)}$ with the $H_2O_{(l)}$ in 98.5 mass% H_2SO_4 , 1.5 mass% H_2O sulfuric acid.
- Industrially, both processes are carried out rapidly and continuously.



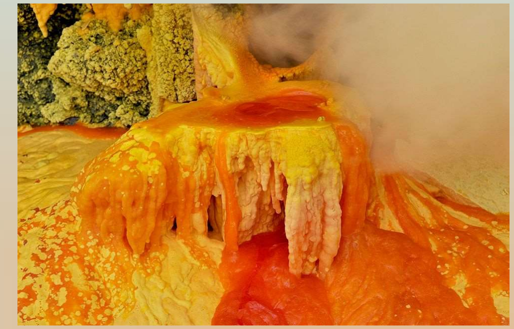
MAIN EQUIPMENT

1. Sulfur melting pit
2. Molten sulfur filter
3. Sulfuric large molten sulfur storage tank.
4. The combustion air filter and air dehydration tower.
5. The sulfur burning furnace
6. Catalytic converter.
7. Twin H_2SO_4 absorption towers.

Catalytic converters are typically 12 m diameter.

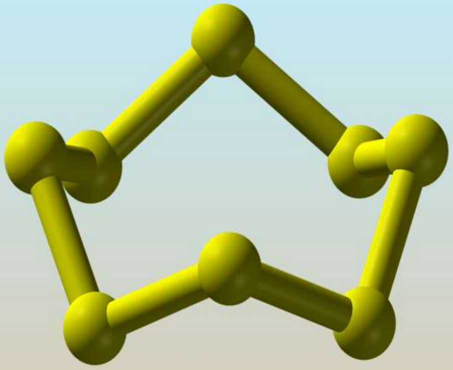
SULFUR MELTING

- Sulfur is non-metallic, a yellow solid at normal temperature, it dissolves in carbon disulphide at normal temperature.
- Liquid sulfur at the melting point is yellow, as the temperature of the liquid is raised up it darkens and becoming deep orange.
- The viscosity of the molten sulfur drops with rising temperature; above 158°C the viscosity increases drastically with rising temperature up to 188°C. Above 188°C its viscosity falls somewhat as the temperature continues to rise.



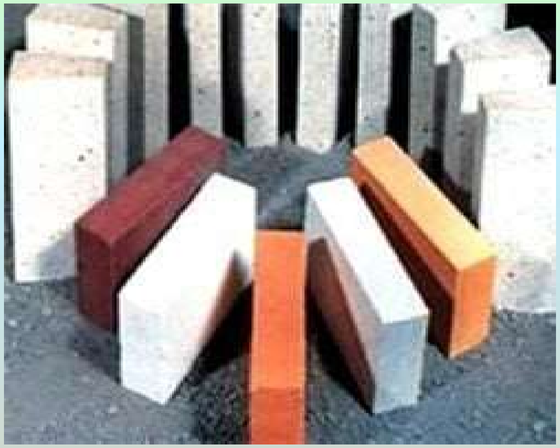
SULFUR MELTING

- Sulfur boils at atmospheric pressure at 445°C, the increase in viscosity as the temperature rises from 158°C to 188°C is assumed to result from rupturing of the puckered rings of S_8 to form chains of varying lengths.
- Sulfur has a melting point of about 116°C to 118°C, viscosity of sulfur affects the flow through pipelines and having high viscosity flows very slowly while liquids having low viscosity can flow easily.
- Solid sulfur is melted by steam coils in the melting pit, these steam coils are made of carbon steel.



SULFUR MELTING

- The molten sulfur is maintained on between 135^{o}C and 145^{o}C for best performance of the pumps.
- The pits are lined with acid proof bricks and mortar; it is recommended to use:
  - ✓ 7 bar steam for sulfur melting pits.
  - ✓ 4 bar steam to maintain the temperature of the sulfur in other pits.
- The impurities in the liquid sulfur are moisture and weak sulfuric acid formation in the solid sulfur.



SULFUR MELTING

- Sulfur when exposed to atmosphere in open space it gets oxidized to SO_2, and further this SO_2 is oxidized to SO_3 .
- And when in contact with moisture it form H_2SO_4
- The H_2SO_4 present in sulfur is highly corrosive to the steam coils and metallic equipment and pumps.
- To reduce the acidity of sulfur, hydrated lime or ammonia gas should be used to act as filter media up to a certain extent.

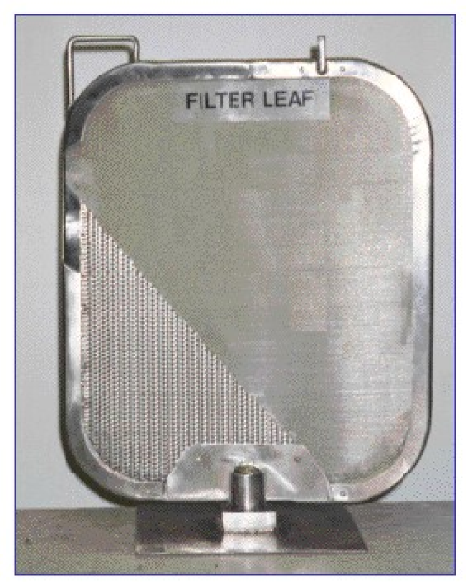
Sulfur FILTRATION

- For filtration of sulfur diatomaceous earth is added.
- Diatomaceous earth consists of tiny skeleton of microorganism called as diatom and is composed of amorphous silica containing a small amount of micro crystalline material.
- The advantages of diatomaceous earth over other filter aid material are that it is:

1. Basically, very economical.
2. Withstand high temperature.
3. Inert to all chemicals except hydrofluoric acid, strong sulfuric acid, and strong alkalis.

SULFUR FILTRATION

- For filtration it is required initially to precoat the filter leaves with this filter aid, the filtration can be done when the coat formation is uniform over all the leaves of the sulfur filter.
- The addition of diatomaceous earth also depends upon the ash content in the sulfur according to the laboratory report.
- The molten sulfur is neutralized with limestone addition on the solid sulfur belt conveyor feeding the smelter.
- The two filters will be operated in parallel each one 20 hours per day. 4 hours foreseen for one filter cleaning.



SULFUR FILTRATION

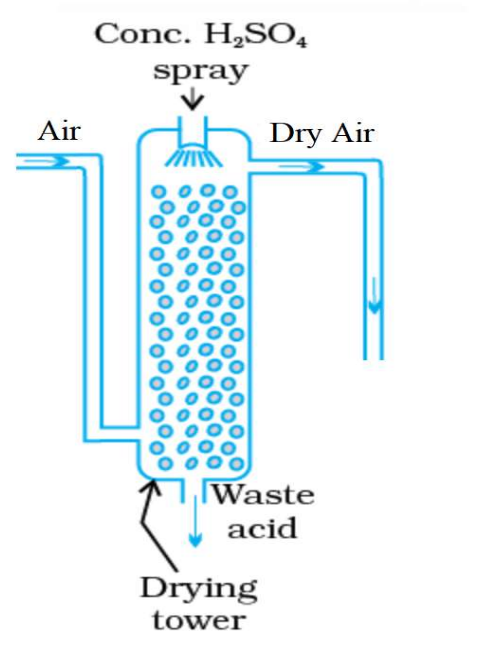
- Each filter is fed from the filtration pit located at the outlet of a sulfur smelter by a vertical pump.
- The filters are located few meters above ground level to allow easy discharge and removal of the cake, when leaving the filters.
- Clean sulfur is sent either to a pit at ground level or to a storage tank.
- Sulfur temperature in each filter is 140ºC and kept by injecting steam at for T=150ºC, P=4.3 bar in a jacket.
- Pipelines carrying molten sulfur should be heated in order to maintain the liquid above its freezing point and below 160ºC, insulation helps to control the temperature.

SULFUR FILTRATION

- Pipelines made from mild steel, galvanized iron.
- Valves are generally steam-jacketed, lubricated, plug valves.
- Pumps are centrifugal, rotary, and reciprocating piston.
- The sulfur stream starts with pumping molten filtered cleaned sulfur to the combustion chamber where it is received in finely divided droplets (spray) by injection through sulfur guns to mix with air where self ignition of the sulfur in the already heated furnace takes places.

FEED GAS DRYINGS

- It starts by pumping air from atmosphere using a blower which is driven electrically or by steam turbine.
- The air leaving the blower sent to sulfur combustion chamber passing firstly through a drying tower where the atmospheric humidity is absorbed by concentrated sulfuric acid 98.5 %.
- The received air at 60^{o}C mixes in the combustion chamber with the sprayed sulfur, the combustion gases constitute of sulfur dioxide, oxygen, and nitrogen and just traces of sulfur trioxide.



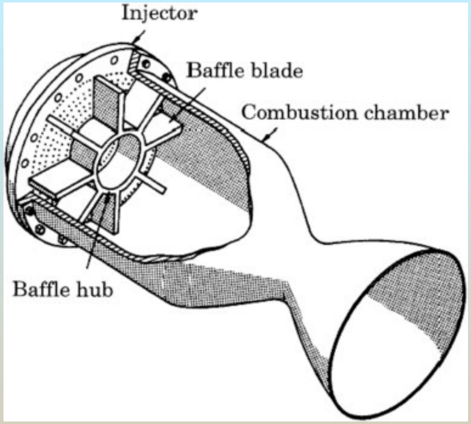
SULFUR BURNING

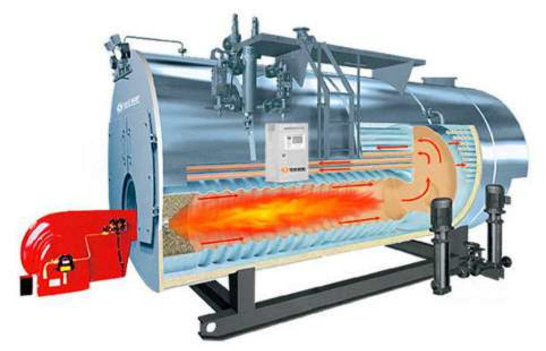
- About 70% of sulfuric acid is made from elemental sulfur while all the sulfur obtained as a byproduct from refining natural gas and petroleum contribute to less than 30%.
- The sulfur is made into SO_2 acid plant feed by:
  1. Melting the sulfur
  2. Spraying it into a hot furnace
  3. Burning the droplets with dried air.
- The reaction is:

$$S_{(s)} + O_{2\,(g)} \xrightarrow{1420\ K} SO_{2\,(g)} \qquad \Delta H_R = -297\ \mathrm{MJ}/kmol$$

SULFUR BURNING

- Very little SO_3 (g) forms at the 1150 °C flame temperature of this reaction.
- This explains the need for two-step oxidation, i.e.:
  - (a) Burning of sulfur to SO_2 then:
  - (b) Catalytic oxidation of SO_2 to SO_3 , 425 °C.
- The product of sulfur burning is hot, dry SO_2 , O_2 , N_2 gas.
- After cooling to 425 °C, it is ready for catalytic SO_2 oxidation and subsequent H_2SO_4 making.
- The gases at 800 – 1000 °C flow through the baffled chamber to leave at this temperature and pass in a fire tube boiler where the steam is generated.



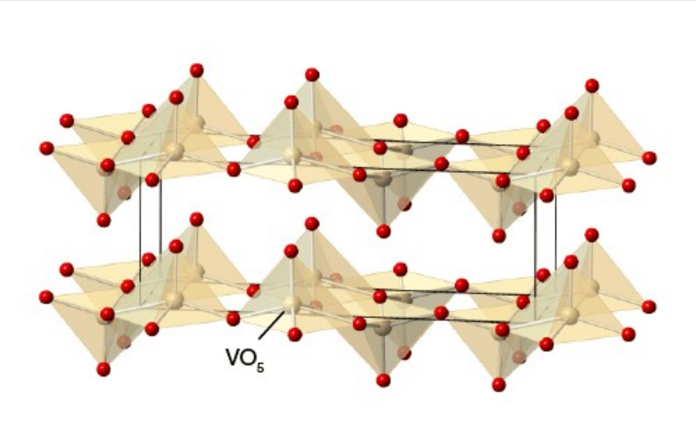


SULFUR BURNING

- Gases enter the convertor at a controlled temperature of 410 – 425 ºC where SO_2 is converted to SO_3 on the surface of the vanadium catalyst.
- Feed gas is always dry. This dryness avoids:
  - (a) Accidental formation of H_2SO_4 by reaction of $H_2O_{(g)}$ with the $SO_{3\ (g)}$ product of catalytic SO_2 oxidation.
  - (b) Condensation of the H_2SO_4 in cool flues and heat exchangers.
  - (c) Corrosion.
- The $H_2O_{(g)}$ is removed by cooling/condensation and by dehydration with $H_2SO_{4\ (g)}$.

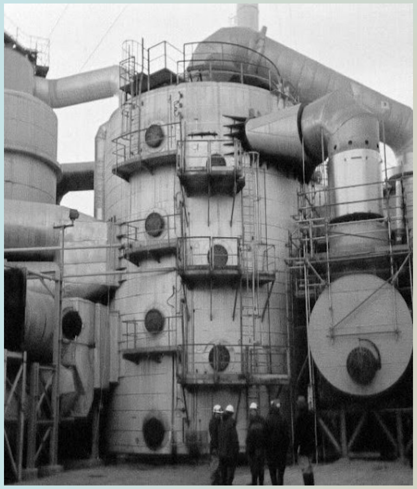
CATALYST

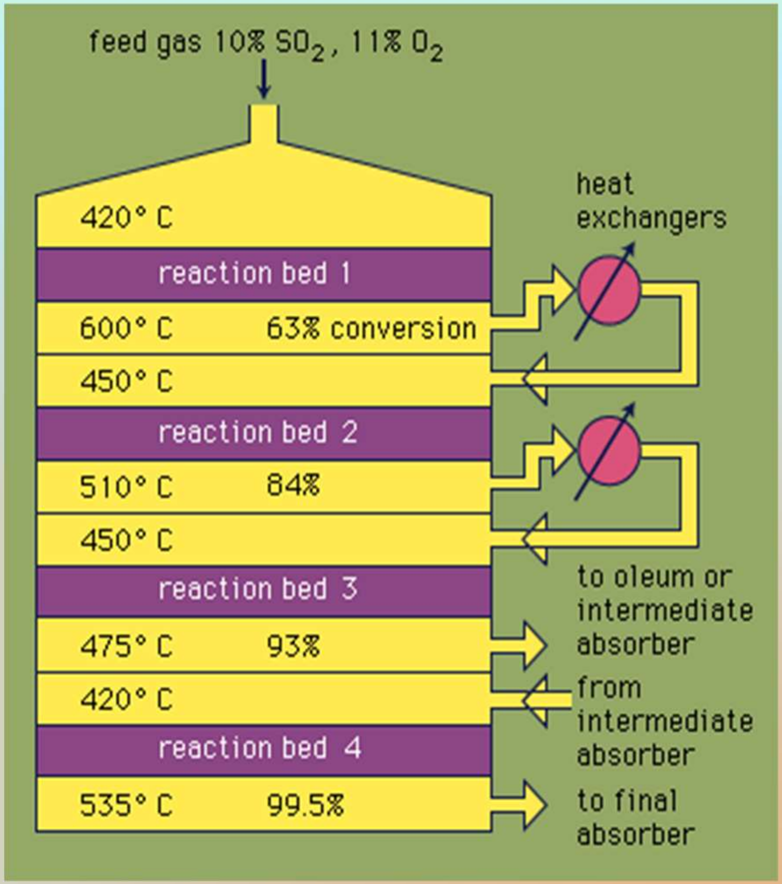
- At its operating temperature, 375 – 480 ºC, SO_2 oxidation catalyst consists of a molten film of V, K, Na, (Cs) pyrosulfate salt on a solid porous SiO_2 substrate.
- The molten film rapidly absorbs $SO_{2\ (g)}$ and $O_{2\ (g)}$ - and rapidly produces and desorbs $SO_{3\ (g)}$.



TYPICAL CATALYST DISTRIBUTION

Catalyst Bed	% Catalyst	Conversion %
1	19.4	63
2	25	84
3	26.7	93
4	28.9	99.5





Converters are 15 m high and 12 m in diameter.

They typically contain four, 0.5 - 1.0 m thick catalyst beds.

FACTORS AFFECTING CATALYST

1. Arsenic (As) (10 ppm in gas): It cause poisoning which is partially reversible, and the arsenic maybe removed from the catalyst by contacting it with gas containing hydrogen chloride.
2. Selenium (Se): Partially harmful to the catalyst surface.
3. Ammonia (NH_3): Harmful to the catalyst surface and when exists it will be oxidized to nitrogen oxides.
4. Chlorides (1 ppm in gas): Chlorides causes vanadium loss and a reduction in catalyst activity.
5. Fluorides (0.3 ppm in gas) : Attacks the catalyst carrier.
6. Iron oxide will plug the catalyst bed causing an increase in pressure drop.

VANADIUM LOSS

1. Formation of oxychloride or oxyfluorides of vanadium which are volatile compounds.
2. Ash and dust accumulated on the surface of the catalyst; this decreases the surface area available for catalysis.

CATALYST REGENERATION

- The regeneration of the catalyst is carried out by screening.
- Factors affecting screening loss:

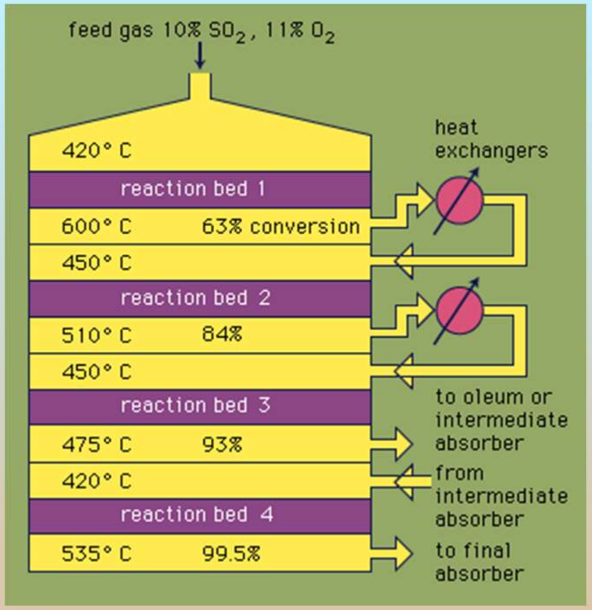
1. Condition of catalyst:
    - ✓ Pellet hardness
    - ✓ Pellet size
    - ✓ Pellet environment
2. Screen size
3. Screening rate/technique.

CONVERTOR

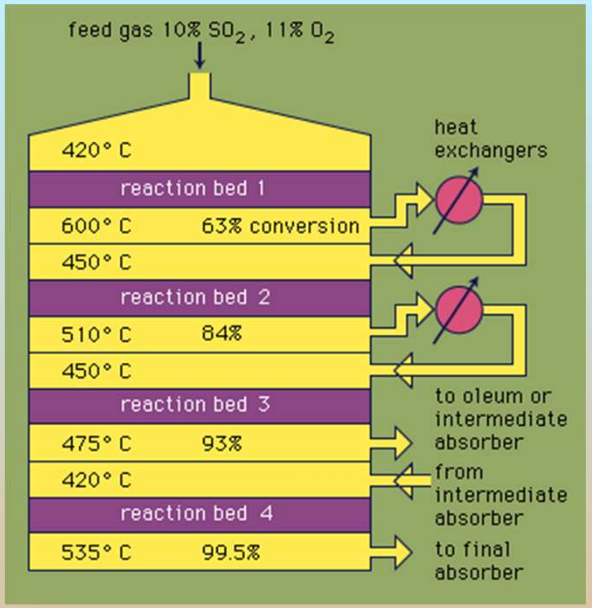
- The conversion of SO_2 to SO_3 is exothermic reversible reaction producing heat.
- In order to achieve the maximum conversion, the convertor is split into number of beds with provision of removing heat of reaction after each stage.
- This will tend to increase the forward reaction.
- At each time the gas leaves any of the catalyst beds has to enter another equipment (super heater or heat exchanger) where the heat in excess is eliminated with another medium.

CONVERTOR

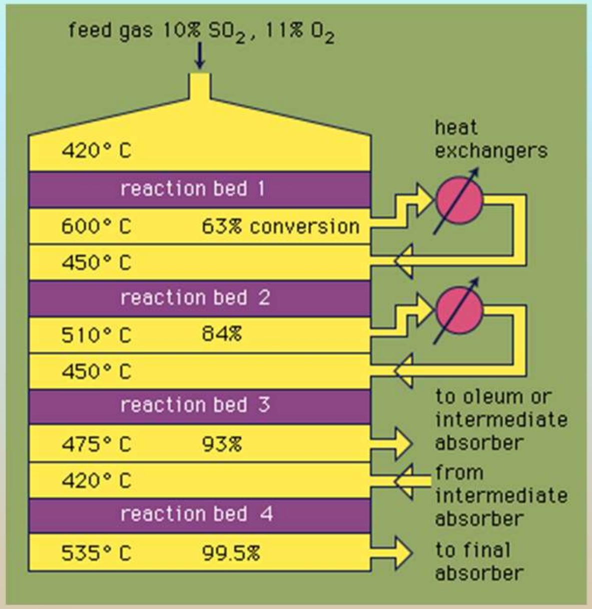
- The gas leaving the heat exchanger enters the other bed at controlled predetermined lower temperature of 420-440ºC
- The sulfurous gases enters 1st catalyst bed at 420ºC and leaves at 600ºC.
- Gas enters a super heater at 600ºC and leaves at 450ºC where it superheats the steam generated in the boiler.
- Gas enters the 2nd catalyst bed at 450ºC and leaves at 510ºC.
- Gas enters a hot gas-gas heat exchanger at 510ºC and leaves at 450ºC.



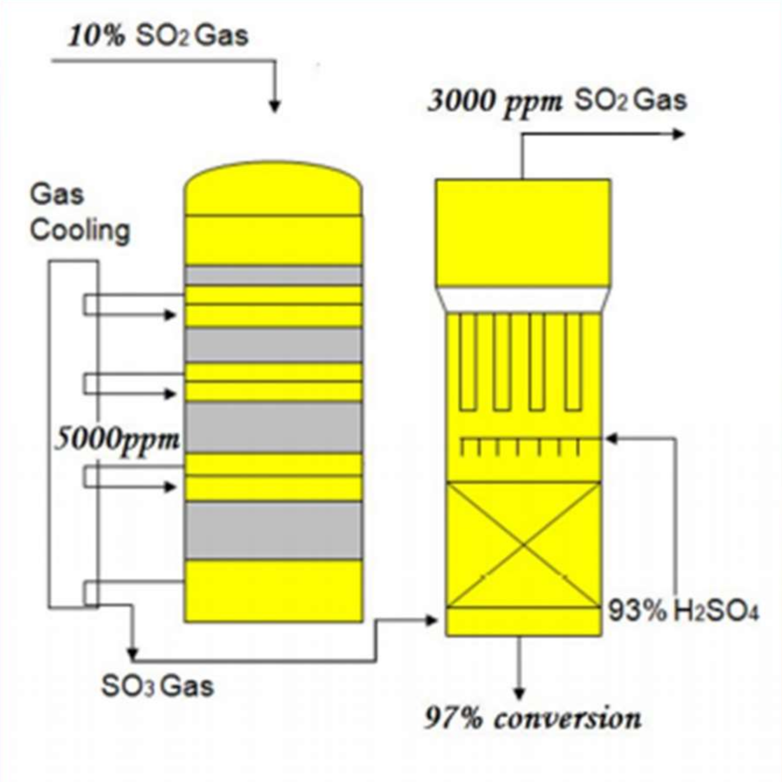
- Gas enters the 3rd catalyst bed at 450°C and leaves at 475°C.
- Gas passes through two gas heat exchanger and water economizer successively where it is cooled down from 475 to 200°C.
- After water economizer the gas enters inter- pass absorbing tower where SO_3 is absorbed by the downward flowing concentrated sulfuric acid 98.5%.
- Gas leaving the tower passes through the gas- gas heat exchanger where it gains heat and temperature elevated from 75 up to 420°C.



- Gas enters the 4th catalyst bed at 420ºC and leaves at 535ºC.
- Gas enters a final water economizer and leaves to a final absorbing tower where the SO_3 is absorbed also with the downward flowing concentrated sulfuric acid 98.5%.
- The gas leaves the absorbing tower to the atmosphere at 80ºC.

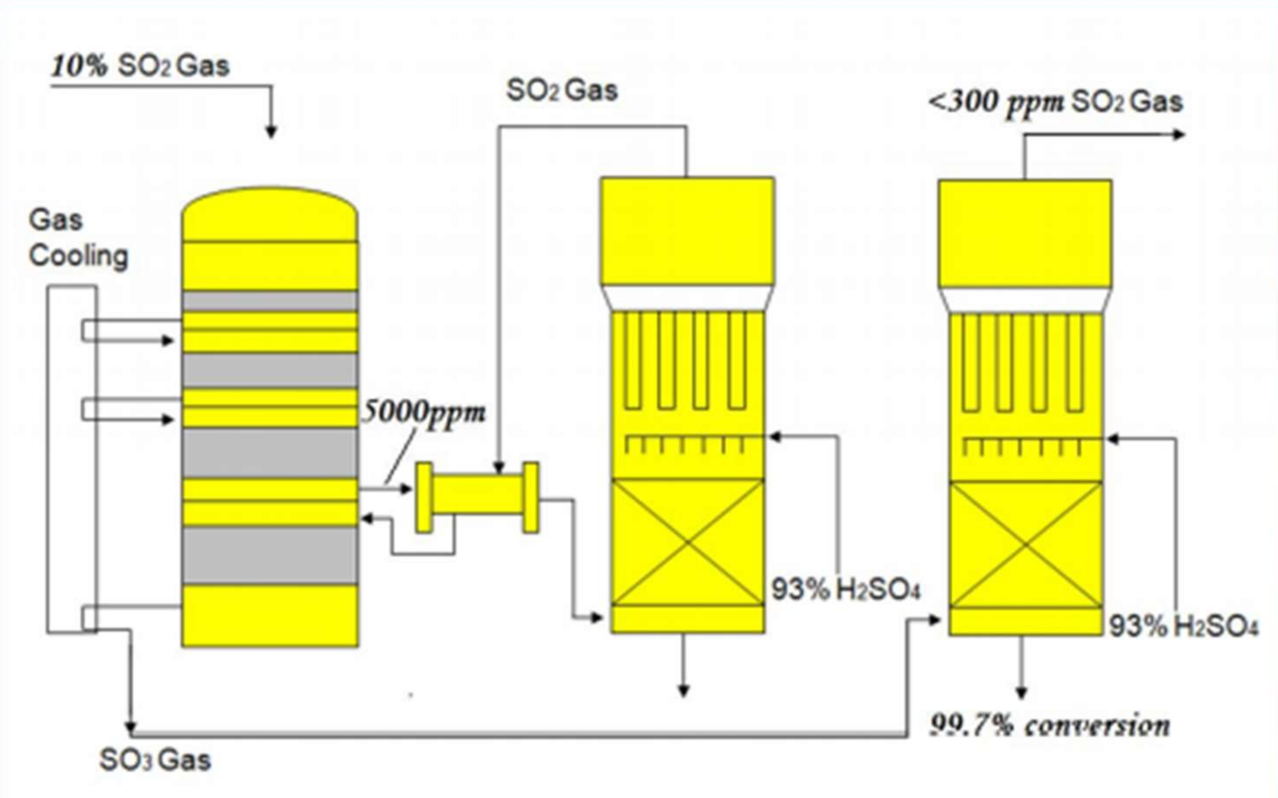


SINGLE ABSORPTION



Single Absorption

DOUBLE ABSORPTION



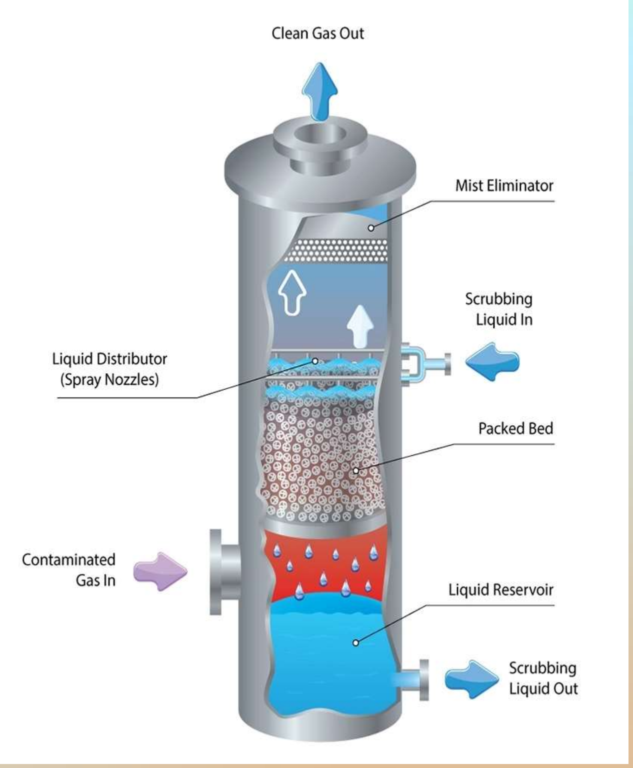
Double Absorption

H_2SO_4 PRODUCTION

- Catalytic oxidation's SO_3 (g) product is made into H_2SO_4 by contacting catalytic oxidation's exit gas with strong sulfuric acid (98.5% Acid and 1.5% H_2O).
- The reaction is:

$$SO_{3\,(g)} + H_2O_{(l)} \xrightarrow{350\text{-}380\ K} H_2SO_{4\,(l)}$$

- This reaction produces strengthened sulfuric acid because it consumes $H_2O_{(l)}$ and makes $H_2SO_{4\,(l)}$.
- It is strongly exothermic (ΔH = -132 MJ per kg- mole of SO_3).

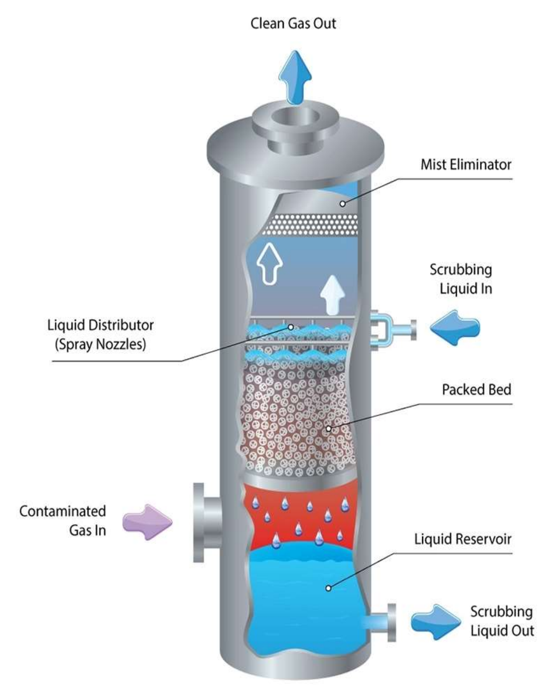


H_2SO_4 PRODUCTIONS

- Catalytic H_2SO_4 (l) is not made by reacting SO_3 (g) with water.
- This is because the reaction of SO_3 (g) with water (l) is so exothermic that the product of the SO_3 (g) + H_2O (l) $\longrightarrow$ H_2SO_4 reaction would be hot H_2SO_4 vapor- which is difficult and expensive to condense.
- The small amount of H_2O (l) and the massive amount of H_2SO_4 (l) in the reaction's input acid avoids this problem.
- The small amount of H_2O (l) limits the extent of the reaction.
- The large amount of H_2SO_4 (l) warms only 25 ^{o}C while it absorbs the reaction's evolved heat.

ABSORPTION TOWER

- The most common type of absorption tower is packed columns which is used in order to bring intimate contact between the two fluids.
- A gas and liquid of counter current flow is normally employed with the gas entering at the bottom and the liquid at the top.
- The shell of the tower maybe constructed of metal ceramic material, or it maybe steel a corrosion-resistance lining.
- The packing is supported on a rigid or screen which must be of an open pattern so as not to offer a high resistance to flow.



ABSORPTION TOWER

- The liquid is introduced at the top and must be evenly distributed over the whole cross section.
- The smaller the packing the larger is the interfacial area for a given volume of column and in general the greater the transfer per unit height, but the higher the ΔP so the backing should be of uniform size so as to produce a bed of high voidage, and low pressure drop.
- Towers used are constructed of shell lined by anti acid resistant plastic lining of polyisobutylene sheets and anti acid stone, the backing is anti-acid ceramic saddles or rings.
- The liquid distributer is made of cast iron.

ABSORPTION TOWER

- The tower is packed with ceramic saddles.
- 98.5 mass% H_2SO_4 , 1.5 mass% H_2O sulfuric acid is distributed uniformly across this packed bed.
- The acid flows through slots in the downcomers down across the bed.
- It descends around the saddles while SO_3 - rich gas ascends, giving excellent gas - liquid contact.
- The result is efficient H_2SO_4 production.
- A tower is 7 m diameter; its packed bed is 4 m deep.
- About 25 m^3 of acid descends per minute.

ABSORPTION TOWER

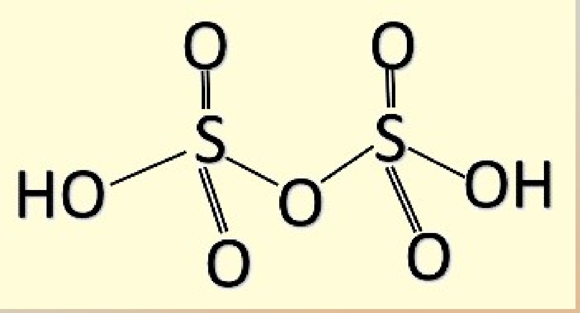
- The absorption of SO_3 in H_2SO_4 is believed to be taking place in the following manner:

$$SO_{3\,(g)} + H_2SO_{4\,(l)} \longrightarrow H_2S_2O_{7\,(l)}$$

$$H_2S_2O_{7\,(l)} + H_2O_{\,(l)} \longrightarrow 2H_2SO_{4\,(l)}$$

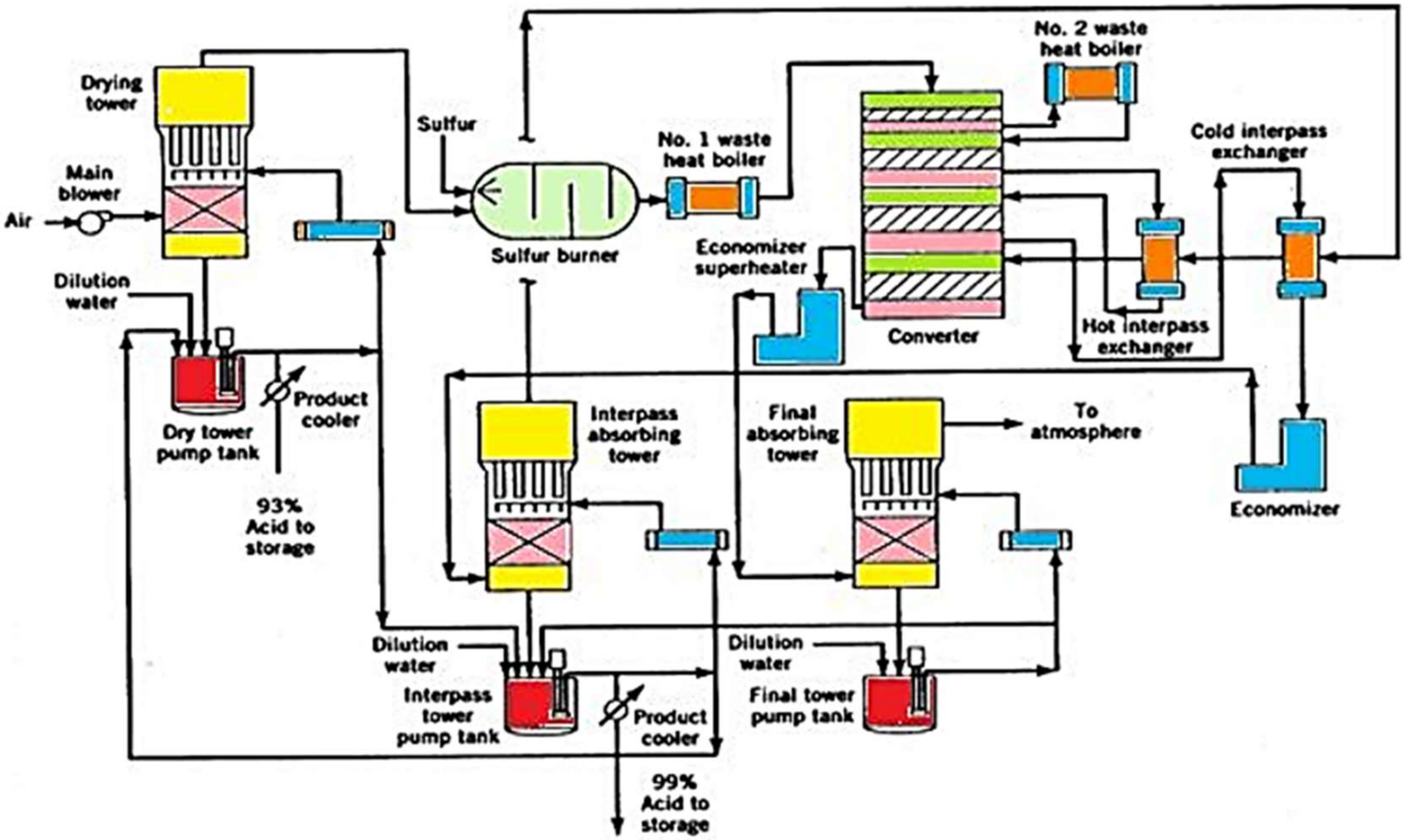
$$H_2SO_{4\,(l)} + xH_2O_{\,(l)} \longrightarrow 98.5\%\ H_2SO_{4\,(l)}$$

- The formula $H_2S_2O_7$ is called oleum.
- Oleum is a term referring to solutions of various compositions of sulfur trioxide in sulfuric acid.



COOLERS

- To cool down the hot H_2SO_4 acid, seawater is used as a cooling medium.
- Anodic protection is applied to decrease the corrosion of the cooler.
- Usually, the number of tubes in the cooler is greater than the required number because whenever a tube is corroded it will be closed from both sides “in and out”.
- H_2SO_4 produce from the absorber is 99.5% concentration, then in the dilute tank water is added to get 98.5% acid concentration.


Drying tower
Main blower
Air
Dilution water
Sulfur
Sulfur burner
No. 1 waste heat boiler
No. 2 waste heat boiler
Converter
Cold interpass exchanger
Economizer superheater
Hot interpass exchanger
Dry tower pump tank
Product cooler
93% Acid to storage
Interpass absorbing tower
Final absorbing tower
To atmosphere
Economizer
Dilution water
Interpass tower pump tank
Product cooler
Dilution water
Final tower pump tank
99% Acid to storage