

# CHEMICAL ENGINEERING

## Chemical Technology



Comprehensive Theory  
*with Solved Examples and Practice Questions*



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**Chemical Technology**

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# Inorganic Chemical Industries

## 1.1 Sulphur and Sulphuric Acid Industry

### 1.1.1 Sulphur Industry

- Sulphur is the basic raw material for manufacture of sulphuric acid ( $\text{H}_2\text{SO}_4$ ), which typically occurs as a rhombic crystal.
- 80 - 90% of sulphur is used for manufacture of sulphuric acid.
- 7% to paper and pulp, 3% to  $\text{CS}_2$  making.
- And the rest is used in the manufacture of  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{CS}_2$ ,  $\text{P}_2\text{S}_5$ .

#### Properties:

Chemical formula : S

Atomic weight : 32.07

Melting point : Rhombic crystal ( $112.8^\circ\text{C}$ )

Monoclinic crystal ( $119^\circ\text{C}$ )

Boiling point :  $444.6^\circ\text{C}$

Various process are employed in the manufacture of sulphur.

They are:

1. Frasch process : Elemental sulphur mining from salt domes.
2. By oxidation - reduction of  $\text{H}_2\text{S}$
3. Finnish process : Elemental sulphur from pyrites

#### Process:

Recovery of elemental sulphur during the refining of crude petroleum.

#### 1. Frasch Process:

- Treated water at suitable temperature and pressure is pumped into wells of sulphur deposit, water moves upward and the collected discharge is undergone a few more steps to collect sulphur.
- No chemical reaction involved.

#### Raw materials:

- Sulphur deposits in salt domes.
- Hot water supply

**Process description:**

- Treated water is sent to domes at 160–180° and 25 atm.
- Molten sulphur sinks to the bottom of casing.
- Sump-separation units are used.
- Filtration is sometimes used to remove contaminants.
- Treated water is used to avoid scaling and corrosion.

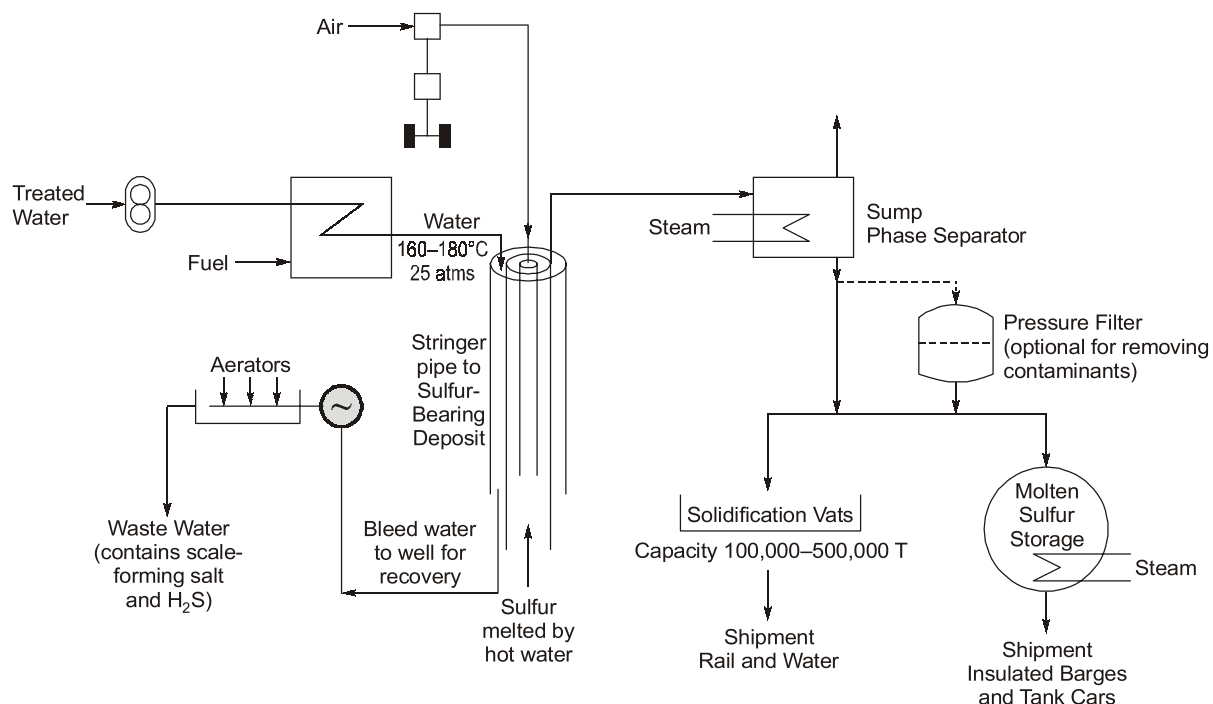


Fig. : Elemental sulfur mining by Frasch process

## 2. Oxidation and Reduction of $H_2S$ :

Raw materials:

- $H_2S$  from natural gas and petroleum refinery.

Reactions:

- $2H_2S + 3O_2 \rightleftharpoons 2SO_2 + 2H_2O$  (Exothermic)
- $4H_2S + 2SO_2 \rightarrow S_6(g) + 4H_2O$  (Exothermic)

**Process:**

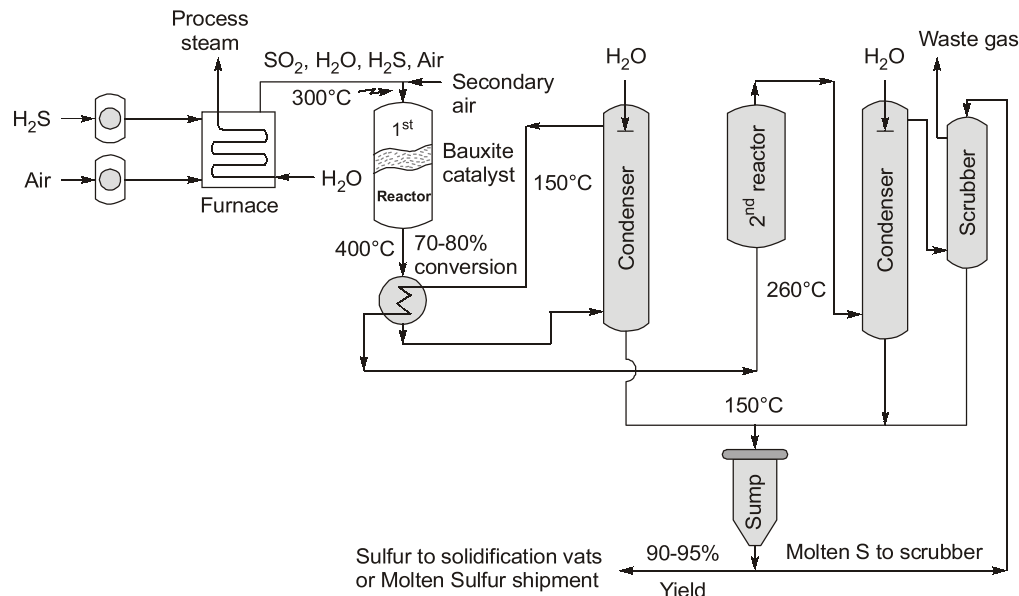
It consists of two-stage catalytic converter with interstage cooling.

**First stage:**

- Catalyst: Bauxite
- Operated at 300° - 400° C
- 70 - 80% conversion achieved
- Exothermic  $SO_2$  oxidation of  $H_2S$

**Second stage:**

- Operated at 250 - 300° C



**Fig. :** Sulfur production by oxidation-reduction of  $H_2S$

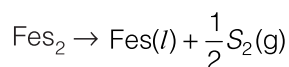
**3. Elemental Sulphur from Pyrites (Finnish Process):**

Raw materials:

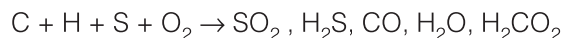
- Pyrites ore [200 mesh]
- Limestone [To remove Silica]
- Water

**Chemical reactions:**

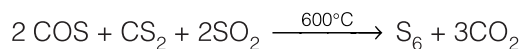
Thermal dissociation:



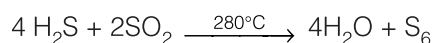
- General combustion reaction :**



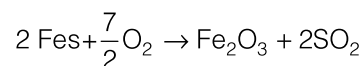
- Hot stage (sulphur recovery)**



- Cold stage (sulphur recovery):**



- Roasting of  $FeS$



**Co-products:**

- $\text{SO}_2$  [From Fes roasting]
- $\text{Fe}_2\text{O}_3$  [From Fes rotating]

**1.2 Sulphuric Acid**

Sulphuric acid is a highly corrosive strong dibasic mineral acid with the molecular formula ( $\text{H}_2\text{SO}_4$ ). It is a pungent, colorless to slightly yellow viscous liquid which is soluble in water at all concentrations.

**Physical Properties:**

- Molecular formula :  $\text{H}_2\text{SO}_4$
- Molecular Weight : 98.08 gram/mole
- Melting point :  $10^\circ\text{C}$
- Boiling point :  $290^\circ$
- Density :  $1840\text{ kg/m}^3$
- Solubility : Miscible with water in all proportions

**1.2.1 Chemical Properties**

- **Dehydrating agent:**
  - It is hygroscopic, readily absorbing water vapour from air.
  - Has great affinity for water and the reaction is extremely exothermic.
  - It forms mono and dihydrate with water,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .
- **Oxidising agent:**
  - Gives  $\text{O}_2$  on strong heating.
  - Hot con  $\text{H}_2\text{SO}_4$  also acts as an oxidising agent.
- **Acidic nature:**
  - Strong basic acid
  - Forms two types of salts with alkalis  
Bisulphates [ $\text{HSO}_4^-$ ] ...  $\text{NaHSO}_4$   
Sulphates [ $\text{SO}_4^{2-}$ ] ...  $\text{Na}_2\text{SO}_4$
- **Manufacturing process:**  
The industrial manufacture of sulphuric acid is done mainly by two processes.
  - The lead chamber process
  - The contact process

**1.2.2 The Lead Chamber Process**

1. This is an old process and uses Nitrogen oxides as oxygen carrying catalysts for the conversion of sulphur dioxide ( $\text{SO}_2$ ) to sulphur trioxide ( $\text{SO}_3$ ).
2. The production of sulphur trioxide and sulphuric acid takes place in the huge lead chambers and that's why the name lead chamber process.
3. Produces acid of concentration less than 80%.
4. All new plants use contact process, although.
5. Gives an yield of 98%.



**Disadvantages:**

1. Produces acid of low quality and concentration.
2. Limitations in throughput.

**1.2.3 The Contact Process**

In the contact process, sulphur dioxide is converted to sulphur trioxide using  $V_2O_5$  catalyst. Platinum was initially used, but now replaced by  $V_2O_5$  catalyst because of platinum's susceptibility to poisoning.

**Catalyst:**

6.2 - 6.5%  $V_2O_5$  supported on silica and 1% potassium sulphate.

The  $V_2O_5$  is dispersed on a porous carrier in a pellet form.

**Raw materials:**

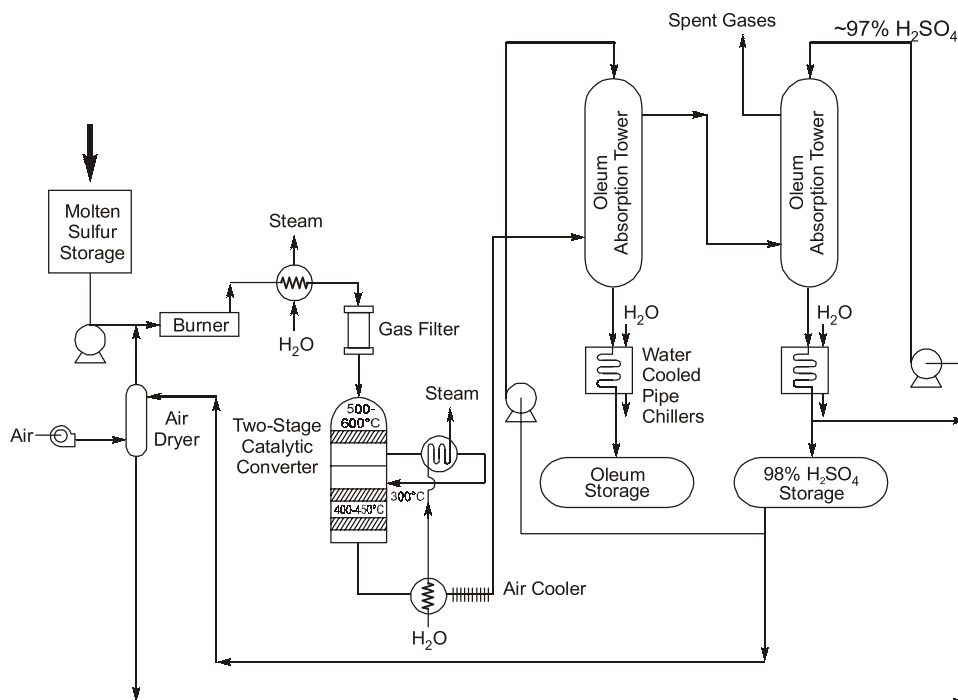
- Sulphur dioxide or pyrites ( $FeS_2$ )
- Air

**Chemical reactions:**

Oxidation:  $S + O_2 \rightarrow SO_2$  (Exothermic)

$2SO_2 + O_2 \rightleftharpoons 2SO_3$  (Exothermic)

Hydration:  $SO_3 + H_2O \rightarrow H_2SO_4$

**Process Description:**

The steps in the process are as follows:

1. Buring of sulphur
2. Catalytic oxidation of  $SO_2$  to  $SO_3$
3. Hydration of  $SO_3$  (oleum absorption)
4. Scrubbing with 97%  $H_2SO_4$ .

## 1. Buring of sulphur:

- Burning of sulphur in presence of dry air is carried out in sulphur pyrite burner.
- Dry air is used to prevent corrosion.

2. Catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ :

This takes place in two stages:

Stage-1: High temperature (500 - 600°C)

Stage-2: Low temperature (400 - 450°C)

- Air -  $\text{SO}_2$  mixture from burner containing 7 - 10%  $\text{SO}_2$  and 11 - 14%  $\text{O}_2$  is preheated if necessary.
- This mixture is sent into the high temperature stage which contains 30% of the catalyst and conversion about 80% of  $\text{SO}_2$  is achieved.
- The converter product is cooled to 300° C and fed to second stage.
- In second stage, the yield increases to 97%.

3. Hydration of  $\text{SO}_3$  [oleum absorption]:

- Sulphur trioxide hydration is done by absorption of  $\text{SO}_3$  in 98 - 99% sulphuric acid in the oleum absorption tower.
- Oleum concentration upto 40% are achieved.

4. Surubbing with 97%  $\text{H}_2\text{SO}_4$ :

- The oleum from the oleum absorption tower is surubbed with 97%  $\text{H}_2\text{SO}_4$  and the sulphuric acid of 98% concentration is achieved.

**NOTE:** Concentration of oleum is expressed in terms of sulphur trioxide and sulphuric acid.

Ex. 40% oleum means 40 kg to  $\text{SO}_3$  in 60 kg to  $\text{H}_2\text{SO}_4$ .

## 1.2.4 Kinetics and Thermodynamics

The most important step that decides the yield of  $\text{SO}_3$  in turn  $\text{H}_2\text{SO}_4$  is the catalytic conversion of  $\text{SO}_2$  to  $\text{SO}_3$ .

**Effect of temperature:**

- Being an exothermic reaction, this reaction can't be conducted at a higher temperature, because that decreases the formation of  $\text{SO}_3$ .
- At low temperature, the rate of combustion of  $\text{SO}_2$  is very low.
- Hence, an optimum temperature of 450° C is selected as the operating temperature.

**Effect of pressure:**

- Formation of  $\text{SO}_3$  is associated with decrease in volume, so increase in pressure is expected to increase the rate of formation of  $\text{SO}_3$ .
- But no significant increase in yield is observed at high pressures.
- Hence a pressure of 1.5 - 1.7 atms is selected.

### 1.3 Comparison of Vanadium and Platinum Catalyst

	Characteristic	Platinum	V <sub>2</sub> O <sub>5</sub>
1.	Investment	High investment, Lower life time	Initially less investment 5% replacement is required per year
2.	Catalyst poisoning	Easily poisoned, mainly by arsenic	Relatively immune to poisoning
3.	Handling of SO <sub>2</sub>	8 - 10%	7 - 8%
4.	Conversion	Lower	Higher

**Example - 1.1**

Which one of the following oxides is used as oxygen carrying catalyst in lead chamber process?

- (a) Carbon oxides (b) Sulphur oxides  
(c) Nitrogen oxides (d) None

**Solution : (c)**

**Example - 1.2**

Reason for using only 7–8% SO<sub>2</sub> in the input stream of catalytic converter?

- (a) Catalyst (V<sub>2</sub>O<sub>5</sub>) limitation  
(b) Converter limitation because of heat accumulation problem  
(c) To increase H<sub>2</sub>SO<sub>4</sub> concentration  
(d) For better flow patterns inside the converter

**Solution : (a)**

**Example - 1.3**

What does DCDA mean?

- (a) Double Converter Double Absorption (b) Double Contact Double Absorption  
(c) Diverging Contact Double Absorption (d) Double Contact Diverging Absorption

**Solution : (b)**

### 1.4 Chlor-Alkali Industry

This industry represents production of three major industrial chemicals.

1. Na<sub>2</sub>CO<sub>3</sub> [Sodium Carbonate, Soda Ash]
2. NaOH [Caustic Soda, Sodium Hydroxide]
3. Cl<sub>2</sub> [Chlorine]

#### Soda Ash (Na<sub>2</sub>CO<sub>3</sub>):

Also known as washing soda is a sodium salt of carbonic acid. Most commonly occurs as a crystalline substance (Na<sub>2</sub>CO<sub>3</sub> · 7H<sub>2</sub>O). It is synthetically produced in large quantities from salt and limestone.

**Properties:**

Molecular weight - 106  
MP - 851°C

BP - Decomposes  
Solubility - Soluble in water

**Consumption:**

Soda ash is the low-cost, highly available, reasonably pure alkali.

**Manufacture:**

Sodium carbonate is manufactured by these following processes.

1. Leblanc process
2. Solvay [ammonia soda] process
3. Dual process

**1. Leblanc process:**

The Leblanc process was discovered in 1773 and was used universally but replaced by Solvay process.

**Reaction:**

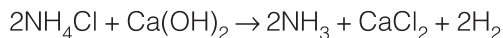
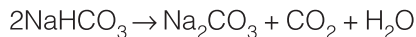
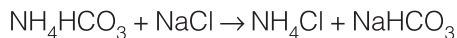
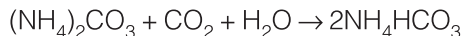
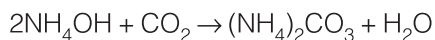
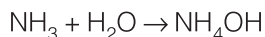
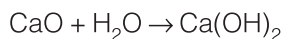
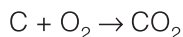
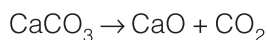
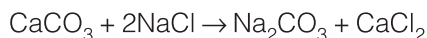
Sodium sulphate in reaction with lime stone (calcium carbonate) to give soda ash and gypsum.

**2. Solvay [Ammonia soda] process:**

The widely used and acclaimed process in the world for manufacture of soda Ash.

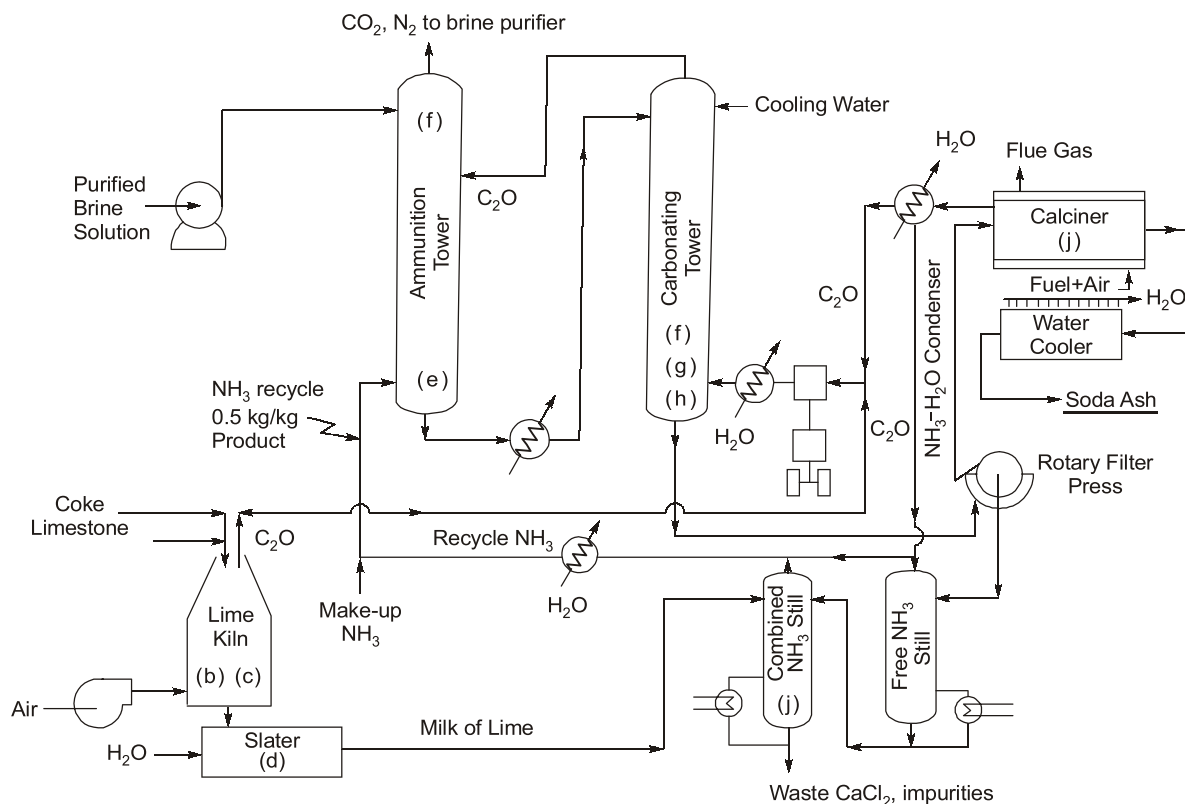
Raw materials:

- (i) Sodium chloride (NaCl)
  - (ii) Lime stone ( $\text{CaCO}_3$ )
  - (iii) Coke
  - (iv) Ammonia
  - (v) Stream of cooling water.
- NaCl is obtained from sea water.
  - Limestone is obtained from mineral calcite.

**Reactions:****Overall reaction:**

**Process:**

Ammonia is dissolved in a salt solution and the obtained ammoniate brine solution is reacted with carbon dioxide ( $\text{CO}_2$ ). A precipitate of  $\text{NaHCO}_3$  obtained is calcined to give high purity  $\text{Na}_2\text{CO}_3$

**Ammoniation of brine:**

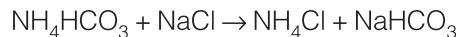
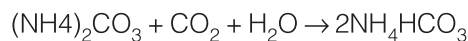
The purified brine is brought into contact with ammonia ( $\text{NH}_3$ ) gas in a countercurrent fashion. i.e. Brine from top and ammonia from bottom of the absorber tower.

The brine solution takes up necessary amount of ammonia and liberates heat. Some carbon dioxide is also absorbed by ammonia, because of which some insoluble carbonate is also precipitated.

The ammoniated brine is allowed to settle, cooled to  $30^\circ\text{C}$  and sent to carbonate tower.

**Carbonation of ammoniated brine:**

- Ammoniated brine and compressed carbon dioxide are also contacted in counter-current fashion. Brine from top and  $\text{CO}_2$  from bottom of carbonation tower.
- Carbonating tower operates in series.
- Temperature is maintained at  $20 - 25^\circ\text{C}$  at both ends and  $45 - 55^\circ\text{C}$  at the middle.
- The exit stream of carbonating tower contains sodium bicarbonate ( $\text{NaHCO}_3$ ), Ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ).
- This steam is sent into a tower called making tower.
- Ammonium carbonate reacts with  $\text{CO}_2$  to form ammonium bicarbonate, and now ammonium bicarbonate reacts with salt forming  $\text{NaHCO}_3$ .



**Filtration:**

$\text{NaHCO}_3$  slurry is then filtered using rotary vacuum filter.

- The salt and  $\text{NH}_4\text{Cl}$  are removed by washing with water.
- The resulting mixture is sent to a centrifugal filter to remove moisture and then sent to calcination.

**Calcination:**

- $\text{NaHCO}_3$  is calcined at about  $200^\circ\text{C}$ .
- The soda ash obtained is passed through a rotary cooler.
- The exit gases ( $\text{NH}_3$ ,  $\text{CO}_2$ ) are condensed to give  $\text{NH}_3$  (liquid),  $\text{CO}_2$  (sent to carbonating tower)

The product of calciner is light soda ash. To produce dense soda ash, sufficient water is added to light soda ash to form a monohydrate and the mixture is recalcined.

**Engineering problems:**

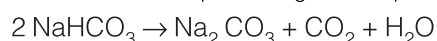
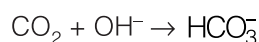
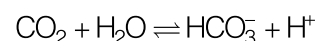
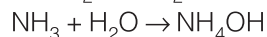
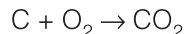
- Most  $\text{NaHCO}_3$  forms cake on sides of the Kiln, which results in poor heat transfer.

**1.5 Dual Process [Modified Solvay Process]****1.5.1 Raw materials**

- Crystalline salt ( $\text{NaCl}$ )
- Ammonia

**Coproduct:**

- $\text{NH}_4\text{Cl}$  (Ammonium chloride)

**Reactions.****Process:**

The important modification of the dual process is the production of  $\text{NH}_4\text{Cl}$  as a coproduct rather than liberation of the ammonia (from  $\text{NH}_4\text{Cl}$ ) for recycle is Solvay process.

- The liquor from bicarbonate filter is mixed with salt feed for the precipitation of  $\text{NH}_4\text{Cl}$  which later and is crystallized in a refrigerated tank at  $0^\circ\text{C}$ .
- The slurry is centrifuged and ammonium chloride crystals are dried in a rotary drum hot air dryer.

**Engineering problem:**

- $\text{NH}_4\text{Cl}$  solution is quite corrosive. Durtmet-20 (or) rubber lined units required.
- The refrigeration cost is almost twice as that of Solvay process.

**Advantages of Solvay process:**

- Less corrosion problem.
- Low quality brine can be used.
- The disposal of coproduct is not a problem.
- Does not require ammonia plant.



### Student's Assignments

- Q1** Which of the following catalysts is employed for converting  $\text{SO}_2$  to  $\text{SO}_3$  in the contact process for sulphuric acid manufacture?
- (a)  $\text{P}_2\text{O}_5$  (b)  $\text{V}_2\text{O}_5$   
(c)  $\text{N}_2\text{O}_5$  (d)  $\text{PCl}_5$
- Q2** In the contact process for sulphuric acid manufacture, the feed gas entering the converter (where  $\text{SO}_2$  is oxidized to  $\text{SO}_3$ ) contains:
- (a) 0.1 – 1%  $\text{SO}_2$  (b) 7–10%  $\text{SO}_2$   
(c) 20–30%  $\text{SO}_2$  (d) 60–70%  $\text{SO}_2$
- Q3** There are two industrial processes for sulphuric acid manufacture (contact process and lead chamber process). The produced acid of lead chamber process is of concentration :
- (a) Less than 10%  
(b) Less than 30%  
(c) Less than 60%  
(d) Less than 80%
- Q4** In the normal contact process of sulphuric acid manufacture, sulphur dioxide to sulphur trioxide conversion efficiency is around
- (a) 20% (b) 50%  
(c) 90% (d) 98%
- Q5** In the double contact double absorption process for sulphuric acid manufacture, sulphur dioxide to sulphur trioxide conversion is more than that in normal contact process and is equal to
- (a) 98.2% (b) 98.5%  
(c) 99.5% (d) 100%
- Q6** In contact process, sulphur dioxide required can be produced either by burning elemental sulphur or by roasting iron, copper or zinc pyrites. In India majority of sulphuric acid plants still use
- (a) Elemental Sulphur  
(b) Iron Pyrites  
(c) Zinc Pyrites  
(d) Copper Pyrites
- Q7** Commercial catalyst used for sulphuric acid manufacture contains:
- (a) 6.2–6.5% vanadium pentoxide supported on silica and 1% potassium sulphate.  
(b) 25% vanadium pentoxide supported on silica and 1% potassium sulphate.  
(c) 50% vanadium pentoxide and 50% potassium sulphate mixture.  
(d) 100% pure vanadium pentoxide.
- Q8** 20% oleum is
- (a) 20%  $\text{SO}_3$  in 80%  $\text{H}_2\text{SO}_4$   
(b) 20%  $\text{SO}_3$  in 100%  $\text{H}_2\text{SO}_4$   
(c) 80%  $\text{SO}_3$  in 100%  $\text{H}_2\text{SO}_4$   
(d) None of those
- Q9** In the manufacture of sulphuric acid, the absorption of sulphur trioxide is done in
- (a) concentrated sulphuric acid  
(b) water  
(c) Both (a) and (b)  
(d) Oleum
- Q10** Advantages of  $\text{V}_2\text{O}_5$  catalyst are :
- (a) Relatively immune to poisons  
(b) Low initial investment  
(c) Both (a) and (b)  
(d) Catalyst is less active
- Q11** Sulphur dioxide is dried by passing it through concentrated sulphuric acid. It is because concentrated sulphuric acid has a very strong affinity for water and reacts with it to form
- (a)  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (b)  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$   
(c)  $\text{H}_2\text{S}_2\text{O}_7$  (d)  $\text{H}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
- Q12** Sulphur dioxide is one of the starting compounds of sulphuric acid industry. It can be obtained by
- (a) Burning sulphur in air or oxygen  
(b) By roasting zinc sulphide in air  
(c) By roasting iron pyrites in air  
(d) All of the above

- Q.13** Which one of the following compounds is called anhydride of sulphuric acid  
(a)  $\text{SO}_3$  (Sulphur trioxide)  
(b)  $\text{SO}_2$  (Sulphur dioxide)  
(c)  $\text{H}_2\text{S}_2\text{O}_7$  (Oleum)  
(d)  $\text{H}_2\text{SO}_3$  (Sulphorous acid)
- Q.14** Which one of the following compounds is used as bleaching agent  
(a)  $\text{SO}_2$  (Sulphur Dioxide)  
(b)  $\text{SO}_3$  (Sulphur Trioxide)  
(c)  $\text{N}_2\text{O}$  (Nitrous Oxide)  
(d)  $\text{CO}_2$  (Carbon Dioxide)
- Q.15** Sulphuric acid is mainly used in  
(a) Fertilizer Industry  
(b) Polymer Industry  
(c) Petroleum Industry  
(d) Automobile Industry
- Q.16** In the contact process of sulphuric acid manufacture, 98% sulphuric acid is stored in  
(a) Hastelloy steel  
(b) Stainless steel  
(c) Cast iron  
(d) Duralumin
- Q.17** Vanadium pentoxide is used as catalyst in sulphuric acid industry for conversion of  $\text{SO}_2$  to  $\text{SO}_3$ , what are the disadvantages of vanadium pentoxide catalyst  
(a) Sulphur dioxide content in incoming air mixture should be limited to 7–10%.  
(b) Require high  $\text{O}_2 : \text{SO}_2$  ratio to give economic conversion.  
(c) Catalyst is less active initially.  
(d) Catalyst is easily poisoned by arsenic.
- Q.18** The conversion of Sulphur dioxide ( $\text{SO}_2$ ) to Sulphur trioxide ( $\text{SO}_3$ ) is favoured by : (strictly according to thermodynamics)  
(a) Increase in temperature above  $500^\circ\text{C}$   
(b) Increase in pressure  
(c) Decrease in temperature  
(d) Decrease in pressure
- Q.19** Which one of the following catalysts is used in conversion of sulphur dioxide to sulphur trioxide in the manufacture of sulphuric acid before vanadium pentoxide  
(a) Platinum (Pt)  
(b) Nitrogen oxides  
(c) Chromium oxide  
(d) Nickel
- Q.20** Sulphur dioxide is produced by oxidation of Hydrogen sulphide ( $\text{H}_2\text{S}$ ). Which one of the following catalysts is used during this process?  
(a) Platinum (Pt)  
(b) Vanadium Pentoxide ( $\text{V}_2\text{O}_5$ )  
(c) Bauxite ( $\text{Al}_2\text{O}_3$ )  
(d) Iron Oxide
- Q.21** Which of the following methods is correct for diluting sulphuric acid?  
(a) Slowly mixing and adding water in sulphuric acid.  
(b) Slowly mixing and adding sulphuric acid in water.  
(c) Rigorous addition of water and sulphuric acid.  
(d) All of the above
- Q.22** Sulphur is the primary raw material for the manufacture of sulphuric acid. Which of the following processes is used for the production of sulphur.  
(a) Frasch process  
(b) Claus process  
(c) Finnish process  
(d) Oxidation, reduction of  $\text{H}_2\text{S}$
- Q.23** The reason why treated water is used in Frasch process (elemental sulphur mining from salt domes using treated water)  
(a) To avoid scaling of the equipment  
(b) Treated water is lighter than untreated water  
(c) Solubility of sulphur is more in treated water  
(d) All of the above
- Q.24** Finnish process is used for the manufacture of sulphur, which is the raw material of sulphuric acid industry. What are the co-products of this process?



- (a) Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ )  
 (b) Sodium Bicarbonate ( $\text{NaHCO}_3$ )  
 (c) Ammonium Chloride ( $\text{NH}_4\text{Cl}$ )  
 (d) Calcium Chloride ( $\text{CaCl}_2$ )

**Q.44** Which of the following processes for producing Sodium Hydroxide ( $\text{NaOH}$ ) has denuding as an intermediate step?

- (a) Diaphragm Cell (b) Mercury Cell  
 (c) Membrane Cell (d) All of the above

**Q.45** Diaphragm cell, Mercury cell and Membrane cell processes produce Sodium Hydroxide, but the product slurry has some  $\text{NaCl}$ . Which one of the following sequence is correct for the content of  $\text{NaCl}$  present in the product slurry?

- (a) Diaphragm > Membrane > Mercury  
 (b) Diaphragm cell < Membrane cell < Mercury cell  
 (c) Membrane cell < Diaphragm cell < Mercury cell  
 (d) Mercury cell < Membrane cell < Diaphragm cell

**Answers :**

- |               |                  |            |               |
|---------------|------------------|------------|---------------|
| 1. (b)        | 2. (b)           | 3. (d)     | 4. (d)        |
| 5. (c)        | 6. (a)           | 7. (a)     | 8. (a)        |
| 9. (a)        | 10. (c)          | 11. (a, b) | 12. (d)       |
| 13. (a)       | 14. (a)          | 15. (a)    | 16. (c)       |
| 17. (a, b, c) | 18. (b,c)        | 19. (a)    | 20. (c)       |
| 21. (b)       | 22. (a, b, c, d) | 23. (a)    | 24. (a, b)    |
| 25. (c)       | 26. (b)          | 27. (c)    | 28. (c)       |
| 29. (a, b, c) | 30. (a)          | 31. (d)    | 32. (b)       |
| 33. (b)       | 34. (c)          | 35. (a)    | 36. (a, c, d) |
| 37. (b)       | 38. (a)          | 39. (b)    | 40. (c)       |
| 41. (c)       | 42. (c)          | 43. (b)    | 44. (b)       |
| 45. (a)       |                  |            |               |

