Chemical Engineering

Chemical Technology

Comprehensive Theory

with Solved Examples and Practice Questions

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Chemical Technology

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CHAPTER 1

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 (H_2SO_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 CS_2 making
- And the rest is used in the manufacture of SO_2 , SO_3 , CS_2 , P_2S_5

Properties:

Chemical formula	:	S
Atomic weight	:	32.07
Melting point	:	Rhombic crystal (112.8° C)
		Monoclinic crystal (119° C)
Boiling point	:	444.6° 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 H_2S
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.

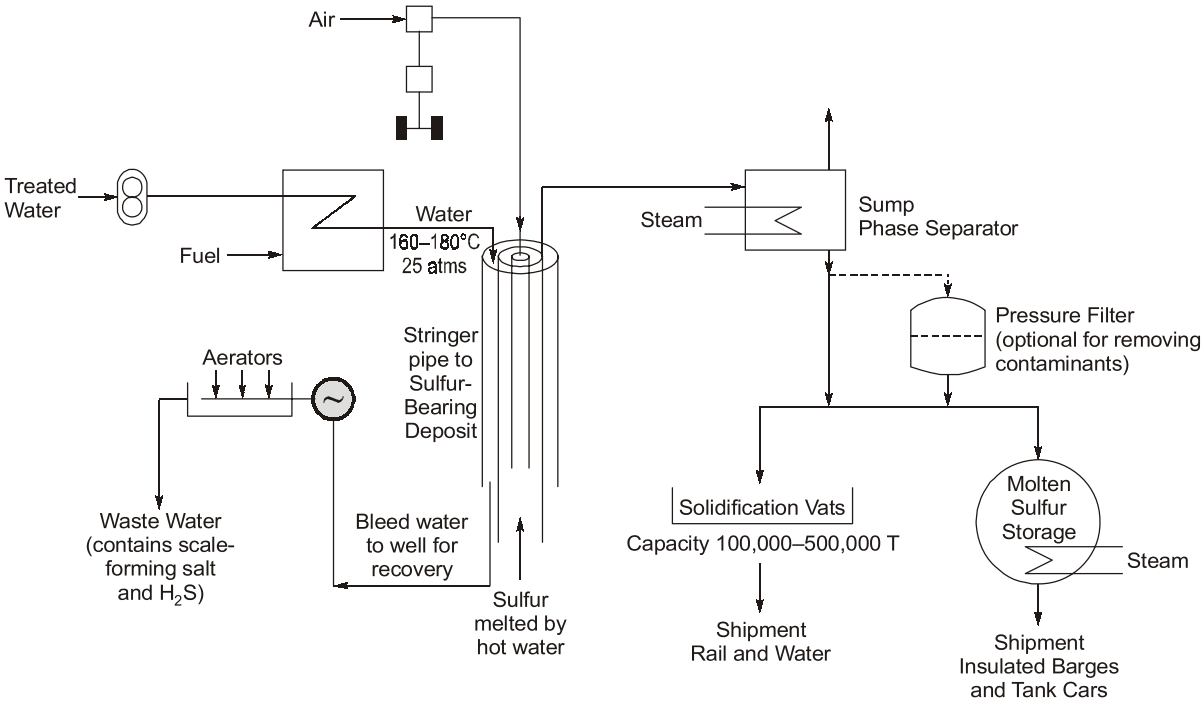


Fig. : *Elemental sulfur mining by Frasch process*

2. Oxidation and Reduction of H_2S :

Raw materials:

- H_2S from natural gas and petroleum refinery.

Reactions:

(i) $2H_2S + 3O_2 \rightleftharpoons 2SO_2 + 2H_2O$ (Exothermic)

(ii) $4H_2S + 2SO_2 \rightarrow S_6\,(g) + 4H_2O$ (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

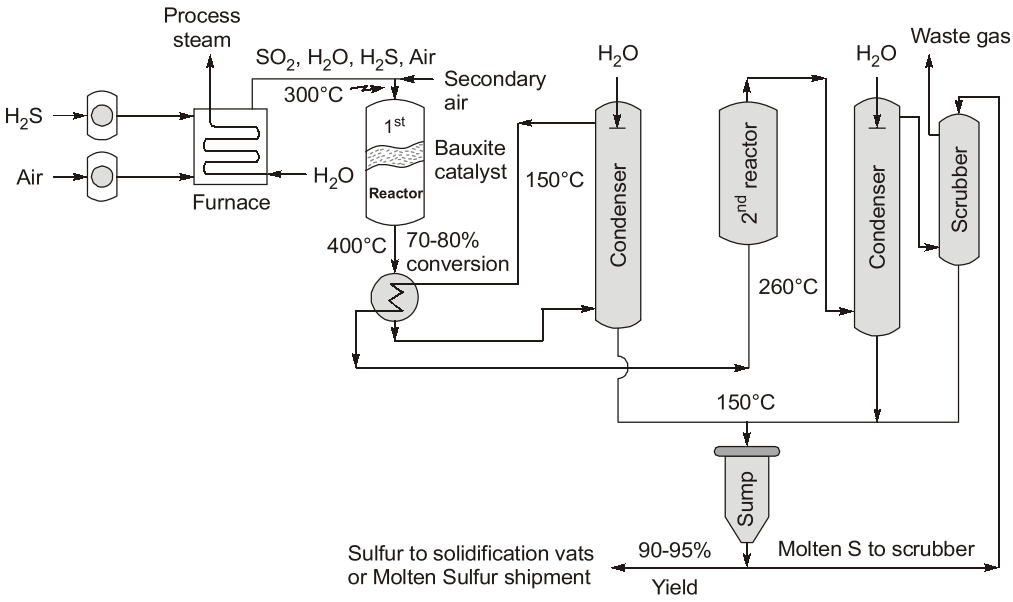


Fig. : *Sulfur production by oxidation-reduction of H_2S*

3. Elemental Sulphur from Pyrites (Finnish Process):

Raw materials:

– Pyrites ore [200 mesh]

– Limestone [To remove Silica]

– Water

Chemical reactions:

Thermal dissociation:

$$Fes_2 \rightarrow Fes(l) + \frac{1}{2}S_2(g)$$

- General combustion reaction :

  $C + H + S + O_2 \rightarrow SO_2, H_2S, CO, H_2O, H_2CO_2$

- Hot stage (sulphur recovery)

  $$2\,COS + CS_2 + 2SO_2 \xrightarrow{600°C} S_6 + 3CO_2$$

- Cold stage (sulphur recovery):

  $$4\,H_2S + 2SO_2 \xrightarrow{280°C} 4H_2O + S_6$$

- Roasting of Fes

  $$2\,Fes + \frac{7}{2}O_2 \rightarrow Fe_2O_3 + 2SO_2$$

Co-products:

- SO_2 [From Fes roasting]
- Fe_2O_3 [From Fes rotating]

1.2 Sulphuric Acid

Sulphuric acid is a highly corrosive strong dibasic mineral acid with the molecular formula (H_2SO_4). It is a pungent, colorless to slightly yellow viscous liquid which is soluble in water at all concentrations.

Physical Properties:

- Molecular formula : H_2SO_4
- Molecular Weight : 98.08 gram/mole
- Melting point : 10° C
- Boiling point : 290°
- Density : 1840 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, $H_2SO_4 . H_2O$, $H_2SO_4 . 2 H_2O$.
- Oxidising agent:
  - Gives O_2 on strong heating.
  - Hot con H_2SO_4 also acts as an oxidising agent.
- Acidic nature:
  - Strong basic acid
  - Forms two types of salts with alkalis

    Bisulphates [HSO_4^-] ... $NaHSO_4$

    Sulphates [SO_4^{2-}] ... Na_2SO_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 (SO_2) to sulphur trioxide (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

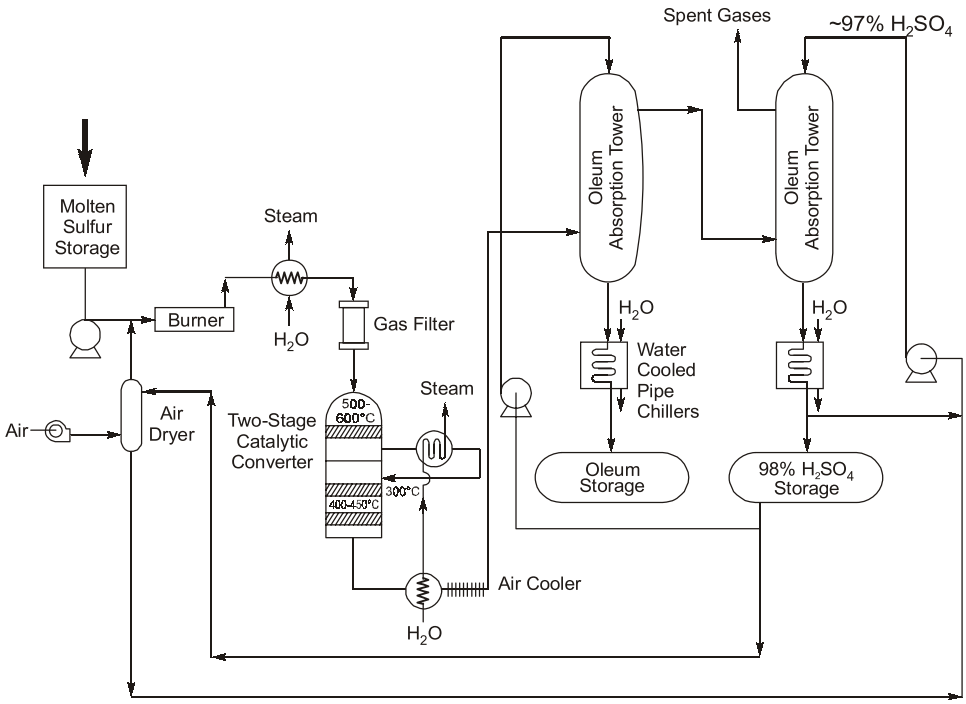
Chemical reactions:

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 SO_2 to SO_3 :**

   This takes place in two stages:

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

   Stage-2 : Low temperature (400 - 450° C)
   - Air - SO_2 mixture from burner containing 7 - 10% SO_2 and 11 - 14% 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 SO_2 is achieved.
   - The converter product is coolded to 300° C and fed to second stage.
   - In second stage, the yield increases to 97%.
3. **Hydration of SO_3 [oleum absorption] :**
   - Sulphur trioxide hydration is done by absorption of SO_3 in 98 - 99% sulphuric acid in the oleum absorption tower.
   - Oleum concentration upto 40% are achieved.
4. **Surubbing with 97% H_2SO_4 :**
   - The oleum from the oleum absorption tower is surubbed with 97% H_2SO_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 SO_3 in 60 kg to H_2SO_4.

1.2.4 Kinetics and Thermodynamics:

The most important step that decides the yield of SO_3 in turn H_2SO_4 is the catalytic conversion of SO_2 to SO_3 .

$$SO_2 + O_2 \rightleftharpoons SO_3 \text{ (Exothermic)}$$

Effect of temperature:

- Being an exothermic reaction, this reaction can't be conducted at a higher temperature, because that decreases the formation of SO_3.
- At low temperature, the rate of combustion of SO_2 is very low.
- Hence, an optimum temperature of 450° C is selected as the operating temperature.

Effect of pressure:

- Formation of SO_3 is associated with decrease in volume, so increase in pressure is expected to increase the rate of formation of 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_2O_5
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_2	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_2 in the input stream of catalytic converter?

(a) Catalyst (V_2O_5) limitation
(b) Converter limitation because of heat accumulation problem
(c) To increase H_2SO_4 concentration
(d) For better flow patterns inside the converter

Solution : (a)

Example - 1.3 What does DCDA mean?

(a) Double Convertor 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_2CO_3 [Sodium Carbonate, Soda Ash]
2. NaOH [Caustic Soda, Sodium Hydroxide]
3. Cl_2 [Chlorine]

Soda Ash (Na_2CO_3):

Also known as washing soda is a sodium salt of carbonic acid. Most commonly occurs as a crystalline substance (Na_2CO_3 , $7H_2O$). It is synthetically produced in large quantities from salt and limestone.

Properties:

Molecular weight - 106
MP - 851° C

Student's Assignments

Q.1 Which of the following catalysts is employed for converting SO_2 to SO_3 in the contact process for sulphuric acid manufacture?
(a) P_2O_5 (b) V_2O_5
(c) N_2O_5 (d) PCl_5

Q.2 In the contact process for sulphuric acid manufacture, the feed gas entering the converter (where SO_2 is oxidized toSO_3) contains :
(a) 0.1 – 1% SO_2 (b) 7–10% SO_2
(c) 20–30% SO_2 (d) 60–70% SO_2

Q.3 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%

Q.4 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%

Q.5 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%

Q.6 In contact process, sulphur dioxide required can be produced either by burning elemental sulphur on 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

Q.7 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.

Q.8 20% oleum is
(a) 20% SO_3 in 80% H_2SO_4
(b) 20% SO_3 in 100% H_2SO_4
(c) 80% SO_3 in 100% H_2SO_4
(d) None of those

Q.9 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

Q.10 Advantages of V_2O_5 catalyst are :
(a) Relatively immune to poisons
(b) Low initial investment
(c) Both (a) and (b)
(d) Catalyst is less active

Q.11 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) $H_2SO_4.H_2O$ (b) $H_2SO_4.2H_2O$
(c) $H_2S_2O_7$ (d) $H_2SO_4 \cdot \frac{1}{2}H_2O$

Q.12 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) SO_3 (Sulphur trioxide)
(b) SO_2 (Sulphur dioxide)
(c) $H_2S_2O_7$ (Oleum)
(d) H_2SO_3 (Sulphorous acid)

Q.14 Which one of the following compounds is used as bleaching agent
(a) SO_2 (Sulphur Dioxide)
(b) SO_3 (Sulphur Trioxide)
(c) N_2O (Nitrous Oxide)
(d) 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) Hastealloy steel (b) Stainless steel
(c) Cast iron (d) Durmet-20

Q.17 Vanadium pentoxide is used as catalyst in sulphuric acid industry for conversion of SO_2 to 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 O_2 : 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 (SO_2) to Sulphur trioxide (SO_3) is favoured by : (strictly according to thermodynamics)
(a) Increase in temperature above 500° 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 (H_2S). Which one of the following catalysts is used during this process?
(a) Platinum (Pt)
(b) Vanadium Pentoxide (V_2O_5)
(c) Bauxite (Al_2O_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 H_2S

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) Sulphur dioxide (SO_2)
(b) Fe_2O_3
(c) FeS
(d) SO_3

Q.25 The lead chamber process was initially used for the manufacture of sulphuric acid. Which one of the following catalysts is used in the lead chamber process?
(a) Platinum
(b) Vanadium Pentoxide (V_2O_5)
(c) Nitrogen oxides
(d) Cobalt (Co)

Q.26 Most sea water contains approximately :
(a) 0.5% dissolved Sodium Chloride
(b) 2.6% dissolved Sodium Chloride
(c) 7.5% dissolved Sodium Chloride
(d) 19.7% dissolved Sodium Chloride

Q.27 Solvay is the most important process for the production of Sodium Carbonate (Soda Ash). What are the raw materials used in the solvay process?
(a) Ammonia and Sodium Chloride
(b) Carbon Dioxide and Sodium Chloride
(c) Carbon Dioxide, Ammonia and Sodium Chloride
(d) Carbon Dioxide, Ammonia

Q.28 Carbon Dioxide is one of the raw materials required for the production of Sodium Carbonate (Soda Ash) by solvay process. Carbon Dioxide used in the solvay process is obtained by
(a) Burning 100% pure coke
(b) Burning coal
(c) By heating limestone
(d) By heating carbonic acid

Q.29 Sodium Hydroxide is produced by :
(a) Mercury Cell Process
(b) Membrane Cell Process
(c) Diaphragm Cell Process
(d) Dual Process

Q.30 Sodium Hydroxide is produced by membrane cell, diaphragm cell, mercury cell processes. Which one of the following gives the purest sodium hydroxide?
(a) Mercury Cell (b) Membrane Cell
(c) Diaphragm Cell (d) All of the above

Q.31 Solvay process is the most important process used in the production of sodium carbonate (soda ash). Which one of the following compounds is the byproduct of the solvay process?
(a) Sodium Sulphate (Na_2S)
(b) Ammonium Chloride (NH_4Cl)
(c) Gypsum ($CaSO_4.2H_2O$
(d) Calcium Chloride ($CaCl_2$)

Q.32 Diaphragm cell process is one of the processes used for the production of Sodium Hydroxide. Which of the following statement(s) is/are correct about Diaphragm cell process?
(a) NaOH produced is pure, Cl_2 gas is contaminated.
(b) NaOH produced is dilute, Cl_2 gas is contaminated.
(c) NaOH produced is dilute, Cl_2 gas is contaminated by hydrogen gas.
(d) NaOH produced is pure, Cl_2 gas is contaminated by hydrogen gas.

Q.33 Diaphragm cell, mercury cell, membrane cell processes are the important methods/processes used for the production of Sodium Hydroxide. Arrange these processes in the order of their purity of Sodium Hydroxide produced.
(a) Diaphragm cell > Membrane cell > Mercury cell
(b) Diaphragm cell < Membrane cell < Mercury cell
(c) Diaphragm cell < Membrane cell > Mercury cell
(d) Membrane cell < Diaphragm cell > Mercury cell

Q.34 NaOH is commercially sold based upon the Na_2O content. The commercially available sodium hydroxide has the Na_2O content of about
(a) 50% (b) 89%
(c) 76% (d) 42%

Q.35 Sodium carbonate is produced by solvay process or Ammonia soda process. Which one of the following reactions represents the overall reaction being conducted in solvay process?
(a) $2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$
(b) $2NaOH + CaCO_3 \rightarrow Na_2CO_3 + Ca(OH)_2$
(c) $2NaOH + 2CaCO_3 + H_2O \rightarrow 2NaHCO_3 + 2Ca(OH)_2$
(d) $2NaCl + MgCO_3 \rightarrow Na_2CO_3 + MgCl_2$

Q.36 Which of the following statement(s) is/are correct about Diaphragm cell, Membrane cell, Mercury

cell processes used for the production of Sodium Hydroxide.
(a) Chlorine gas produced is contaminated in diaphragm cell.
(b) Chlorine gas produced is contaminated in mercury cell.
(c) Chlorine gas produced is contaminated in membrane cell.
(d) Chlorine gas produced is not contaminated in mercury cell.

Q.37 Arrange Diaphragm cell, Mercury cell, Membrane cell processes in the order of the power requirement for the production of sodium hydroxide.
(a) Diaphragm cell > Mercury cell > Membrane cell
(b) Diaphragm cell < membrane cell < Mercury cell
(c) Membrane cell > Mercury cell > Diaphragm cell
(d) Membrane cell < Diaphram cell < Mercury cell

Q.38 Which one of the following processe(s) is/are not used for the production of Sodium Carbonate?
(a) Solvay Process (b) Dual Process
(c) DCDA Process (d) Le-Blanc Process

Q.39 Diaphragm cell, Membrane cell, Mercury cell processes are employed for the production of Sodium Hydroxide (NaOH). Which of the following statement(s) is/are correct about these processes?
(a) Chlorine gas and Sodium carbonate are by-products.
(b) Chlorine gas and Hydrogen gas are by-products.
(c) Sodium carbonate and Hydrogen gas are by-products.
(d) Chlorine gas is not a byproduct.

Q.40 Carbon Dioxide is one of the raw materials used in the solvay process for the production of Sodium Carbonate (Soda Ash). Which one of the following statement is correct about addition of Carbon Dioxide gas?
(a) To adjust the pH of the ammoniated brine solution
(b) For the bleaching of ammoniated brine solution
(c) To remove the impurities of Ca, Mg and Fe
(d) To reduce the scale formation by Sodium Bicarbonate.

Q.41 Synthetically produced Sodium Carbonate is sold based on the percentage of Na_2O present commercially available Sodium Carbonate has the Na_2O content of about
(a) 28% (b) 48%
(c) 58% (d) 88%

Q.42 The ammoniated brine is treated with Carbon Dioxide gas in a carbonating tower for the production of Sodium Carbonate by solvay process. Which one of the following materials is used for carbonating tower?
(a) Hastealloy Steel (b) Stainless Steel
(c) Cast Iron (d) Pig Iron

Q.43 In solvay process for the production of Sodium Carbonate, one of the disadvantages of the products obtained is the formation of scale (fouling) on the equipment. Which one of the following compounds is responsible for the scale formation?
(a) Sodium Carbonate (Na_2CO_3)
(b) Sodium Bicarbonate ($NaHCO_3$)
(c) Ammonium Chloride (NH_4Cl)
(d) Calcium Chloride ($CaCl_2$)

Q.44 Which of the following processes for producing Sodium Hydroxide (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 NaCl. Which one of the following sequence is correct for the content of 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)

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