MANUFACTURE OF SULPHURIC ACID BY OXIDATION OF SULPHUR DIOXIDE

A Report

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in partial fulfilment of the requirements for the award of the degree of

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Under the guidance of

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CERTIFICATE

This is to certify that the thesis titled "Manufacture of Sulphuric acid by Oxidation of Sulphur Dioxide" submitted by Yash Goyal (R900211032), Pramika Bhardwaj (R900211022), Naman Shukla (R900211018) and Asams NJ (R900211007) to the University of Petroleum & Energy Studies, for the award of the degree of BACHELOR OF TECHNOLOGY in Chemical Engineering with specialization in Refining & Petrochemicals is a bonafide record of project work carried out by them under my supervision.

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NOMENCLATURE

- $T_{\rm f}$ = Temperature at Combustion Chamber
- C_p = Specific Heat at constant pressure
- F_t = Temperature Correction Factor
- A = Heat transfer area
- $B_c = Baffle cut$
- C_{pL} = Heat capacity of liquid phase
- $D_b = Bundle \ diameter$
- $D_s =$ Shell diameter
- $D_v =$ Vessel diameter
- $d_e = Equivalent diameter$
- $d_i = Tube$ inside diameter
- $d_o = Tube outside diameter$
- G_s = Shell-side mass flow-rate per unit area
- G_t = Tube-side mass flow-rate per unit area
- $h_i = Film$ heat-transfer coefficient inside a tube
- $h_s =$ Shell-side heat-transfer coefficient
- j_h = Heat transfer factor
- j_H = Heat-transfer factor
- $l_b = Baffle spacing (pitch)$
- $N_t = Number of tubes in a tube bundle$
- $P_s =$ Shell-side pressure drop



 $P_t = Tube-side pressure drop$

- Q = Heat transferred in unit time
- $T_{lm} = Logarithmic mean temperature difference$
- T_m = Mean temperature difference
- T_s =Temperature change in vapour (gas) stream
- U = Overall heat-transfer coefficient
- U_o = Overall heat-transfer coefficient based on tube outside area
- \mathbf{H}_{G} = Height of gas film transfer unit
- \mathbf{H}_{L} = Height of liquid film transfer unit
- \mathbf{H}_{OG} = Height of overall gas phase transfer unit
- \mathbf{H}_{OL} = Height of overall liquid phase transfer unit
- N_{OG} = Number of overall gas-phase transfer units

 $\mu = Viscosity$

- μ_w = Viscosity of water at 20° C
- y_1 = Concentration of solute in gas phase at column base
- y_2 = Concentration of solute in gas phase at column top
- Z= Height of packing
- Dimensionless numbers
- Nu = Nusselt number
- Pr = Prandtl number
- Re = Reynolds number

ABSTRACT

Sulfuric acid is a dense clear liquid. Worldwide, about 180 million tonnes of sulfuric acid are consumed per year. The raw material for sulfuric acid is sulfur dioxide gas. It is obtained by:

(a)Burning elemental sulfur with air

(b)Smelting and roasting metal sulfide minerals

(c)Decomposing contaminated (spent) sulfuric acid catalyst.

Manufacturing of sulfuric acid takes place by active sulfur dioxide oxidation using catalyst consists of molten vanadium-alkali metal pyro sulfate layer on porous solid silica substrate. This reaction gives rapid sulfur dioxide oxidation at moderate temperatures. Catalyst deactivates when it is cooled below its solidification temperature. This happens when a catalyst bed is fed with cold gas or when the acid plant is shut down. Fortunately, catalyst solidification and melting are reversible so that the catalyst reactivates, when it is once again heated and remelted.

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Sulfuric acid is mostly used for making phosphate fertilizers. It is also used extensively as a solvent for ores and catalyst for petroleum refining and polymer manufacturing.

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CHAPTER 1

INTRODUCTION

1.1. SULFURIC ACID

Sulfuric (or sulphuric) acid, H_2SO_4 , is a strong mineral acid. It is soluble in water at all concentrations. Sulfuric acid has many applications, and is one of the top products of the chemical industry. World production in 2001 was 165 million tonnes, with an approximate value of US\$8 billion. Principal uses include lead-acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis.

Sulphuric acid (American English: **Sulfuric**), H_2SO_4 , is a strong mineral acid (not an organic acid). It can form any concentration in water. The old name for sulphuric acid is oil of vitriol. When high concentrations of SO_3 are added when making the acid, a solution of SO_3 in H_2SO_4 results. This is called fuming sulphuric acid or Oleum or Nordhausen acid.

Sulphuric acid has many applications, including in many chemical reactions and production processes. It is the most widely used chemical. Principal uses include fertilizer manufacturing, ore processing, chemical synthesis, wastewater processing and oil refining.

In combination with nitric acid it forms the nitronium ion, which is used in the nitration of compounds. The process of nitration is used to manufacture a great many explosives, including trinitrotoluene, nitroglycerine, and guncotton. It is also the acid used in lead-acid batteries, and so is sometimes known as battery acid.

The energy of the hydration reaction with sulphuric acid is highly exothermic, and if water is added to concentrated sulphuric acid it can boil. Always add the acid to the water rather than the water to the acid. Note that part of this problem is due to the relative densities of the two liquids. Water is less dense than sulfuric acid and will tend to layer above the acid, and not mix well, if added to the acid.

Because the hydration of sulfuric acid is thermodynamically favorable, sulphuric acid is an excellent dehydration agent, and is used to prepare many dried fruits. When in the atmosphere it is part of many chemicals which make up acid rain.

1.2. STATEMENT OF PROBLEM

"Sulfuric Acid plant of capacity 1000 tons per day. Using molten sulphur as raw material and designing a heat exchanger and Absorption Tower"

1.3. OBJECTIVE

The objectives of our project work are:

- To determine the demand for H_2SO_4 in the current market.
- To identify a suitable method for production of H_2SO_4 .
- To select a suitable catalyst for production of H₂SO₄.
- To determine the material and energy balance for the plant.
- To design a heat exchanger and absorption column.
- To determine the investment costs for the plant and prepare the break-even analysis chart

1.4. HISTORY OF SULFURIC ACID

Sulfuric acid was known to medieval alchemists under of variety of names including *oil of vitriol* and *spirit of vitriol*. These substances were produced by the dry distillation of minerals including ferrous sulfate heptahydrate, $FeSO_4 \cdot 7 H_2O$, called green vitriol, and cupric sulfate pentahydrate, $CuSO_4 \cdot 5 H_2O$, called blue vitriol. When heated, these compounds decompose to ferrous and cupric oxides, respectively, giving off water and sulfur trioxide, which combine to produce a dilute solution of sulfuric acid. Preparations like these have been ascribed to alchemists including the 12th-century Arab About Bekr al-Rhases and the 13th-century German Albertus Magnus.

In the 17th century, the German-Dutch chemist Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter (potassium nitrate, KNO₃), in the presence of steam. As the saltpeter decomposes, it oxidizes the sulfur to SO₃, which combines with water to produce sulfuric acid.

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

John Roebuck's sulfuric acid was only about 35-40% sulfuric acid, and later refinements in the lead-chamber process improved this to 78%. However, the manufacture of some dyes and other chemical processes require a more concentrated product, and throughout the 18th century, this could only be made by dry distilling minerals in a technique similar to the original alchemical processes. The expense of this process prevented the large-scale use of concentrated sulfuric acid.

In 1831, the British merchant Peregrine Phillips patented a far more economical process for producing sulfur trioxide and concentrated sulfuric acid. In this process sulfur dioxide, SO_2 , produced by roasting either sulfur or pyrite in air, is combined with additional air and passed

over a platinum catalyst at high temperatures, where it combines with oxygen from the air to produce nearly pure SO_3 . Even so, there was little demand for highly concentrated sulfuric acid at the time, and the first sulfuric acid plant using this *contact process* was not built until 1875 in Freiburg, Germany.

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

1.5. USES OF SULPHURIC ACID

Some of the Important Applications of Sulphuric acid are as follows:

- Phosphate fertilizer production.
- Petroleum refining and polymer manufacture.
- The purification of petroleum to wash impurities out of gasoline
- Manufacture of chemicals.
- Processing of metals,
- Manufacture of Rayon.
- Lead-Acid storage batteries.

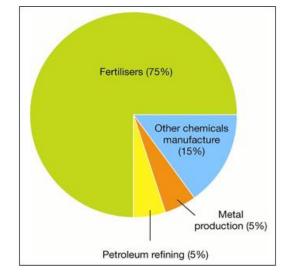


Fig. 1.1

CHAPTER 2

LITERATURE SURVEY

2.1. MAJOR SULPHURIC ACID PLANTS- INDIA

| COMPANY | LOCATION | OTHER PRODUCTS | TECHNOLOGY USED | CAPACITY (MTPA) | |
|----------------------------------|--------------|---|--------------------|--------------------|--|
| FACT. * | KERALA | CAPROLACTUM, FERTILIZERS | - | 330,000 | |
| GSFC GUJARAT | | METHANOL, OLEUM, CAPROLACTUM | - | 450,000 | |
| HINDALCO- BIRLA CU | GUJARAT | DAP, PHOSPHORIC ACID | DCDA** | 1,470,000 | |
| TATA CHEMICALS LTD. | WEST BENGAL | PHOSPHORIC ACID, CAUSTIC SODA, CHLORINE BASED | DCDA | 162,000 | |
| MANGLORE C&F MANGLORE | | AMMONIUM BI CARBONATE, FORMALDEHYDE | | 330,000 | |
| PARADEEP FERT. ORISSA | | DAP, APS | | 330,000 | |
| RAMA PHOSPHOROUS | INDORE, PUNE | SSP | DCDA | 1,02,000 | |
| ANKUR FERT. MUZZARFARNAGAR, (UP) | | - | ΔΤΤ | 36,000 | |

*Sulphuric acid as Intermediate Product

Total number of Plants = 140

Production Capacity = 12 MMTPA

Current Production = 5.5 MMTPA

2.2. Process Involved in Manufacturing of Sulfuric Acid

2.2.1. Chamber process:

Dr. Roebuck of Birmingem introduced the lead chamber in 1746. The chamber process with various modifications and on an even increasing scale, was employed exclusively for manufacture of sulfuric acid and until the letter part of the 19th century when the contact process was developed. The notable improvement in the process was the invention of the Gay Lussac tower for the recovery of nitrogen oxide as nitrogen virtriol. This was followed in 1859 by the invention of the Glover tower for denitrofication of the nitrous virtriol.

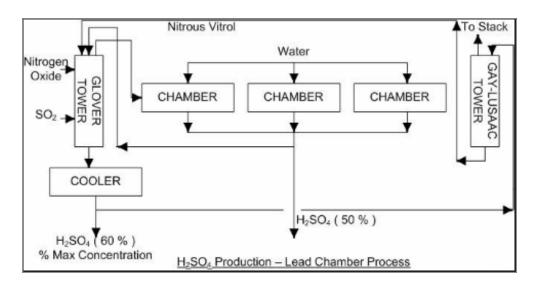


Figure 2.1: Lead Chamber Process (courtesy: Dryden's Chemical Technology)

2.2.2. Contact process:

The Contact process was first discovered in 1831 by Pergrine Phillips. His patent include the essential future of the modern contact process, namely, the passing of a mixture of sulfur dioxide over a catalyst followed by absorption of SO_3 in 98.5 to 99.0% sulfuric acid. Many investigations followed by the process, but with no practical success for more than forty years probably because of following reason:

- I. Lack of demands for fuming acids.
- II. Inadequate knowledge of catalytic gas reactions and
- III. The slow progress of chemical technology.

In 1889 it was demonstrated that excess of oxygen in the gaseous mixture for the contact process was advantageous. The contact process has now been improved. More than 90% of sulfuric acid produced is made by the contact process.

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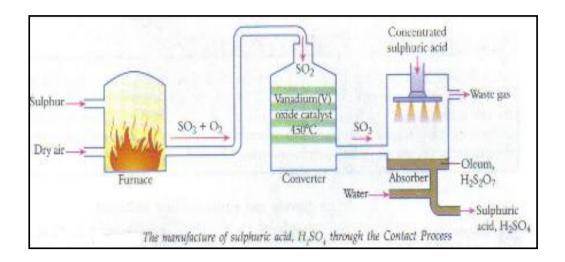


Figure 2.2.: Contact Process (courtesy: BASF)

Worldwide, about 180 million tonnes of sulfuric acid are consumed peryear (Kitto, 2004). The Sources raw materials (Sulfur and Sulfur dioxide) for Contact Process are :

1. Sulfur from mines.

2. Sulfur or hydrogen sulfide recovered from petroleum desulfurization.

3. Recovery of sulfur dioxide from coal or oil-burning public utility stack gases.

4. Recovery of sulfur dioxide from the smelting of metal sulfide ores:

 $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

5. Decomposing contaminated (spent) sulfuric acid catalyst. (Regeneration)





Fig. 2.3.

Schematic of sulfur burning sulfuric acid plant, courtesy Outokumpu OYJ www.outokumpu.com The main components are the catalytic $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ 'converter' (tall, back), twin H_2SO_4 making ('absorption') towers (middle distance) and large molten sulfur storage tank (front). The combustion air filter and air dehydration ('drying') tower are on the right. The sulfur burning furnace is hidden behind. Catalytic converters are typically 12 m diameter.



Fig. 2.4. Catalyst pieces in a catalytic SO_2 oxidation 'converter'. Converters are ~15 m high and 12 m in diameter. They typically contain four, $\frac{1}{2}$ -1 m thick catalyst beds. SO_2 -bearing gas descends the bed at ~3000 Nm³ per minute. Individual pieces of catalyst are shown in Fig. 8.1. They are ~0.01 m in diameter and length.

2.3. Sulfur Burning

About 70% of sulfuric acid is made from elemental sulfur. All the sulfur is obtained as a byproduct from refining natural gas and petroleum.

The sulfur is made into SO₂ acid plant feed by:

- Melting the sulfur
- Spraying it into a hot furnace
- Burning the droplets with dried air.

$$S + O_2 \rightarrow SO_2$$
 $\Delta H = -300 \text{ kJ mol-1}$

Very little SO₃ (g) forms at the 1400 K flame temperature of this reaction, This explains twostep oxidation, i.e.:

(a)Burning of sulfur to SO₂ then

(b)Catalytic oxidation of SO₂ to SO₃, 700 K.

 $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \qquad \Delta H = -100 \text{ kJ mol}-1$

The product of sulfur burning is hot, dry SO₂, O₂, N₂ gas. After cooling to -700 K, it is ready for catalytic SO₂ oxidation and subsequent H_2SO_4 making.

2.4 Catalytic Oxidation of SO₂ to SO₃

 O_2 does not oxidize SO_2 to SO_3 without a catalyst. All industrial SO_2 oxidation is done by sending SO_2 bearing gas down through 'beds' of catalyst. The reaction is:

700-900K

It is strongly exothermic ($\Delta H \sim 100$ MJ per kg-mole of SO₃). Its heat of reaction provides considerable energy for operating the acid plant.

2.4.1. Catalyst

At its operating temperature, 700-900 K, SO₂ oxidation catalyst consists of a molten film of V, K, Na, (Cs) pyrosulfate salt on a solid porous SiO₂ substrate. The molten film rapidly absorbs $SO_2(g)$ and $O_2(g)$ - and rapidly produces and desorbs $SO_3(g)$,

The only function of catalyst is to increase the rate of reaction.

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

Oxidation is a key step in sulfuric acid manufacture. The SO3 (g) is essential for H2SO4 making, i.e. for the reaction:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4$$

V, K, Na, Cs, S, O, SiO₂ catalyst is a key ingredient in ensuring rapid, efficient SO2 oxidation. Without catalyst, SO₂ oxidation is slow at temperatures where the oxidation is thermodynamically efficient.

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Catalytic Reactions

Active SO₂ oxidation catalyst consists of molten vanadium-alkali metal pyro sulfate layer on porous solid silica substrate. Catalytic SO₂ + SO₃ oxidation takes place with dissolved V S O ionic complexes by reactions. N2 and CO2 don't react during the SO₂ oxidation process.

Reactions with catalyst have smaller activation energies than Reaction. They give rapid SO_2 oxidation at moderate temperatures. Rapid reaction between gases and ions requires that the vanadium ion salt be molten. Melting at moderate temperatures (-~650 K) is obtained by combining high melting point: Vanadium pentoxide (melting point, 943 K).

Catalyst deactivates when it is cooled below its solidification temperature. This happens when a catalyst bed is fed with cold gas or when the acid plant is shut down. Fortunately, catalyst solidification and melting are reversible so that the catalyst reactivates when it is once again heated.

Composition and Manufacture

Compositions and methods of manufacturing commercial catalysts are proprietary. Roughly, however, commercial catalysts contain (mass%)

- 4-9% V₂O₅
- 15 20% potassium sulfate/pyrosulfate (S0₄/S₂0₇)
- 2 5% sodium sulfate/pyrosulfate
- 5 15% cesium sulfate/pyrosulfate (when present)
- 55 70% porous silica substrate.

Commercially Used Catalysts

Table 2.2. Catalyst Used

| STAGE | CATALYST NAME | ТҮРЕ | PRICE |
|-----------------------------------|---------------|---------------|---------------------|
| 1 st | VK- 38 | Na-K based | 200 ₹ / ltr |
| 2 nd & 3 rd | VK -48 | Na-K based | 200 ₹ / I tr |
| 4 th | VK -69 | Caesium based | 400 ₹ / ltr |

Industrially Used catalyst (Courtesy: TATA Chemicals)

| CATALYST | VK-38 | VK-69 |
|--------------------|----------------------------|----------------------------|
| INLET TEMP. (° C) | 440 | 390 |
| OVERALL COVERSION | 99.0 | 99.88 |
| SO2 IN STACK (ppm) | 375 (2.0 Kg/MT of acid) | 150 (0.8 Kg/MT of acid) |

Source: Sulphur No. 249. (What's new for Sulphuric Acid Services - by Lisa Connock).

2.4.2. Feed gas drying

Eqn. (2.1) indicates that catalytic oxidation feed gas is always dry avoids:

This dryness

- (a) Accidental formation of H₂SO₄ by reaction of H₂O(l) with the SO₃(g) product of catalytic SO₂ 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 $H_2SO_4(l)$.

2.5. H₂SO₄ Production

Catalytic oxidation's SO₃ (g) product is made into H_2SO_4 by contacting catalytic oxidation's exit gas with strong sulfuric acid, Fig. 1.3. The reaction is:

$$SO_{3}(g) + H_{2}O(l) \longrightarrow H_{2}SO_{4}(l) \quad (2.2)$$

in SO₃,SO₂,O₂, in 98.5% H₂SO₄, in strengthened
N₂ gas 1.5% H₂O sulphuric acid sulphuric acid

Reaction (1.2) produces strengthened sulfuric acid because it consumes H_2O (l) and makes H_2SO_4 (l). H_2SO_4 (l) is not made by reacting SO_3 (g) with water. This is because Reaction (2.2) is so exothermic that the product of the

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4$$

reaction would be hot H₂SO₄ vapour - which is difficult and expensive to condense.

Prior to 1900, the **lead chamber process** was used to manufacture sulphuric acid. As late as 1940, up to 50% of sulphuric acid manufactured in the US was produced by chamber process plants.

However today, nearly all of the world's sulphuric acid is produced using contact process

2.6. Recent Developments

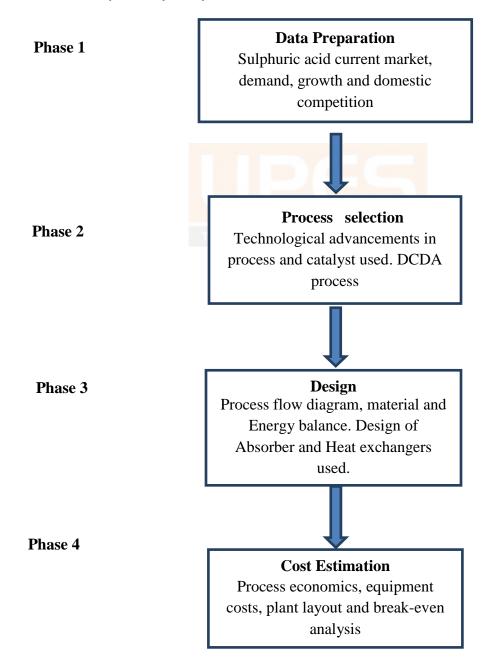
The major developments in sulfuric acid making are as follows:

- (a) Improved materials of construction, specifically more corrosion resistant materials (Salehi and Hopp, 2001, 2004; Sulphur, 2004).
- (b) Improved SO₂ (g) + $\frac{1}{2}$ O₂ = SO₃ (g) catalyst, specifically V, Cs, K, Na, S, O, SiO2 catalyst with low activation temperatures (Hansen, 2004).
- (c) Improved techniques for recovering the heat from Reactions.
- (d) At present most of the Sulphur based Sulphuric Acid Plants are based on Double Conversion Double Absorption (DCDA) process except for a few Smelter based plants, which are working on Single Conversion Single Absorption (SCSA) process.
- (e) Plants are coming up with 5-stage converter.
- (f) The sulphur-based plants are using heat of combustion and conversion for producing superheated steam. In high capacity plants and upcoming plants, heat of absorption is also utilized for producing low-pressure steam.
- (g) Use of sulphur filter for minimizing ash content.
- (h) Selection of high efficiency mist eliminators ensuring minimum acid mist exhaust.

CHAPTER 3

METHODOLOGY

- To assess the current demand for sulphuric acid in today's market.
- On this basis a 1000MTPD capacity plant is modelled.
- The Double Absorption Double Conversion process was identified as the best suited technology giving the maximum yield with best purity Sulphuric Acid. This technology is currently used by many industries in India.



CHAPTER 4

EQUIPMENT DESIGN

4.1. Design of Absorption Column

Packed Columns

Packed columns are used for distillation, gas absorption, and liquid-liquid extraction; only distillation and absorption will be considered in this section. Stripping (desorption) is the reverse of absorption and the same design methods will apply. The gas liquid contact in a packed bed column is continuous, not stage-wise, as in a plate column. The liquid flows down the column over the packing surface and the gas or vapour, counter-currently, up the column. In some gas-absorption columns co-current flow is used. The performance of a packed column is very dependent on the maintenance of good liquid and gas distribution throughout the packed bed, and this is an important consideration in packed-column design.

A schematic diagram, showing the main features of a packed absorption column, is given in Figure 4.01.

Choice of plates or packing:

The choice between a plate or packed column for a particular application can only be made with complete assurance by costing each design. However, this will not always be worthwhile, or necessary, and the choice can usually be made, on the basis of experience by considering main advantages and disadvantages of each type; which are listed below:

- 1. Plate columns can be designed to handle a wider range of liquid and gas flow-rates than packed columns.
- 2. Packed columns are not suitable for very low liquid rates.

3. The efficiency of a plate can be predicted with more certainty than the equivalent term for packing (HETP or HTU).

- 4. Plate columns can be designed with more assurance than packed columns. There is always some doubt that good liquid distribution can be maintained throughout a packed column under all operating conditions, particularly in large columns.
- 5. It is easier to make provision for cooling in a plate column; coils can be installed on the plates.
- 6. It is easier to make provision for the withdrawal of side-streams from plate columns.

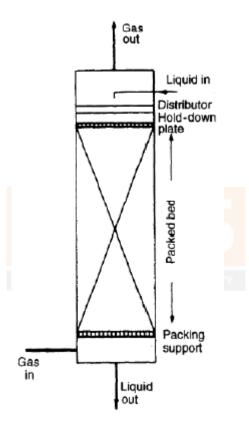


Fig. 4.01. Packed Absorption column

- 7. If the liquid causes fouling, or contains solids, it is easier to make provision for cleaning in a plate column; man ways can be installed on the plates. With small diameter columns it may be cheaper to use packing and replace the packing when it becomes fouled.
- 8. For corrosive liquids a packed column will usually be cheaper than the equivalent plate column.

- 9. The liquid hold-up is appreciably lower in a packed column than a plate column. This can be important when the inventory of toxic or flammable liquids needs to be kept as small as possible for safety reasons.
- 10. The pressure drop per equilibrium stage (HETP) can be lower for packing than pl ates; and packing should be considered for vacuum columns.

Packing should always be considered for small diameter columns, say less than 0.6 m, where plates would be difficult to install, and expensive. Packed columns are more suitable for h

| | Size | Size Bulk density | | Surface area a | Packing factor |
|-----------------------------|-------|----------------------|----------------------|-------------------|-------------------|
| | in. | mm | (kg/m ³) | (m^2/m^3) | $F_p m^{-1}$ |
| Raschig rings | 0.50 | 13 | 881 | 368 | 2100 |
| ceramic | 1.0 | 25 | 673 | 190 | 525 |
| | 1.5 | 38 | 689 | 128 | 310 |
| | 2.0 | 51 | 651 | 95 | 210 |
| | 3.0 | 76 | 561 | 69 | 120 |
| Metal | 0.5 | 13 | 1201 | 417 | 980 |
| (density for carbon steel) | 1.0 | 25 | 625 | 207 | 375 |
| · · · · | 1.5 | 38 | 785 | 141 | 270 |
| | 2.0 | 51 | 593 | 102 | 190 |
| | 3.0 | 76 | 400 | 72 | 105 |
| Pall rings | 0.625 | ULD 165 UI | IVER=593 | 341 | 230 |
| metal | 1.0 | 25 | 481 | 210 | 160 |
| (density for carbon steel) | 1.25 | 32 | 385 | 128 | 92 |
| | 2.0 | 51 | 353 | 102 | 66 |
| | 3.5 | 76 | 273 | 66 | 52 |
| Plastics | 0.625 | 16 | 112 | 341 | 320 |
| (density for polypropylene) | 1.0 | 25 | 88 | 207 | 170 |
| (| 1.5 | 38 | 76 | 128 | 130 |
| | 2.0 | 51 | 68 | 102 | 82 |
| | 3.5 | 89 | 64 | 85 | 52 |
| Intalox saddles | 0.5 | 13 | 737 | 480 | 660 |
| ceramic | 1.0 | 25 | 673 | 253 | 300 |
| | 1.5 | 38 | 625 | 194 | 170 |
| | 2.0 | 51 | 609 | 108 | 130 |
| | 3.0 | 76 | 577 | .50 | 72 |

Table 4.1. Data for various packings

Packing size: In general, the largest size of packing that is suitable for the size of column should be used, up to 50mm. Small sizes are appreciably more expensive than the larger sizes. Above 50 mm the lower cost per cubic metre does not normally compensate for the lower mass transfer efficiency. Use of too large a size in a small column can cause poor liquid distribution.

Recommended size ranges are:

| Column | Use diameter packing and size |
|--------------------------|-------------------------------|
| <0.3 m (1 ft) | <25 mm (1 in.) |
| 0.3 to 0.9 m (1 to 3 ft) | 25 to 38 mm (1 to 1.5 in.) |
| >0.9 m | 50 to 75 mm (2 to 3 in. |

Table.4.2. Packing size range

4.1.1. Absorption

Though packed absorption and stripping columns can also be designed as staged process, it is usually more convenient to use the integrated form of the differential equations set up by considering the rates of mass transfer at a point in the column.

or
$$Z = Hog Nog$$

$$Z = Hol Nol$$
4.01a
4.01b

For design purpose it is convenient to write equations 4.01a and 4.01b in terms of "transfer units" (HTU); where the value of integral is the number of transfer units, and the group in front

$$\mathbf{H}_{OG} = \mathbf{H}_{G} + m \frac{G_{m}}{L_{m}} \mathbf{H}_{L}$$

$$4.02a$$

$$\mathbf{H}_{OL} = \mathbf{H}_{L} + \frac{L_{m}}{mG_{m}} \mathbf{H}_{G}$$

$$4.02b$$

The relationship between the overall height of a transfer unit and the individual filmtransfer units H_L and H_G , which are based on the concentration driving force across the liquid and gas films, is given by the integral sign, which has units of length, is the height of a transfer unit.

Where, *m* is the slope of the equilibrium line and G_m/L_m the slope of the operating line.

4.1.2. Prediction of the height of a transfer unit (HTU)

There is no entirely satisfactory method for predicting the height of a transfer unit. In practice the value for a particular packing will depend not only on the physical properties and flow-rates of the gas and liquid, but also on the uniformity of the liquid distribution throughout the column, which is dependent on the column height and diameter. This makes it difficult to extrapolate data obtained from small size laboratory and pilot plant columns to industrial size columns. Whenever possible estimates should be based on actual values obtained from operating columns of similar size to that being designed

4.1.3. Cornell's method

Cornell (1960) reviewed the previously published data and presented empirical equations for predicting the height of the gas and liquid film transfer units. Their correlation takes into account the physical properties of the system, the gas and liquid flow-rates; and the column diameter and height. Equations and figures are given for a range of sizes of Raschig rings and Berl saddles. Only those for Berl saddles are given here, as it is unlikely that Raschig rings would be considered for a new column. Though the mass-transfer efficiency of Pall rings and Interlox saddles will be higher than that of the equivalent size Berl saddle, the method can be used to make conservative estimates for these packings. Bolles and Fair (1982) have extended the correlations given in the earlier paper to include metal Pall rings.

Cornell's equations are:

$$\mathbf{H}_{G} = 0.011 \psi_{h} (Sc)_{v}^{0.5} \left(\frac{D_{c}}{0.305}\right)^{1.11} \left(\frac{Z}{3.05}\right)^{0.33} / (L_{w}^{*} f_{1} f_{2} f_{3})^{0.5}$$

$$\mathbf{H}_{L} = 0.305 \phi_{h} (Sc)_{L}^{0.5} K_{3} \left(\frac{Z}{3.05}\right)^{0.15}$$

$$4.03a$$

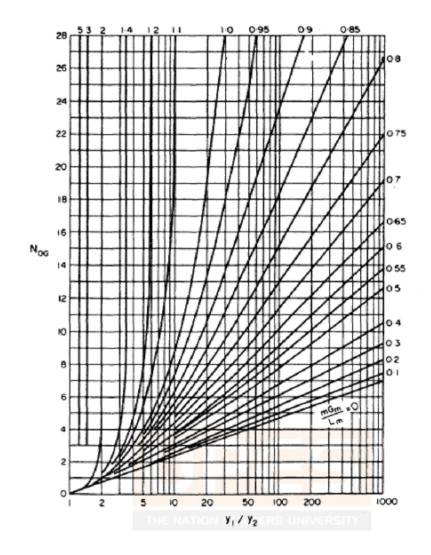


Fig.4.2. Number of transfer units $N_{\text{OG}}\,as\,a$ function of y_1/y_2 with mG_m/L_m as parameter

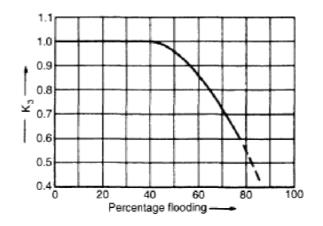


Fig.4.3.Percentage flooding correction factor

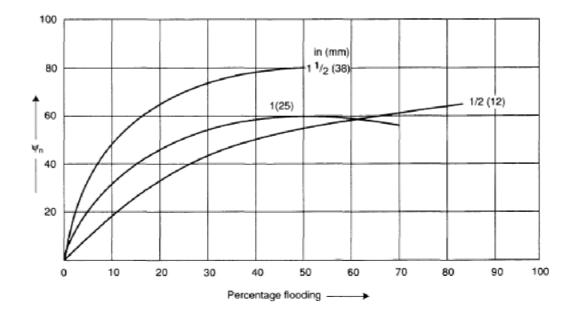


Fig.4.4.Factor for H_Gfor Berl Saddles

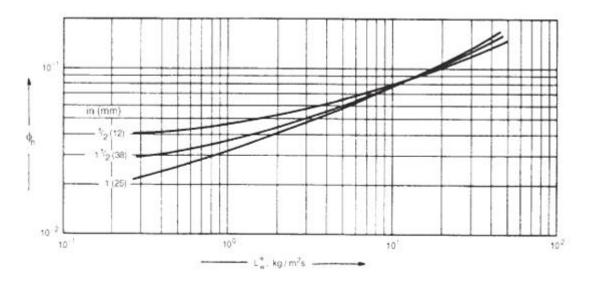


Figure 4.5. Factor for HL for Berl saddles

Percentage flooding =
$$\left[\frac{K_4 \text{ at design pressure drop}}{K_4 \text{ at flooding}}\right]^{1/2}$$
 (4.04)

4.1.4. Column diameter (capacity)

The capacity of a packed column is determined by its cross-sectional area. Normally, the column will be designed to operate at the highest economical pressure drop, to ensure good liquid and gas distribution. For random packing the pressure drop will not normally exceed 80 mm of water per meter of packing height.

At this value the gas velocity will be about 80 per cent of the flooding velocity. Recommended design values, mm water per m packing, are:

- Absorbers and strippers 15 to 50
- Distillation, atmospheric and moderate
- Pressure 40 to 80 where the liquid is likely to foam, these values should be halved.

For vacuum distillations the maximum allowable pressure drop will be determined by the process requirements, but for satisfactory liquid distribution the pressure drop should not be less than 8 mm water per m. If very low bottom pressures are required special low pressure-drop gauze packing should be considered.

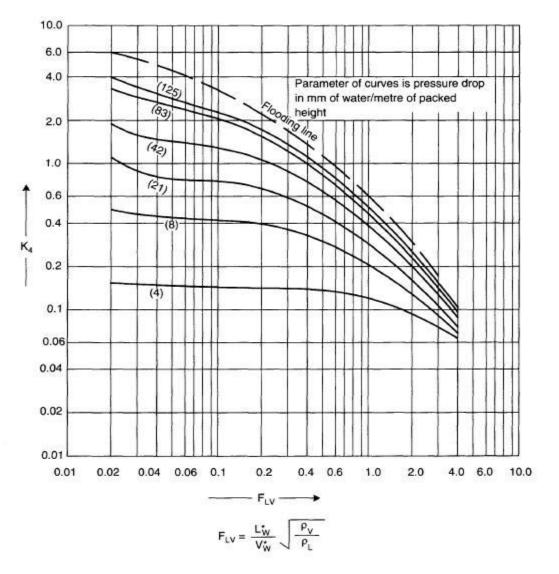


Fig.4.6.Generalized Pressure Drop Correlations (Courtesy: Norton Co.)

4.2. Basic Economizer Design Procedure and Theory

The general equation for heat transfer across a surface is:

$$\mathbf{Q} = \mathbf{U}\mathbf{A}\Delta\mathbf{T}_{\mathbf{m}} \tag{4.05}$$

Where Q = Heat transferred per unit time, W,

 $U = \text{Overall heat transfer coefficient, W/m}^{2\circ}\text{C},$

A = Heat-transfer area, m²,

 ΔT_m = the mean temperature difference, the temperature driving force, °C.

The prime objective in the design of an exchanger is to determine the surface area required for the specified duty (rate of heat transfer) using the temperature differences available. The overall coefficient is the reciprocal of the overall resistance to heat transfer, which is the sum of several individual resistances. For heat exchange across a typical heat exchanger tube 21 the relationship between the overall coefficient and the individual coefficients, which are the reciprocals of the individual resistances, is given by:

$$\frac{1}{U_o} = \frac{1}{h_o} + \frac{1}{h_{od}} + \frac{d_o \ln\left(\frac{d_o}{d_i}\right)}{2k_w} + \frac{d_o}{d_i} \times \frac{1}{h_{id}} + \frac{d_o}{d_i} \times \frac{1}{h_i}$$
(4.06)

where U_o = the overall coefficient based on the outside area of the tube, W/m² °C

 h_o = outside fluid film coefficient, W/m²°C,

 h_i = inside fluid film coefficient, W/m² °C,

 h_{od} = outside dirt coefficient (fouling factor), W/m² °C,

 h_{id} = inside dirt coefficient, W/m² °C,

 k_w = thermal conductivity of the tube wall material, W/m°C,

 d_i = tube inside diameter, m,

 d_o = tube outside diameter, m.

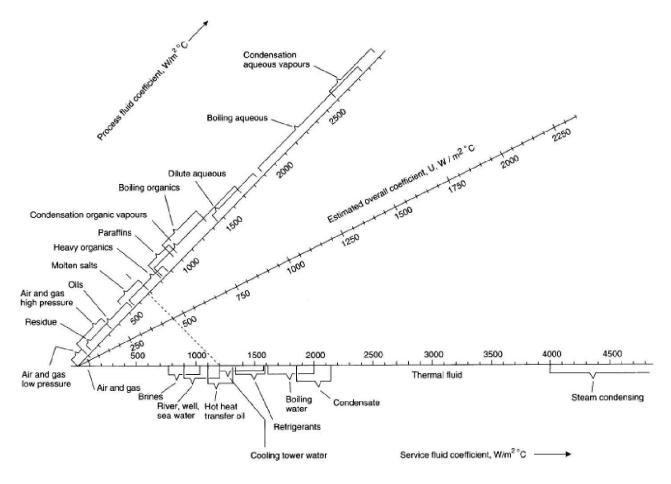


Fig.4.7. Overall Coefficients

4.2.1 Tube

Dimensions: Tube diameters in the range 0.63 in. (16 mm) to 2 in. (50 mm) are used. The smaller diameters to 0.63 in.(16 to 25 mm) are preferred for most duties, as they will give more compact, and therefore cheaper, exchangers. Larger tubes are easier to clean by mechanical methods and would be selected for heavily fouling fluids. The tube thickness (gauge) is selected to withstand the internal pressure and give an adequate corrosion allowance. Steel tubes for heat exchangers are covered by BS 3606 (metric sizes); the standards applicable to other materials are given in BS 3274. Standard diameters and wall thicknesses for steel tubes are given in Table 4.2.

| Outside diameter (mm) | | Wall | thickness | (mm) | |
|-----------------------|-----|------|-----------|------|-------|
| 16 | 1.2 | 1.6 | 2.0 | | - |
| 20 | | 1.6 | 2.0 | 2.6 | - |
| 25 | - | 1.6 | 2.0 | 2.6 | 3.2 |
| 30 | | 1.6 | 2.0 | 2.6 | 3.2 |
| 38 | - | _ | 2.0 | 2.6 | 3.2 |
| 50 | | | 2.0 | 2.6 | 3.2 |

Table 4.3. Standard Dimensions for Steel Tubes

The preferred lengths of tubes for heat exchangers are: 6 ft. (1.83 m), 8 ft (2.44 m), 12 ft (3.66 m), 16 ft (4.88 m) 20 ft (6.10 m), 24 ft (7.32 m). For a given surface area, the use of longer tubes will reduce the shell diameter; which will generally result in a lower cost exchanger, particularly for high shell pressures. The optimum tube length to shell diameter will usually fall within the range of 5 to 10. If U-tubes are used, the tubes on the outside of the bundle will be longer than those on the inside. The average length needs to be estimated for use in the thermal design. U-tubes will be bent from standard tube lengths and cut to size. The tube size is often determined by the plant maintenance department standards, as clearly it is an advantage to reduce the number of sizes that have to be held in stores for tube replacement. As a guide, 3/4 in. (19 mm) is a good trial diameter with which to start design calculations.

4.2.1.1. Tube Arrangements

The tubes in an exchanger are usually arranged in an equilateral triangular, square, or rotated square pattern. The triangular and rotated square patterns give higher heat-transfer rates, but at the expense of a higher pressure drop than the square pattern. A square, or rotated square arrangement, is used for heavily fouling fluids, where it is necessary to mechanically clean the outside of the tubes. The recommended tube pitch (distance between tube centers) is 1.25 times the tube outside diameter; and this will normally be used unless process requirements dictate otherwise. Where a square pattern is used for ease of cleaning, the recommended minimum clearance between the tubes is 0.25 in. (6.4 mm).

4.2.1.2. Tube-sheet layout (Tube Count)

The bundle diameter will depend not only on the number of tubes but also on the number of tube passes, as spaces must be left in the pattern of tubes on the tube sheet to accommodate the pass partition plates. An estimate of the bundle diameter D_b can be obtained from equation 4.07b,

$$N_t = K_1 \left(\frac{D_b}{d_o}\right)^{n_1},$$

$$D_b = d_o \left(\frac{N_t}{K_1}\right)^{1/n_1},$$
(4.07a)
(4.07a)

Where, N_t=Number of tubes,

D_b=Bundle diameter, mm,

d_o=Tube outside diameter, mm.

The tube layout for a particular design will normally be planned with the aid of computer programs. These will allow for the spacing of the pass partition plates and the position of the tie rods. Also, one or two rows of tubes may be omitted at the top and bottom of the bundle to increase the clearance and flow area opposite the inlet and outlet nozzles.

Table.4.4. Constants for Use in Eq.4.07

| Triangular pitch, $p_t = 1.25d_o$ | | | | | |
|-----------------------------------|-----------------|----------------|----------------|-----------------|-----------------|
| No. passes | 1 | 2 | 4 | 6 | 8 |
| K_1 n_1 | 0.319 2.142 | 0.249 2.207 | 0.175 2.285 | 0.0743 2.499 | 0.0365 2.675 |
| Square pitch, p | $a_t = 1.25d_o$ | | | | |
| No. passes | 1 | 2 | 4 | 6 | 8 |
| $\frac{K_1}{n_1}$ | 0.215 2.207 | 0.156 2.291 | 0.158 2.263 | 0.0402 2.617 | 0.0331 2.643 |

4.2.2. Mean Temperature Difference (Temperature Driving Force)

Before determining the heat transfer area required for a given duty, an estimate of the mean temperature difference ΔT_m must be made. This will normally be calculated from the terminal temperature differences: the difference in the fluid temperatures at the inlet and outlet of the exchanger. The well-known "logarithmic mean" temperature difference is only applicable to sensible heat transfer in true co-current or counter-current flow (linear temperature enthalpy curves). For counter-current flow, Figure 12.18a, the logarithmic mean temperature is given by:

$$\Delta T_{\rm lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \frac{(T_1 - t_2)}{(T_2 - t_1)}}$$
(4.08)

Where, $\Delta T_{lm} = \log$ mean temperature difference,

 T_1 = hot fluid temperature, inlet, T_2 = hot fluid temperature, outlet, t_1 = cold fluid temperature, inlet, t_2 = cold fluid temperature, outlet.

The equation is the same for co-current flow, but the terminal temperature differences will be $(T_1 - t_1)$ and $(T_2 - t_2)$. Strictly, equation 4.08 will only apply when there is no change in the specific heats, the overall heat-transfer coefficient is constant, and there are no heat losses. In design, these conditions can be assumed to be satisfied providing the temperature change in each fluid stream is not large.

The usual practice in the design of shell and tube exchangers is to estimate the "true temperature difference" from the logarithmic mean temperature by applying a correction factor to allow for the departure from true counter - current flow:

$$\Delta T_{\rm m} = F_{\rm t} \, \Delta T_{\rm lm} \tag{4.09}$$

Where, ΔT_m = True difference, the mean temperature difference for use in the design equation 4.05

 F_t = Temperature correction factor

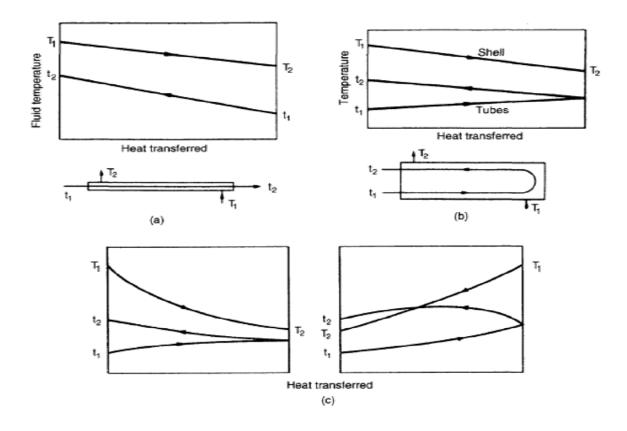


Fig.4.8. Temperature Profiles a) Counter-current flow, b) 1:2 Exchanger, c) Temperature Cross

4.2.3. Fluid allocation: Shell or Tubes

Where no phase change occurs, the following factors will determine the allocation of the fluid streams to the shell or tubes.

Corrosion. The more corrosive fluid should be allocated to the tube-side. This will reduce the cost of expensivealloy or clad components.

Fouling. The fluid that has the greatest tendency to foul the heat-transfer surfaces should be placed in the tubes. This will give better control over the design fluid velocity, and the higher allowable velocity in the tubes will reduce fouling. Also, the tubes will be easier to clean.

Fluid temperatures. If the temperatures are high enough to require the use of special alloys placing the highertemperature fluid in the tubes will reduce the overall cost. At moderate temperatures, placing the hotter fluid in thetubes will reduce the shell surface temperatures, and hence the need for lagging to reduce heat loss, or for safety reasons.

Operating pressures. The higher pressure stream should be allocated to the tube-side. High-pressure tubes will becheaper than a high-pressure shell

Pressure drop. For the same pressure drop, higher heat-transfer coefficients will be obtained on the tube-side thanthe shell-side, and fluid with the lowest allowable pressure drop should be allocated to the tube-side.

Viscosity.Generally, a higher heat-transfer coefficient will be obtained by allocating the more viscous material tothe shell-side, providing the flow is turbulent. The critical Reynolds number for turbulent flow in the shell is in the region of 200. If turbulent flow cannot be achieved in the shell it is better to place the fluid in the tubes, as the tube-side heat-transfer coefficient can be predicted with more certainty.

Stream flow-rates. Allocating the fluids with the lowest flow-rate to the shell-side will normally give the mosteconomical design.

4.2.4. Tube-Side Heat-Transfer Coefficient And Pressure Drop (Single Phase)

Heat transfer:

Turbulent flow: Heat-transfer data for turbulent flow inside conduits of uniform cross-section are usually correlated by an equation of the form:

$$Nu = CRe^{a}Pr^{b}\left(\frac{\mu}{\mu_{w}}\right)^{c} \tag{4.10}$$

Where, Nu =Nusselt number = $(h_i d_e / k_f)$,

- Re = Reynolds number =($\rho u_t d_e / \mu$),
- $Pr = Prandtl number = (\mu C_p / k_f)$
- $h_i = inside \ coefficient, \ W/m^{\circ}C$,
- d_e = equivalent (or hydraulic mean) diameter, m
- $u_t =$ fluid velocity, m/s,
- $k_f =$ fluid thermal conductivity, W/m°C,
- G_t = mass velocity, mass flow per unit area, kg/m² s,
- μ = fluid viscosity at the bulk fluid temperature, sN/m²,

 $\mu_{\rm w}$ = fluid viscosity at the wall, sN/m²

Cp = fluid specific heat, heat capacity, J/kg°C

Laminar Flow

Below a Reynolds number of about 2000 the flow in pipes will be laminar. Providing the natural convection effects are small, which will normally be so in forced convection, the following equation can be used to estimate the film heat-transfer coefficient:

$$Nu = 1.86(RePr)^{0.33} \left(\frac{d_e}{L}\right)^{0.33} \left(\frac{\mu}{\mu_w}\right)^{0.14}$$
(4.11)

Where, L is the length of the tube in metres.

If the Nusselt number given by equation 4.11 is less than 3.5, it should be taken as 3.5. In laminar flow the length of the tube can have a marked effect on the heat-transfer rate for length to diameter ratios less than 500.

Tube-side pressure drop

The flow in a heat exchanger will clearly not be isothermal, and this is allowed for by including an empirical correction factor to account for the change in physical properties with temperature. Normally only the change in viscosity is considered:

$$\Delta P = 8j_f(L'/d_i)\rho \frac{u_t^2}{2} \left(\frac{\mu}{\mu_w}\right)^{-m}$$
(4.12)

m = 0.25 for laminar flow, Re < 2100,

= 0.14 for turbulent flow, Re > 2100.

$$\Delta P_t = N_p \left[8j_f \left(\frac{L}{d_i} \right) \left(\frac{\mu}{\mu_w} \right)^{-m} + 2.5 \right] \frac{\rho u_t^2}{2}$$
(4.13)

Where, ΔP_t = tube-side pressure drop, N/m² (Pa),

 N_p = number of tube-side passes,

 $u_t = tube-side velocity, m/s$

L = length of one tube.

4.2.5. Shell-Side Heat-Transfer and Pressure Drop (Single Phase)

Kern's method

This method was based on experimental work on commercial exchangers with standard tolerances and will give a reasonably satisfactory prediction of the heat-transfer coefficient for standard designs. The prediction of pressure drop is less satisfactory, as pressure drop is more affected by leakage and bypassing than heat transfer. The shell-side heat transfer and friction factors are correlated in a similar manner to those for tube-side flow by using a hypothetical shell velocity and shell diameter. As the cross-sectional area for flow will vary across the shell diameter, the linear and mass velocities are based on the maximum area for cross-flow: that at the shell equator. The shell equivalent diameter is calculated using the flow area between the

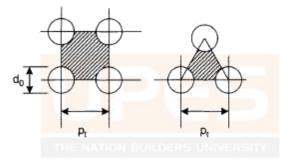


Fig.4.9. Equivalent diameter, cross-section area and wetted perimeter

Shell-side j_h and j_f factors for use in this method are given in Figure 4.10, for various baffle cuts and tube arrangements. These figures are based on data given by Kern (1950) and by Ludwig (1965). The procedure for calculating the shell-side heat-transfer coefficient and pressure drop for a single shell pass exchanger is given below:

Procedure

1. Calculate the area of cross-flow A_s for the hypothetical row of tubes at the shell equator, given by:

$$A_{s} = \frac{(p_{t} - d_{o})D_{s}l_{B}}{p_{t}}$$
(4.14)

Where, p_t = tube pitch

d_o= tube outside diameter,

 D_s = shell inside diameter, m,

l_B= baffle spacing, m

The term $(p_t - d_o)/p_t$ is the ratio of the clearance between tubes and the total distance between the tube centre.

2. Calculate the shell-side mass velocity G_s and the linear velocity u_s:

$$G_{s} = \frac{W_{s}}{A_{s}} \qquad (4.15a) \qquad \qquad u_{s} = \frac{G_{s}}{\rho} \qquad (4.15b)$$

Where, W_s = fluid flow=rate on the shell-side, kg/s

 ρ = shell=side fluid density, kg/m³

3. Calculate the shell-side equivalent diameter (Hydraulic Diameter), figure 4.9.

For a square pitch arrangement

$$d_e = \frac{4\left(\frac{p_t^2 - \pi d_o^2}{4}\right)}{\pi d_o} = \frac{1.27}{d_o}(p_t^2 - 0.785d_o^2)$$
(4.16a)

For an equilateral triangle pitch arrangement

$$d_{e} = \frac{4\left(\frac{p_{t}}{2} \times 0.87 p_{t} - \frac{1}{2}\pi \frac{d_{o}^{2}}{4}\right)}{\frac{\pi d_{o}}{2}} = \frac{1.10}{d_{o}}(p_{t}^{2} - 0.917 d_{o}^{2})$$
(4.16b)

4. Calculate the shell-side Reynolds number, given by:

$$Re = \frac{G_s d_e}{\mu} = \frac{u_s d_e \rho}{\mu} \tag{4.17}$$

5. For the calculated Reynolds number, read the value of j_h , then calculate the shell-side heat transfer coefficient h_s from:

$$Nu = \frac{h_s d_e}{k_f} = j_h Re P r^{1/3} \left(\frac{\mu}{\mu_w}\right)^{0.14}$$
(4.18)

6. For the calculated shell-side Reynolds number, calculate the shell-side pressure drop from:

$$\Delta P_s = 8j_f \left(\frac{D_s}{d_e}\right) \left(\frac{L}{l_B}\right) \frac{\rho u_s^2}{2} \left(\frac{\mu}{\mu_w}\right)^2 \tag{4.19}$$

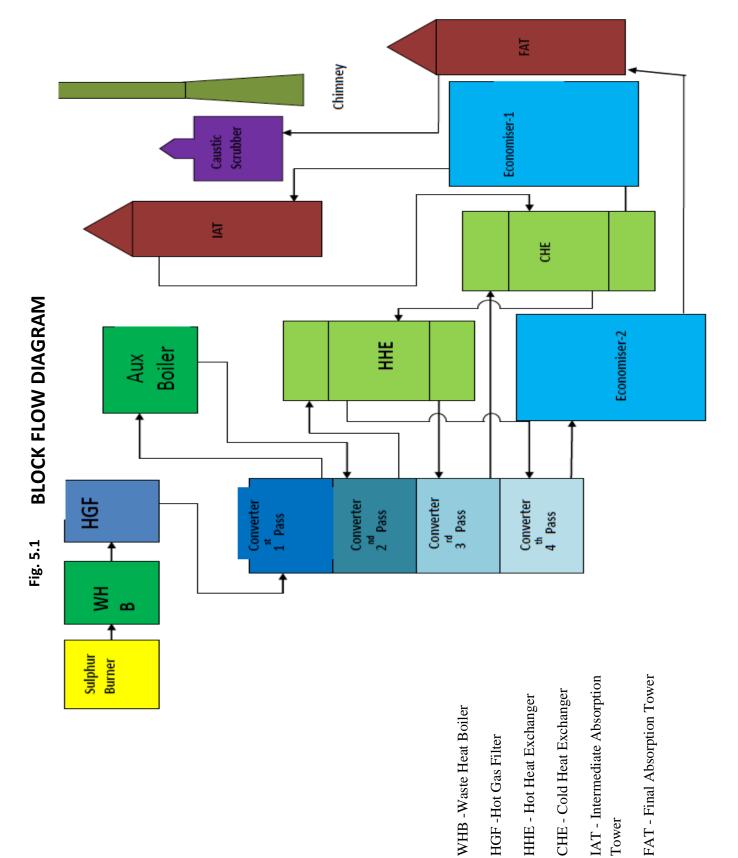
Where L = tube length, l_B = baffle spacing

The term (L/l_b) is the number of times the flow crosses the bundle = (N_b+1)

CHAPTER 5

DESIGN CALCULATIONS





Tower

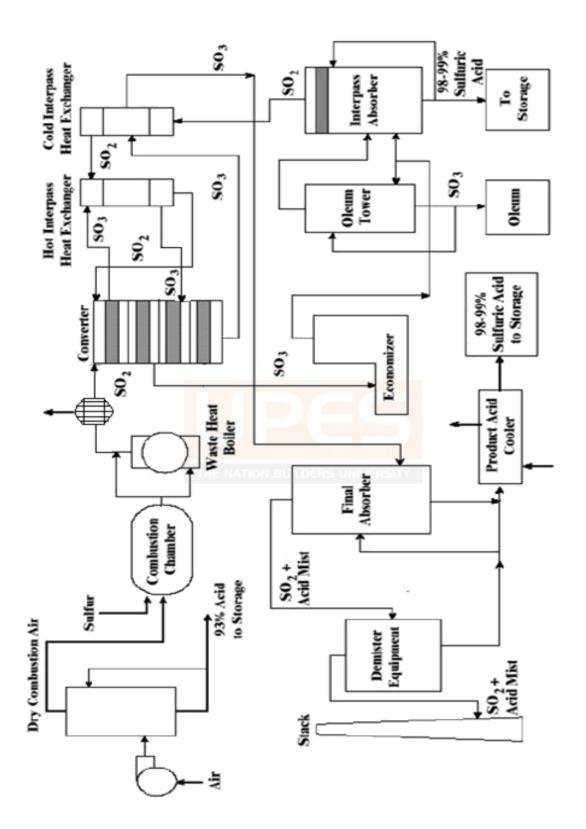
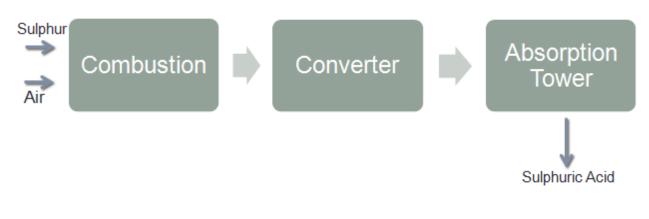


Fig. 5.2. Layout of Sulphuric Acid Plant

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5.1. OVERALL MATERIAL BALANCE



ASSUMPTIONS:

- Conversion efficiency: 99.6%
- Absorption efficiency: 99%
- Gases from combustion chamber contain 12% SO₂

1000 Tpd, 98 % pure H₂SO₄

$$\Rightarrow$$
 980 Tpd H₂SO₄

 \Rightarrow 980000/98

 \Rightarrow 10,000 kmol of H₂SO₄ per day

Reaction:

$S + O_2 {\rightarrow} SO_2$

Therefore,

1 kmol of S + 1 kmol of $O_2 = 1$ kmol of SO_2

Now,

$SO_3 + H_2O \rightarrow H_2SO_4$

So,

- 1 kmol of $H_2SO_4 = 1$ kmol of SO_2 required
- Efficiency at Converter = 99.6%
- Absorption efficiency = 99%
- 1 kmol of $H_2SO_4 = 1/(0.996*0.99)$

= 1.01415 kmol of SO₂

Therefore,

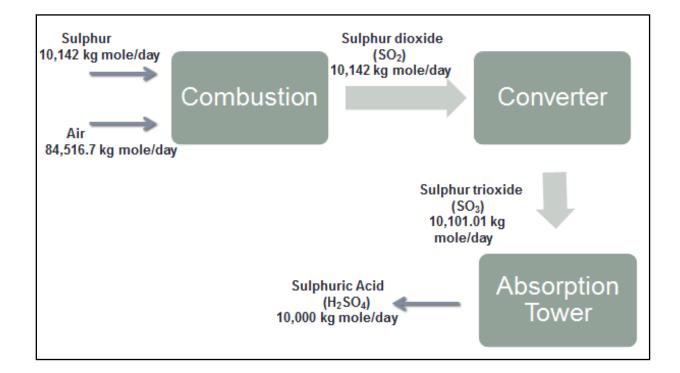
- 10,000 kmol of H_2SO_4 = 10142 kmol of SO_2
- Sulphur required at inlet = 10142 kmol per day
- O_2 required for combustion = 10142 kmol per day

COMBUSTION CHAMBER

Gases from combustion chamber contain 12% SO₂

(21% O_2 and 79% N_2 in air)

| • SO ₂ outlet from combustion chamber | =10142 kmol |
|---|----------------|
| • Total amount of mixture of gases | = 10142/0.12 |
| required per day | = 84516.7 kmol |
| • O ₂ inlet in the combustion chamber | = 84516.7*0.21 |
| | =17748.5 kmol |
| • N ₂ inlet in the combustion chamber | = 84516.7*0.79 |
| | = 66768.2 kmol |
| • O ₂ outlet from combustion chamber | =17748.5-10142 |
| | = 7606.5 kmol |
| • N ₂ outlet in the combustion chamber | = 66768.2 kmol |



| GAS | % of GAS | Kg Mole per day |
|-----------------|----------|-----------------|
| SO ₂ | 12 | 10142 |
| 0 ₂ | 9 | 7606.5 |
| N ₂ | 79 | 66768.2 |
| Total | | 84516.7 |

Total air used = 84516.7*29 = 2450984.3 kg

= 2450.9 ton

CONVERTER:

Reaction:

 $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

- SO_2 at the inlet = 10142 kmol per day
- O_2 at the inlet = $(\frac{1}{2})* 10142 = 5071$ kmol per day
- Efficiency = 99.6%

Therefore,

• Amount of SO_3 formed = 10142×0.996

= 10101.01 kmol per day

ABSORPTION TOWER:

Reaction:

 $SO_3 + H_2O \longrightarrow H_2SO_4$

- SO_3 at the inlet = 10101.01 kmol per day
- 1 kmol of $SO_3 + 1$ kmol of $H_2O = 1$ kmol of H_2SO_4
- Efficiency = 99%

Therefore,

• Amount of H₂ SO₄ formed = 0.99*10101.01 kmol

=10,000 kmol per day

5.1.1. Material balance across converter

It is four stage converter. Let assume converter conversion efficiency is 99%.

 1^{st} stage conversion efficiency = 60%

 2^{nd} stage conversion efficiency = 25%

 3^{rd} stage conversion efficiency = 8%

 4^{th} stage conversion efficiency = 6.6%

Total = 99.6%

<u>Material balance across 1st bed (1st stage)</u>

 SO_2 in gas mixture =10142 kmol/day

 1^{st} bed 60% SO₂ is converted into SO₃

 SO_2 converted = 60 / 100 * 10142 = 6085.2 kmol/day

 SO_3 formed = 6085.2 kmol/day

 SO_2 remaining = 10142 - 6085.2 = 4056.8 kmol/day

 $SO_2 + \frac{1}{2}O_2 = SO_3$

 SO_2 for 1 mole of SO_3 formed = 0.5 mole of O_2 required

 O_2 present = 7606.5 kmol

 O_2 consumed = 6085.2 * 0.5 = 3042.6 kmol/day

 O_2 required = 7606.5 - 3042.6 = 4563.9 kmol/day

Thus gas consumption after 1st bed/stage

| Gas | Composition (Kmol/day) |
|-----------------|------------------------|
| SO ₂ | 4056.8 |
| O ₂ | 4563.9 |
| SO ₃ | 6085.2 |
| N ₂ | 66768.2 |

Material Balance across Auxiliary Boiler:

Gases entering from 1st bed at 620°C and leave at 440°C.

| Gas | Composition (Kmol/day) |
|-----------------|------------------------|
| SO ₂ | 4056.8 |
| O ₂ | 4563.9 |
| SO ₃ | 6085.2 |
| N ₂ | 66768.2 |

Material Balance across 2nd Bed:

99% gas is pass to 2nd stage

(2nd stage converter 85% conversion)

 SO_2 in= 0.99* 4056.8 = 4016.23kmol /day

 $O_2 \text{ in} = 0.99 * 4563.9 = 4518.26 \text{ kmol}/\text{day}$

 $SO_3 in = 0.99* \ 6085.2 = 6024.35 \ kmol \ /day$

 N_2 in = 0.99*66768.2= 66100.518 kmol /day

$$SO_{2} \text{ consumed in } 2^{nd} \text{ bed} = 4016.23 - [(6024.35 + 4016.23) - (6024.35 + 4016.23)* 0.85 \\ = 2510.143 \text{ kmol /day}$$

$$SO_{2} \text{ remaining after } 2^{nd} \text{ bed converter} = 4016.23 - 2510.14 \\ = 1506.08 \text{ kmol/day}$$

$$SO_{3} \text{ produced after } 2^{nd} \text{ bed converter} = (6024.35 + 4016.23)* 0.85 \\ = 8534.5 \text{ kmol/day}$$

 O_2 consumed in 2nd bed = 2510.143*0.5

= 1255.07 kmol/day

 O_2 remaining after 2^{nd} bed converter = 4518.26 - 1255.07

= 3263.18 kmol /day

| Gas | Composition (Kmol/day) |
|-----------------|------------------------|
| SO ₂ | 1506.08 |
| O ₂ | 3263.18 |
| SO3 THE NATION | 8534.50 |
| N2 | 66100.52 |

Material Balance in Hot Heat Exchanger:

Gases entering from 2nd bed at 525°C and leave at 450°C.

| Gas | Composition (Kmol/day) |
|-----------------|------------------------|
| SO ₂ | 1506.08 |
| O ₂ | 3263.18 |
| SO ₃ | 8534.50 |
| N2 | 66100.52 |

Material Balance across 3rd Bed:

99% gas is pass to 3rd stage (3rd stage converter 93% conversion)

 SO_2 in= 0.99* 1506.08 = 1491.02 kmol /day O_2 in = 0.99* 3263.18= 3230.53 kmol /day SO_3 in = 0.99* 8534.5= 8448.15 kmol /day N_2 in = 0.99*66100.52= 65439.5 kmol /day

 $SO_2 \text{ consumed in } 3^{rd} \text{ bed} = 1491.02 - [(8449.15 + 1491.02) - (8449.15 + 1491.02)* 0.93$ = 2510.143 kmol /day $SO_2 \text{ remaining after } 3^{rd} \text{ bed converter} = 1491.02 - 795.208$ = 695.81 kmol /day $SO_3 \text{ produced after } 3^{rd} \text{bed converter} = (8449.15 + 1491.02)* 0.93$

 SO_3 produced after 3⁻⁻bed converter = (8449.15 + 1491.02)*0.93 = 9244.36 kmol /day

 O_2 consumed in 3rd bed = 795.208*0.5 non-numbers university = 397.604 kmol /day

 O_2 remaining after 3rd bed converter = 3230.55 - 397.604

= 2832.95 kmol /day

| Gas | Composition (kmol /day) |
|-----------------|-------------------------|
| SO ₂ | 695.81 |
| O ₂ | 2832.95 |
| SO ₃ | 9244.36 |
| N ₂ | 65439.50 |

Material Balance in Cold Heat Exchanger:

Gases entering from 3rd bed at 475°C and outlet gases enter Economiser 1.

| Gas | Composition (kmol /day) |
|-----------------|-------------------------|
| SO ₂ | 695.81 |
| O ₂ | 2832.95 |
| SO ₃ | 9244.36 |
| N ₂ | 65439.50 |

Material Balance in Economiser 1:

Gases entering from Cold heat exchanger at 300°C and leave at 220°C.

| Gas | Composition (kmol /day) |
|---------------------|-------------------------|
| SO ₂ | <u>69</u> 5.81 |
| O ₂ | 2832.95 |
| SO ₃ | <mark>924</mark> 4.36 |
| N_2 The nation bu | DERS UNIVERS 65439.50 |

Material Balance in Intermediate Absorption Tower:

Absorption Efficiency = 99%

| $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$ | | | |
|---|--|--|--|
| Amount of SO_3 present in gas = 9244.36 kmol /day | | | |
| Amount of SO_3 absorbed = 0.99*9244.36 | | | |
| = 9152 kmol /day | | | |
| SO_3 remaining = 9244.36 - 9152 | | | |
| = 92.36 kmol /day | | | |
| SO_2 remaining = 695.81 - (695.81*0.99) | | | |
| = 6.958 kmol /day | | | |
| O_2 remaining = 2832.95 - (0.99*2832.95) | | | |
| = 28.33 kmol /day | | | |
| Material Balance across 4 th Bed: | | | |
| Conversion = 99.6 % | | | |

Gas enters from Intermediate Absorption Tower through Cold heat Exchanger followed by Hot Heat Exchanger.

$$\begin{split} &\text{SO}_2 \text{ in} = 6.958 \text{ kmol /day} \\ &\text{O}_2 \text{ in} = 28.33 \text{ kmol /day} \\ &\text{SO}_3 \text{ in} = 92.36 \text{ kmol /day} \\ &\text{N}_2 \text{ in} = 65439.5 \text{ kmol /day} \\ &\text{SO}_2 \text{ consumed in 4}^{\text{th}} \text{ bed} = 6.9581 - [(92.36 + 6.9581) - (92.36 + 6.9581)^*0.97] \\ &= 3.98 \text{ kmol /day} \\ &\text{SO}_2 \text{ remaining after 4}^{\text{th}} \text{ bed} = 6.9581 - 3.98 \\ &= 2.98 \text{ kmol /day} \\ &\text{O}_2 \text{ consumed in 4}^{\text{th}} \text{ bed} = 3.98^*0.5 \\ &= 1.99 \text{ kmol /day} \end{split}$$

 O_2 remaining after 4th bed = 28.33 - 1.99

= 26.34 kmol /day

 SO_3 produced after 4th bed = (92.36 + 6.9581)*0.97

= 96.34 kmol /day

| Gas | Composition (kmol /day) |
|-----------------|-------------------------|
| SO ₂ | 2.98 |
| O ₂ | 26.34 |
| SO ₃ | 96.34 |
| N ₂ | 65439.50 |

Material Balance in Final Absorption Tower:

Absorption Efficiency = 99%

 $SO_{3}(g) + H_{2}O(l) \longrightarrow H_{2}SO_{4}(l)$ 1 mole of SO₃ = 1 mole of H₂SO₄ Amount of SO₃ present in gas = 96.34 kmol /day one on we refer to the second state of SO₃ absorbed = 0.99*96.34 = 95.38 kmol /day

Therefore, Water used = 95.38*18

= 1716.78 kg/day

1716.78 kg of water will give = 1716.78 *98 = 168,244.32 kg H₂SO₄

5.2. ENERGY BALANCE

Energy Balance across Combustion Chamber

Temperature at Combustion chamber = $T_f^{o}C$

Temperature of Molten Sulphur = $115 \ ^{\circ}C$

Dry air inlet at 100 °C

Reference Temperature = $25^{\circ}C$

Specific Heat :

 $C_p \text{ of } N_2 = 6.45 + 0.000325 \text{ T}$

 C_p of S= 4.38 + 0.0044 T

 $C_p \text{ of } O_2 = 8.27 + 0.000258 \text{ T}$

 $C_p \text{ of } SO_2 = 7.7 + 0.0053 \text{ T}$

Inlet Heat :



Sulphur in = $10142 \int (4.38 + 0.0044 \text{T dT})$

 $= 10142[4.38(115-25) + 0.0044(115^2 - 25^2)/2]$

= 4279112.6 kcal/day

Oxygen in = $17748.5 \int (8.27 + 0.000258T dT)$

 $= 17748.5 [8.27 (100-25) + 0.000258(100^2-25^2)/2]$

= 11029971.7 kcal/day

Nitrogen in = $66768.2 \int (6.45 + 0.000325 \text{T dT})$

 $= 66768.2[6.45 (100-25) + 0.000325(100^2-25^2)/2]$

= 32400833.93 kcal/day

Total Heat Inlet = 32400833.93+11029971.7+4279112.64

= 47709918.27 kcal/day

Heat of Reaction (Evolved):

 $\Delta H_s = -70.9 \text{ kcal/mole}$

 $\Delta H_r = 10142*70.9*10^3 = 719067800 \text{ kcal/day}$

Outlet Heat :

| Oxygen out | $= 7606.5 \int (8.27 + 0.000258 \text{T dT})$ |
|--------------|---|
| | $= 7606.5[8.27(T_f-25) + 0.000258((T_f)^2-25^2)/2]$ |
| | $= 0.9812 (T_f)^2 + 62905.75 T_f - 1573257.14$ |
| Nitrogen out | $= 66768.2 \int (6.45 + 0.000325 \text{T dT})$ |
| | $= 66768.2 \ [6.45(T_f - 25) + 0.000325((T_f)^2 - 25^2)/2]$ |
| | $= 10.849(T_f)^2 + 430654.8 T_f - 10773153.4$ |

Sulphur dioxide out = $10142 \int (7.7 + 0.0053 \text{ T dT})$

| | $= 10142 \left[7.7 (T_{\rm f} - 25) + 0.0053 ((T_{\rm f})^2 - 25^2)/2 \right]$ |
|----------------|---|
| | = 26.875 (T _f) ² + 78093.4 T _f - 3161755 |
| Total heat out | $= 38.71(T_f)^2 + 571653.9 T_f - 15508165.14$ |

<u>Heat of Reaction = Heat Out – Heat In</u>

 $= 38.71(T_f)^2 + 571653.9 T_f - 63218083.41$

Therefore,

 $38.71(T_f)^2 + 571653.9 T_f - 63218083.41 = \Delta H_r = 719067800$

 $38.71(T_f)^2 + 571653.9 T_f - 782285883.4 = 0$

T_f= 1260 °C

Outlet Temperature of Waste Heat Boiler = 400° C

Heat Extracted:

Oxygen = 7606.5 $\int (8.27 + 0.000258T dT)$ = 7606.5[8.27(400-1260) + 0.000258(400²-1260²)/2] = - 5.549 * 10⁷ Nitrogen = 66768.2 $\int (6.45 + 0.000325T dT)$ = 66768.2 [6.45(400-1260) + 0.000325(400²-1260²)/2] = - 3.858 * 10⁸ Sulphur Dioxide = 10142 $\int (7.7 + 0.0053 T dT)$ = 10142 [7.7(400-1260) + 0.0053(400²-1260²)/2]

Heat extracted from Waste Heat Boiler = $(-1.055 - 3.858 - 0.5549)10^8$

 $= -5.468 \times 10^8 \text{ kcal/day}$

Let x kg mol/day amount of water be used.

 $= -1.055 * 10^{8}$

Let water temperature be 90°C and atmospheric temperature be 25°C.

 C_p of water = 17.97 cal/mol K

Heat taken by water = x * 17.97 (90-25) = 1670 x

Heat taken by water = Heat extracted by boiler

Therefore,

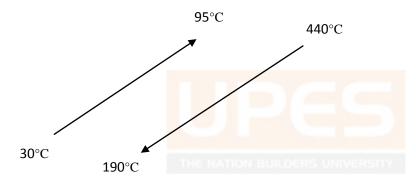
$$1670x = 5.468*10^{8}$$

x= 3.274*10⁵kmol/day

5.3. ECONOMISER DESIGN

ASSUMPTIONS

- Only the thermal design considered.
- Coolant is corrosive, so assigned to tube side.
- In tube side water is taken and shell side SO₂ and air (mixture of both) is taken.
- Water will be used as a coolant, with a temperature rise from 30°C to 95°C, and SO₂ and air mixture will be cooled to 440°C to 190°C.



| Gas | Inlet | Inlet C _p | Inlet (MC _p) |
|-----------------|-----------|----------------------|--------------------------|
| | Kgmol/day | KCal/Kmol. K | |
| SO ₂ | 3.01 | 4307.34 | 12965.09 |
| O ₂ | 2355.68 | 3486.17 | 8.7*10 ⁶ |
| N ₂ | 65439.5 | 2744.92 | 1.8*10 ⁸ |
| SO ₃ | 747.82 | 7731.55 | 5.78*10 ⁶ |
| Total | | | 1.94*10 ⁸ |

Heat of Feed to Economizer

Heat of Products from Economizer

| Gas | Outlet | OutletC _p | Outlet (MC _p) |
|-----------------|-------------|----------------------|---------------------------|
| | V a mal/day | kcal/Kmol. | |
| | Kg mol/day | К | |
| SO ₂ | 3.01 | 1734.68 | $5.22*10^3$ |
| | | | |
| O ₂ | 2355.88 | 1387.15 | $3.28*10^{6}$ |
| | | | |
| N ₂ | 65439.5 | 1092.71 | $7.15*10^{7}$ |
| | | | |
| SO ₃ | 747.82 | 3443.2 | $2.57*10^{6}$ |
| | | | |
| Total | | | 7.73*10 ⁷ |
| | | | |

Heat to be Fed = Heat of Feed - Heat of Product

= q(feed) - q(product) = $1.94*10^8 - 7.73*10^7$ = $1.16*10^8$ kcal/day.K Heat of gas in economizer = $1.16*10^8*(440-190)$ = $2.9*10^{10}$ kcal/day

Water used for heat extracted = x ton mol/day

Energy balance:

 $2.9*10^7 = x*18.3*(95 - 25)$ x = 2.44*10⁴ ton mol/day x = 43.92*10⁴ tons/day (water used)

$$\Delta T_{Lm} = \left[\frac{(440 - 95) - (190 - 30)}{Ln \left(\frac{440 - 95}{190 - 30} \right)} \right] = 240.8^{\circ}C$$

Use one shell pass and two tube passes

From figure 12.6 and 12.7 (Coulson & Richardson vol.6 "Chemical engineering design"), the values of R and S are:

$$R = \frac{440 - 190}{95 - 30} = 3.84$$

$$S = \frac{95 - 30}{440 - 30} = 0.158$$

From figure 12.19, correction factor $F_t = 0.98$ Hence, corrected Temp. $\Delta T_m = 240.8*0.98 = 236.858 \sim 236^{\circ}C$

$$Q = \frac{2.9*10^{10}*4.18}{24*3600} = 1.4*10^{6} \text{ J/s} = 1.40 \text{ MW}$$

Let assume U =100W/m².s (for air-gas mixture)

Q = UA
$$\Delta$$
T
A= $\frac{Q}{U\Delta T}$ = $\frac{1.4*10^6}{100*236}$ = 59.32 m²

Let 16 mm outer diameter, 12.8 mm inner diameter, and 3.88 ft. or 4 m long tubes, made by cupro-nickel material.

Area of one tube = $\pi^* D^* L$ = 3.14*16*10⁻³*4 = 0.201 m² No. of Tubes = $\frac{59.32}{0.201}$ = 295 tubes As the shell side fluid is relatively clean, use 1.25 triangular pitch.

Bundle diameter

$$D_{b} = 16 \left[\frac{295}{0.249} \right]^{\binom{1}{2.207}} = 395.17 \text{ mm}$$
 (by equation)

Assume split ring floating head from figure 12.10. Bundle diameter clearance = 56 mm

Shell diameter $D_s = D_b$ + clearance = 395.17 + 56 = 451.17 mm

Tube side coefficient (take H₂O in tube side)

Mean water temp. = $(95 + 30) / 2 = 62.5^{\circ}C$

Tube cross sectional area = $\pi / \frac{4}{2} N_i^2$

 $= 3.14 / 4*12.8^2 = 128.6 \text{ mm}^2$ c nation builders university

Tube per pass = $N_t/2 = 148$

Total flow area = $148*128.6*10^{-6} = 0.02 \text{ m}^2$

Water mass velocity = $\frac{water \ flow \ rate}{flow \ area} = \frac{43.92*1000}{3600*24*0.02} = 254.2 \ \text{kg/m}^2\text{-s}$

Density of water = 1000 kg/m^3

Water linear velocity $(u_t) = 254.2 / 1000 = 0.254 \text{ m/s}$

hi =
$$\frac{4200(1.35 + 0.02*T_m)*0.265^{0.8}}{12.8^{0.2}} = 3648 \text{w/m}^2 \text{°C}$$

Viscosity of water = 0.89 Ns/m^2

Specific Heat= 4.18 KJ/Kg K

Thermal conductivity = $0.59 \text{ W/m}^{\circ}\text{C}$

Reynolds Number:

 $Re = (\rho * u_t * D_i) / \mu = 1000 * 0.254 * 0.0128 / 0.00089 = 3653$

Prandtl Number:

 $Pr = (C_p {}^*\mu) \ / \ K_f = 4.2 {}^*1000 {}^*0.00089 \ / \ 0.59 = \ 6.3$

Neglect wall viscosity effect

 $L/d_i = 4000/12.8 = 312.5$

From figure 12.23

 $J_{h} = 5.5 * 10^{-3}$

From equation $h_i = 0.0055*30$ = 1700 W/n



Assume baffle spacing = Ds / 5 = 451.1 / 5 = 90.2 mmTube pitch Pt = 1.25*Do = 1.25*16 = 20 mm

Cross flow area
$$A_s = (P_t - D_o)^* D_s^* l_b = (20 - 16)^* 451.17^* 90.23^* 10^{-6}$$

Pt 20 =
$$8.14 * 10^{-3} m^2$$

Mass velocity
$$G_s = W_s / A_s$$

 $W_s = (28*65439.5) + (64*3.01) + (2355.88*32) + (747.82*80)$

 $= 1.96 * 10^{6} \text{ kg/day}.$

| n 12.27 : 653*6.3 ^{0.33} *0.59 n ² °C | / 0.0128 | |
|---|----------|--|
| | | |

 $G_s = 2797.8 \text{ kg/m}^2 \text{s}$ (from above)

Equivalent Diameter: $d_e = 1.1/d_0(P_t^2 - 0.917d_0^2)$ $d_e = 11.36 \text{ mm}$ Mean shell side temp. = $(440 + 190) / 2 = 315^{\circ}C$ Density of mixture N₂. O₂, SO₂, SO₃ at 1 atm and 588 K (315°C) By formula $\rho = PM/RT$ Where, P=1 atm, R=0.0821 kJ/atm K , T= 588 K Density of N₂ = 0.58 kg/m³ Density of O₂ = 0.662 kg/m³ Density of SO₂ = 1.325 kg/m³ Density of SO₃ = 1.657 kg/m³

Mass Fraction of N₂ = $(28*65439.5)/(1.96*10^6) = 0.935$ Mass Fraction of O₂ = $(32*2355.88)/(1.96*10^6) = 0.0385$ Mass Fraction of SO₂ = $(64*3.01)/(1.96*10^6) = 9.8*10^{-5}$ Mass Fraction of SO₃ = $(80*747.82)/(1.96*10^6) = 0.0305$

 ρ of mixture = (0.58*0.935) + (0.662*0.0385) + (1.325*9.8*10⁻⁵) + (1.657*0.0305) = 0.6184 kg/ m³

 $Log \mu = A \left[\frac{1}{T} - \frac{1}{B} \right] at temperature 661K$

The viscosities of the gases :

| N_2 | A = 90.3 | B = 46.14 | $\mu = 0.011 \text{ Ns/m}^2$ |
|-------|----------|-----------|------------------------------|
| | | | |

O₂, A = 85.68 B = 51.5 $\mu = 0.0303 \text{ Ns/m}^2$

| SO_2 | A = 397.85 | B = 315.99 | $\mu = 0.2615 \text{ Ns/m}^2$ |
|-----------------|------------|------------|-------------------------------|
| SO ₃ | A = 1372.8 | B = 315.99 | $\mu=0.0098~Ns/m^2$ |

Viscosity of Mixture

$$\mu \text{ of mixture} = (0.011*0.935) + (0.2615*9.8*10^{-5}) + (0.0385*0.0303) + (0.0098*0.0305)$$
$$= 0.012 \text{ Ns/m}^2$$

Inlet Heat capacity $C_p = (2744.92*0.935) + (4307.34*9.8*10^{-5}) + (0.0385*3486.17) + (7731.55*0.0305)$

= 2937 kcal/kmol°C

Outlet Heat Capacity $C_p = (1092.71*0.935) + (1734.68*9.8*10^{-5}) + (0.0385*1387.15) + (3443.2*0.0305)$

= 1180.27 kcal/kmol°C

Net Heat Capacity = Inlet Heat Capacity - Outlet Heat Capacity

= 2937-118<mark>0</mark> = 1756.7 kcal/kmol°C 1 900 PCR5 UNIVERSITY

 $\Sigma y_i M_i = (28*0.935) + (64*9.8*10^{-5}) + (0.0385*32) + (80*0.0305)$

= 29.86

 $C_p = 1756.7*(4.18/29.86) = 245.9 \text{ kJ/kg} \circ C$

Thermal conductivity = $0.0515 \text{ W/m}^{\circ}\text{C}$

$$Re = \frac{2797.8 * 11.36 * 10^{-3}}{0.012 * 10^{-3}} = 2.64 * 10^{6} \quad (Re = G_{s} * d_{e} / \mu)$$

$$Pr = \frac{245.9*10^3*0.012*10^{-3}}{0.0515} = 57.3 \quad (Pr = \mu * C_p/K)$$

From figure 12.29, $J_h = 6*10^{-4}$

$$h_{s} = \frac{0.0515*6*10^{-4}*2.64*10^{6}*57.3^{0.33}}{11.36*10^{-3}} = 27.3 \text{ W/m}^{2\circ}\text{C}$$

Overall coefficient

Thermal conductivity of cupro-nikel alloy = $50 \text{ W/m}^{\circ}\text{C}$

Take the fouling coefficient from table 12.2, flue gases = 5000 (from equation 12.2)

 $\frac{1}{U_o} = \frac{1}{27.3} + \frac{1}{5000} + \frac{1600 * 0.001 * 0.224}{100} + \frac{16 * 1}{12.8 * 3000} + \frac{16 * 1}{12.8 * 3648} = 0.011$

 $U_o = 90.9 \text{ W/m}^{2\circ}\text{C}$

Pressure drop in economizer



Tube side

From figure 12.24 for Re = 3653

 $J_f = 6.5 * 10^{-3}$

Neglecting the viscosity factor, from equation 12.2

$$\begin{split} \Delta P_t &= 2 \; [\; 8*6.5*10^{-3}*(\; 4000/12.8) \; *1 + 2.5 \;] \; [(1000*0.254^2)/2] \\ &= 1.21 \; \text{kPa} \\ &= 0.175 \; \text{Psi} \end{split}$$

It is very low, could consider increasing the no. of tube passes

Shell side

Linear velocity $u_s = Gs / \rho = 2797.8 / 0.618 = 4.52*10^3 \text{ m/s}$ From figure 12.30 at Re = $2.64*10^6$

 $J_{\rm f} = 2.5*10^{-2}$

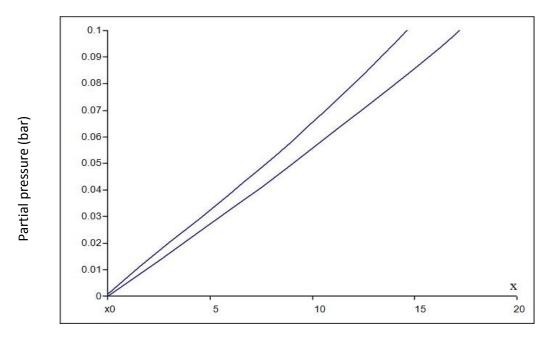
Neglect viscosity factor & from equation12.26

 $\Delta P_t = [8*2.5*10^{-2}*(451.17/11.36)*(4000/90.23)][0.618*(4.52*10^3)^2]/2$ = 2.22 MPa



5.4. ABSORBER DESIGN

| percent of SO ₃ (w/w percent) | 0 | 5 | 10 | 20 |
|---|---|-------|-------|-------|
| Partial Pressure (bar) | 0 | 0.026 | 0.056 | 0.122 |



percent of SO₂ (w/w %)

Feed to final Absorption Tower

| Gas | Inlet Kg mol/day |
|-----------------|---------------------|
| SO ₂ | 3.01 |
| O ₂ | 2355.88 |
| N ₂ | 65439.5 |
| SO ₃ | 747.82 |
| Total | 68546.21 |

Solubility Data of SO₃

Weight percentage of SO_3 (inlet) = 1.1

Partial pressure of SO₃ in the feed = (1.1/100)*1.013 = 0.011 bar

Weight percentage of SO₃ (outlet) = 1.103×10^{-2}

Partial pressure at exit after 99% recovery = $1.1*10^{-4} * 1.013 = 1.114 * 10^{-4}$ bar

Over this range of partial pressure the equilibrium line is straight so figure can be used to estimate no. of stage.

The use of figure slightly over estimated. The no. of stages and a more accurate estimation would be made by graphical integration.

Partial pressure at 10% w/w SO₃ = 0.056 bar

Mole fraction in vapour = 0.056 / 1.013 = 0.055

Mole fraction in liquid = $\frac{\overline{80}}{\left(\frac{0.1}{80}\right) + \left(\frac{0.9}{18}\right)} = 0.024$

Slope m = 0.055 / 0.024 = 2.29

To decide the most economical water flow rate the design should be for optimum no. of stages.

$$Y_1/Y_2 = 0.083/0.00083 = 100$$

| A = mG/L | 0.5 | 0.6 | 0.7 | 0.8 | 0.85 |
|-----------------|-----|-----|-----|-----|------|
| N _{OG} | 6.7 | 9.2 | 13 | 15 | 18.5 |

Optimum value of mG/L = 0.6 to 0.85

Below 0.6 there is only small decrease in no. of stages required with increasing flow rate and above 0.8 the no. of stages increases rapidly on decreasing liquid flow rate.

Mole fraction solute free basis:

$$\begin{split} Y_1 = & [0.011 / (1 - 0.011)] = 0.0111 & Y_2 = & [0.0001103 / (1 - 0.0001103)] = 1.103 * 10^{-4} \\ & L_m * X_1 = G_m * (Y_1 - Y_2) \\ & L_m * X_1 = G_m * (0.0111 - 0.0001103) \end{split}$$

$$X_{1} = \frac{m^{*}G_{m}^{*}0.0884}{2.29^{*}L_{m}} = 0.8$$

 $X_1 = 0.038$ So, $N_{OG} = 15$

Gas flow rate = 68546.21*(1 - 0.011) = 67792.2 kmol/day = 67.8 ton mole/ day For two absorber, flow rate = 67.8/2 = 33.9 ton mole/day

$$G_{\rm m} = \frac{33.89 \times 29.86 \times 1000}{24 \times 3600} = 11.7 \text{ kg/s}$$

$$L_{\rm m} = \frac{2.29 \times 33.89}{0.8} = 97.01 \text{ ton mol/day}$$

$$L_{\rm m} = \frac{97.01*18*1000}{24*3600} = 20.21 \text{ kg/s}$$

Select 25mm, 1 inch, ceramic Intalox saddles.

From table 11.3 (Reference No. 6), packing factor $F_p = 300 \text{ m}^{-1}$

Gas density at 463 K = 0.785 Kg/m^3

Liquid density = 1000 Kg/m^3 THE NATION BUILDERS UNIV

Liquid viscosity = $2.822*10^{-4}$ pa-s

$$\frac{L_w}{V_w}\sqrt{\frac{\rho_v}{\rho_l}} = \frac{20.21}{11.7}\sqrt{\frac{0.78}{1000}} = 0.048$$

Design for 15mm H₂O per meter packing, pressure drop Figure 11.44, (Reference No. 6)

 $K_4 = 0.6$, at flooding $K_4 = 4.2$

Percentage flooding
$$\sqrt{\frac{0.6}{4.2}}$$
 *100 = 38%

From equation 11.118,

$$\mathbf{V}_{\mathbf{w}} = \sqrt{\frac{K_4 \times \rho_v \times (\rho_l - \rho_v)}{13.1 \times F_p \times \left(\frac{\mu_l}{\rho_l}\right)^{0.1}}}$$

 $V_{w} = \left\{ \left[0.6^{*} \ 0.785^{*} \ (1000 - 0.785) \right] / \left[13.1^{*} 300^{*} \ (2.88/1000)^{0.1} \right] \right\}^{1/2}$

$=0.464 \text{ kg/m}^2.\text{s}$

Column area required = $11.7 / 0.464 = 25.2 \text{ m}^2$

Diameter = $[(4/\pi)^*(25.2)]^{1/2} = 5.66 \approx 6m$

Column Area = $(\pi/4)^{*}6^{2} = 28.26$ m

Packing size to column diameter ratio = [6/(0.025)] = 240

Percentage flooding at selected diameter = [38*(25.2/28.2)] = 33.8%

Could consider reducing column diameter.

Estimation of H_{OG}

| CORNELL'S METHOD Viscosity Calculation by using formula: $\mu = \mu_0 \left[\frac{T_0 + C}{T + C} \right] \left[\frac{T}{T_0} \right]^{1.5}$ |
|--|
| Where C (N ₂) = 111, C (O ₂) = 127, |
| Temperature in Kelvin (K) = $(190 + 293) = 463 \text{ K} (\text{T}) \text{ ; } \text{T}_{0} = 298 \text{ K}$ |
| $\mu_{\rm o} \text{ of } N_2 = 17.81^{*}10^{-6} \text{ pa-s} \text{ at } 25^{\circ}\text{C}$ |
| $\mu_{o} \text{ of } O_{2} = 20.18 * 10^{-6} \text{ pa-s} \text{ at } 20^{\circ}\text{C}$ |
| From the above data, |
| $\begin{split} \mu_{N2} &= 2.457*10^{-5} Pa\text{-s} \\ \mu_{O2} &= 2.854*10^{-5} Pa\text{-s} \\ \mu \text{ of mixture} &= \mu \text{ of } N_2*0.79 + \mu \text{ of } O_2*0.21 \\ \mu \text{ of mixture} &= 2.45*10^{-5}*0.79 + 2.85*10^{-5}*0.21 = 21.42*10^{-6} \text{ pa-s} \\ \mu_v &= 2.535*10^{-5} \text{ pa-s} \\ \mu_l &= 2.822*10^{-4} \text{pa-s} \text{ (for water)} \end{split}$ |
| $D_L = 1.76*10^{-9} m^2/s$ (for water) |

Using Empirical Equation by Fuller, Schettler and Giddings (1996)

$$D_{v} \text{ at } 463 \text{ K}, (1.013 \text{ bar}) = \frac{1.013 * 10^{-7} * T^{1.75} \left(\frac{1}{M_{a}} + \frac{1}{M_{b}}\right)^{0.5}}{P\left[\left(\sum_{a} v_{i}\right)^{1/3} + \left(\sum_{b} v_{i}\right)^{1/3}\right]^{2}}$$

| $\sum v_i = (2.31*2) + 5.48$ | $M_a = 18$ |
|------------------------------|---------------|
| $\sum_{b}^{a} v_i = 20.1$ | $M_b = 29.86$ |

| С | 16.5 | H ₂ | 7.07 | CO2 | 26.9 |
|-------------------|-------|----------------|------|------------------|------|
| н | 2.31 | He | 2.88 | N ₂ O | 35.9 |
| 0 | 5.48 | N ₂ | 17.9 | NH3 | 14.9 |
| N | 5.69 | O ₂ | 16.6 | H ₂ O | 12.7 |
| CI | 19.5 | Air | 20.1 | Cl ₂ | 37.7 |
| S | 17.0 | Ar | 16.1 | SO₂ | 41.1 |
| Aromatic ring | -20.2 | Kr | 22.8 | _ | |
| Heterocyclic ring | -20.2 | со | 18.9 | | |

(Table 2.4 Atomic and diffusion volumes, Fuller et al., 1996, Reference No. 7)

 $D_v = 1.727*10^{-5}m^2/s$

 $Sc = (\mu/\ D^*\rho)$

 $(Sc)_v = (2.535*10^{-5}) / (1.72*10^{-5}*0.785) = 1.169$

 $(Sc)_{L} = (2.82*10^{-4}) / (1.70*10^{-9}*1000) = 166$

 $L_w = (L_m/28.26) = (20.21/28.26) = 0.715 \text{ kg/m}^2.\text{s}$

From figure 11.41 at 33.8% flooding $K_3=1$ (ReferenceNo.6)

From figure 11.42 at 33.8% flooding $\Psi_h = 50$

From figure 11.43 at L_w = 0.715, Φ_h = 0.02

Assuming Z to be 26m.For Design Purposes, the diameter correction term should be a fixed value of 2.3 for columns above 0.6 m

From equation 11.110 & 11.111 (Reference No. 6),

$$\mathbf{H}_{L} = 0.305\phi_{h}(Sc)_{L}^{0.5}K_{3}\left(\frac{Z}{3.05}\right)^{0.15}$$
$$\mathbf{H}_{G} = 0.011\psi_{h}(Sc)_{v}^{0.5}\left(\frac{D_{c}}{0.305}\right)^{1.11}\left(\frac{Z}{3.05}\right)^{0.33} / (L_{w}^{*}f_{1}f_{2}f_{3})^{0.5}$$

where \mathbf{H}_G = height of a gas-phase transfer unit, m,

- \mathbf{H}_L = height of a liquid-phase transfer unit, m,
- $(Sc)_v = \text{gas Schmidt number} = (\mu_v / \rho_v D_v),$
- $(Sc)_L =$ liquid Schmidt number = $(\mu_L / \rho_L D_L)$,
 - $D_c =$ column diameter, m,
 - Z =column height, m,
 - K_3 = percentage flooding correction factor, from Figure 11.41,
 - $\psi_h = \mathbf{H}_G$ factor from Figure 11.42,
 - $\phi_h = \mathbf{H}_L$ factor from Figure 11.43,
 - L_{w}^{*} = liquid mass flow-rate per unit area column cross-sectional area, kg/m²s,
 - $f_1 =$ liquid viscosity correction factor = $(\mu_L/\mu_w)^{0.16}$,
 - $f_2 =$ liquid density correction factor = $(\rho_w / \rho_L)^{1.25}$,
 - f_3 = surface tension correction factor = $(\sigma_w/\sigma_L)^{0.8}$,

$H_L = 0.305 * 0.02 * (166)^{0.5} * 1 * (26/3.05)^{0.15} = 0.108 \text{ m}$

As the liquid taken is water so, $f_1 = f_2 = f_3 = 1$ from equation 11.110,

$$H_{\rm G} = \frac{0.011*50*1.86^{0.5}*2.3*(26/3.05)^{0.33}}{0.715^{0.5}} = 1.87 \text{ m}$$

 $H_{OG} = H_G + A^* H_L = 1.87 + 0.8^{*}0.108 = 1.95 \text{ m}$

$$Z = H_{OG} * N_{OG} = 1.95 * 15 = 29.3 m$$

Close enough to estimated value, with an error percentage of 11.3%

CHAPTER 6

PLANT LAYOUT & COST ESTIMATION

6.1. Plant Layout

The layout of the plant should be given a very practical consideration. The layout, space available and process adopted .The following six principal should be kept in mind while deciding the layout:-

i) Principal of overall integration:

The best layout integrates the men, materials; machinery supporting activates in a way which results in the best compromise.

ii) Principal of minimum distance:

Other things being equal, the best layout is that in which the materials and men move the minimum distance between operations.

iii) Principal of flow:

Other things being equal, the best lay out is that which arranges the work area for each operation or in the same order or sequence that forms, treats, or assembles the materials.

iv) Principal of cubic space :

The Best layout is that in which all available space, both vertical and horizontal is economically and effectively utilized.

v) Principal of satisfaction & safety:

Other things being equal, the best layout is that which makes work satisfying, pleasant and safe for workers.

vi) Principal of flexibility:

Other things being equal, the best layout is that which can be adjusted and rearranged at a minimum cost and inconvenience.

Thus, one of the possible plant layout for smelter gas based sulphuric acid plant is that all the three tower are placed in a line close to each other having their individual pumps and supports .The floor of the tanks is covered with acid bricks .The converter C1 can be placed in the middle surrounded by the four heat exchanger allowing a suitable place for SO2 blower .The storage tank is at one corner of the plant. All the acid coolers can be taken to one side of the plant ad the floor can be made of acid resistant bricks.

6.1.1. Staff and Labour Requirements

Labour

The plant will be operated 24 hours per day by 3 operators each working on eight hours shift. Apart from unskilled labors for zinc blends handling one other personnel will be needed in the plant.

Organisation Structure:

The plant in charge will report to the general manager or technical director. The project consist of technical and commercial personnel.Commercial personnel's are included for project accounting, making various applications with government bodies, financial institutions, etc. Technical personnel consists of process equineers, and mechanical and electrical engineers for maintenance.

6.1.2. Material of Construction & Corrosion Prevention

1. For Pumps, valves, pipings & tubing:

In early pumps, three basic construction materials were in common use:

a) 7 percent Antimonical lead:

This material was used for low acid strengths and temperature. It found its use in chamber process plants

b) Grey- Cast Iron:

This material was used for acid at 60 degree be and strong and temperature not greater than 50 degree centigrade. At higher temperature, special alloy cast iron was used.

c) Silicon cast iron: These materials containing 13 to 15% silicon were used primarily in wearing and bearing components. These were highly resistant to all concentrations to very high temperatures, but they lacked mechanical strength, were brittle and not readily mechinable.

The use of illium for shaft bearing, wearing rings and impeller began during 1924-25. With the introduction of alloy 20 in1951, it represent standard material for this item . In recent years heat shrunk ploytertaflouro ethylene converting have been applied to the alloy 30 shafts to extend their resistance to the corrosive effect of very high temperature acids. Pump impellers in illium G were upgraded in 1963 to illium B, because of its combination of properties-resistance to corrosion by not conc. Acid, and ability to be age hardened for improved wear resistance was especially developed for use in shaft journals and bearings as well as impeller and casing wearing rings.

As outstanding improvement came about in 1970, with the introduction of lawnet 55, another nickel based alloy (Chromine level as high as 30%). It exhibits excellent corrosion resistance to the very hot conc.. sulfuric acid H_2SO_4 even in the presence of trace amounts of chlorides or fluorides. This alloy is finding more & more application other than pumps.

i) Orifice plats

ii)Sulfuric Acid valves

iii)Spray pipe hole assemblies.

6.1.3. Safety & Hazards

Sulfuric Acid is injurious to the skin, mucosa and eyes. Dangerous amounts of Hydrogen may develop in reactions between weakened acid and metals. Sulfuric acid at high concentrations reacts vigorously with water, organic compounds, and reducing agents. The following general handling precautions should be observed:

1. Do not get in eyes, on skin, on clothing. Wear chemical goggles, face shields, rubber gloves and full protective clothing whenever there is dangerous of exposure. Wash thoroughly after handling.

2. Avoid breathing mist or vapors. Handle only in areas with sufficient ventilation to prevent irritation, or wear a suitable respirator.

3. Keep containers closed. Do not allow awaiter to enter containers because of violent reactions. When diluting, add the acid slowly with agitation to the surface of the aqueous solution to avoid violent spattering, boiling and eruption.

4. Handling containers and pipelines also requires special precautions. An emptied container retains vapor and product residue. Drum should be periodically vented to prevent accumulations of Hydrogen. To avoid Hydrogen Explosion when welding any vessel that has contain sulfuric acid must be thoroughly purged and tested for explosive conditions before welding commence.

5. In case of contact immediately flush eyes of skin with plenty of water for at least 15 min while removing contaminated clothing or shoes. Call the physician. Wash clothing before.

6. In case of inhalation remove the fresh air if necessary, give artificial respiration, preferably mouth to mouth or give oxygen, call physician.

7. Safety shower should be available at appropriate location in the plant.

8. In case of spill or leak, keep people away and upwind of the spill. Dike the area with sand or earth to contain the spill. Finish the area with water. Neutralize washing with lime soda or ash. Notify pollution control authorities of any surn off into streams or swears and of any air pollution incidents.

6.1.4. Safety Operation and Testing

1. Leakage of SO_2 and SO_3 containing gases from the contact plan equipment can cause a nuisance. Stop the plant in such case. Periodical checking of instruments is necessary.

2. Circulation of sulfuric acid from the acid pump tank through coolers, IAT, FAT etc. is a possible hazard to the operational staff in case of leakage of the acid. Thus, continuous testing of the pipes must be done for thickness and for maximum acid pressure.

3. Stoppage of Sulfuric Acid circulation due to failure of acid circulating pump during plant operation can cause a serious safety hazard. In such an eventuality 8 to 10 % SO₃ containing acid will escape into the atmosphere. Immediately stop the plant.

4. The recommended material of construction for storage of the sulfuric acid is K. S. Tanks. Large quantities of sulfuric acid are stored in these tanks. It is essential to have dyke walls around the storage so that in case of leakage of acid, the leakage can be confined to a restricted area and thus spillage can be collected by pumping and subsequently the area can be washed and neutralize with lime.

5. According to the present regulations laid down by the central pollution control board, sulfur dioxide mission in the stack gases of DCDA plant should not exceeded 600ppm. The conventional DCDA process incapable of controlling the emission within these limits. However, at the time of start up of a sulfuric acid plant the so₂ concentration in exhaust gases exceeds 600ppm and is in the range of 2000 to 10000ppm for the first 3 to 6 hours. However, when a proper preheating system for converter passes is installed to ensure that the catalyst is at the right

temperature, it is possible to reduce the period of higher SO_2 emission to less than 2 hours. Acid mist should also be controlled below 50 mg/m³ using high efficiency mist eliminators.

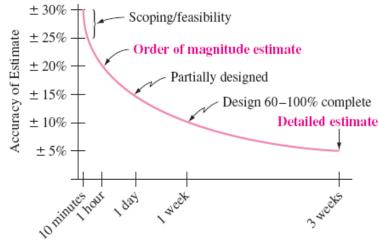
6. Sudden stoppage of failures in power supply severely affect the working of sulfuric acid plant.

7. The disposal of spent vanadium catalyst from sulfuric acid plants should not be overlooked because of high toxicity of the vanadium chemicals. The catalyst can be buried under ground where it does not affect the underground water.

6.2. Cost Analysis

Types of Capital Cost Estimates :

- 1. Order of Magnitude Ratio (Ratio Estimate) : based on similar previous cost data (+/- 30%)
- Study Estimate (Factored Estimate) : based on knowledge of major items of equipment(+/-30%)
- 3. Preliminary Estimate (budget authorization estimation) : based on sufficient data to permit the estimate to be budgeted(+/- 20%)
- 4. Definitive Estimate : based on almost complete data but before completion of drawings and specifications(+/- 10%)
- Detailed Estimate : based on complete engineering drawings, specifications and site surveys. (+/- 5%)



Time Spent on Estimate

Fig. 6.1. Characteristic curve of accuracy vs. time to make estimate

6.2.1. Cost Estimation

A study estimate has been done on the 1000MTPD capacity sulphuric acid plant. Table 6.1. shows the total cost of equipments installed.

The total purchased equipment cost is then further on used as a basis to calculate the total capital investment required (Table 6.2).

A breakeven analysis has been done using the figures calculated.



| Equipments | Quantity | Lifetime (years) | Cost per Cost (R unit(Rs) Crore) | | *Salvage Value (Rs) | #Depreciation (Rs/yr) | |
|--|----------|---------------------|-------------------------------------|---------|------------------------|--------------------------|--|
| Heat exchangers | 13 | 4 | 32,00,000 | 4.16 | 1,60,000 | 76,00,000 | |
| Absorption column | 2 | 10 | 70,00,000 | 1.4 | 3,50,000 | 13,30,000 | |
| Reactor | 1 | 10 | 2,50,00,000 | 2.5 | 12,50,000 | 23,75,000 | |
| Pumps : | | | , , , | | , , | , , | |
| Acid circulation | 5 | 3 | 70,000 | 70.000 | | 44,333 | |
| Dosing | 2 | 3 | 32,000 | | 1600 | 20,267 | |
| Boiler Feed Water | 3 | 3 | 50,000 | 7.021 | 2500 | 47,500 | |
| Sulphur | 5 | 3 | 5,00,000 | | 25,000 | 7,92,000 | |
| Turbine | 4 | 5 | 1,25,00,000 | | 6,25,000 | 47,50,000 | |
| Tanks : | | | | | | | |
| sulphuric acid | 2 | 10 | 1,80,00,000 | | 9,00,000 | 17,10,000 | |
| Boiler Feed Water | 2 | 10 | 7,00,000 | 5.37 | 35,000 | 66,500 | |
| | | 10 | 3,20,000 | | 16,000 | 60,800 | |
| Process Machinery: | | | | | | | |
| Agitators | 8 | 5 | 10,00,000 | | 50,000 | 15,20,000 | |
| Burner | 1 | 5 | 20,00,000 | | 1,00,000 | 3,80,000 | |
| Cooling Tower | 4 | 10 | 12,50,000 | | 62,500 | 2,37,500 | |
| Waste heat boiler | 1 | 10 | 1,25,00,000 | VERSITY | 6,25,000 | 11,87,500 | |
| Steam drum | 1 | 10 | 20,00,000 | 10 | 1,00,000 | 1,90,000 | |
| Air blower | 2 | 5 | 3,20,000 | | 16,000 | 1,21,600 | |
| Mist Eliminator | 5 | 5 | 60,00,000 | | 3,00,000 | 34,20,000 | |
| Wet Scrubber | 1 | 5 | 40,00,000 | | 2,00,000 | 7,60,000 | |
| Total | | | | 30.46 | | 2,66,13,000 | |
| *Salvage Value = 5% c as given by manufactu # Depreciation calcula | urer | | hod | | | | |

Table 6.1. Method : Percentage of Delivered Equipment Cost

| Components | Cost (Rs crore) |
|---|-----------------|
| Purchased equipment delivered | 30.46 |
| Purchased equipment installation 47% | 14.32 |
| Instrumentation & controls (installed) 18% | 5.48 |
| Piping (installed) 66% | 20.1 |
| Electrical (installed) 11% | 3.35 |
| Buildings (including services) 18% | 5.48 |
| Yard improvements 10% | 3.046 |
| Service facilities (installed) 70% | 21.32 |
| Total direct plant cost | 73.01 |
| Indirect Costs | |
| Engineering & supervision 33% | 10.05 |
| Construction expenses 41% | 12.49 |
| | |
| Total indirect & direct plant costs | 95.64 |
| Contractor's fee(about 5% of indirect & direct plant costs) | 4.78 |
| Contingency (about 10% of indirect & direct plant costs) | 9.564 |
| Fixed capital investment | 110 |
| Working Capital(about 40% of total | 73 |
| capital investment) | |
| Total Capital Investment | 183 |

Table 6.2. Estimation of Capital Investment

Break Even Analysis:

The current selling price of Sulphuric acid is Rs 14000 /ton.

Based on the annual production and revenue, a break even chart has been prepared as shown below. From the graph, we can say that the plant needs to be operated at a minimum of 287 TPD to avoid any losses.

| Production (10 ³ tonnes per year) | Sales (Rs crore per annum) |
|--|----------------------------|
| 0 | 0 |
| 73 | 102.2 |
| 146 | 204.4 |
| 219 | 306.6 |
| 292 | 408.8 |
| 365 | 511 |

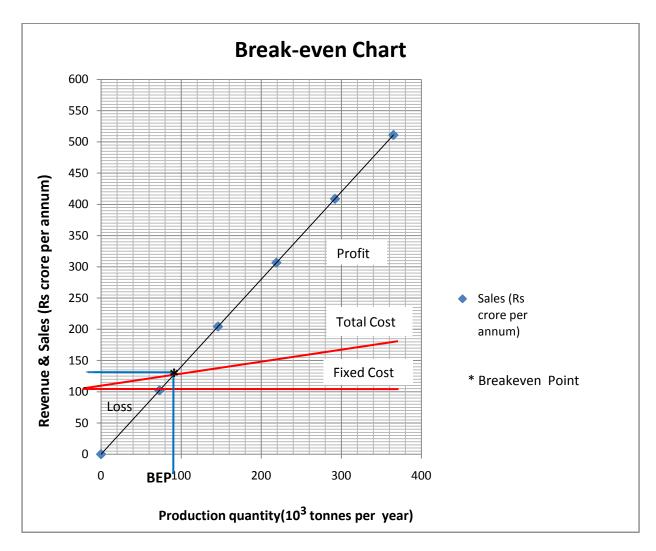


Fig. 6.2. Break-even Analysis

CHAPTER 7

RESULTS & CONCLUSIONS

| 1 | Total H ₂ SO ₄ produced | 10.00 ton mole/day |
|---|---|--------------------|
| 2 | Total sulfur used | 10.26 ton mole/day |
| 3 | Total air used | 2450.9 ton |

HEAT EXCHANGER DESIGN

| 1 | Shell side fluid | mixture of SO ₃ , SO ₂ & air |
|---|-----------------------------------|--|
| 2 | Tube side fluid | water at 30°C |
| 3 | Diameter of tube | 16mm (od), 12.8mm (id) |
| 4 | Length of tube | 4 m |
| 5 | Diameter of the shell | 451.2mm |
| 6 | Pressure drop in shell side | 2.22 MPa |
| 7 | Pressure drop in tube side | 0.1755 psi |
| 8 | Overall heat transfer coefficient | 91W/m ² .°C |
| 9 | Overall heat transfer area | 59.32m ² |

ABSORBER DESIGN

| 1 | Total water used | 13326.12 kg/day |
|---|-------------------------------------|-------------------------|
| 2 | Total No. of stages N _{OG} | 15 |
| 3 | Absorber diameter | 6.0 m |
| 4 | Total height | 26 m |
| 5 | Type of packing used | ceramic Intalox Saddles |
| 6 | Size of packing | 1" 25mm |

CONCLUSIONS

- The demand for H_2SO_4 in the current market was determined to be 5.5 MMTPA
- The DCDA process was found to be the most efficient method for production of H₂SO₄.
- VK-68 (by Haldor Topsoe) was the suitable catalyst for production of H₂SO_{4.}
- Material and energy balance was made for 1000 MTPD
- Heat exchanger (Kern's method) and absorption column (Cornell's method) was designed.
- Total capital investment was found to be 183 crores (as on 11th April 2015)
- Break even chart was prepared and the plant has to be operated at 287 TPD minimum to avoid loss.

| Literature survey | | | | | F | | | | F |
|-----------------------------|-----|-----|-----|-----|----------------------------|-----|-----|-----|----------------------------|
| Process Flow chart | | | | | I R S | | | | I N A |
| Material Balance | | | | | T | | | | L |
| Energy balance | | | | | P R | | | | P R |
| Design of Reactor | | | | | E S | | | | E S |
| Design of equipments | | | | | E N | | | | E N |
| Material of construction | | | | | T A T I O N | | | | T A T I O N |
| Economic analysis | | | | | | | 24 | | |
| Time Period | Sep | Oct | Nov | Dec | Dec | Jan | Feb | Mar | Ар |

WORK PLAN FOLLOWED

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