

# **Chemical Process Industries**

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University of Technology

Chemical Engineering Department

Fourth Edition

# CHEMICAL PROCESS INDUSTRIES

R. Norris Shreve  
Joseph A. Brink, Jr.



INTERNATIONAL STUDENT EDITION

# Shreve's Chemical Process Industries

Fifth Edition

GEORGE T. AUSTIN



McGraw-Hill INTERNATIONAL EDITIONS  
Chemical Engineering Series

# Process classification

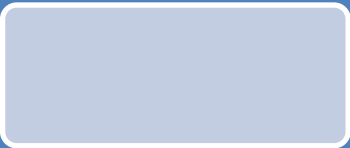
**Physical process**

**Chemical process**

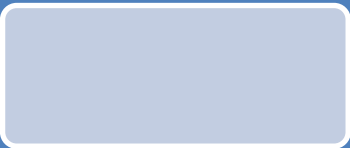
# Operating conditions



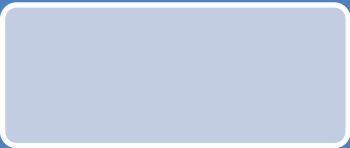
temperature



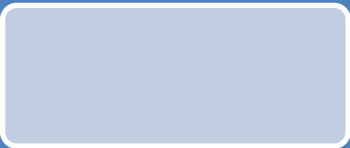
pressure



Surface area, purity, concentration



catalyst

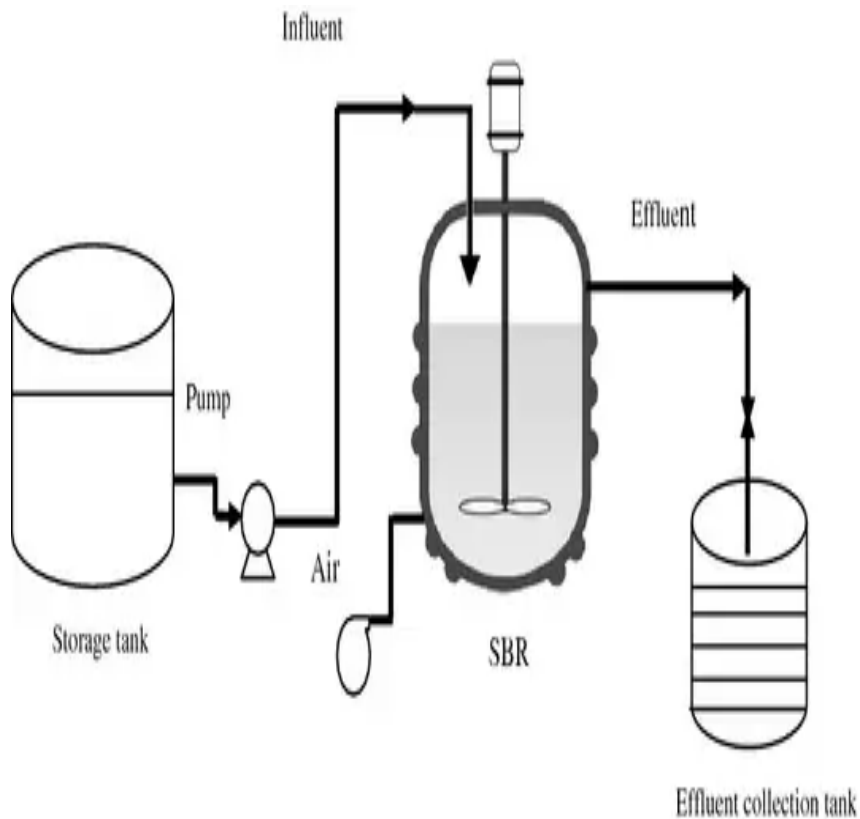


Equilibrium rate

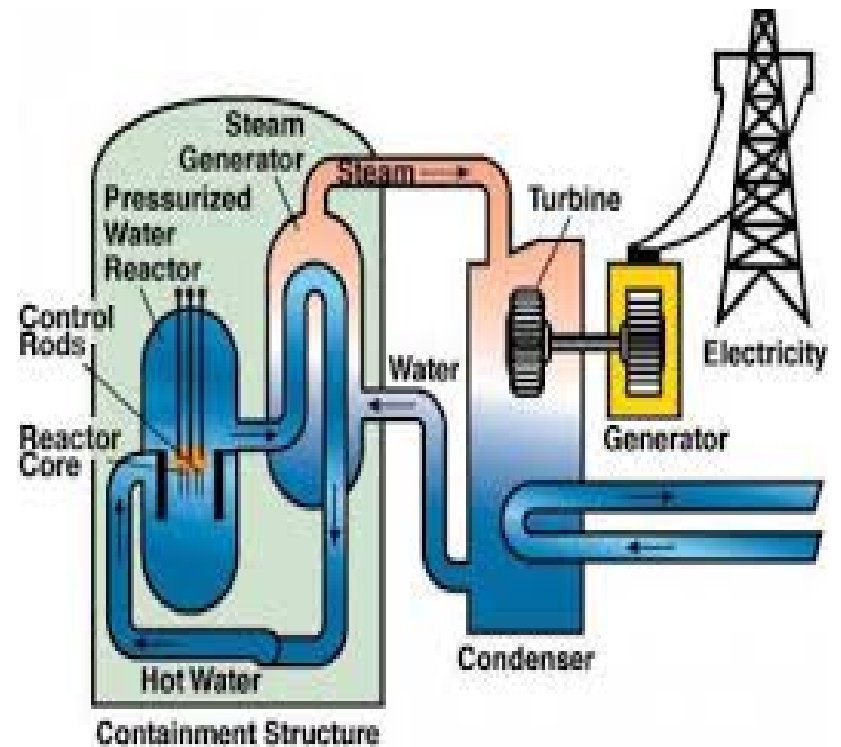


# Process types

## Batch Process

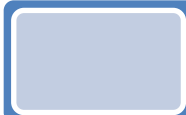


## Contentious Process



# Unit operations

## Chemical unit operation



Oxidation



hydrogenation



calcinations



fermentation

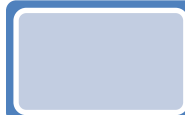


polymerization



carbonization

## Physical unit operation



distillation



evaporations



drying



filtration

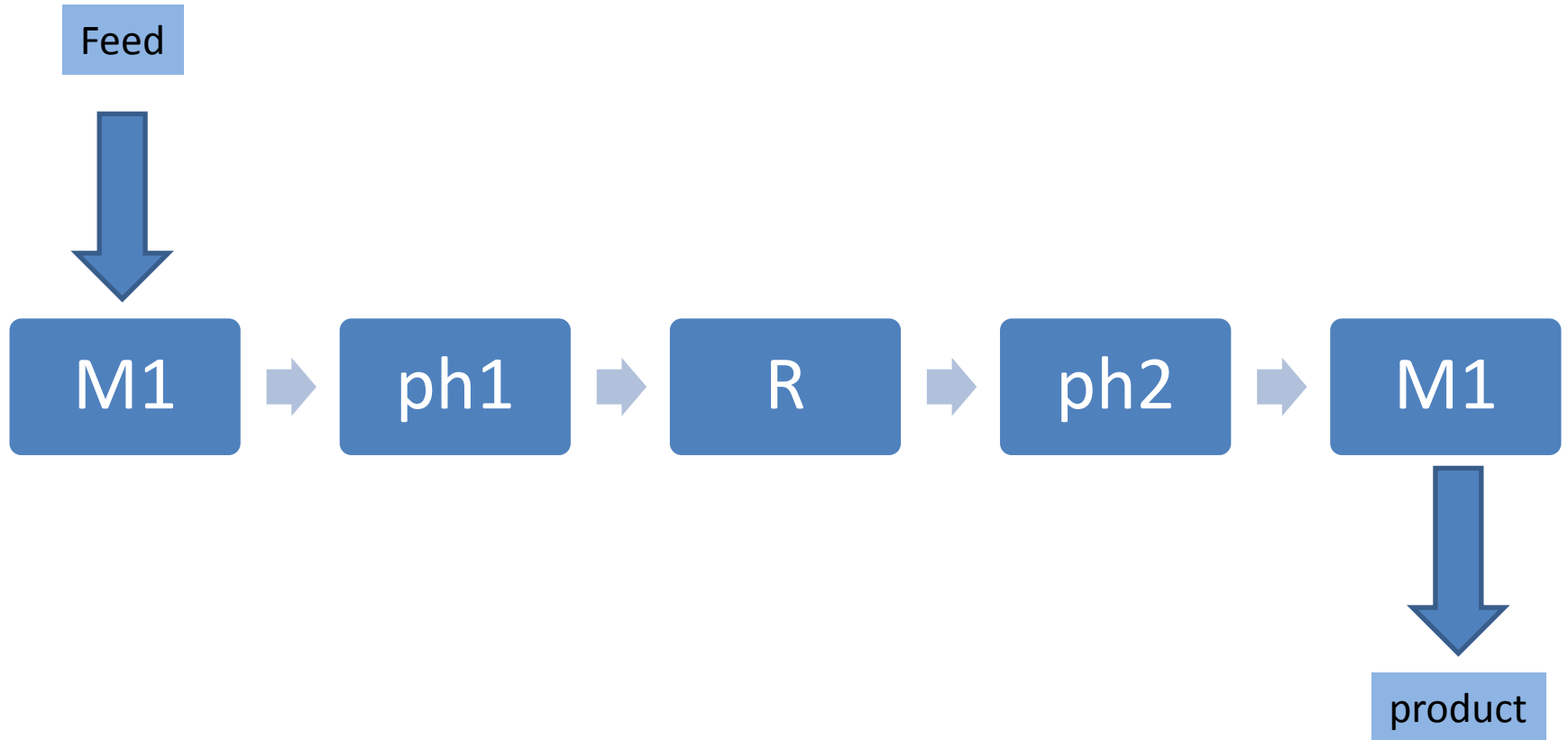


extraction



crystallization

# Flow chart (process structure)



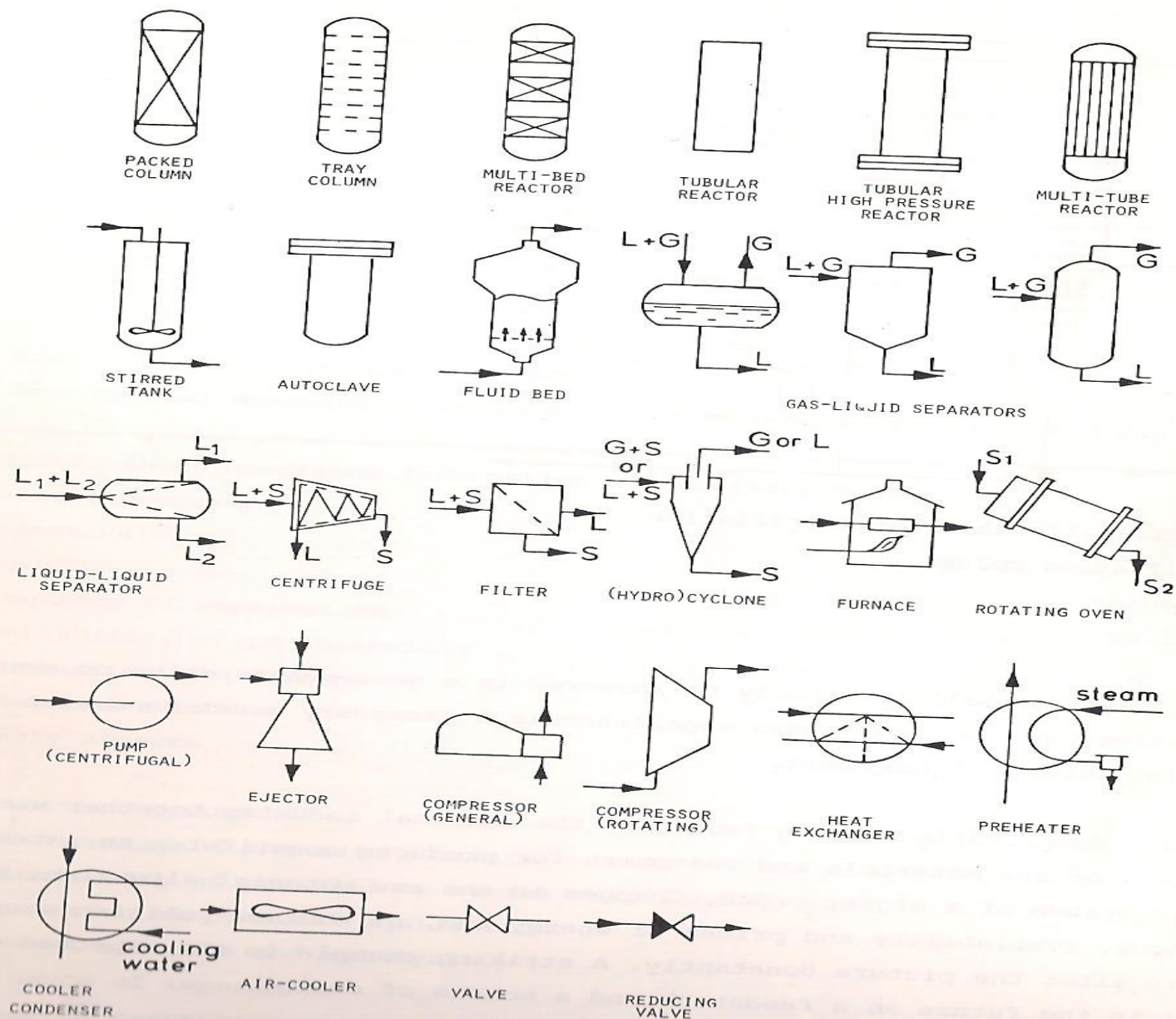
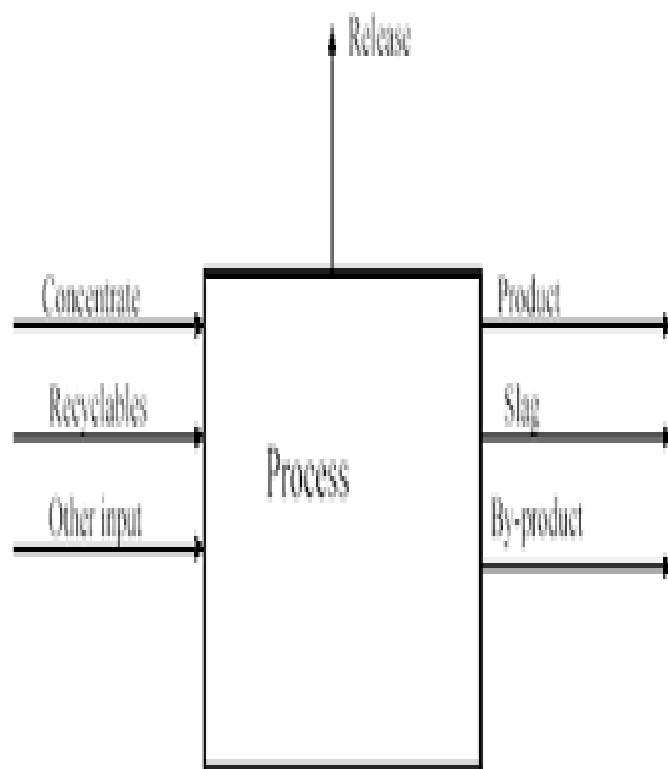


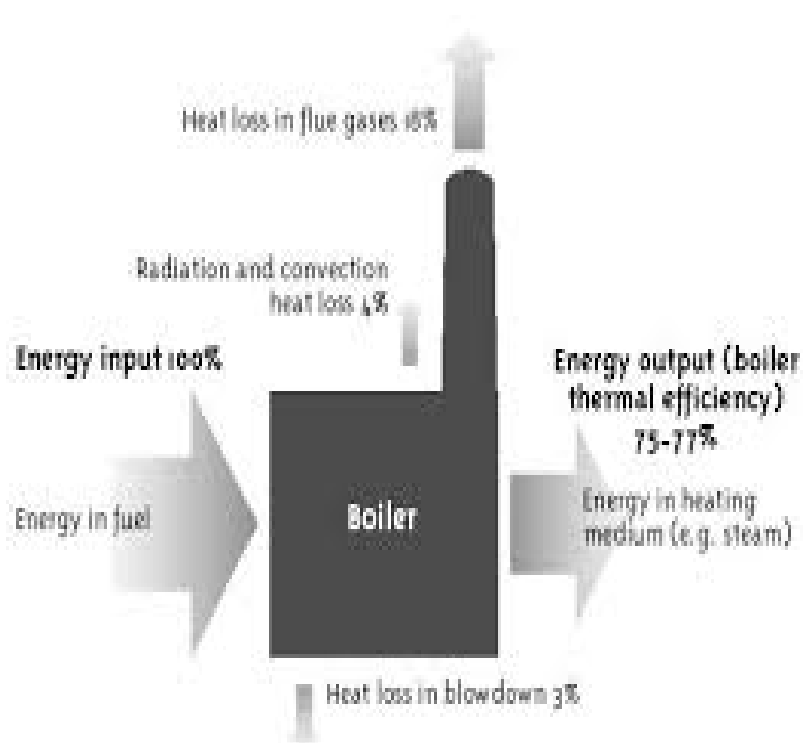
Figure II.2. Symbols used in flow charts

# Industrial stoichiometry

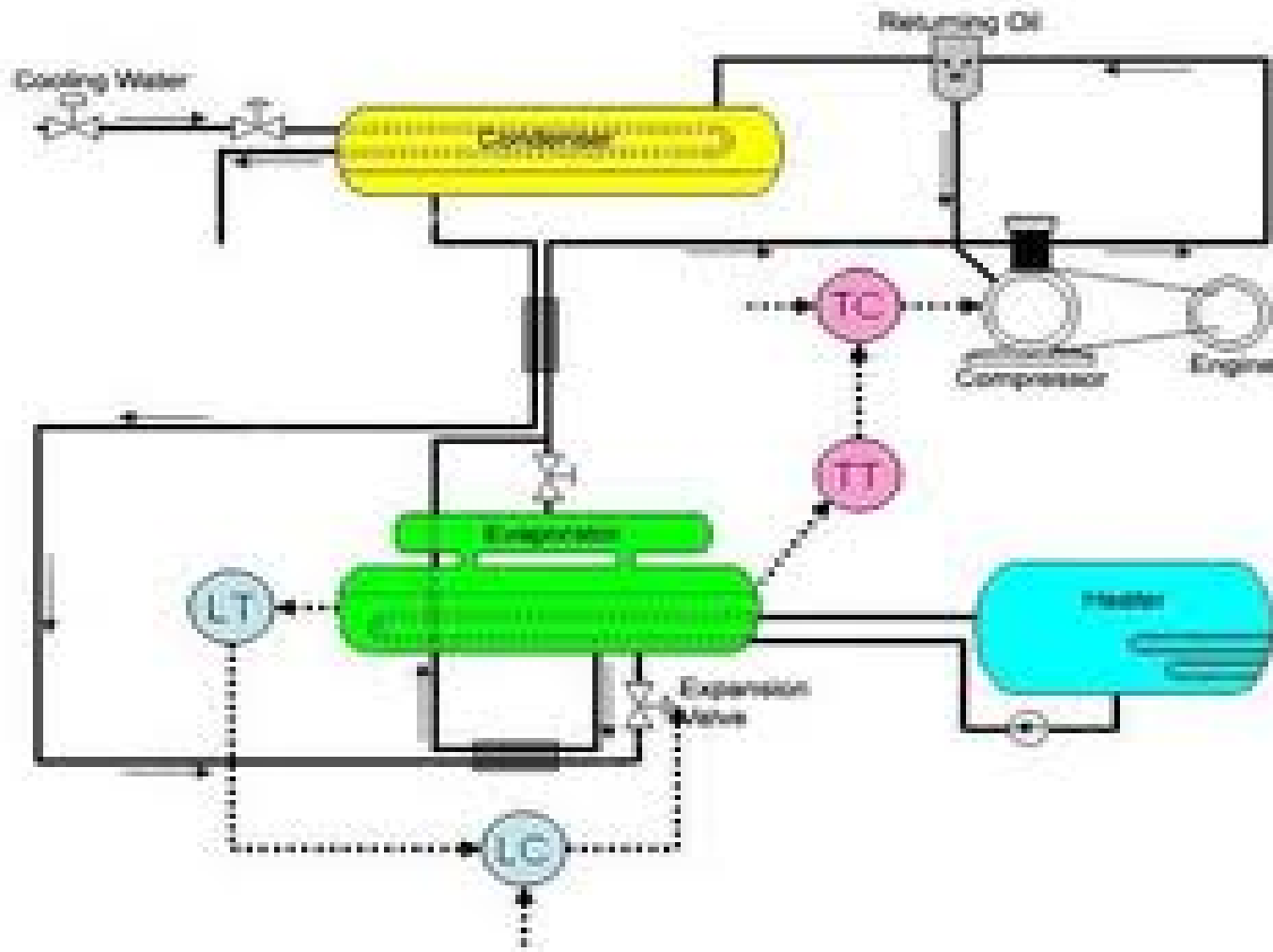
## Mass Balance



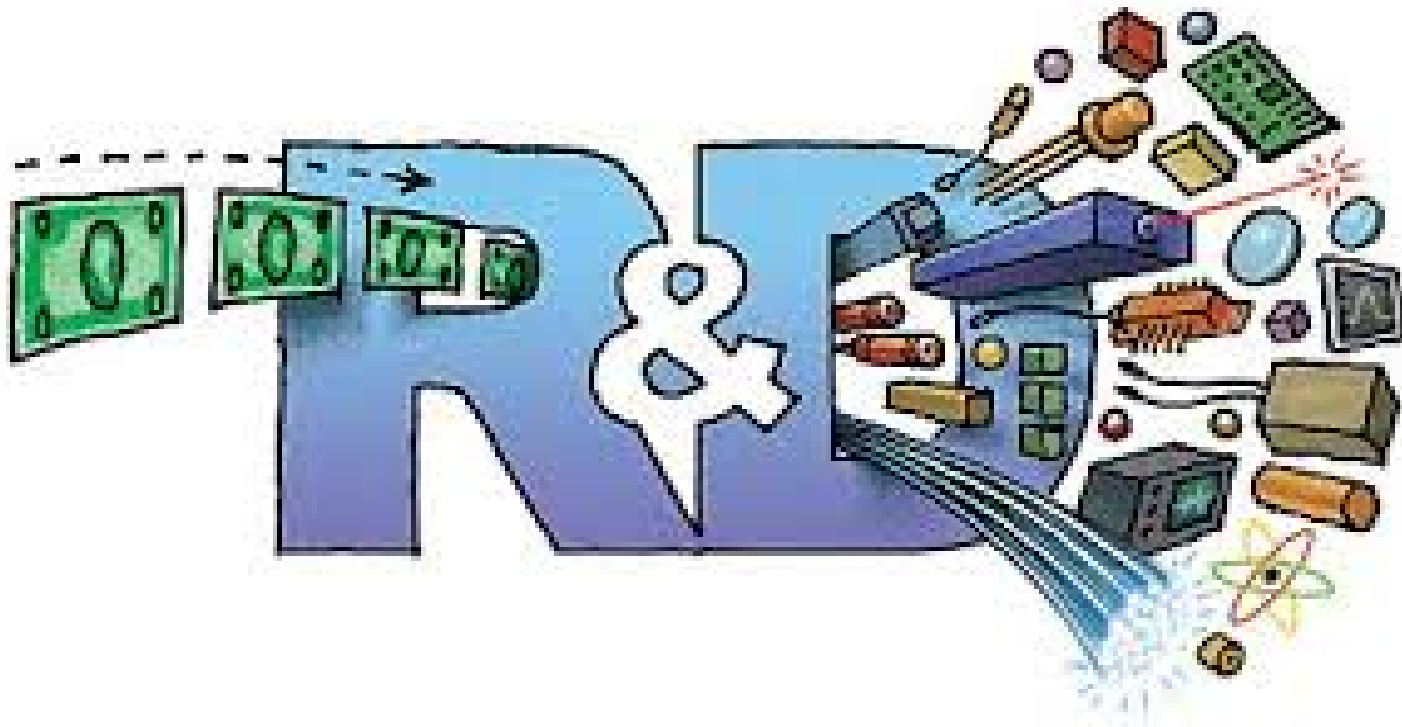
## Energy Balance



# control



# R&D (Research and Development)



# Sulfuric acid





# Raw materials

sulfur

Sulfide  
ore

Coal, NG  
,fuel gas

Waste  
 $\text{H}_2\text{SO}_4$

$\text{MgSO}_4$

$\text{CaSO}_4$

$\text{H}_2\text{S}$

$\text{SO}_2$

# Raw materials (cont.)

## Homogenous Catalysis

**Chamber Tower**

**60-80% $\text{H}_2\text{SO}_4$**

## Heterogeneous catalysis

**Contact Process**

**100% and Stronger acid**



Fertilizer industry :



Coke oven



Superphosphate  
industry



Chemical Industry



Organic dye stuffs



intermediates



explosive



Petroleum refining

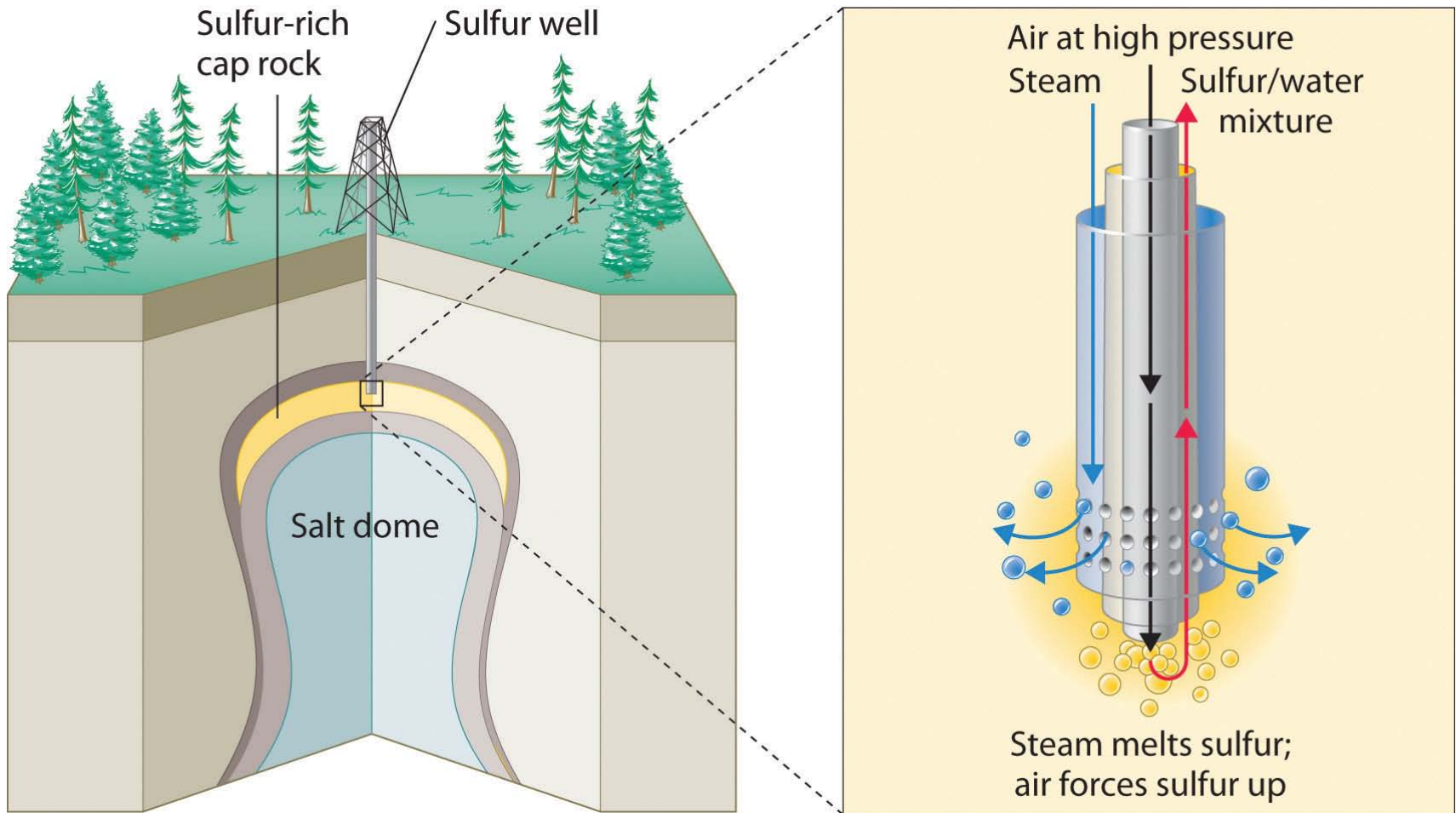


Synthetic fibers

# Mining and manufacture of Sulfur

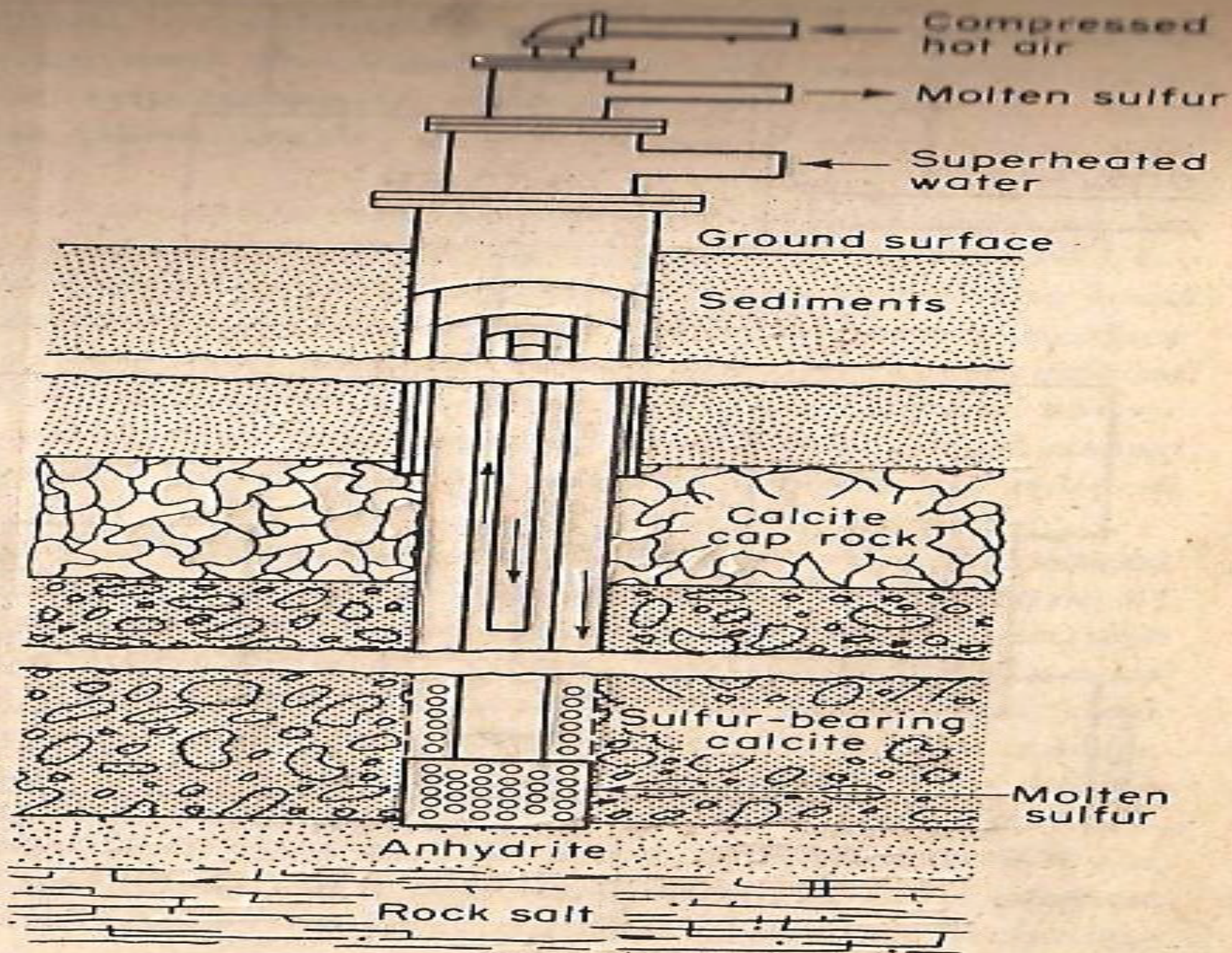


# Frasch process



-

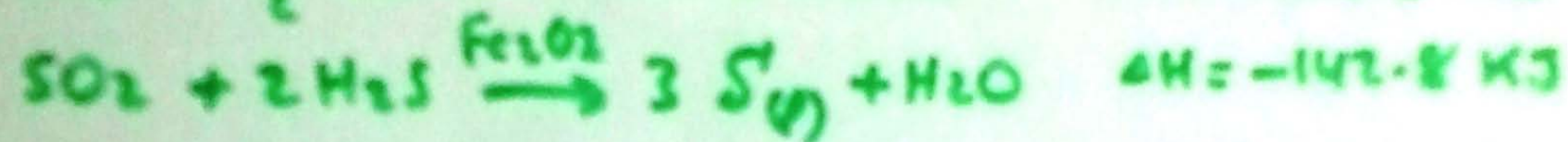
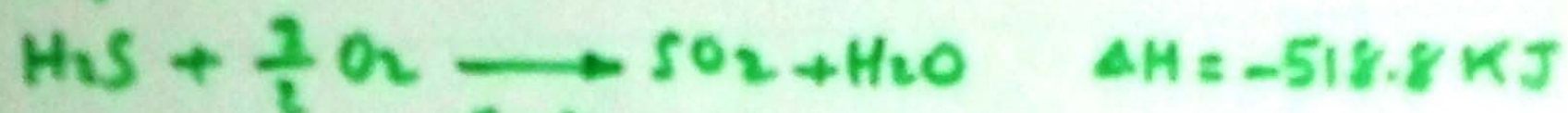






## Sulfur from fuel gas (Claus process)

removing  $\text{H}_2\text{S}$  gas during purification of sour N.G., coke-oven gas, and from petroleum refinery gas, by **absorption** in the  $\text{K}_2\text{CO}_3$  sol. or MEA solvent. followed by **stripping** to regenerate it. The  $\text{H}_2\text{S}$  produced is **burning** to give  $\text{SO}_2$  for  $\text{H}_2\text{SO}_4$ . However, the majority is **converted** by modified **Claus process** :-



Conversion = 98-99.5 % to prevent air pollution

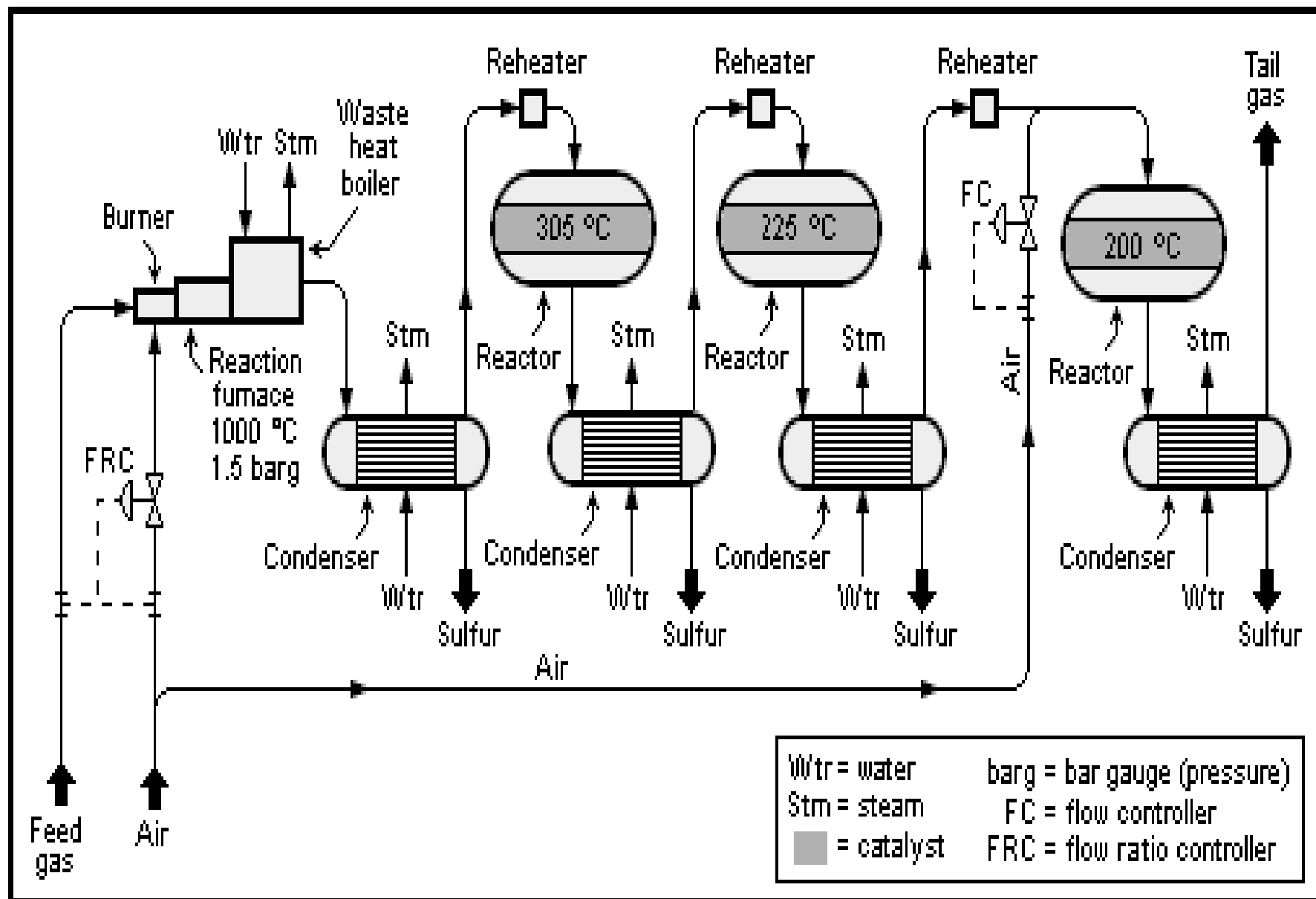
H.W Claus plant, fig 19.2, P.324, Shreve, 5ed

# Clause Process

- Sulfur from fuel gases:
- H<sub>2</sub>S gas from purification of sour NG , coke oven gas, and petroleum refinery gas. H<sub>2</sub>S gas convert to S by Clause process
- Conversion 98-99.5% to prevent air pollution







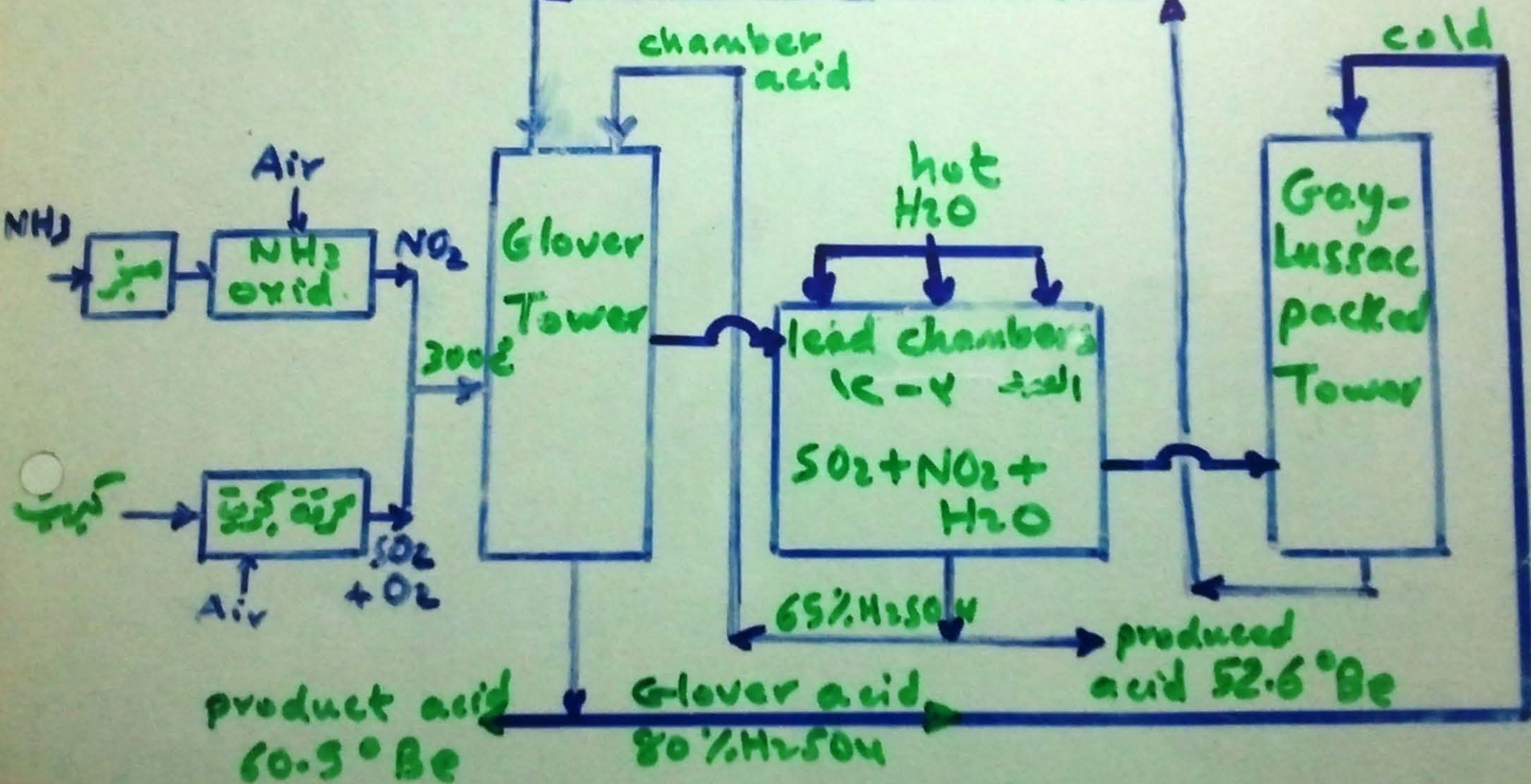
### Sulfur from other sources :

removing and utilize  $\text{SO}_2$  in the gas resulting from the roasting of sulfide ores, smelting of ores, and burning of spent  $\text{H}_2\text{SO}_4$  acid or acid sludge from petroleum refining. liquid  $\text{SO}_2$  is preferred product from these sources. Electrical furnaces and flash smelters produce more conc.  $\text{SO}_2$  suitable for the recovery of sulfur or sulfuric acid.

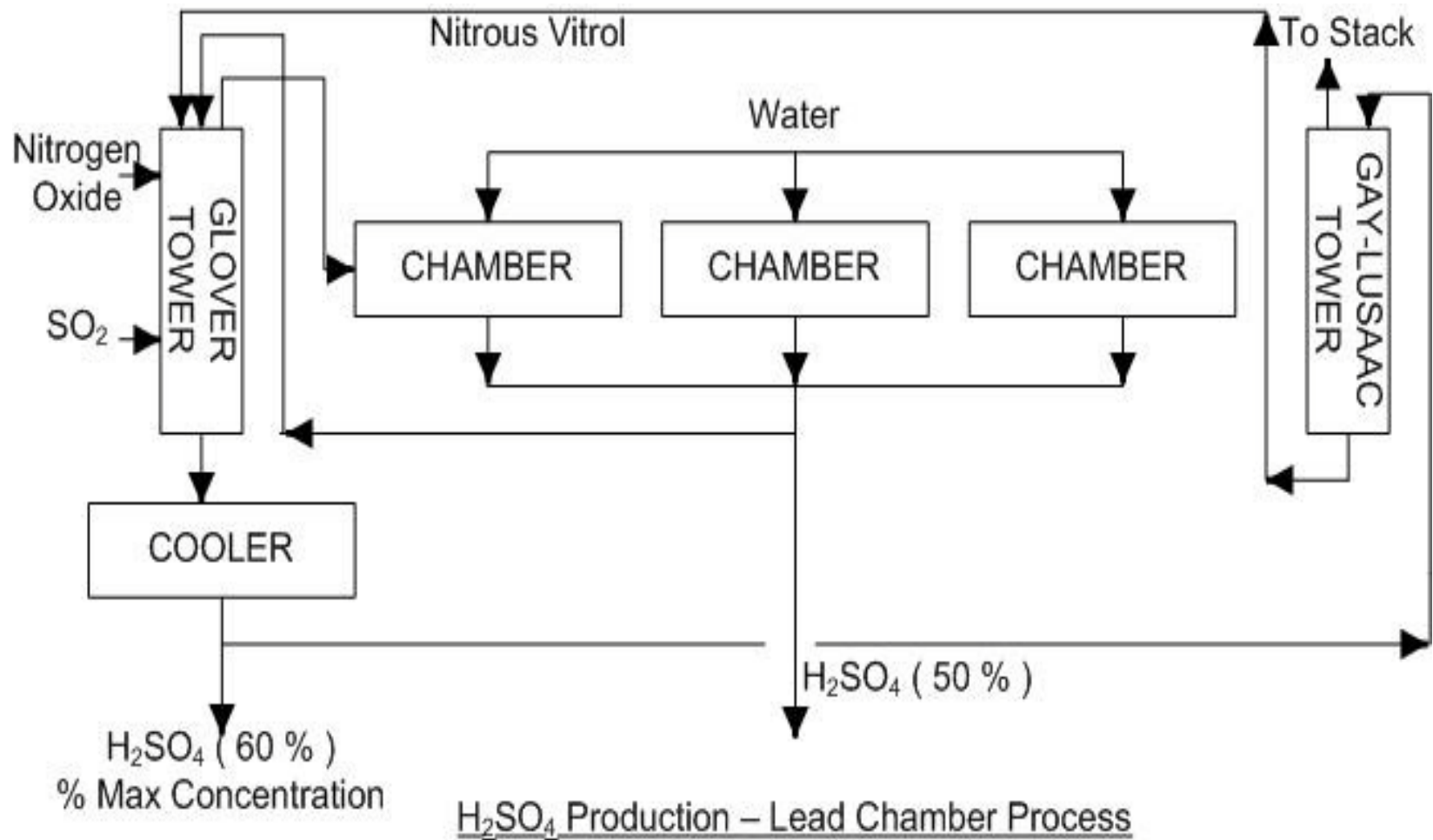
Sulfuric acid

Sulfuric acid : manufacture in two ways  
 chamber process & contact process  
chamber process (nitrous, or tower process) :

use  $\text{NO}_x$  gases as catalyst  
 $\text{N}_2\text{O}_5 + \text{acid } 60.5^\circ \text{Be (nitrous vitriol)}$



# Chamber process (nitrous or tower process)





- Use NOX as catalyst
- There are three essential stages:
  - Purification & cooling of roast gases in Glover tower with concentration & denitrification of the 65% chamber acid.
  - Oxidation of SO<sub>2</sub> in the lead chambers.
  - Recovery of the nitrous gases in the Gaylussac tower.

# theory : Main reactions in chambers & towers

type of reaction	Reaction eq.	Site of reaction
Gas reaction	$2NO + O_2 = 2NO_2$	In all parts
Dissolution react. (at gas-liquid phase boundary)	(a) $SO_2 + H_2O = H_2SO_3$ (b) $NO + NO_2 + H_2O = 2HNO_2$ (c) $NO + NO_2 + 2H_2SO_4 =$ $2H_2SO_4 \cdot NO + H_2O$ <small>sulfonitric acid (or violet acid)</small> large liquid surfaces are necessary	Glover tower, chambers, or towers  Gay Lussac tower and partially in chambers and towers
Hydrolysis reactions (liquid phase)	$H_2SO_4 \cdot NO + H_2O = H_2SO_4 + HNO_3$	Glover tower, chambers and towers
oxidation reactions (liquid phase)	$H_2SO_3 + 2HNO_2 = H_2SO_4 +$ $2NO + H_2O$	Glover tower, chambers and towers

CONTACT PROCESS : All plant must perform the following operations:

- 1) produce  $\text{SO}_2$  from a suitable raw material
- 2) cool, purify, and dry the  $\text{SO}_2$  gases.
- 3) preheat the gases to the kindling temperature for conversion to  $\text{SO}_3$ .
- 4) catalytically oxidize the  $\text{SO}_3$ .
- 5) cool the converted gases.
- 6) absorb the  $\text{SO}_3$  in strong  $\text{H}_2\text{SO}_4$ .



contact plant fall into general categories:

hot - gas - purification

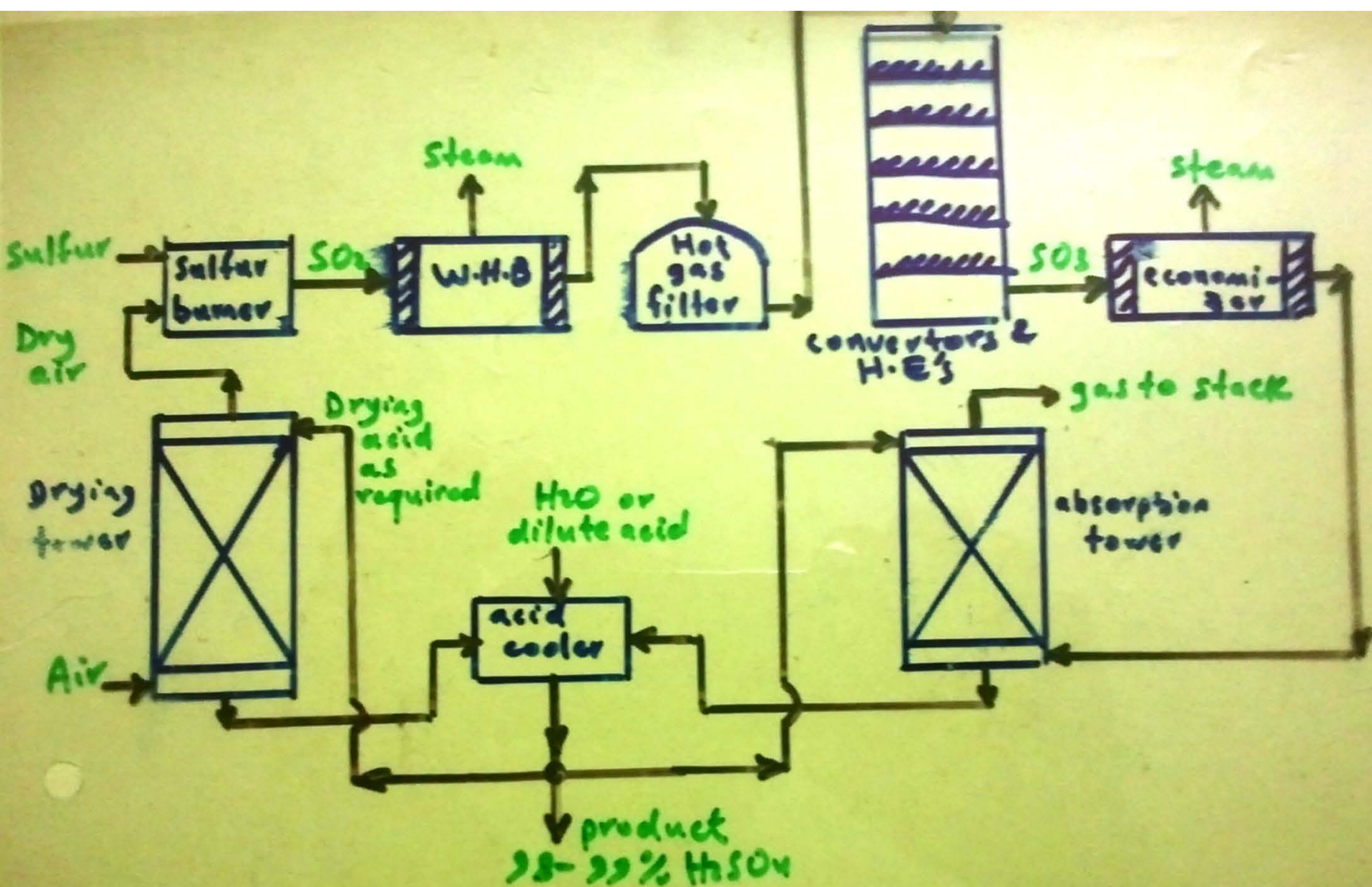
- 1) plant operate on Frasch or recovered sulfur
- 2) combustion gases contains mainly  $SO_2$  (low impurities)
- 3) required simple purification, consist of filtration at high Temp. ( $800 - 850^{\circ}F$ ) ( $422 - 454^{\circ}C$ )
- 4) low costs

cold - gas - purification

- 1) plant operate on metallurgical gases, pyrites & acid sludges.
- 2) combustion gases contains  $SO_2$ , water, dust, acid mist & other impurities.
- 3) required extensive purification consist of cooling gases to about room temp., condensing out moisture, filtering & drying before sending to converter
- 4) higher costs

(fig. 19.3, 19.4) 5<sup>th</sup> ed shreve (fig. 19.5)

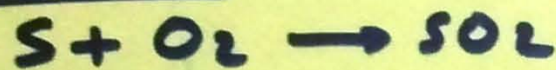




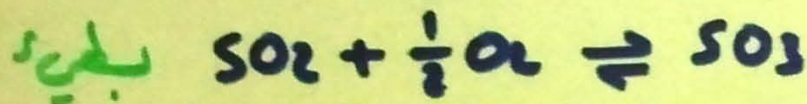
Typical hot gas purification contact plant  
(co-generation plant)



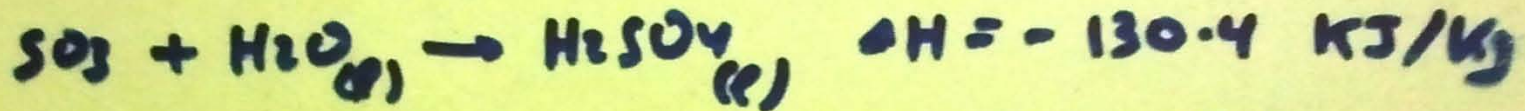
## Reactions :



$$\Delta H = -298.3 \text{ KJ/Kg, } 25^\circ\text{C}$$



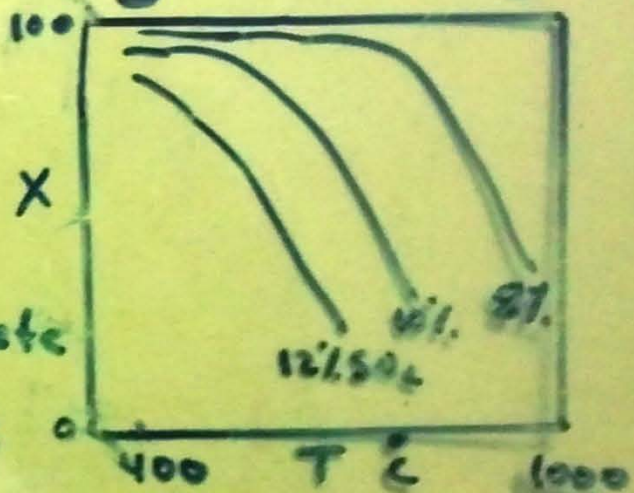
$$\Delta H = -98.3 \text{ KJ/Kg, } 25^\circ\text{C}$$



according to Le Chatelier principle, the equilibrium reaction can be shifted to  $SO_3$  formation by lowering  $T$  & increasing  $P$

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \cdot P_{O_2}} = \frac{N \cdot n_{SO_3}^2}{n_{SO_2}^2 \cdot n_{O_2} \cdot P}$$

$$n_{SO_3}^2 = \frac{n_{SO_2}^2 \cdot n_{O_2} \cdot K_p \cdot P}{N}$$



at below  $400^\circ\text{C}$ , the reaction complete

but above  $400^\circ\text{C}$ , the reaction go left

thus this problem solved by using :

1) low Temp. (i.e chamber process)

2) catalyst (i.e contact process)



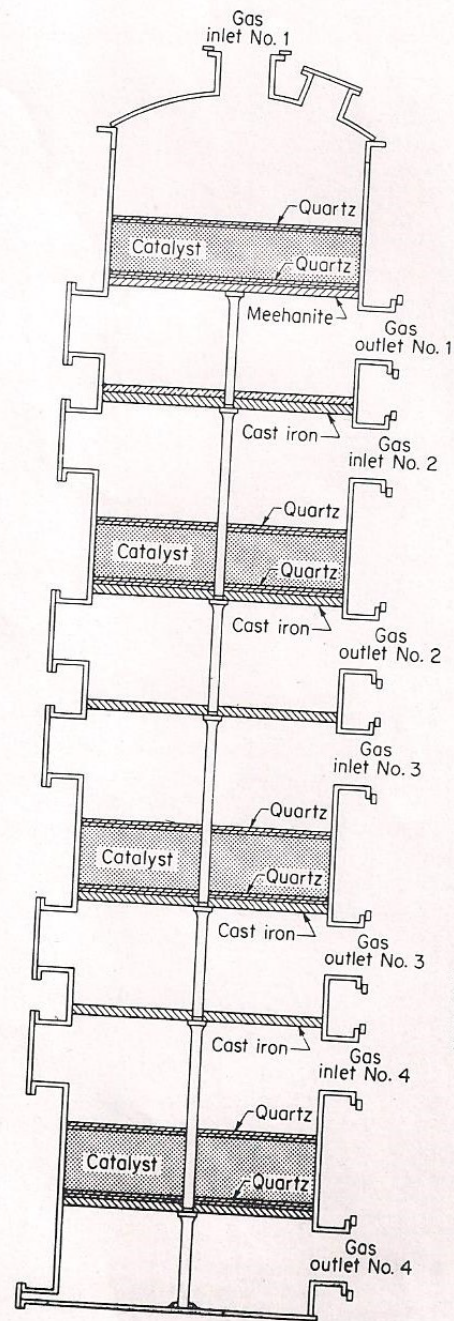
Catalyst      Pt, Fe, V

- 1) Pt. catalyst
  - \* lower conv. which declines with use
  - \* lower life being highly fragile (脆)
  - \* Is poisoned especially by As
  - \* Handles richer gas 8 to 10% SO<sub>2</sub>
  
- 2) Fe oxide
  - \* less in cost
  - \* not poisoned by As
  - \* act only above 625 °C (when  $x_e < 7\%$ )
  - \* Handles lower SO<sub>2</sub> contact gas (7% SO<sub>2</sub> & 11% O<sub>2</sub>)
  - \* therefore, used in initial stage oxidation to reach 50-60% X<sub>e</sub>

### 3) Vanadium Cat.

- \* Higher conv. efficiency
- \* longer life with high efficiency
- \* freedom from poisoning
- \* Handles lower  $\text{SO}_2$  contact gas, 7-8%  $\text{SO}_2$ , hence capital cost of plant is higher.
- \* employed at 400-600 °C
- \* low cost
- \* contain 7%  $\text{V}_2\text{O}_5$  +  $\text{K}_2\text{O}$  - promoter  
+ porous aluminosilicate - carrier  
diatomaceous earth
- \* are shaped into porous granules, tablet, or rings.





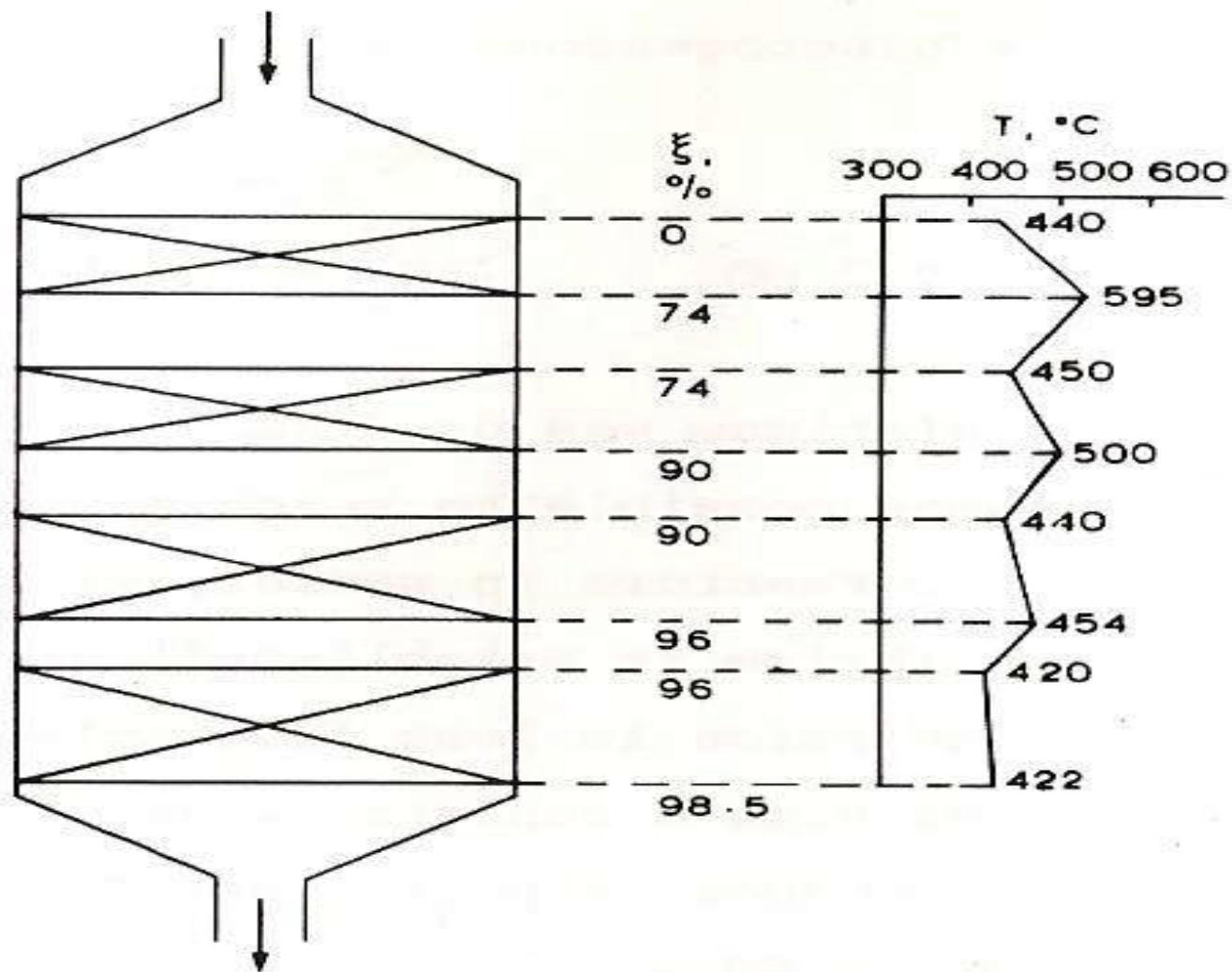
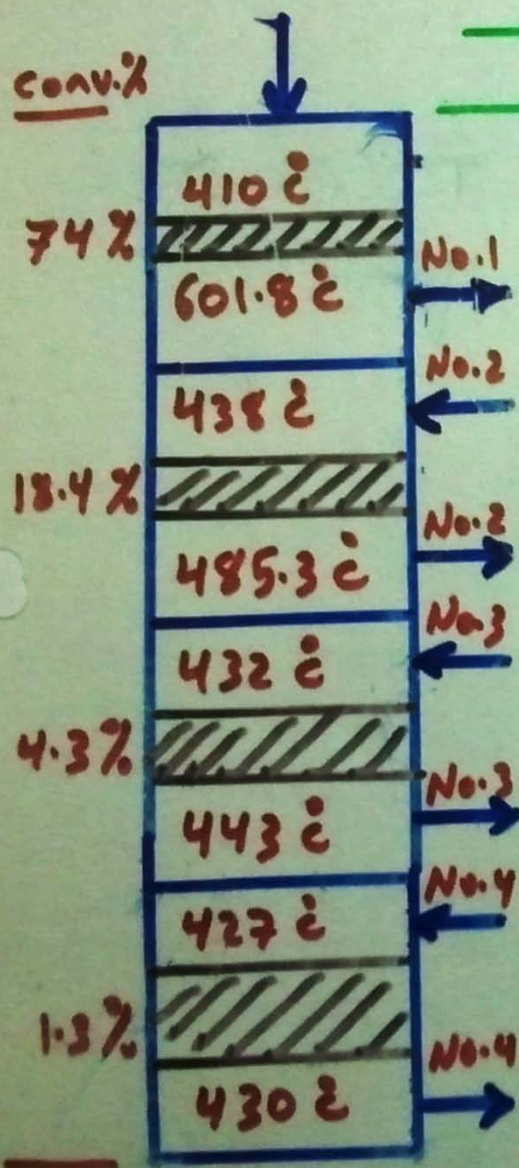


Figure VII.3. Temperature profile in a multi-bed  $\text{SO}_2$  convertor

# Converters : fixed-bed with interstage cooling :



Sulfur-burning plant (hot-gas-purification)		cold-gas-purif. (ore roasting)
dual absorption	single abs.	single abs.
fig (19.6) $\Delta b$	fig (19.4) $\Delta b$	fig (19.5) $\Delta b$
fig (19.4) $\Delta b$	fig (19.3) $\Delta b$	fig (19.5) $\Delta b$
W.H.B	H.E	hot H.E
hot H.E	dry cold Air	intermediate H.E
cold H.E	dry cold Air	cooling loop
economizer	economizer	cold H.E

total 98%



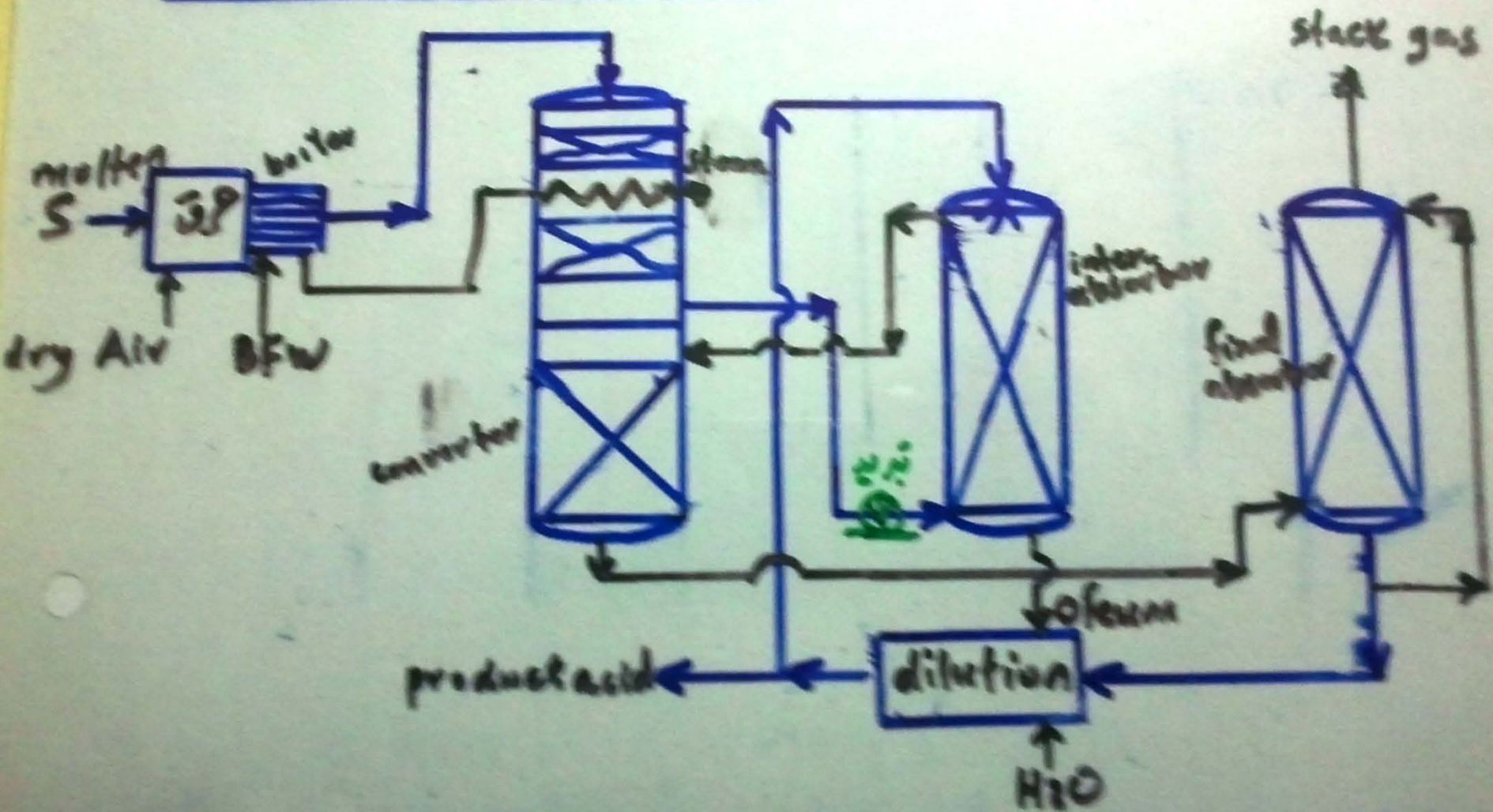
convertors, sometimes, have two grade of catalysts used, in 1<sup>st</sup> pass by less active but hard type. and for other passes, be more active but soft type ..

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H.W / fig (19.3), (19.4), (19.5), shreve, 5<sup>th</sup> ed.

.. fig (19.4), (19.5), (19.6), shreve, 4<sup>th</sup> ed.

## absorption of SO<sub>2</sub> (dual process)





$\text{SO}_2$  scrubbed, using strong acid (98.5 - 99%  $\text{H}_2\text{SO}_4$ ) because  
direct contact of  
with a more diluted acid (or water) gives rise to persistent  
acid mist which is difficult to absorb, and a more  
conc. acid does not absorb all the  $\text{SO}_2$ . To make  
sure that no mist is carried away the gas is passed  
through mist eliminator (to prevent corrosion). The  
reason that the strong acid is optimum is that vapor  
pressure of  $\text{H}_2\text{SO}_4$  goes through minimum at this conc.  
and hence the tendency to form  $\text{H}_2\text{SO}_4$  mist is a minimum.

However, the double absorption-contact plant (fig  
reducing  $\text{SO}_2$  emission in the tail gas. (fig

Typical flowchart for single-absorption plant  
is shown in (fig. 19.3, 19.5)  $^{\circ}\text{b}$   
or (fig. 19.4, 19.5)  $\text{E}_\text{b}$



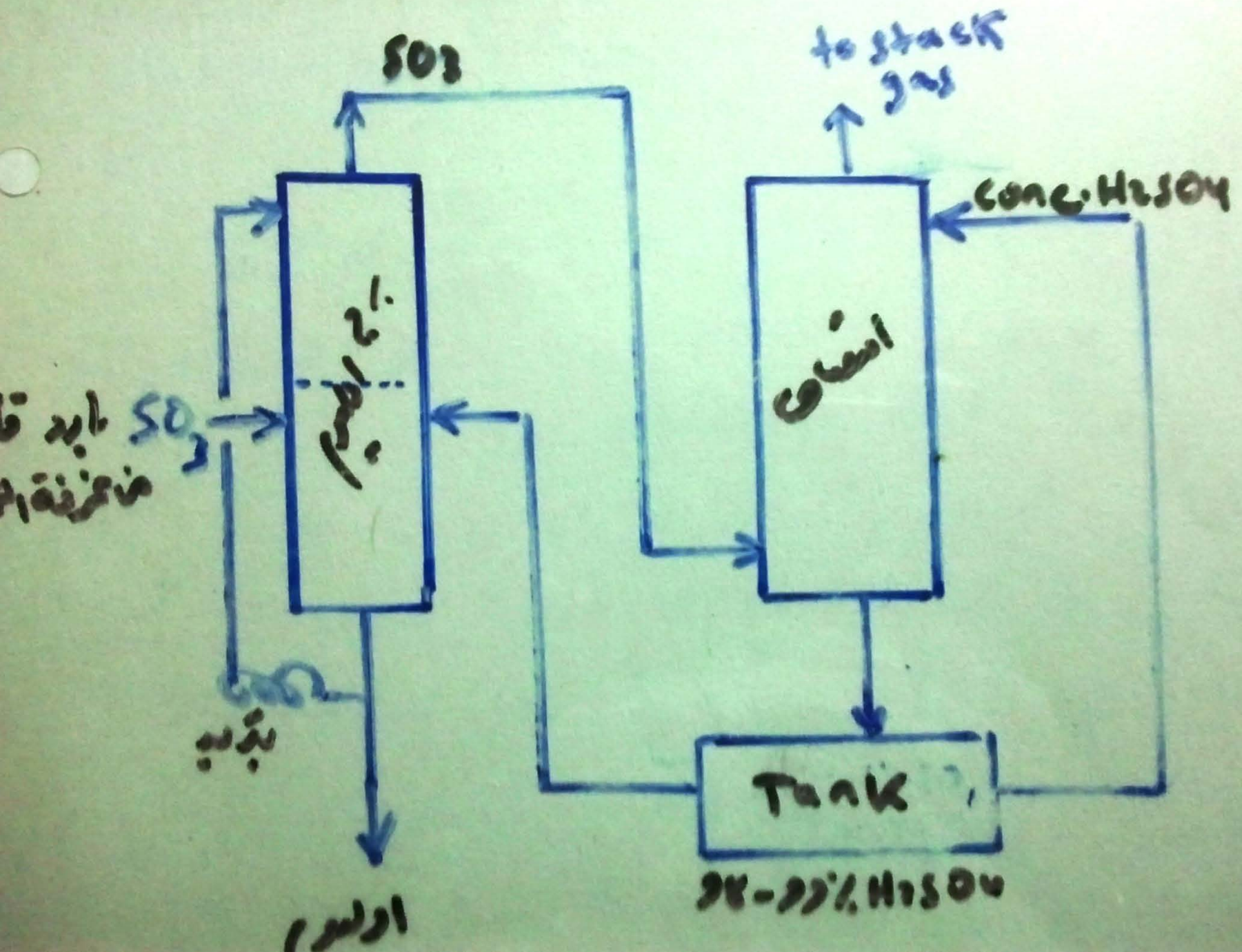
## manufacture of Oleum : ( $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ )

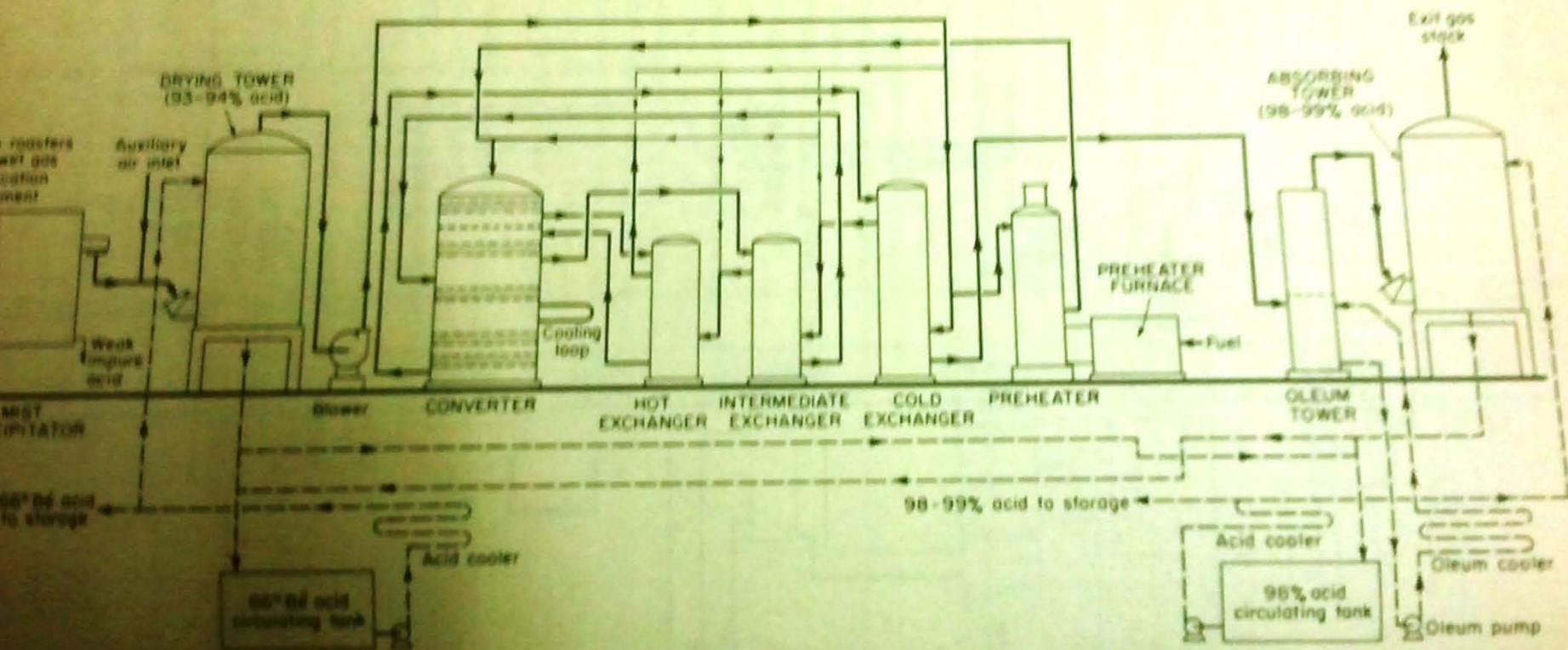
fuming  $\text{H}_2\text{SO}_4$ , or oleum can be made directly from contact process by installing an oleum tower before the  $\text{H}_2\text{SO}_4$  absorbing tower. The 20% oleum is made in an oleum tower as shown in (fig 19.3 & fig 19.5, Shreve 5<sup>th</sup> ed) by adding 98-99%  $\text{H}_2\text{SO}_4$  to the oleum.

if 60-65% Oleum is wanted, it may be prepared by producing 30-35% oleum in the tower and distilling it in steel boiler <sup>(batch dist.)</sup> the  $\text{SO}_3$  driven off may be blended with other oleum to get the desired concentration.

if full capacity of 60-65% oleum is required it may be used two oleum tower in series.











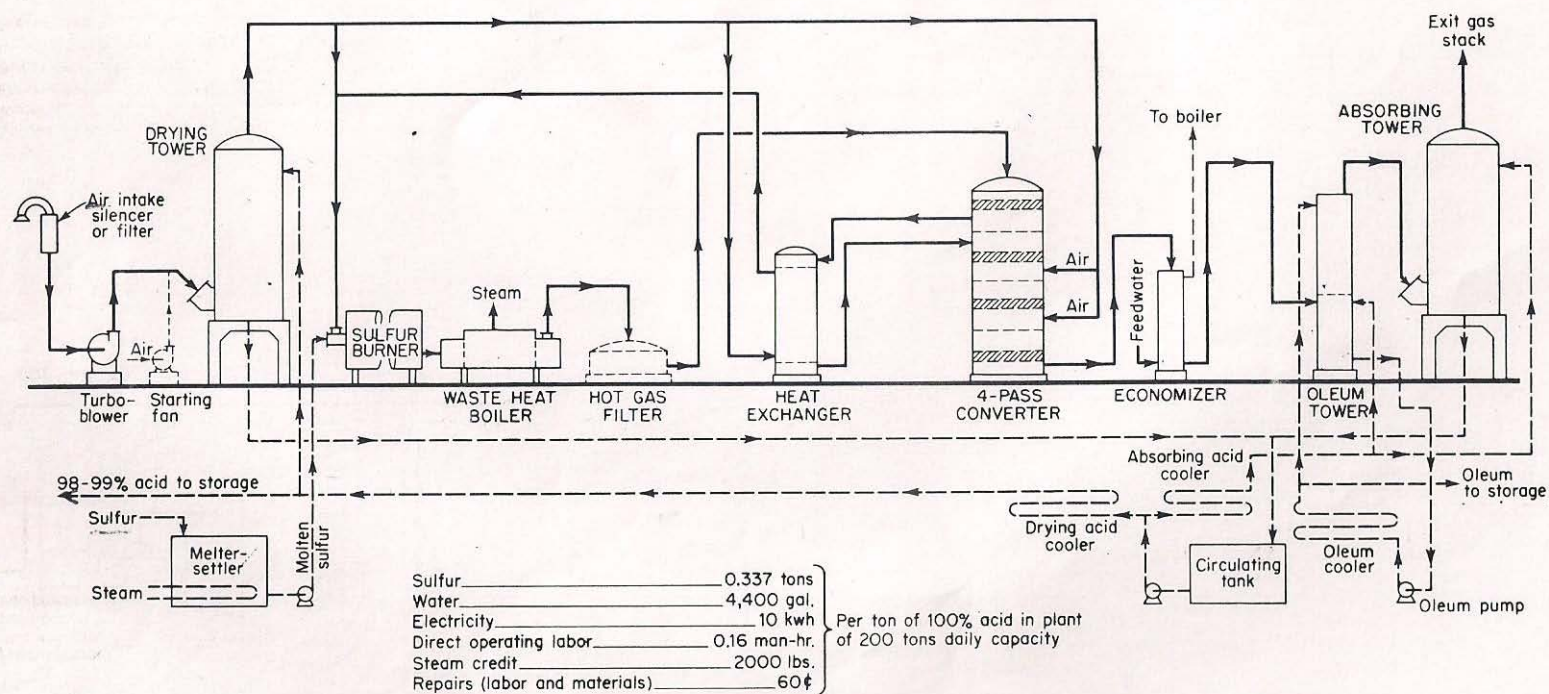
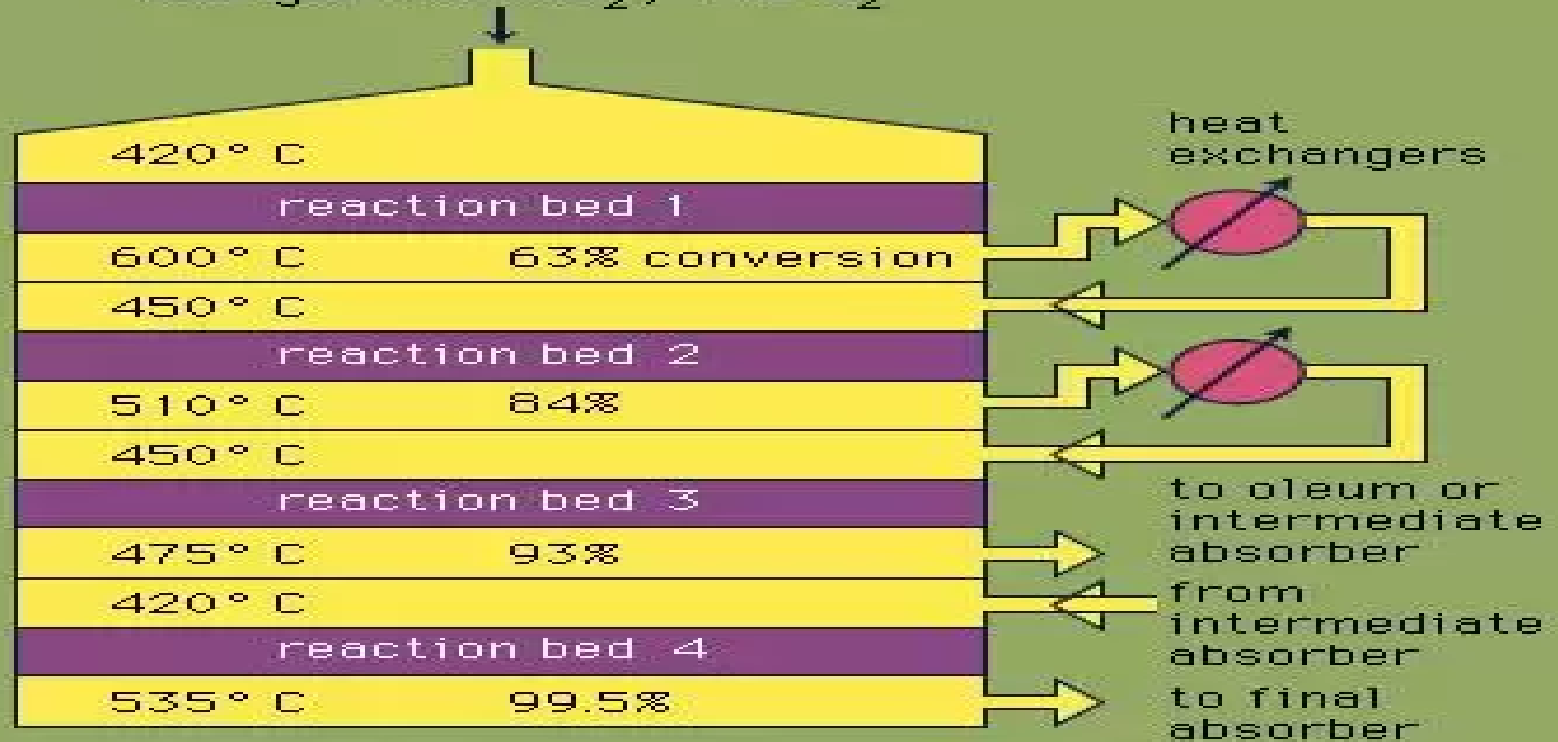


Fig. 19.4 Typical flowchart for a sulfur-burning contact sulfuric acid plant. (Monsanto Co.)



feed gas 10%  $\text{SO}_2$ , 11%  $\text{O}_2$





# AMMONIA NH<sub>3</sub>

## Ammonia NH<sub>3</sub>

Raw materials : H<sub>2</sub> & N<sub>2</sub>

feed stocks :

- 1) Coal lignite/bituminous coal and coke.
- 2) Gases, i.e. coke oven gas, N.G., Refinery gas
- 3) Electrolytic H<sub>2</sub>
- 4) petroleum : naphtha, furnace oil, low sulfur heavy stock.

manufacture,  $N_2 + 3H_2 \xrightleftharpoons[\text{Cat}]{\text{high P, (400-500)}} 2NH_3$   $\Delta H_{25^\circ C} = -46 \text{ kJ}$

$\Delta H_{650^\circ C} = -55.4$

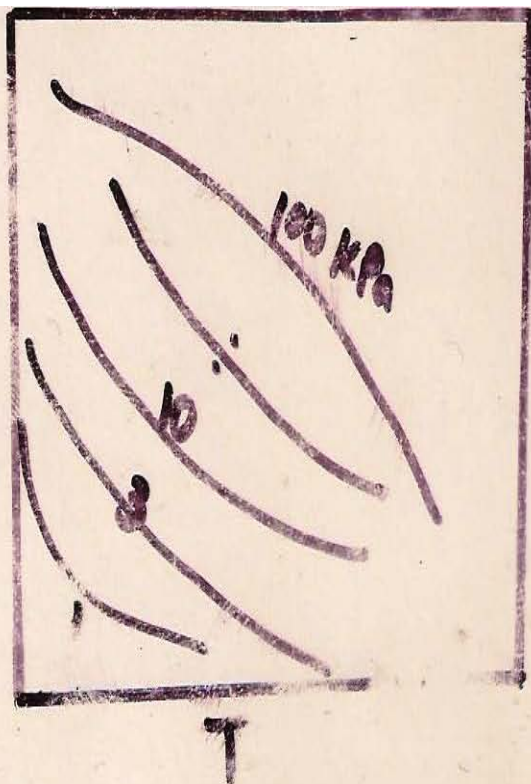
$$K_p = \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}$$

The basic conditions for high productivity and stable operation of  $\text{NH}_3$  synthesis unit are:

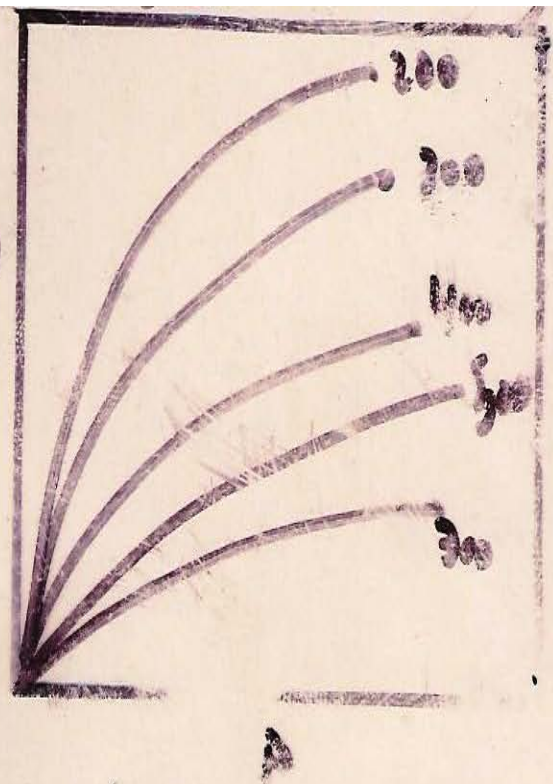
- 1) effective purification of the  $\text{N}_2$ - $\text{H}_2$  mixture to remove catalyst poisons and inert admixtures.
- 2) maintaining the  $\text{N}_2$ :  $\text{H}_2$  ratio close to 1:3
- 3) optimal temperature conditions over the length of the catalyst zone.
- 4) a low  $\text{NH}_3$  content at the inlet to the catalytic reactor.
- 5) a well designed converter (synthesis tower).



%NH<sub>3</sub>



%NH<sub>3</sub>



**TABLE 18.3 Synthetic Ammonia Systems Arranged in Order of Increased Conversion Pressure**

<i>Conversion pressure, atm</i>	<i>Designation</i>	<i>Temp., °C</i>	<i>Catalyst</i>	<i>Conversion, %</i>	<i>Recirculation purge inerts</i>	<i>Hydrogen sources</i>
120-160	Mont Cenis	400-425	Iron cyanide	9-20	Yes	Electrolytic or by-product H <sub>2</sub>
150	American* (large)	500	Doubly promoted iron	14	Yes	Natural gas
200-300	Haber-Bosch	550	Promoted iron	8	Yes	Water gas, producer gas
200-300	Fausser-Montecatini	500	Promoted iron	12-22	Yes	Electrolytic cells and waste nitric gas
+ 300	American* (small)	500	Doubly promoted iron	20	Yes	Natural gas, hydrocarbon
± 600	Casale	500	Promoted iron	15-25	Yes	Various
± 900	Claude	500-650	Promoted iron	40-85†	Not	Coke-oven gas
900	Du Pont‡	500	Promoted iron	40-85	Yes	Natural gas



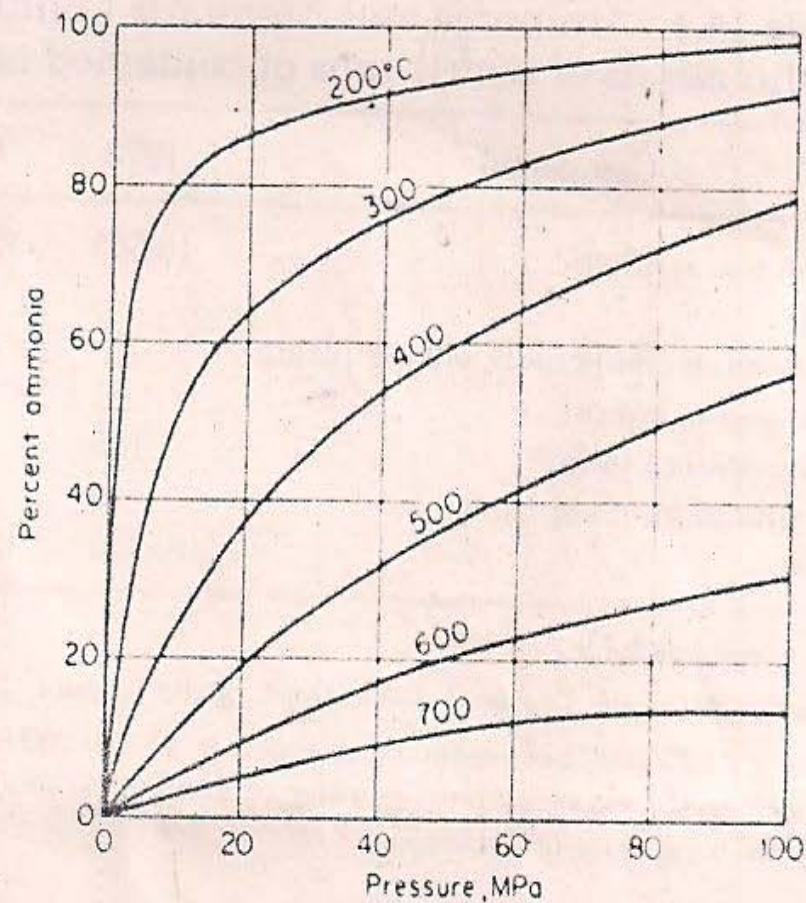
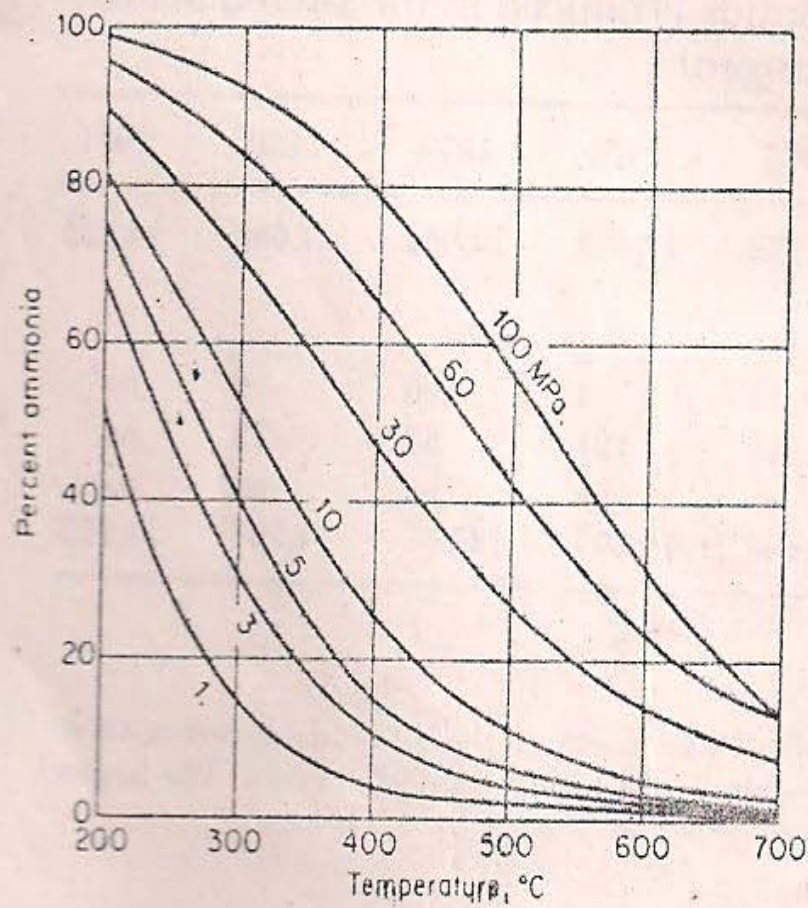


Fig. 18.2. Percentage of ammonia at equilibrium from an initial mixture of 3:1  $\text{H}_2/\text{N}_2$  gas at various temperatures and pressures. (Comings, *High Pressure Technology*, p. 410. Compare Frear and Baber, *ECT*, 2d ed., vol. 2, 1963, p. 260.)

Manufacturing procedure : consist essentially of  
six phase : (1) manufacture of reactant gas .

(2) purification . (3) compression (4) catalytic reaction  
(5) recovery of  $\text{NH}_3$  formed , and (6) recirculation .

Cost depend on P, T, catalyst & raw materials.



A) manufacture of raw synthesis gas ( $N_2/H_2 = 1:3$ )

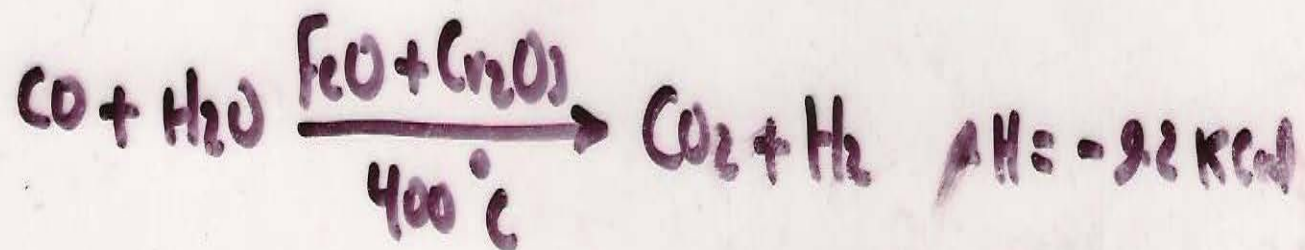
1- purification the hydrocarbon by adsorption

2. Reforming conversion of hydrocarbons (mostly N.G.) in a primary reformer by steam and in secondary reformer by air to supply  $N_2$ .



Combustion of unconverted  $CH_4$  with  $O_2$  (from air) furnishes heat for the secondary reforming reaction.

B) shift conversion of CO to CO<sub>2</sub> with steam using (FeO + Cr<sub>2</sub>O<sub>3</sub>) catalyst.



C) purification by removal CO<sub>2</sub> using MEA or hot K<sub>2</sub>CO<sub>3</sub> or Sulfinol in two stages.

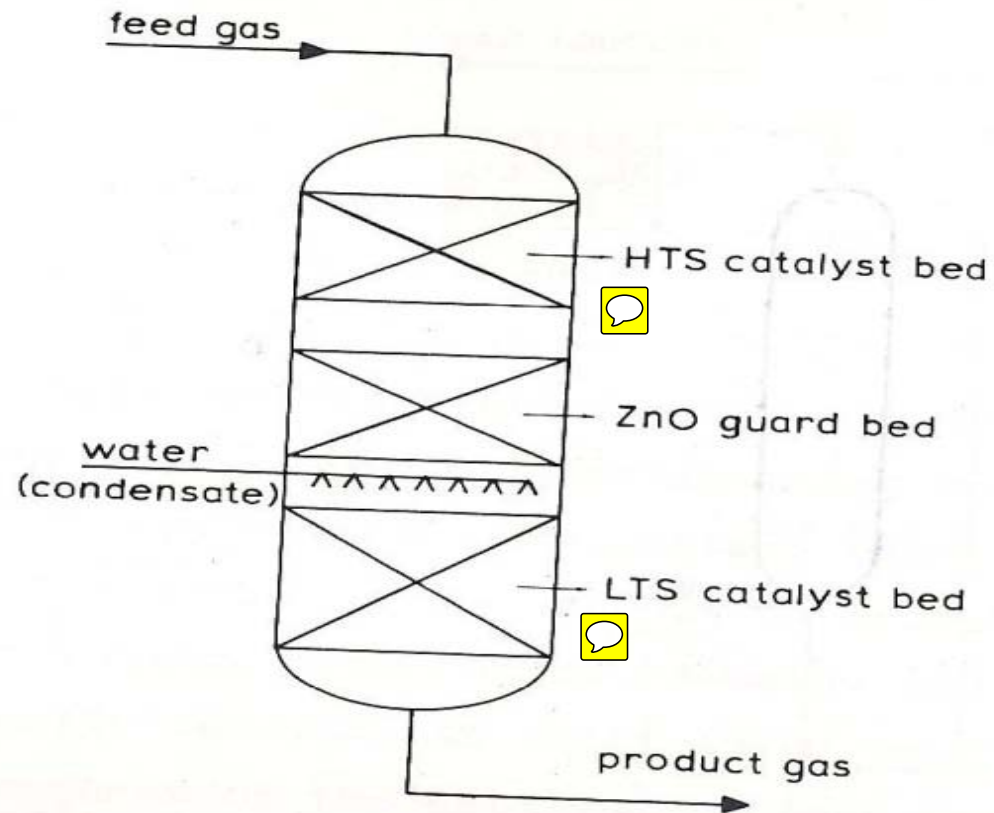


Figure IV.3. CO shift converter

D) removal of residual amount of  $\text{CO}_2$  and  $\text{CO}$  to less than 10ppm total by methanation over a nickel catalyst (some times followed by MEA or by a  $\text{N}_2$  wash or an ammoniated copper carbonate wash).



E)  $\text{NH}_3$  synthesis at various P & T, with varying % conversion. (see Table 18.3, Shreve)



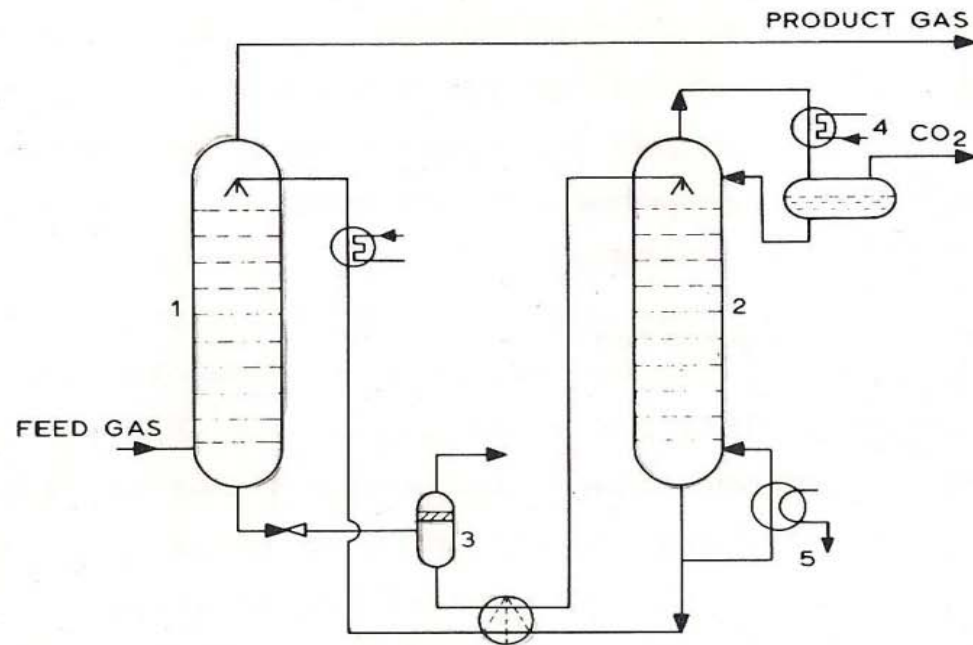


Figure IV.4. Principle of CO<sub>2</sub> removal by absorption in an aqueous alkanolamine solution.

1. absorber
2. regenerator
3. flash vessel
4. cooler/condenser
5. reboiler

- F) cooling, condensing, and separation of  $\text{NH}_3$  formed.
- G) Recirculation, with repressuring of unreacted  $\text{N}_2$  &  $\text{H}_2$  after addition of fresh  $\text{N}_2$  &  $\text{H}_2$ .
- H) purging to primary reformer, to reduce inerts. Recovery of purge gas

H.W	Kellogg plant, fig 18.3, p. 306, shreve 5 <sup>th</sup> ed Lummus plant, fig 18.4, p. 281, shreve 4 <sup>th</sup> ed
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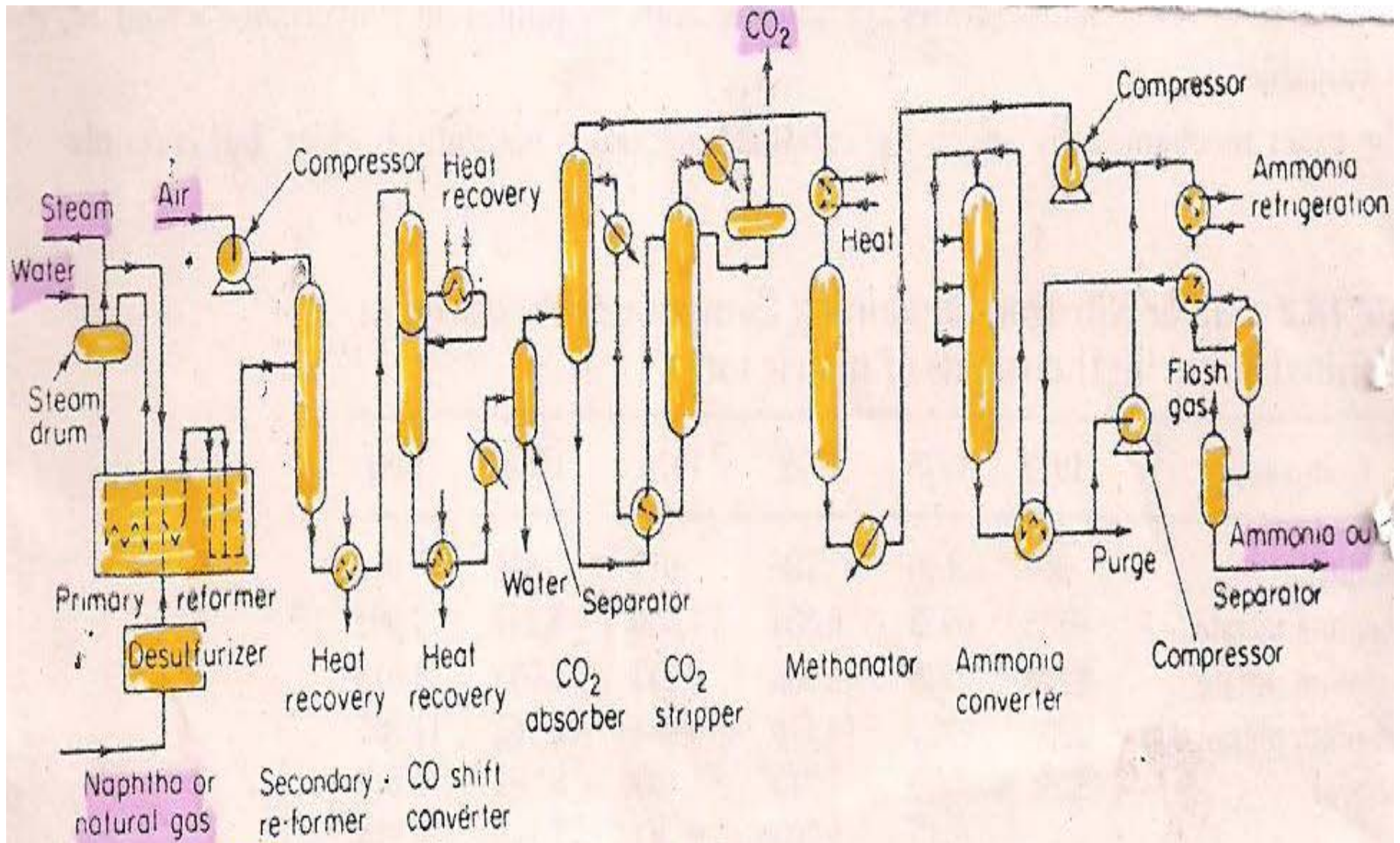
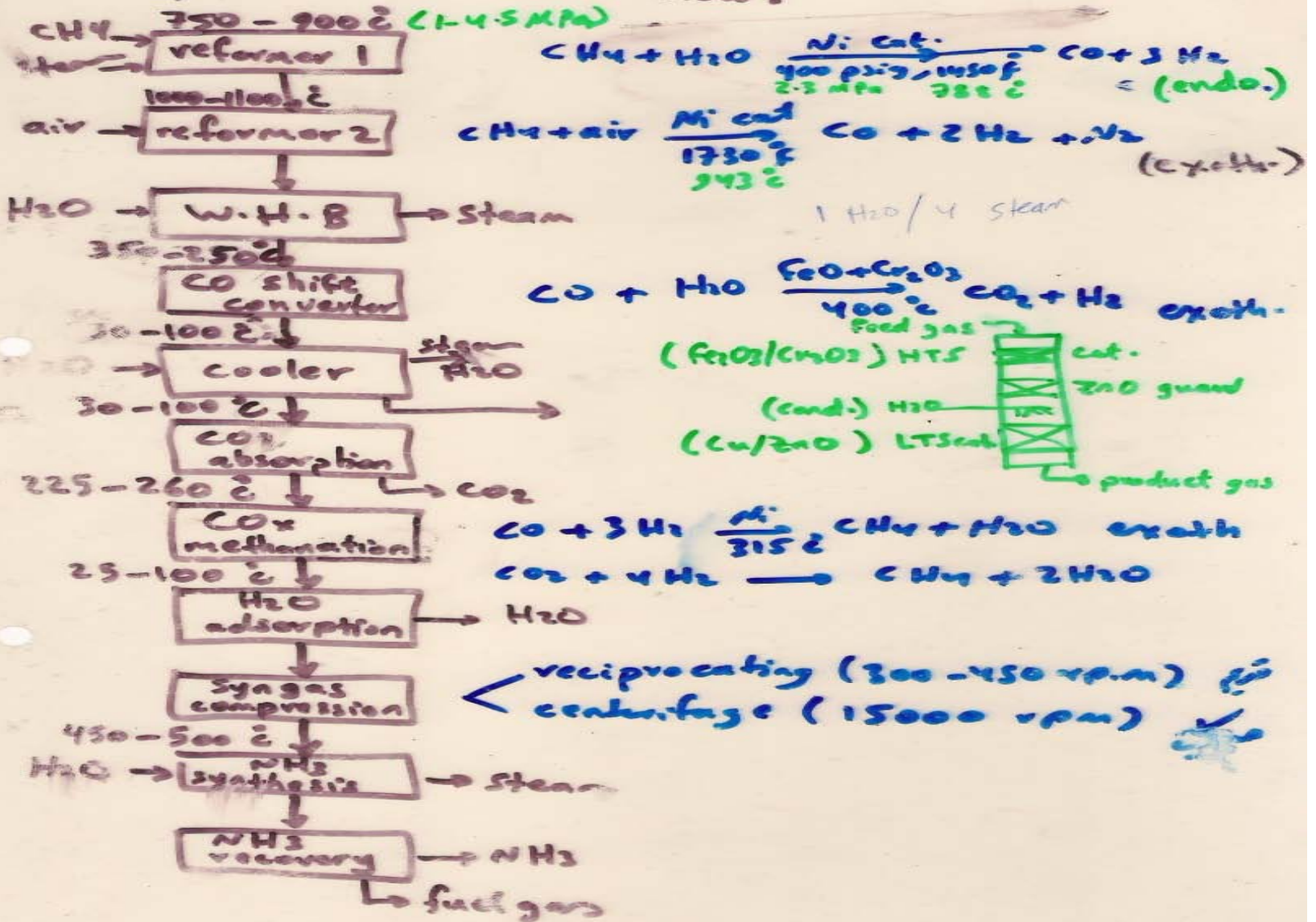


Fig. 18.3. The Kellogg ammonia process. (M. W. Kellogg Co.)

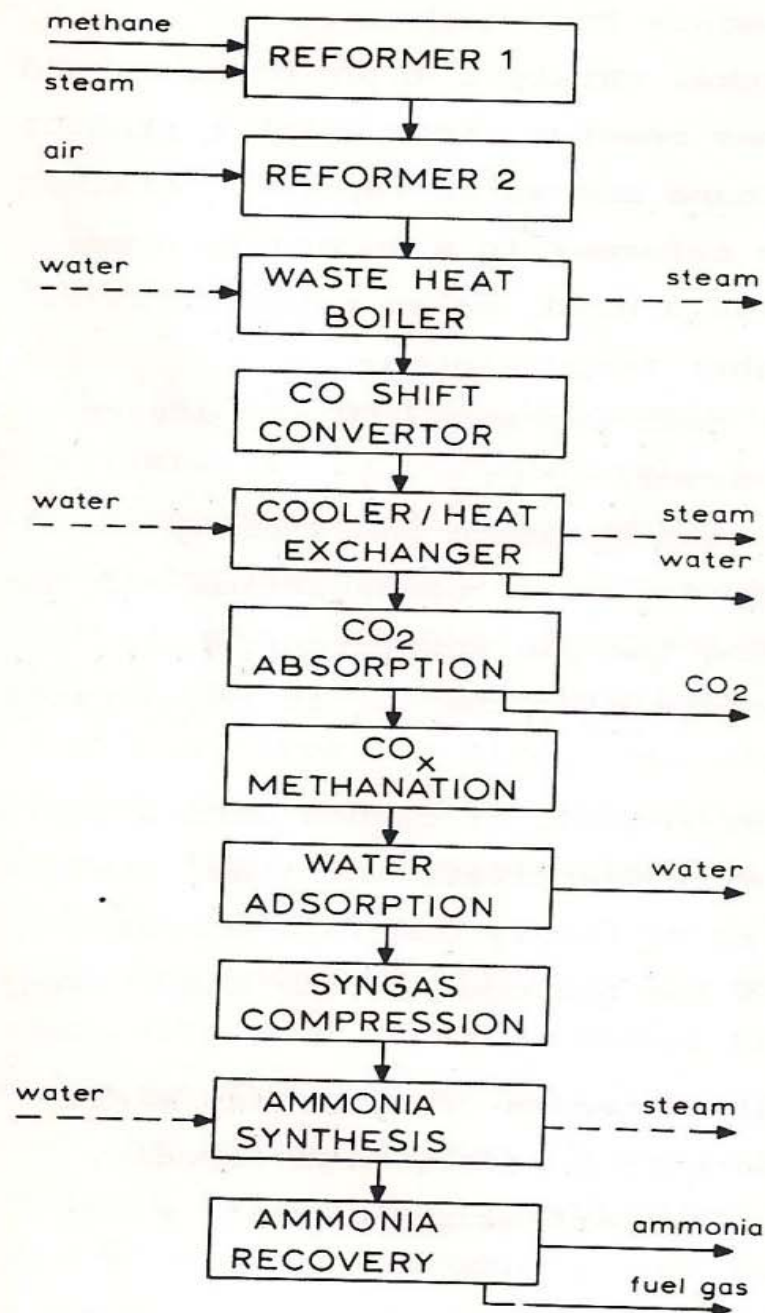




A block diagram of the process for making  $\text{NH}_3$  from  $\text{CH}_4$  or  $\text{CH}_4$ -rich N-Gas shown below:







Gas composition

Temperature  
°C  
750 - 900

$H_2, CO_2, CO, H_2O, CH_4$

1000 - 1100

$N_2, H_2, CO_2, CO, H_2O, CH_4, Ar$

350 - 250

$N_2, H_2, CO_2, CO, H_2O, CH_4, Ar$

30 - 100

$N_2, H_2, CO_2, CO, H_2O, CH_4, Ar$

30 - 100

$N_2, H_2, CO_2, CO, H_2O, CH_4, Ar$

225 - 260

$N_2, H_2, CO_2, CO, H_2O, CH_4, Ar$

25 - 100

$N_2, H_2, CO_2, CO, H_2O, CH_4, Ar$

450 - 500



Catalysts  $\text{FeO}$  + promoters

promoters: 3% (oxides of Al, Zr, Si)  
1% ( $\text{K}_2\text{O}$ )

promoters used to: (1) prevent the catalyst Sinterizing  
at high Temperature

(2) make catalyst more porous.

for (non-promoted)  $\text{FeO}$  produce 3-5% conversion

Singly promoted  $\text{FeO}$  " 8-9% conv.

doubly promoted  $\text{FeO}$  " 13-14% conv.

$\text{FeO}$  disadvantage : (1) lose their activity rapidly  
if heated above  $520^\circ\text{C}$ .

(2) deactivated by contact with  
 $\text{Cu}$ ,  $\text{P}$ ,  $\text{As}$ ,  $\text{S}$  &  $\text{CO}$ .

the exact mechanism by catalyst suggest as :

either N and H chemisorbed with cat. surface,  
then migrate forming H, N, NH, NH<sub>2</sub> and NH<sub>3</sub>  
followed by desorption.

the % NH<sub>3</sub> produced (for a given catalyst, T, P)  
decreased with increasing space velocity.

The space velocity is volume of gas (at 0°C, 101 KPa)  
that pass over one volume of catalyst per unit  
time.



## Types of converters :

various converters design to work at low, medium & high pressure can be divided into two types :

(1) in first type, the catalyst is arranged in the form of a bed and temperature of every catalyst bed controlled by allowing incoming cold gas to exchange heat with outgoing hot gases after every bed i.e point to point and bed to bed control . This type includes :  
Fausser-Monte, Catini, Udhe & Kellogg converters.

(2) second type is where the catalyst is not arranged in the form of different bed but in the form of single continuous bed, the temperature of which is controlled by embedded cooling pipes . Examples are : Casale, Claude, TVA, NEC, etc.



Modern Trend : The modern trend is to use radial flow type of converters rather than the above axial flow type. In radial flow type, the gases flow radially instead of axis (i.e. axial flow type). The chief advantages

- (1) lower pressure drop
- (2) excellent heat economy, because the gases have to cross less thick catalytic beds.
- (3) less operating pressure
- (4) low costs.

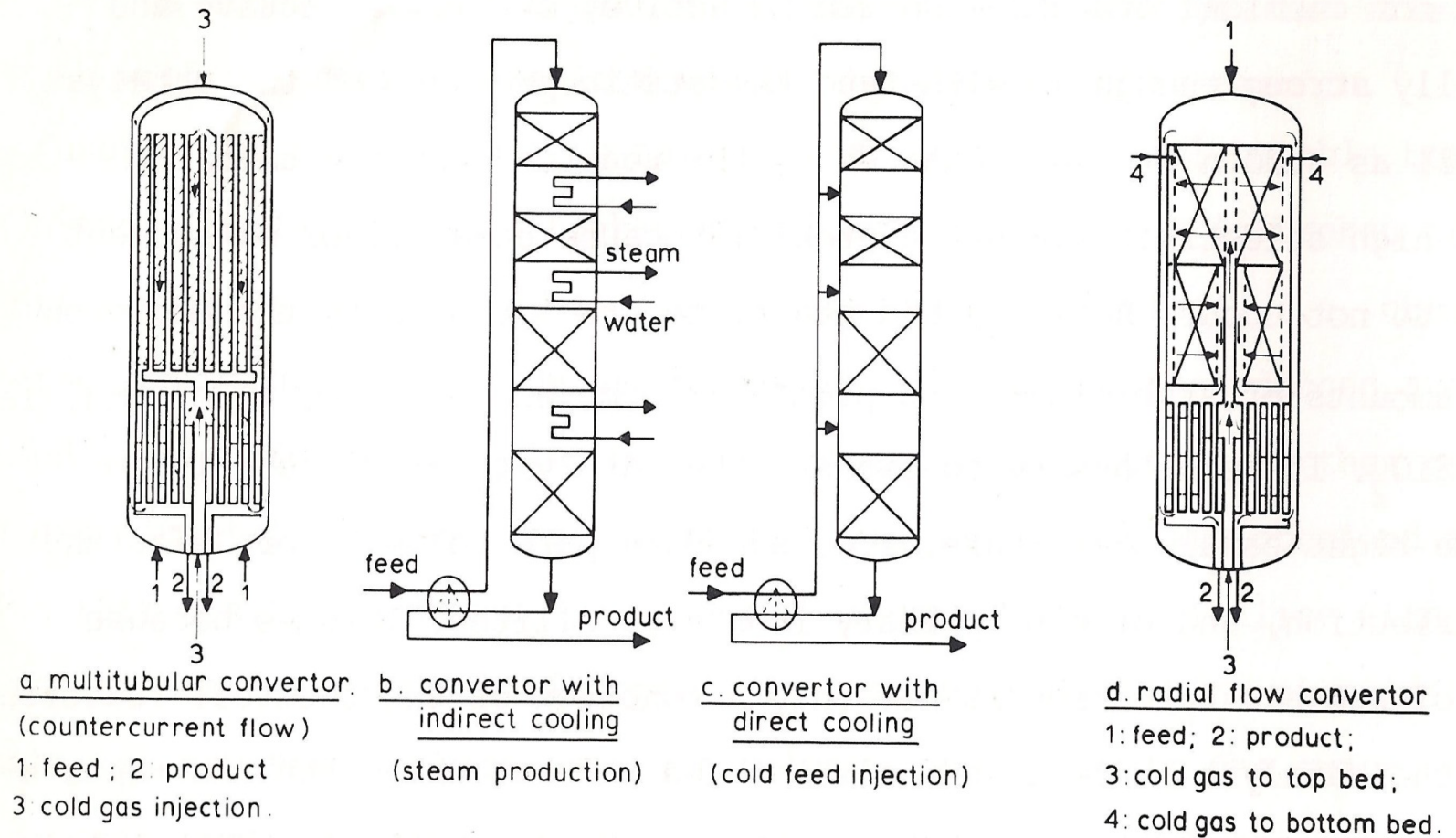


Figure IV.8. Four types of ammonia synthesis reactor