PROCESS TECHNOLOGY & ECONOMICS-I

INTRODUCTION

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Unit operation and Unit process concepts

Commercial production= *f* (Chemical change + Physical change)

Unit operation: It is an operation where physical change occurs only.

- distillation in batch and continuous fractionators
- drying of solids in spray, rotary and tunnel driers
- evaporation in single and multiple effect evaporators
- extraction (liquid-liquid) in extractor and (solid-liquid) in leaching
- fluid handling by centrifugal, reciprocating pump or compressor
- fluid solid contactors such as fluidized bed and fixed bed
- fluid-solid separation in centrifugation, settling tank, crystallizer, filter, cyclone separator, thickener-classifier
- gas-liquid separation in absorption and stripping column
- heat transfer equipment heat exchangers, reboiler, condenser
- mixer
- size reduction in a crusher, grinder
- solid handling in conveyor, elevator
- solid-solid separation by screening, elutriation, jigging etc.

Unit process: It is a process where the both chemical and physical changes occur.

- alkylation (petroleum organic chemicals)
- calcination (cement)
- combustion (process heating)
- condensation (organic chemical, dyestuff)
- cracking or pyrolysis (petroleum, coal)
- dehydrogenation (synthetic rubber, oil refining)
- esterification (oil, fat, soap)
- halogenation
- hydrogenation
- hydrolysis
- isomerization (petroleum)
- nitration
- polymerization
- sulfonation.

General principles applied in studying chemical industry

Market and sales – justification of the industry

Methods of production, Flowsheet

Chemical engineering problems deals with manufacturing and economics

Within any chemical industry the following principles of science and engineering are continually being used:

Chemistry

- *Analytical chemistry* for process control, yield determination and optimization by modern and electronic instrumentation, such as, vapor phase chromatography, UV visible and infrared spectroscopy, nuclear magnetic resonance, etc.
- *Physical chemistry* in physical property determination, phase diagram studies in separation process, chemical kinetics and catalysis.
- *Inorganic chemistry* is essential in types of bonding, metal organic complexes. Organic chemistry is essentials in the production of aromatic and aliphatic compounds.

Thermodynamics

- Determination of chemical equilibria, phase equilibria for ideal and non ideal system
- Energy applications like, heat of reaction in chemical reaction, heat of formation in mixing process, work of compression and work of expansion for real gases.

Chemical reaction kinetics and Chemical Reaction Engineering and:

- It is studied for the design of reactor
- reacting phases, like, homogeneous and heterogeneous reactions
- mechanisms- molecular, chain initiated, photochemical initiated
- catalysis- catalytic, noncatalytic
- energy transfer- adiabatic, isothermal, non-adiabatic
- chemical equation- simple reaction, parallel reaction, series reaction, reversible reaction; effect of temperature, pressure, reactant concentration, flow pattern and transport properties.
- For reversible gas phase reaction quench tower is used downstream to the reactor to lower back ward reaction and to improve product yield. Reversible series reaction is carried out in a tubular reactor with quench tower for producing high yield.
- Types of reactors are simple batch homogeneous reactor, semi batch reactor, continuous homogeneous reactor (CSTR), continuous heterogeneous reactor (fluid bed and fixed bed catalytic reactor).

Process design

- Flow sheeting and piping and instrumentation diagram
- Process steps - prepare the reactants, reaction, product separation, product purification
- Design steps – collect laboratory and process development information, prepare flow sheet, design unit operations, design unit process, select control instrumentation for process monitoring and analysis, select material handling and transportation equipments like, pumps, piping, conveyors, make plant lay out and estimate cost.

Economics: Profitability analysis of a project.

- Capital investment= Fixed capital+ working capital
- Total product cost= Manufacturing cost + general expenses
- Profitability analysis and breakeven point analysis.

Reference

- Rao, M.G. and Sittig, M., Dryden's Outlines of Chemical Technology for the 21st Century Affiliated East West Press (1998) 3rd ed.

Thank You

Project Engineering & Economics for Chemical Engg.

Introduction:

A chemical engineer requires the knowledge of fundamental science and related engineering subjects like, thermodynamics, transport of fluid, mass, heat/energy, chemical reaction engineering, unit operation, process control, ~~etc~~ computer technology etc. Moreover, the chemical engineer have to be able to apply the knowledge ~~of~~ and skill to real situations for the solution of engineering problems for the benefit of society.

In the application of knowledge and skill, an engineer must recognize economic implecation, social benefit, safety etc.

Design of a chemical plant and revision or modification of existing one requires application of engineering principles and theories combined with practical realization or experience.

It is a much complex problem.

A plant design project completes through the sequential stages:

i) Inception of project idea.

ii) Preliminary evaluation of economics and market.

iii) Development of data necessary for final design.

iv) Final Economic evaluation.
v) Detailed Engineering design.
vi) Procurement.
vii) Erection.
viii) Start-up and trial runs.
ix) Production.

Following skills are research, market analysis, design individual pieces of equipment, cost estimation, computer programming. etc.

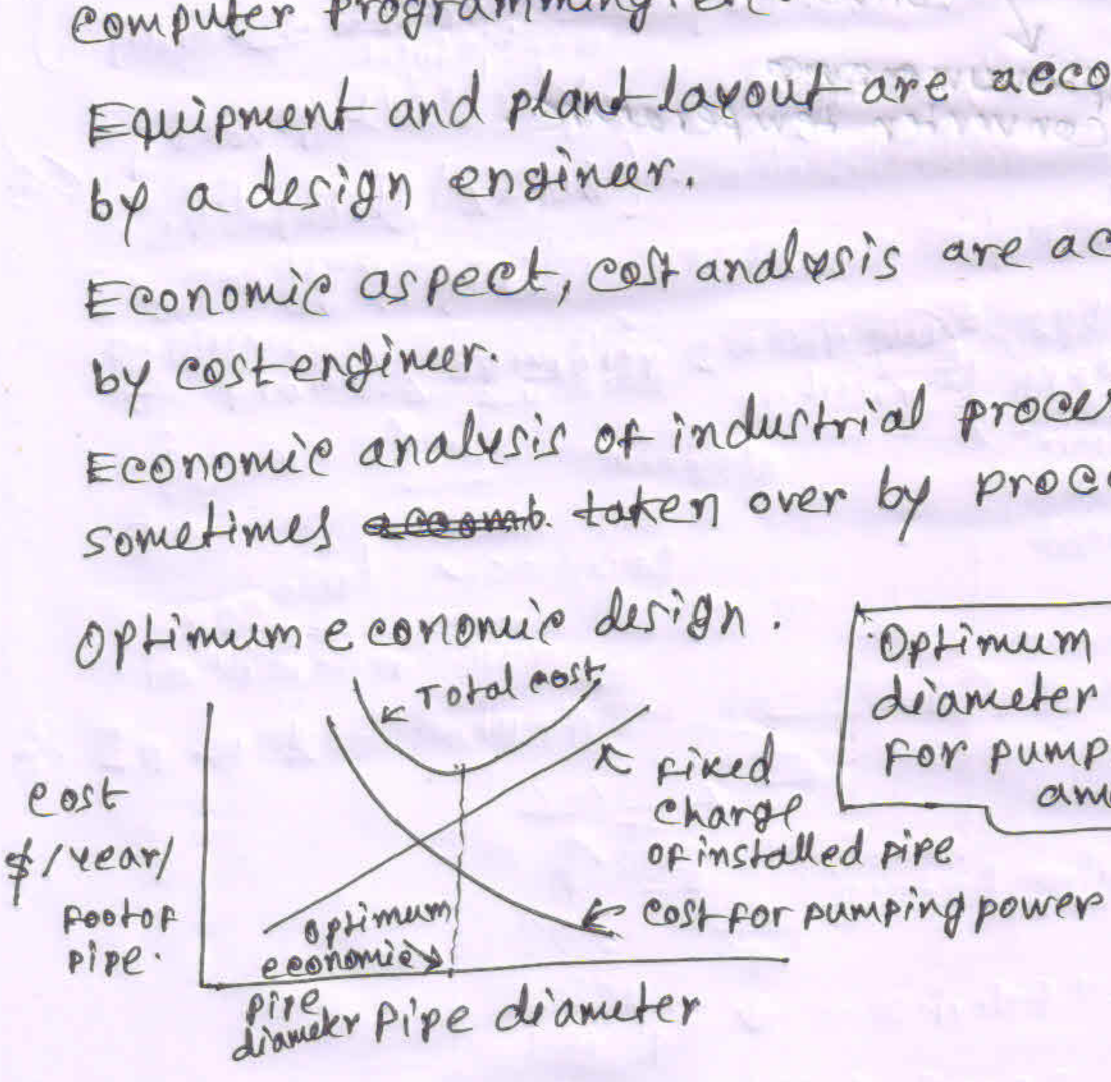
Equipment and plant layout are accomplished by a design engineer.

Economic aspect, cost analysis are accomplished by cost engineer.

Economic analysis of industrial process is sometimes ~~accomb.~~ taken over by process engineer.

Optimum economic design.

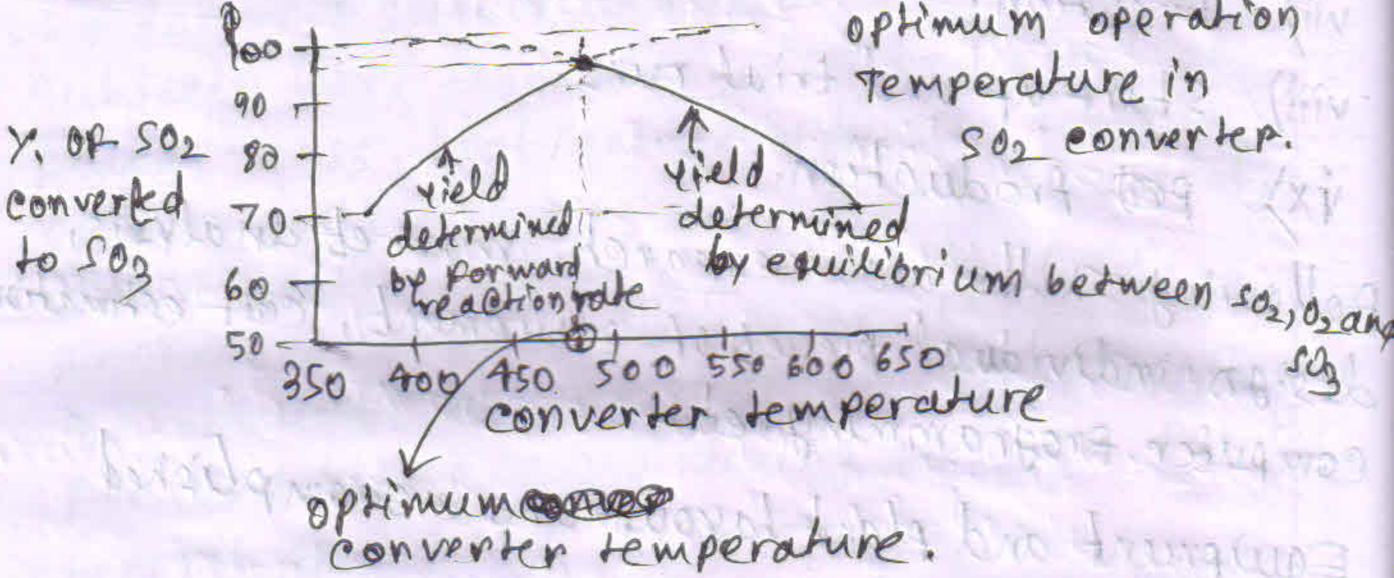
Optimum economic diameter of a pipe for pumping a given amount of fluid.



Optimum Operation Design

$$2SO_2 + O_2 \overset{\text{catalyst}}{\rightleftharpoons} 2SO_3 + \text{heat}.$$

Determination of optimum operation temperature in SO_2 converter.



Sulfur Industries

Elemental Sulfur and Sulfuric Acid

Sulfur Industries

↳ SO_2, SO_3, H_2SO_4, Oleum ($H_2SO_4 + SO_3$)

End use of sulfur Industries.

85% – 90% is used for H_2SO_4 manufacturing
Rest for the production of
SO_2, SO_3, CS_2, P_2S_5 ;
Rubber vulcanization agent ;
sulfur dyes, sulfur concrete;
paper production;

Source of raw material

H_2SO_4 ← elemental sulfer
H_2SO_4 ← pyrites (sulfides of iron)
H_2SO_4 ← H_2S contained in sour gas and petroleum product.

} Raw materials.

waste gases from burning of fuel and smelting operation such as.
pyrites of copper, Fe, Zn, Pb.

Note: smelting operation of metal pyrites produces H_2S gas.

i) chemical reaction ⟶ India

$2H_2S + 3O_2 \rightleftharpoons 2SO_2 + 2H_2O$ ΔH = −247.89 kcal

$4H_2S + 2SO_2 \xrightarrow{Al_2O_3} S_6(g) + 4H_2O$; ΔH = −42.29 kcal

ii) Elemental sulfur can be obtained from mining..

iii) Elemental sulfur from Iron pyrites.

a) Thermal dissociation

$FeS_2 \xrightarrow{1atm} \frac{1}{2}S_2(g) + FeS(liq)$ ΔH = +15.98 kcal

b) general combustion reaction

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

c) $2COS + CS_2 + 2SO_2 \xrightarrow[600°C]{catalyst} S_6 + 3CO_2$

sulfur recovery from hot gases.

d) sulfur recovery from gases – cold state

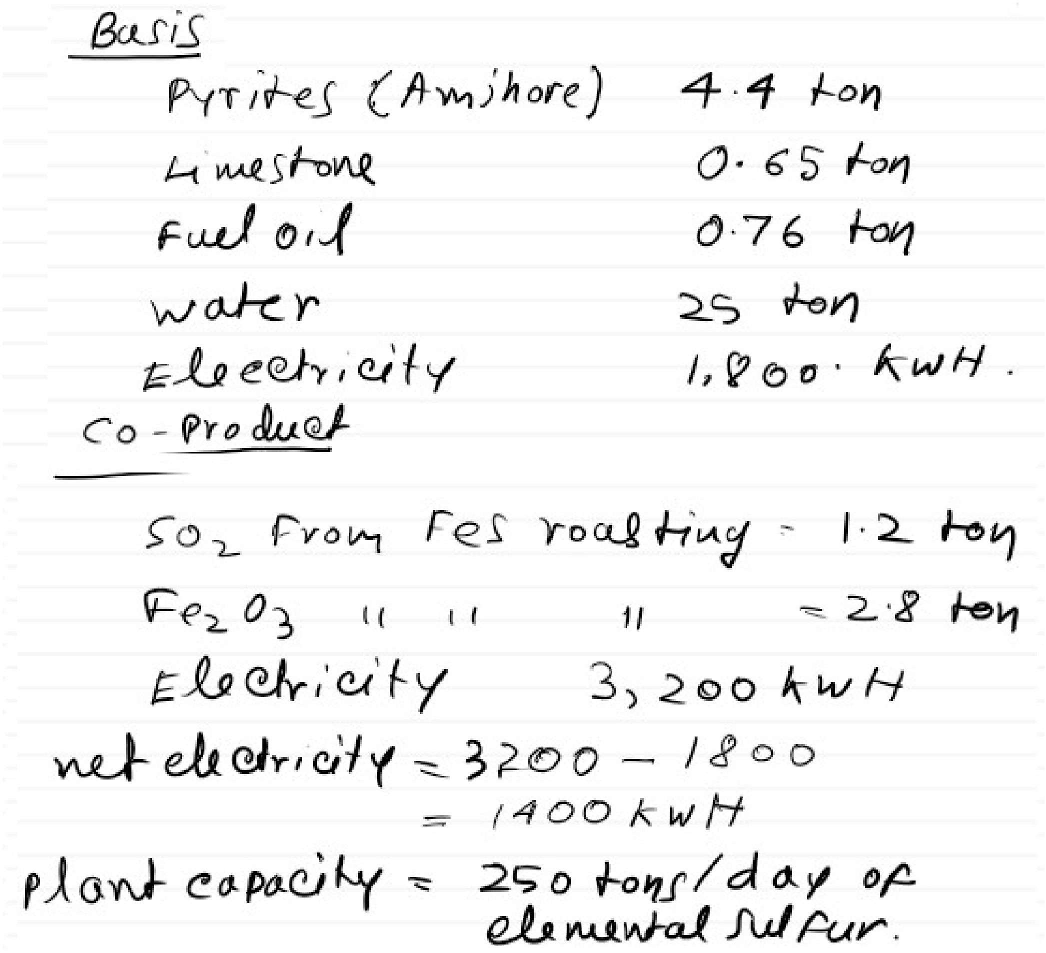
$4H_2S + 2SO_2 \xrightarrow[280°C]{Al_2O_3} S_6 + 4H_2O$

e) Rosting of FeS (pyrrhotite) for SO₂ recovery.

$2FeS + 3\frac{1}{2}O_2 \xrightarrow[1000°C]{1atm} Fe_2O_3 + 2SO_2$

ΔH = −295.02 kcal.

Sulfur From Iron Pyrites



Basis

Pyrites (Amjhore)	4.4 ton
Limestone	0.65 ton
Fuel oil	0.76 ton
water	25 ton
Electricity	1,800. KWH.

Co-Product

SO_2 From FeS roasting = 1.2 ton

Fe_2O_3 " " " = 2.8 ton

Electricity 3,200 KWH

net electricity = 3200 − 1800

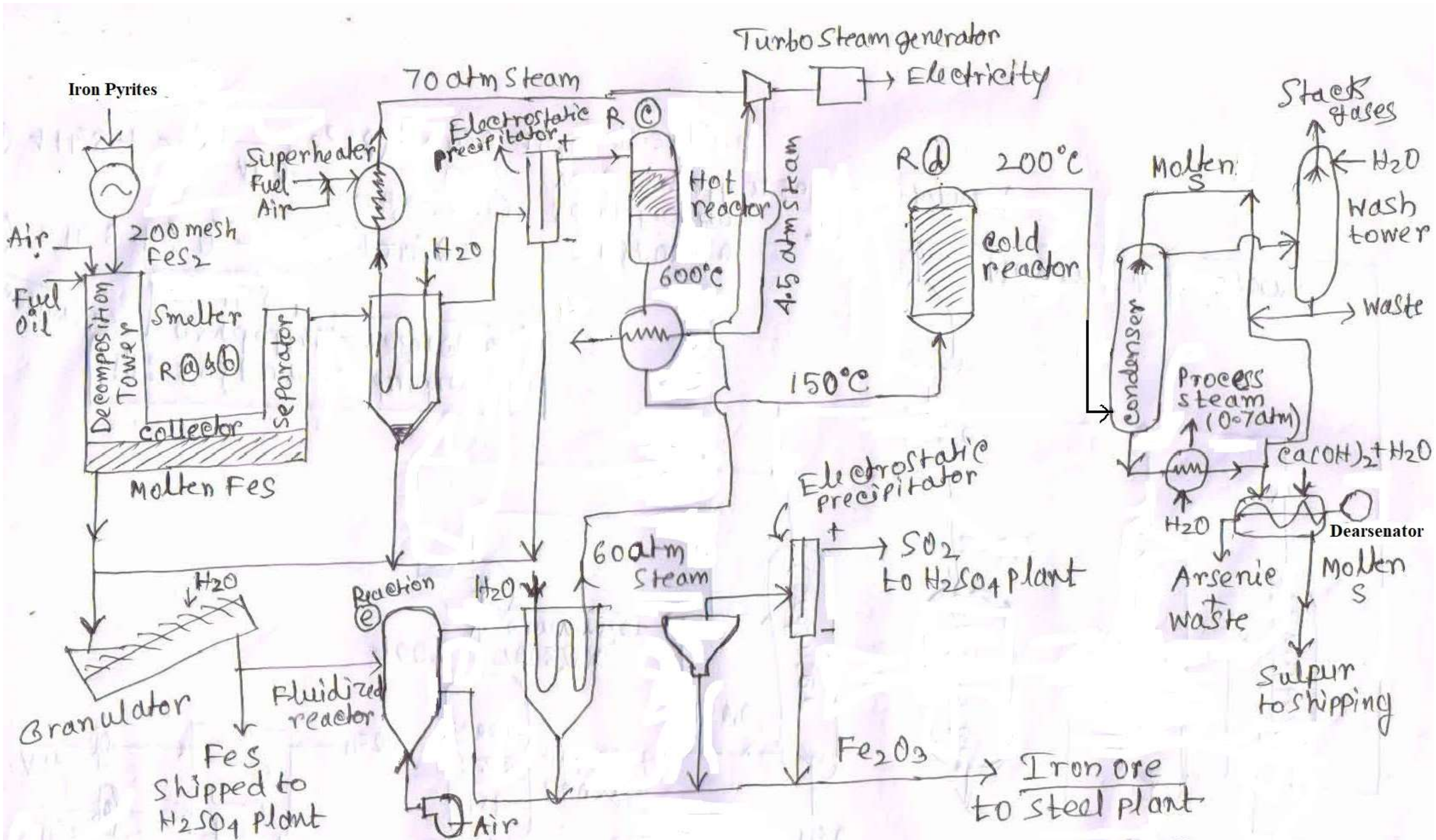
= 1400 KWH

plant capacity = 250 tons/day of elemental Sulfur.

Process description

- Pyrites ore is dried (rotary kiln with flue gas) and ground to – 200 mesh size particles.
- In a vertical and circular shaft furnace (5.5 m diameter, 10 m height), the pyrites particles are dispersed in hot combustion gas from oil burner. As dispersed particles move through the furnace, the dissociation and combustion reactions take place.
- The liquid droplets of FeS are collected at the bottom horizontal batch of the furnace, while hot gases are separated and moves upward through the separator at 1300 ^oC.
- It is sent to the high pressure heat recovery boiler generating 70 atms steam through superheating, while cooled hot gases at 300 ^oC in outlet of the boiler is sent to hot reactor through electrostatic separator for dust separation.
- In the high temperature catalytic reactor, carbon-sulfur compounds are reacted to produce sulfur. The product gases contains SO_2 and H_2S, are cooled to 150 ^oC by passing through low pressure heat recovery boiler generating 4.5 atms gage steam.

- It is sent to the cold stage catalytic reactor catalyzed by aluminum oxide to produce S6 vapor from SO_2 and H_2S gas mixture.
- The sulfur gas is condensed on molten sulfur droplets in a spray condenser. The non condensable gases from condenser releases heat through low pressure boiler generating steam (0.7 atms. gage).
- Exit gases are washed in a water-wased tower to recover uncondensed sulfur.
- Arsenic in the sulfur is removed by reacting it with milk of lime in in a continuous autoclave. (note: The arsenic poison the vanadium or platinum catalyst in the contact process of the sulfuric acid plant (conversion of SO_2 to SO_3).
- Molten FeS from the bottom of the furnace is granulated with water. Roasting of FeS (Pyrrhotite) is carried out in a fluidized bed reactor (fluidized by air) at 1000 ^oC to produce SO_2 gas which is cooled to a heat recovery boiler (generating 60 atms steam).
- The iron ore particles and SO_2 gas are separated sequentially in by cyclone separator and electrostatic precipitator.



{ Sulfur from pyrites -
SO₂ from pyrites

note ⓐ, ⓑ, ⓒ, ⓓ, ⓔ are reactions mentioned earlier.

Major engineering problems

- The process is developed for pyrites ores containing 1.5% SiO_2. The Indian ore at Amjhore contains 5-7% SiO_2, and requires either of flotation or limestone to remove excess silica. The limestone is preferred because is saves 30% loss of ore through beneficiation.
- The optimum particle size for economic process is to –200 mesh size, which must be maintained for obtaining economic balance between heat transfer rate from combustion gases and residence time of the particle in the furnace. Furthermore, the optimum size determines fall of particles, tower height, and grinding cost.
- Smelting of ore by coal saves 20% cost of the process compared to fuel oil which is available at high cost in the Amjhore.
- Complete combustion of fuel without excess air is desirable to prevent unbalance of H_2S-SO_2 ratio. Hence, oxygen/fuel ratio must be controlled precisely in the smelter feed system through high precision and accuracy control system.

Sulfur From Oxidation-Reduction of H_2S

Process description

- H_2S and O_2 are burned in reaction (a) (in fig. next page) and product SO_2 oxidizes H_2S in reaction (b) (in fig. next page) in a two-stage catalytic converter through intercooling and condensing. The final waste gas is scrubbed with molten sulfur.

Major engineering problems

- Design of two-stage reactor for exothermic reactions to obtain favorable equilibrium.
- Heat exchanger for molten sulfur
- Corrosion
- Final cleaning of stack gases

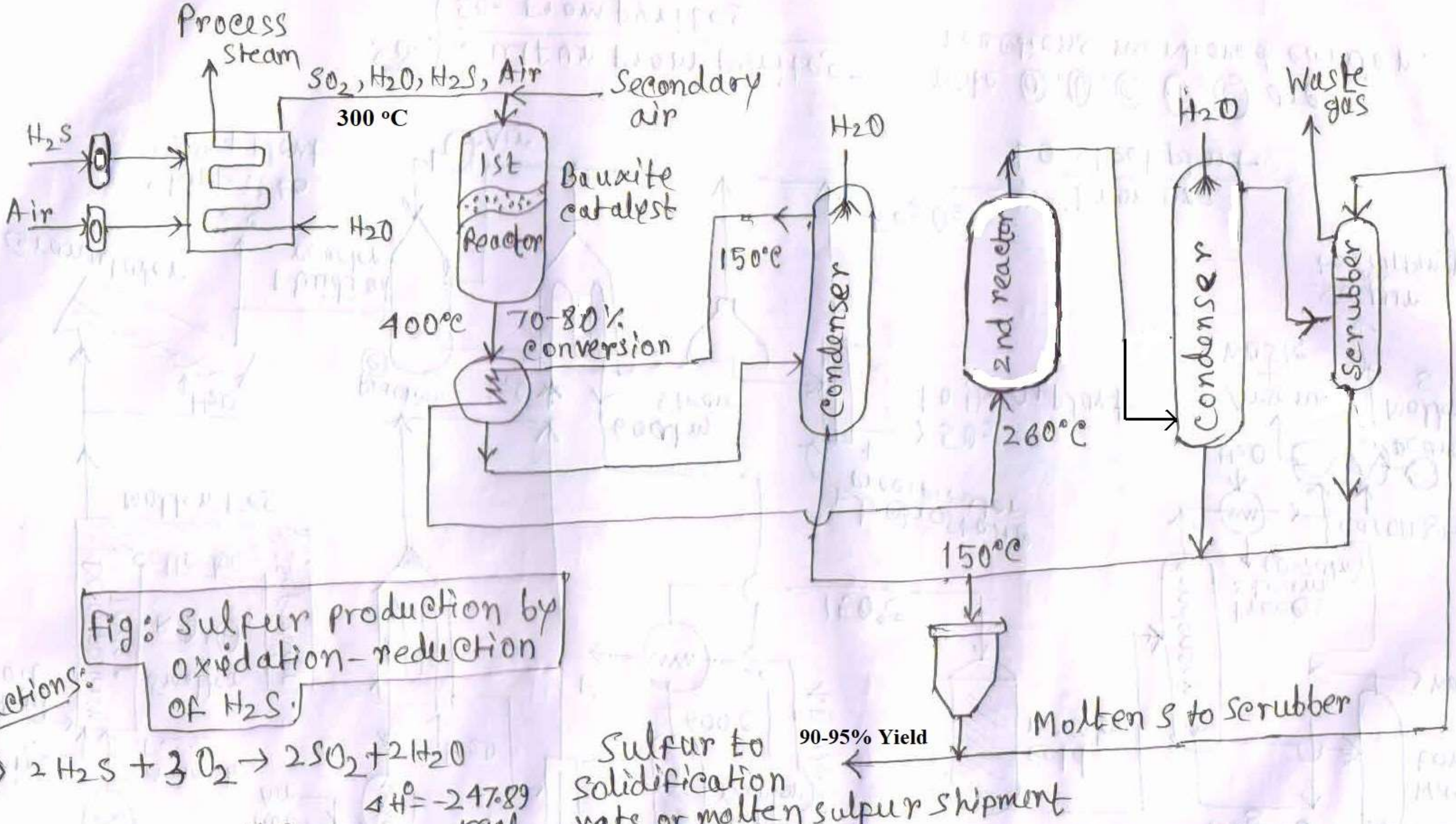


Fig: Sulfur production by oxidation-reduction of H_2S.

Reactions:

a) $2 H_2S + 3 O_2 \rightarrow 2 SO_2 + 2 H_2O$ $\Delta H^0 = -247.89$ kcal

b) $4 H_2S + 2 SO_2 \xrightarrow{Al_2O_3} S_6 (g) + 4 H_2O$ $\Delta H^0 = -42.24$ kcal

Sulfuric Acid

Sulfuric Acid (H_2SO_4)

Grades of H_2SO_4	% H_2SO_4
50° Be (Fertilizer acid)	62.2%
60° Be (Oil of Vitriol)	93.2%
95% Acid	95%
98% Acid	98%
Monohydrate acid	100%
20% oleum (Fuming)	104.5% (20% Free SO_3)
40% oleum (Fuming)	109.0% (40% free SO_3)
65% oleum	114% (65% Free SO_3)

Method of productions

a) chamber process (1746) and obsolete now

b) contact Process. (It is developed process)

a) **Chamber Process**: It yields less than 80% H_2SO_4

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

$$SO_2 + HNO_3 \rightarrow NOHSO_4$$

$$NOHSO_4 + HNO_2 \rightarrow H_2SO_4 + NO + NO_2$$

b) **contact process**

a) $S(s) + O_2(g) \rightarrow SO_2 \; ; \; \Delta H = -70.9\,kcal$

b) $SO_2(g) + \frac{1}{2}O_2(g) \overset{V_2O_5}{\rightleftharpoons} SO_3(g) ; \; \Delta H = -23.0\,kcal$

contact process yield 98% H_2SO_4 and higher concentration which can be diluted if necessary.

Nowadays DCDA (Double contact Double Absorption) is used

For more economic and environmental friendly process.

Source of SO_2

a) sulfur, b) pyrites

c) CuS, ZnS, PbS, MoS_2.

d) waste H_2SO_4

e) H_2S source

Sulfur source → pyrites, smelter source

waste H_2SO_4: $FeSO_4$ from iron and steel industry and H_2SO_4 from petroleum refinery operations are roasted to recover SO_2;

H_2S source: H_2S recovered by scrubbing various fuel and refinery gases with solvent followed by hot stripping.

Catalyst in Contact Process

Vanadium pentoxide is the popular catalyst in the process, which is dispersed on *porous carrier* in *pellet* form. *Platinum* catalyst is easily poisoned, fragile, rapidly heat deactivated, and of high initial investment.

Catalyst Characteristics

- *Porous carrier* of high surface area, controlled pore size, and high temperature resistance: It can be used in fixed bed in pellet form, fluidized bed in powdered form. Examples of *porous carriers* are alumina, silica gel, kieselguhr, zeolite.
- *Active catalytic agent* is V_2O_5. It is fired with porous carrier and water-soluble compounds below sintering point to gel or porous substructure.
- *Promoter* can be alkali, metallic compounds which are added in minute quantity to enhance the activity of catalytic agent.

Advantages of V_2O_5 catalyst

- Immune to poison
- Low initial investment (5% replacement/year)
- Requirement is 10 kg of catalyst mass containing 7-8% V_2O_5 per daily ton of acid (100%).

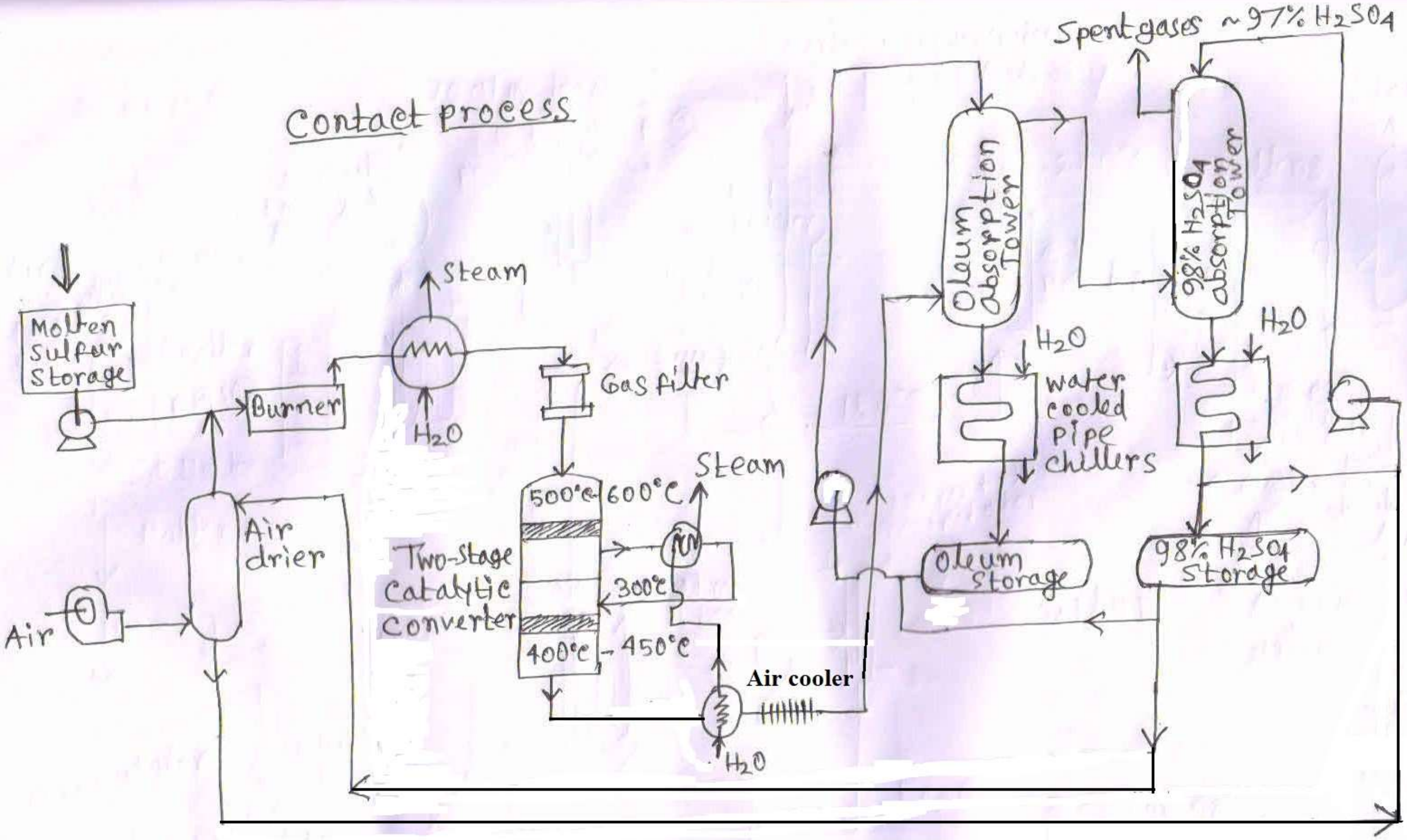
Disadvantages of V_2O_5 catalyst

- It can be used for dilute SO_2 feed concentration (7-10%).
- The catalyst activity is less that requires high O_2/SO_2 ratio for economic production of acid. It requires design of larger convertor reactor of higher initial investment.

Process description

- Feed gas containing 7-10% SO_2 and 11-14% O_2 is preheated by converter gas and sent to first stage (contains 30% of total catalyst) of stainless-steel reactor. At the first stage 80% conversion of SO_2 is achieved at 500-600 ^oC.
- The hot gas from 1st stage is cooled to 300 ^oC by exchanging heat with cooled water and fed to the 2nd stage at 400-450 ^oC to obtain higher conversion SO_2 and total yield of 97%.
- The product gases from the 2nd stage are cooled to 150 ^oC by water and air cooler and sent to the oleum absorption tower where the SO_3 gas is absorbed by oleum feed to produce oleum not over 1% rise in acid strength compared to feed oleum. Bottom product of tower is cooled in water cooled pipe chiller and stored in oleum storage. 40% oleum can be obtained by tower absorption, which can be concentrated to 65% by distillation.
- Scrubbed gas from oleum absorption tower is sent to 98% H_2SO_4 absorption tower where it is finally scrubbed by 97% H_2SO_4 to produce 98% H_2SO_4 in the bottom product which is stored. The 97% H_2SO_4 required for the final scrubbing is obtained from the outlet of the air drier where air is dried by 98% H_2SO_4 and get diluted through moisture intake from air.

Contact process



Flowsheet for manufacture of H_2SO_4 and oleum by contact process.

Thermodynamics of equilibrium SO_2 oxidation

$$SO_2(g) + {}^1/_2\, O_2(g) \leftrightharpoons SO_3(g); \quad \Delta H = -23.0\, Kcal$$

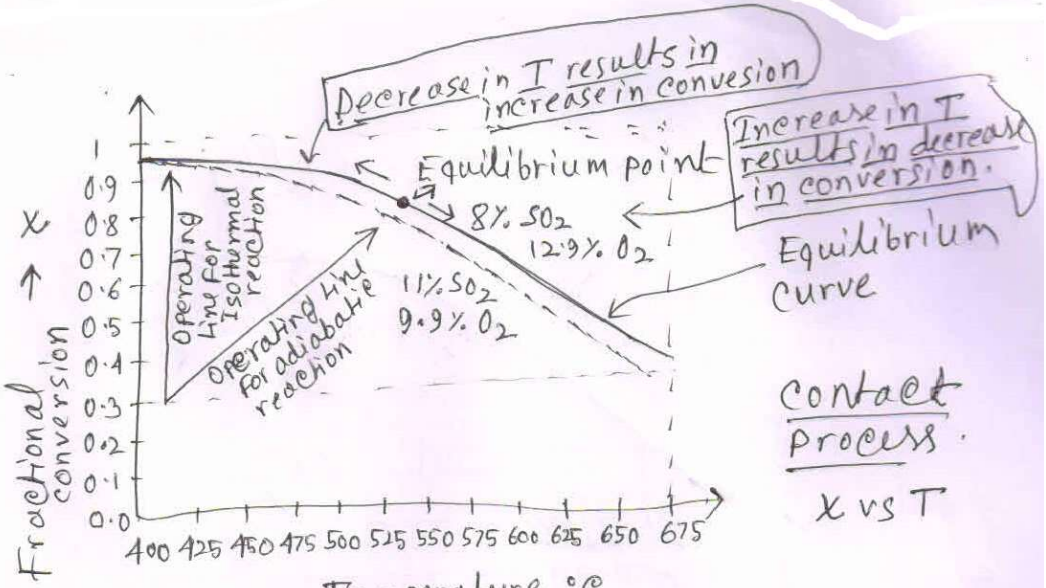
$$K_p = \frac{P_{SO_3}}{P_{SO_2}\left(P_{O_2}\right)^{1/2}} = \frac{Y_{SO_3}}{Y_{SO_2}\left(Y_{O_2} P_T\right)^{1/2}};\ P_i = Y_i P_T$$

From Le Chatelier's principle chemical equilibria of the reaction can be analyzed

- *Change of SO_3 concentration* alters the equilibrium concentrations of SO_2 and O_2 gas and hence equilibrium conversion of the reactant gases. It does not alter the K_p or equilibrium point. So, if the *SO_3 is absorbed* in the one reactor/stage outlet and fed to the next reactor/stage the rate of forward reaction will increase to adjust the K_p or equilibrium point. As a result, overall conversion of reactants will increase and hence production of acid.
- *Change of pressure* alters the equilibrium conversion as there is change in total mole number between reactant (1.5 mole) and product (1). It does not alter the K_p or equilibrium point. So, if P is increased the rate of forward reaction will increase that in turn increases overall conversion to adjust the K_p or equilibrium point.
- *Change of temperature* alters the equilibrium conversion and K_p or equilibrium point, simultaneously. Heat is evolved in the product or forward reaction. With increase in temperature rate of backward reaction will increase to adjust heat energy. As a result, equilibrium conversion of reactant gases will decrease and hence acid production. At the same time, the K_p decreases, or equilibrium point shifted towards backward direction.

Thermodynamic data of SO_2 oxidation

Temperature (°C)	Heat evolved (Kcal/g mole)	K_p
327	23.42	4170
427	23.27	257
527	23.08	32
627	22.87	6.47
727	22.63	2.03



Contact process.

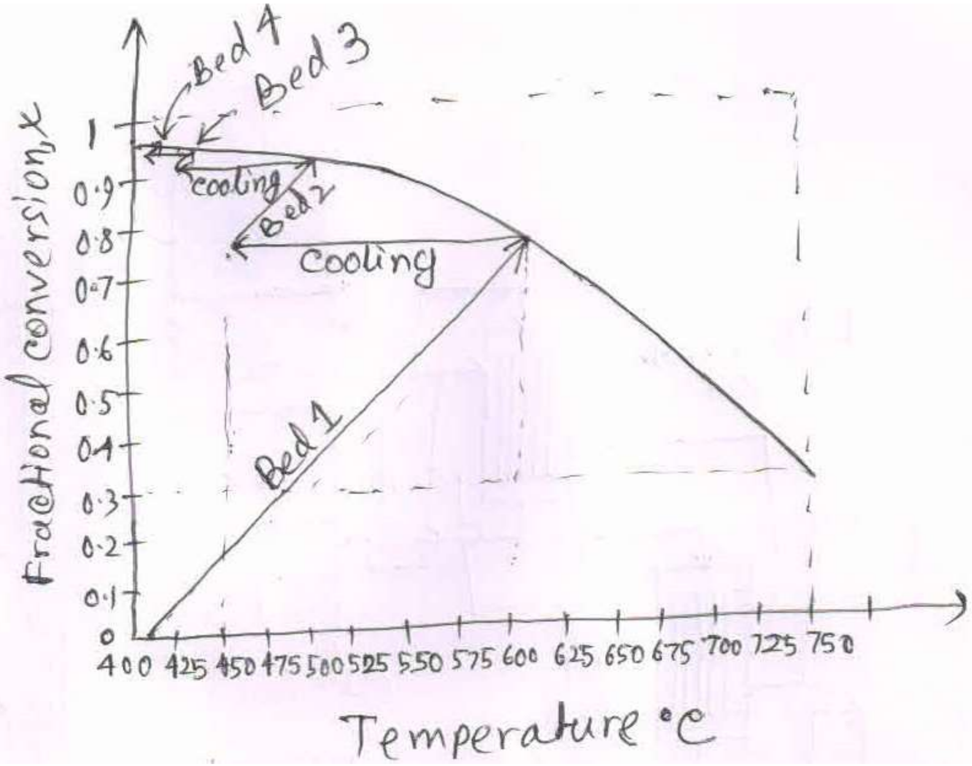
X vs T

Fractional conversion, $X = \dfrac{C_{A0} - C_A}{C_{A0}}$

C_{A0} = concentration of limiting reactant initially present or Initial concentration of reactant. (%, mol/m³)

C_A = concentration of limiting reactant present in the reactor after reaction (mol/m³)

By Douglas Louie, Vancouver, Canada.



Single absorption contact process. with mutiple bed. (4) SO_2 : 9%
O_2 : 13.2%

	concentration	T
Bed 1	72.2%	410°C
Bed 2	92.7%	450°C
Bed 3	96.3%	425°C
Bed 4	97.5%	420°C

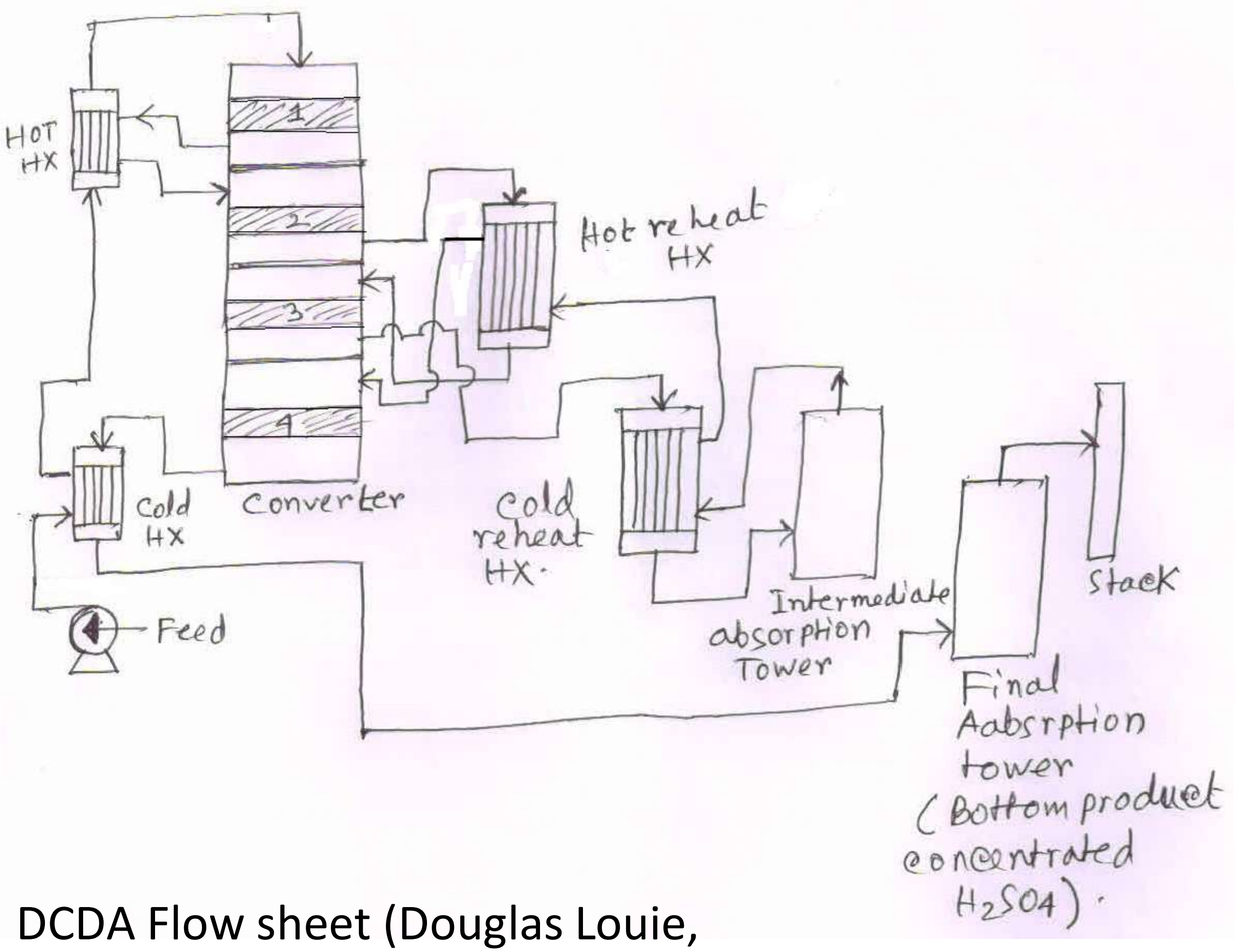
By Douglas Louie, Vancouver, Canada.

Major engineering problems

- *Design of multistage catalytic reactor* for exothermic reactions to obtain favorable equilibrium. The catalytic converter can contain 3 to 4 stages rather than 2-stage reactor for large capacity plant.
- *Optimization of space velocity in catalytic chamber*. Pumping cost increases with space velocity (inversely proportional to time to process one reactor volume of the reactant feed volumetric flow rate of feed/volume of the continuous reactor, sec^{-1}) of the reactor. Fixed cost (cost of reactor material) decreases with increase in space velocity. Then space velocity should be optimized to obtain minimum total cost (Pumping cost + Fixed cost).
- *Corrosion problem* increases with reactor pressure. It is shown that yield of SO_3 gas increases with pressure. $Y_{SO_3} = Y_{SO_2}\left(Y_{O_2}P_T\right)^{1/2}$; But reactor pressure must be not high to avoid corrosion problem.
- For first two problems above, catalyst beds result 30-50 cm height. Yield can drop due to longitudinal mixing if convective gas velocity is low enough.

- Removal of heat of absorption of SO_3 gas in acid. Pipe coolers with water dripping (on the external surface of the pipe) are replaced by cast iron pipe with internal fins to enhance heat transfer rate.

DCDA Process



DCDA Flow sheet (Douglas Louie, COM 2010. Vancouver, Canada)

- Double contact/ Double absorption
- It includes two SO_3 absorption tower
- Higher overall conversion.
- Produce higher concentration of H_2SO_4 (~99.8%).
- Can utilizes higher SO_2 feed concentration (upto 14%).
- Meet current emission restrictions for SO_2 gas (Best available technology BET).
- Economic and produces

Reference

- Dryden's Outlines of Chemical Technology, M. Gopala Rao, M. Sittig, 3rd Edition, East West Press.

Phosphorous Industries

Phosphate Rock

- Elemental phosphorus and its products are derived from commercial deposits of phosphate rock, ***fluorapatite*** **$[Ca_{10}(PO_4)_6F_2]$ or $CaF_2.3Ca_3P_2O_8$.**
- Major products of phosphorus industry are,
- phosphorus, phosphoric acid for detergent and food chemicals.
- ammonium phosphate, calcium phosphate, nitrophosphate as fertilizer,
- sodium phosphate, organic phosphate Tricresyl (TCP) and triphenyl phosphates are organic esters of phosphoric acid and are widely employed as plasticizers..

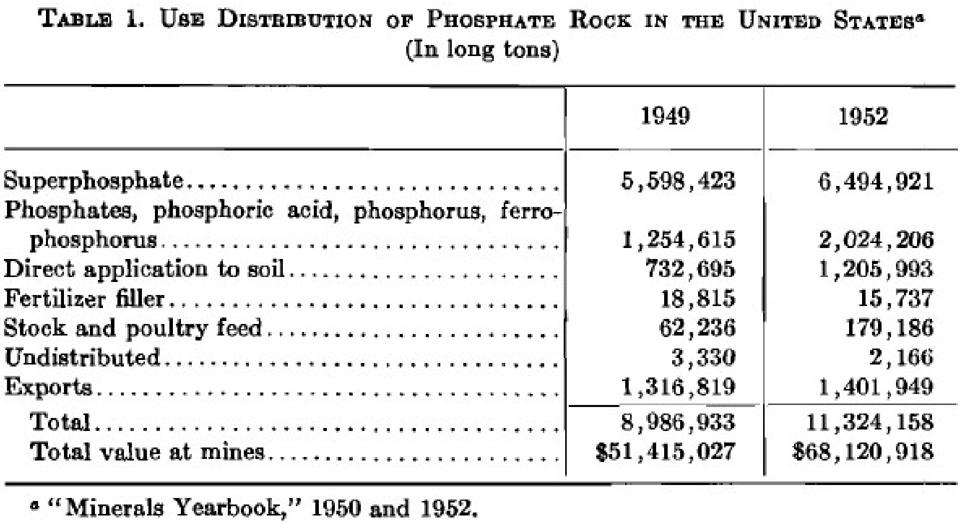


TABLE 1. USE DISTRIBUTION OF PHOSPHATE ROCK IN THE UNITED STATES[a]
(In long tons)

	1949	1952
Superphosphate	5,598,423	6,494,921
Phosphates, phosphoric acid, phosphorus, ferrophosphorus	1,254,615	2,024,206
Direct application to soil	732,695	1,205,993
Fertilizer filler	18,815	15,737
Stock and poultry feed	62,236	179,186
Undistributed	3,330	2,166
Exports	1,316,819	1,401,949
Total	8,986,933	11,324,158
Total value at mines	$51,415,027	$68,120,918

[a] "Minerals Yearbook," 1950 and 1952.

Consumption pattern

- Phosphorus content of phosphate rock is expressed as percentage P_2O_5. In trade, it is expressed as ***bone phosphate of lime*** (BPL), tricalcium phosphate content, i.e., $Ca_3(PO_4)_2$.
- High grade phosphate rock +30% P_2O_5 from Jhamarkotra, Rajasthan is used for superphosphate manufacturing.
- The rock from Jhabua Madhya Pradesh, Chattarpur Delhi is used for the production of elemental phosphorus and fertilizer mixtures. Mussoorie rock is used for direct application.
- About 75% phosphate rock in India are low grade with 10-25% P_2O_5 requires prior beneficiation to improve P_2O_5 content to about 30% to make it usable as fertilizer manufacture.
- Beneficiation plants in India are Hindustan zinc, RSMML Udaipur and Jhamarkotra for high dolomite content.
- Domestic production of rock phosphate was about 5.5 lakh tons during 1990-91. Rest of the bulk rock requirement is met through imports from Jordan, Morocco, Senegal and Togo, which was 3.5 million ton during 1990-91.

MANUFACTURE OF PHOSPHORUS AND PHOSPHORIC ACID

- Two types of elemental phosphorus P_4: Yellow phosphorus and red phosphorus. Later one exists at least six different crystal modifications and can be formed by heating yellow phosphorus to give higher oxidation resistance and stability.
- Reactions: Phosphorus has been produced by both the blast-furnace and the electric-furnace methods. Currently only the electric-furnace method is active. The raw materials are phosphate rock, silica, and coke.
- $\mathrm{CaF_2 3Ca_3P_2O_8 + 9SiO_2 + 15C \rightarrow CaF_2 + 9CaSiO_2 + 6P + 15CO}$
- Or more simply
- $\mathrm{2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4(yellow\ grade) + 10CO}$
- $\mathrm{P_4(yellow\ grade) \xrightarrow{250-450^oC} P_4(red\ grade)}$
- The phosphorus is employed frequently as an intermediate product, being burned or oxidized to P_2O_5, which is dissolved in water to form the acids or other compounds.

Phosphorus pentoxide: $4P + 5O_2 \rightarrow 2P_2O_5$
Metaphosphoric acid: $P_2O_5 + H_2O \rightarrow 2HPO_3$
Pyrophosphoric acid: $P_2O_5 + 2H_2O \rightarrow H_4P_2O_7$
Orthophosphoric acid: $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

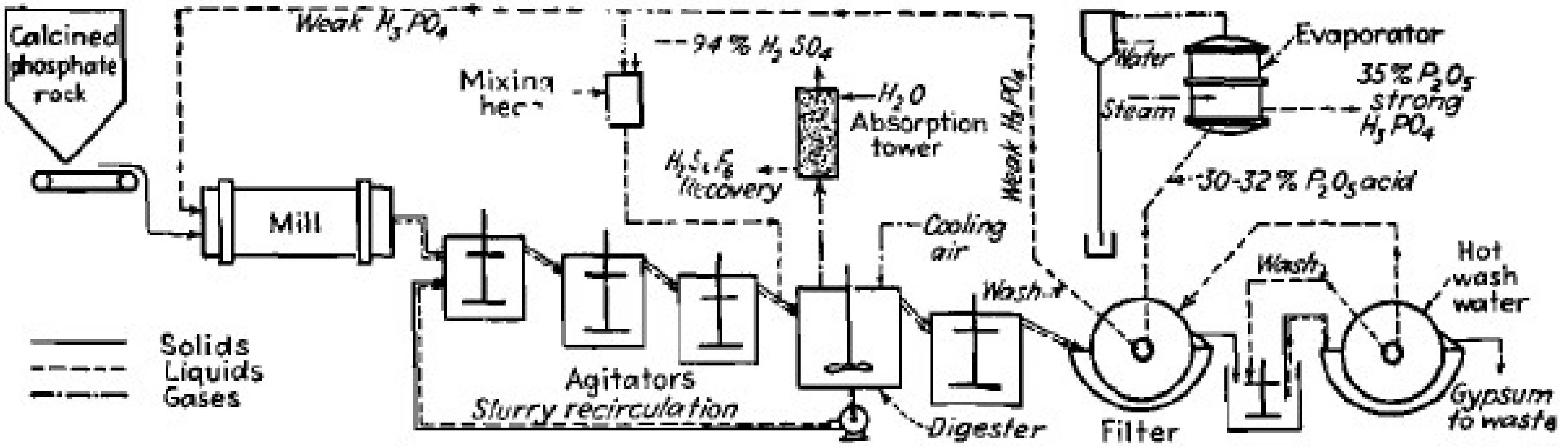
- **Sulfuric Acid or the Wet Method:** The sulfuric acid or wet method is employed to manufacture phosphoric acid directly, by the reaction

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4{\cdot}2H_2O)$$

- Side reaction: $\mathrm{CaF_2} + \mathrm{H_2}SO_4 + 2\mathrm{H_2O} \rightarrow 2HF + \mathrm{CaSO_4}.\,2\mathrm{H_2O}$
- $6HF + SiO_2 \rightarrow \mathrm{H_2}Si\mathrm{F_6} + 2\mathrm{H_2O}$
- In the past, most of the phosphoric acid was prepared by the action of dilute sulfuric acid, 30oBe., on ground phosphate rock or bones. This method has been replaced by the ***Dorr strong-acid process***, which produces a stronger, cheaper, and purer acid.
- The equipment should be lead-lined, and sufficient time provided in the various agitators for the reaction to go to completion. The temperature in the digester should be kept low enough to ensure the precipitation of gypsum, $CaSO_4.2H_2O$, and not anhydrite. If the latter is formed, it hydrates subsequently and causes plugging of pipes. Acid made by this process is almost entirely used in fertilizer production where impurities are unimportant.

- Phosphate rock is ground to 65% -200 mesh and mixed with weak phosphoric acid in a mill that washes it into a reaction tank. Strong sulfuric acid is metered with automatic control which keeps desired acid and rock feed ratio.
- In a single reactor 98% conversion with residence time 4-5 hr and proper baffling is arranged. In other design, a series of 4-5 continuous mixing tanks can be used with better efficiency. 40% phosphoric acid is removed from gypsum-acid slurry in a pan vacuum filter.
- Pyrophosphoric acid is obtained by heating phosphoric acid to 250^{o}C. At 900^{o}C temperature it is red heated to metaphosphoric acid.

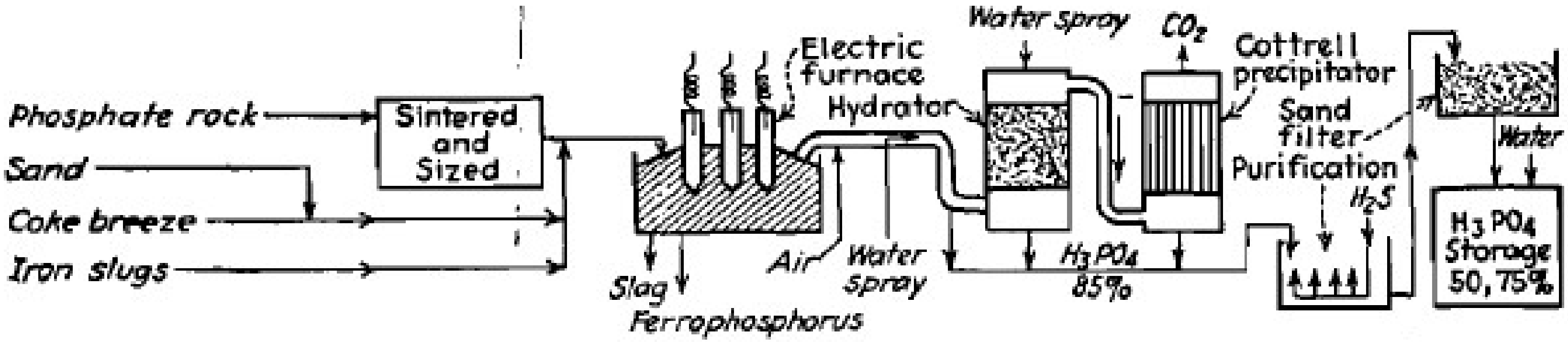
- Phosphate rock ground and calcined. Ground rock reacted in mill with part of weak H_3PO_4. Reaction continued in three agitators. Reaction continued with rest of weak H_3PO_4 and with H_2SO_4. SiF_4 recovered. Calcium sulfate filtered off and washed. This sludge pulped, refiltered, ,and re-washed. Strong acid from first filter evaporated to stronger acid.



Phosphate rock (70 B.P.L.)	2,350 lb.	Per ton of 35% P_2O_5 acid
Sulfuric acid (94 %)	1,950 lb.	
Water (Chiefly cooling)	7,500 gal.	
Steam	780 lb.	
Electricity	52.5 kw.-hr.	
Direct labor	0.8 man-hr.	

FIG. 3. Phosphoric acid by Dorr strong-acid process.

- **Electric-furnace Method:** First employed in 1920. It permits the use of lower grade rock than does the wet process as the slag carries off impurities.
- The phosphate rock must be charged in a lump form. Fine material tends to block the exit of the phosphorus vapors and to cause bridging and uneven descent of the furnace charge, resulting in puffs and the carrying over of excessive quantities of dust.



Phosphate rock (69.8 B.P.L.)	3,970 lb	Iron	depends on ferrophosphorus requirements	Per ton 85% H_3PO_4
Silica rock	1,270 lb	Electricity	3,460 kw-hr.	
Coke breeze	748 lb	Direct labor	(est.) 0.5-1 man-hr.	

FIG. 4. Phosphoric acid flow sheet. Electric-furnace process by one-step system. The two-step system separates the phosphorus after condensation, ships it to consuming centers to save freight, and there oxidizes the phosphorus.

- Phosphate rock ***ground*** (Op.) to mixed with ***coke breeze*** (small particle from coking of coal) and sand which are ***sintered***, and introduced into ***electric furnace*** (Op.) to obtain better ***electrical resistivity*** and to avoid entrainment of fines in the released P_4 and CO vapor.
- Mix heated to reaction temperature (Pr.) 1400-1450 ^oC.
- Molten ***slag*** (8 ton/ton of P) and ferro phosphorus run off (Op.) and trapped from the bottom of the furnace periodically. These are cooled and crushed for rod-bed gravel, soil liming and glass manufacture.
- Phosphorus and CO drawn off, P ***condensed*** or ***oxidized*** with air (Pr.)
- P_2O_5 ***cooled*** and ***hydrated*** (Op. and Pr.)
- Strong H_3PO_4 filtered and purified (Op. and Pr.)

Chemical Reaction:

- $2\mathrm{Ca}_3(\mathrm{PO}_4)_2 + 6\mathrm{SiO}_2 + 10\mathrm{C} \rightarrow 6\mathrm{CaSiO}_3 + \mathrm{P}_4(\text{yellow grade}) + 10\mathrm{CO}$
- $\mathrm{P}_4 + 10\mathrm{CO} + 10\mathrm{O}_2 \rightarrow 2\mathrm{P}_2\mathrm{O}_5 + 10\mathrm{CO}_2$
- $\mathrm{P}_2\mathrm{O}_5 + \mathrm{xH}_2\mathrm{O} \rightarrow 2\mathrm{H}_3\mathrm{PO}_4 + (\mathrm{x} - 3)\mathrm{H}_2\mathrm{O}$

Calcium Phosphate

- Large tonnage of low grade calcium phosphate are made as fertilizer. Two grads are possible based on based on the method of production;
- ***Superphosphate*** is made by reacting ***phosphate rock*** (contains 15-35% P_2O_5) with sulfuric acid.
- ***Triple superphosphate*** is made by reacting phosphate rock (contains 42-50% P_2O_5) with ***phosphoric acid***.
- After 1962 in India, no further licensing of superphosphate plant was permitted to promote the growth of balanced fertilizer that yield better corps.

Superphosphate manufacture

- Raw materials: ***Phosphate rock of high grade*** (30-35% P_2O_5); ***Sulfuric acid*** (62-70%).
- Basis: 1 ton of superphosphate requires 0.5-0.6 ton phosphate rock and 0.3-0.4 ton sulfuric acid.

- Chemical reaction:
- Acidulation

$$\underbrace{[Ca_3(PO_4)_2]_3 \cdot CaF_2}_{\text{Phosphate rock}} + 7H_2SO_4 + 3H_2O \rightarrow \underbrace{3CaH_4(PO_4)_2 \cdot H_2O + 7CaSO_4}_{\text{superphosphate}} + 2HF$$

- SiO_2 impurity removal

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$
$$H_2SiF_6 + NaCl \rightarrow Na_2SiF_6 + 2HCl$$

- Process description: Phosphate rock lumps are crushed in a jaw crusher and ground to – 100 mesh in a hammer mill. A continuous feed of dilute sulfuric acid (65-70%) and powdered rock is monitored by automatic control into a steel trough, lead-lined and brick-lined, covered with a hood to collect SiF_4 and HF fumes. The rotating mechanism, made of cast iron blades on a square shaft, moves the product gradually at the rate of 0.2-0.5 meter per minute through the 12-15 meter reactor-conveyor system. After completion of the reaction the product is sent to a granulator.
- SiF_4 and HF fumes along with CO_2 are scrubbed in water and the silica is recovered.

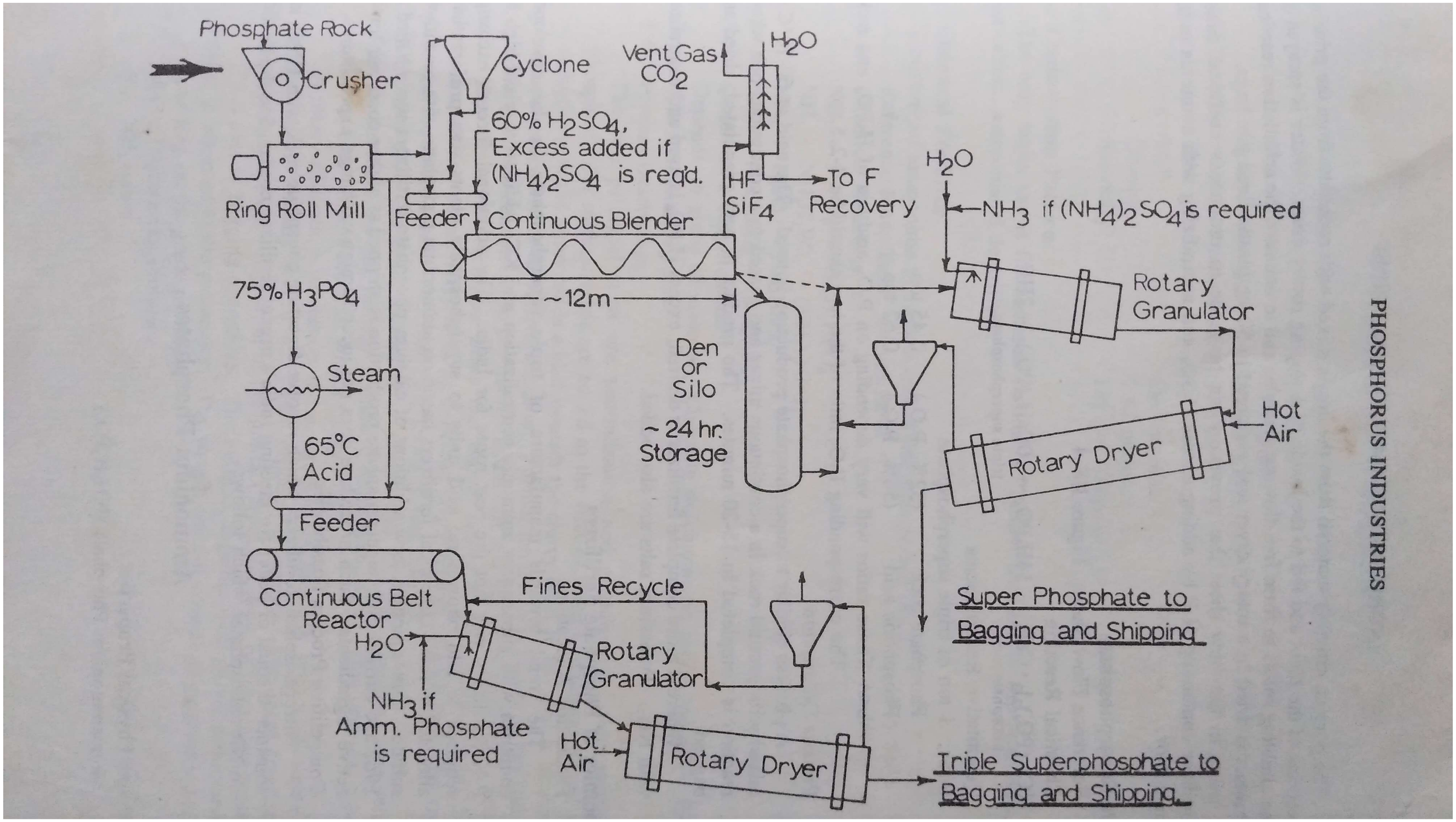


Fig. Superphosphate and triple superphosphate production method

Triple superphosphate manufacture

- Raw materials: ***Phosphate rock of high grade*** (32% P_2O_5); ***Phosphoric acid*** (56% P_2O_5).
- Basis: 1 ton of triple superphosphate requires 0.45 ton phosphate rock and 0.62 ton of phosphoric acid.
- Chemical reaction:

$$\underbrace{[Ca_3(PO_4)_2]_3 \cdot CaF_2}_{\text{Phosphate rock}} + 14H_3PO_4 \rightarrow \underbrace{10CaH_4(PO_4)_2}_{\text{triple superphosphate}} + 2HF$$

- Process description: The phosphoric acid at 60-70 ^{o}C is mixed with ground rock in a continuous mixer and passed to a continuous belt where reaction is completed in 15-20 minute. The product is next granulated, dried and bagged.

Sodium Phosphate

- The industrially important sodium phosphates may be classified: Alkali metal metaphosphates, such as ***sodium metaphosphate*** $NaPO_3$ and ***sodium hexametaphosphate*** $(NaPO_3)_6$, or Graham's salt. Alkali metal polyphosphates, such as ***Sodium Tripolyphosphate***, $Na_5P_3O_{10}$ or ***STTP.*** Alkali metal pyrophosphates, such as $Na_4P_2O_7 \cdot 10H_2O$, sodium or ***tetra-sodium pyrophosphate.*** Alkali metal orthophosphates, such as $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$ and $Na_3PO_4 \cdot 2H_2O$.
- Consumption pattern: The principal use of alkali phosphate is in detergent manufacture. Ecologically its use as detergent formulation has been reduced all over the world. It is still widely used as metal cleaning, boiler water treatment, in textile industry and in foodstuff.
- Method of production: Ortho and polyphosphate are made from varying ratios of sodium carbonate, sodium hydroxide, and othophosphoric acid. Other salts such as, meta and pyro phosphates of sodium made from meta and pyro phosphoric acids, respectively.
- **Sodium Tripolyphosphate** ($Na_5P_3O_{10}$ or ***STTP***): It is white powder of M.W 368. pH of 1% solution is 9.7. Soluble in water: 12.8 gm/cc water at 20^{o}C.
- Chemical reaction:
- $5\mathrm{Na}_3CO_3 + 6\mathrm{H}_3\mathrm{PO}_4 \rightarrow 2\mathrm{Na}_5P_3O_{10} + 9\mathrm{H}_2\mathrm{O} + 5\mathrm{C}O_2$
- Basis: 1 ton of SSTP at 99% yield requires sodium carbonate (58% Na_2O) 8.81 ton and phosphoric acid (75% $\mathrm{H}_3\mathrm{PO}_4$) 1.0 ton.

- **Process description:** Saturated soda ash and technical grade concentrated $\mathrm{H_3PO_4}$ are diluted with water and steam in a batch mixing tank. A 1.67 ratio of Na_2O/P_2O_5 must be attained to form 1 mole of monosodium to 2 mole of disodium phosphate. Produced carbon dioxide is scrubbed by incoming water that is returned to entrain solids.
- The solution is filtered to remove impurities, then dried, dehydrated and cooled along the length of an indirect-fired rotary kiln. The final product then grinded, stored and packaged.

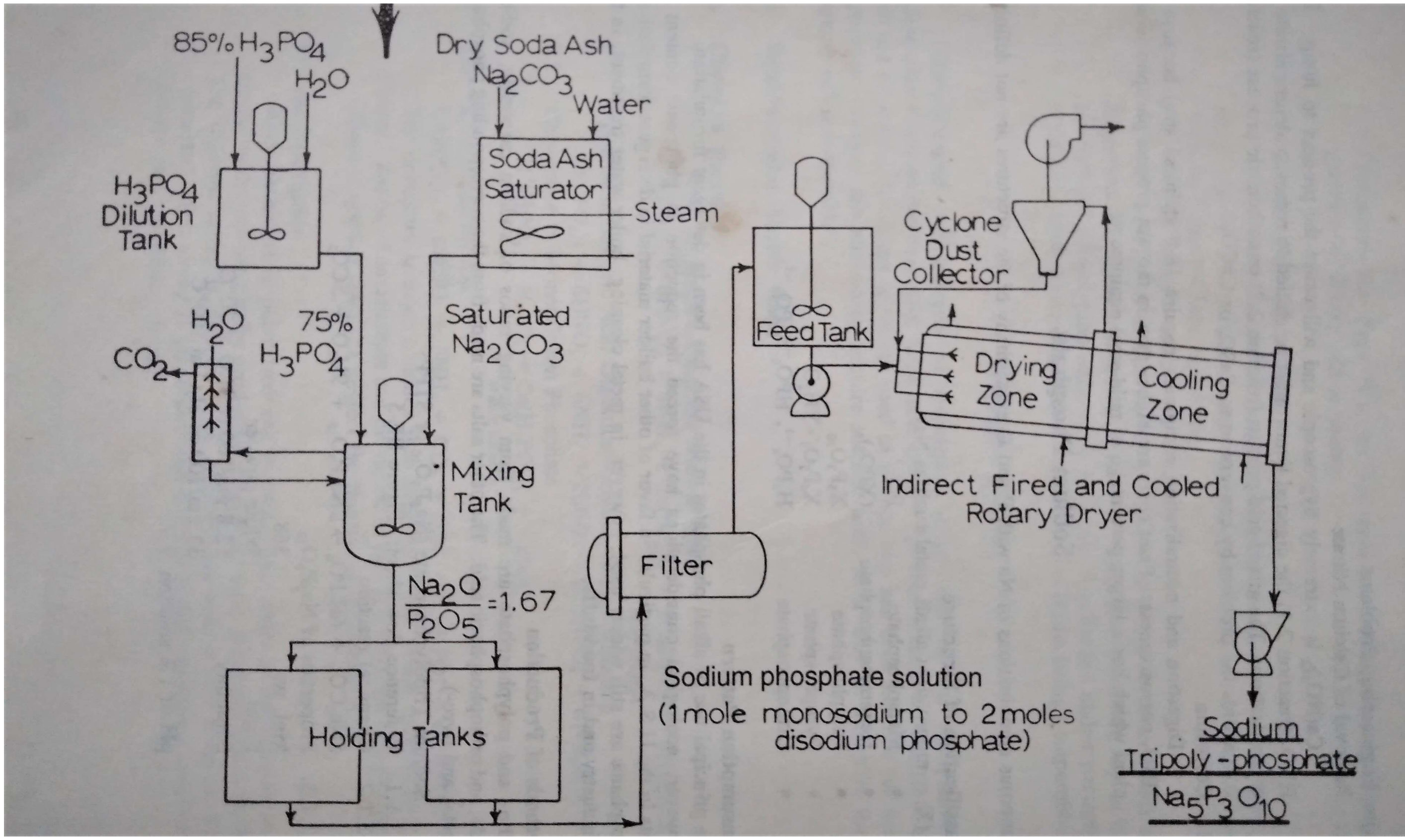
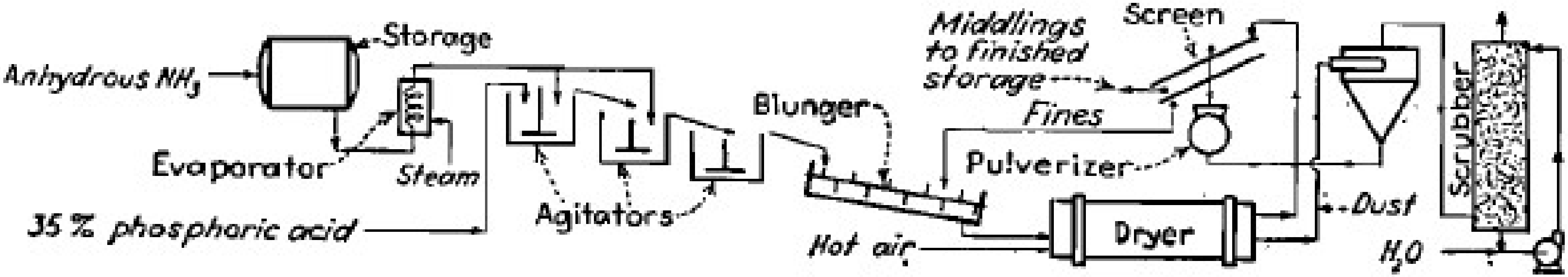


Fig. Manufacture of STTP

Ammonium Phosphates

- Both monoammonium phosphate, $NH_4H_2PO_4$, and diammonium phosphate, $(NH4)_2PO_4$, are used as fertilizers, as yeast nutrients, and as flameproofing agents for paper, wood, and textiles.
- High-grade monoammonium phosphate is, manufactured simply by the absorption of ammonia gas in 75% $\mathrm{H_3PO_4}$ made from elemental P. Considerable heat is given off in the reaction, and the mass becomes pasty and crystallizes almost solid on cooling. The white crystals are centrifuged free from the mother liquor and dried for sale. Wet-process phosphoric acid and ammonia liquor from coking operations are reacted batchwise to form a fertilizer-grade salt.
- The Dorr continuous process for granulated concentrated fertilizers neutralizes phosphoric acid or a mixture of phosphoric and sulfuric acids with ammonia to monoammonium or diammonium phosphate.
- Purified diammonium phosphate is made from phosphoric acid and ammonia in two stages. The NH_3 introduced in the first stage removes the bulk of the Fe, AI, F, Ca, and Mg present in wet-process acid as filterable impurities. The filtrate, practically a pure solution of monoammonium phosphate, is evaporated. It is saturated with ammonia to a NH_3/P_20_5 mole ratio of 2 to 1 in a continuous single-stage saturator. The product is crystallized, centrifuged, and dried for sale.



Ammonia	280 lb.	Per ton of ammonium phosphate
Phosphoric acid (35%)	2,850 lb.	
Dryer fuel	2,000,000 B.t.u.	
Electricity	13 kw-hr.	
Direct labor	0.7 man-hr.	

Fig. Flowsheet for diammonium phosphate

Chemical reaction

- $\mathrm{NH_3 + H_3PO_4 \rightarrow NH_4H_2HPO_4}$
- $\mathrm{NH_3 + NH_4H_2HPO_4 \rightarrow (NH_4)_2HPO_4}$
- $\mathrm{NH_3 + H_2SO_4 \rightarrow NH_4HSO_4}$
- $\mathrm{NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4}$

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2. Shreve’s Chemical Process Industries, George T. Austin, 5th Edition, Tata McGraw Hill Edition.