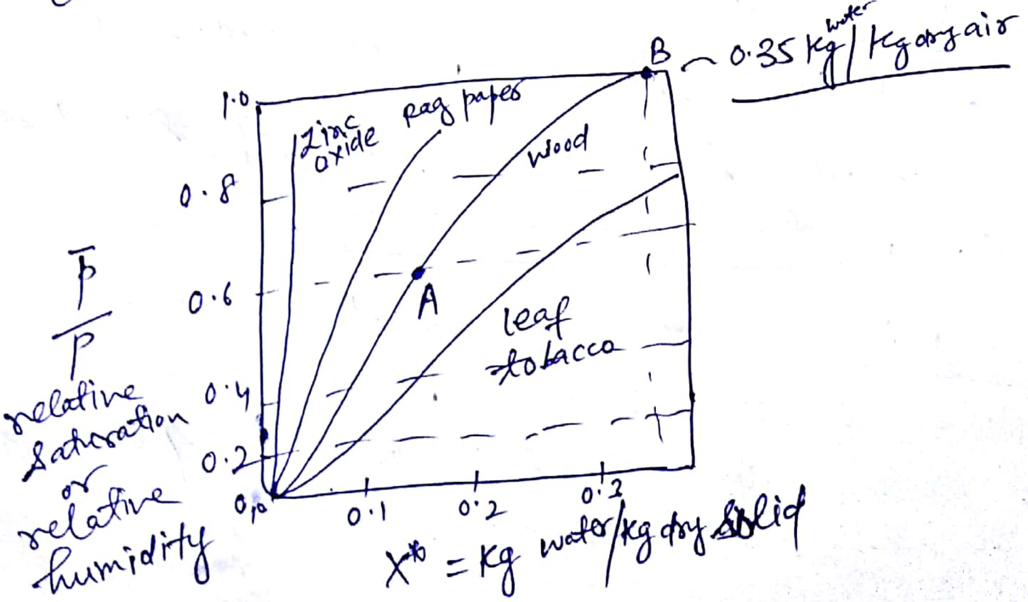
Drying :- The term drying refers generally to the removal of moisture from a substance.

Equilibrium :-

The moisture contained in a wet solid or liquid solution exerts a vapor pressure to an extent depending upon the nature of moisture, the nature of solid, and the temperature. If then a wet solid is exposed to a continuous supply of fresh gas containing a fixed partial pressure of the vapor $\bar{p}$, the solid will either lose moisture by evaporation or gain moisture from the gas until the vapor pressure of the moisture of the solid equals $\bar{p}$. The solid and the gas are then in equilibrium, and the moisture content of the solid is termed its equilibrium moisture content at the prevailing conditions.



Definitions

Moisture content, wet basis:-

$$\frac{\text{Kg moisture}}{\text{Kg wet solid}} \times 100 = \frac{\text{Kg moisture}}{(\text{Kg moisture} + \text{Kg dry solid})} \times 100$$

$$\frac{100X}{(1+X)} \qquad X = \frac{\text{Kg moisture}}{\text{Kg of dry solid}}$$

Moisture Content dry basis :-

$$\frac{\text{Kg moisture}}{\text{Kg of dry solid}} = X$$

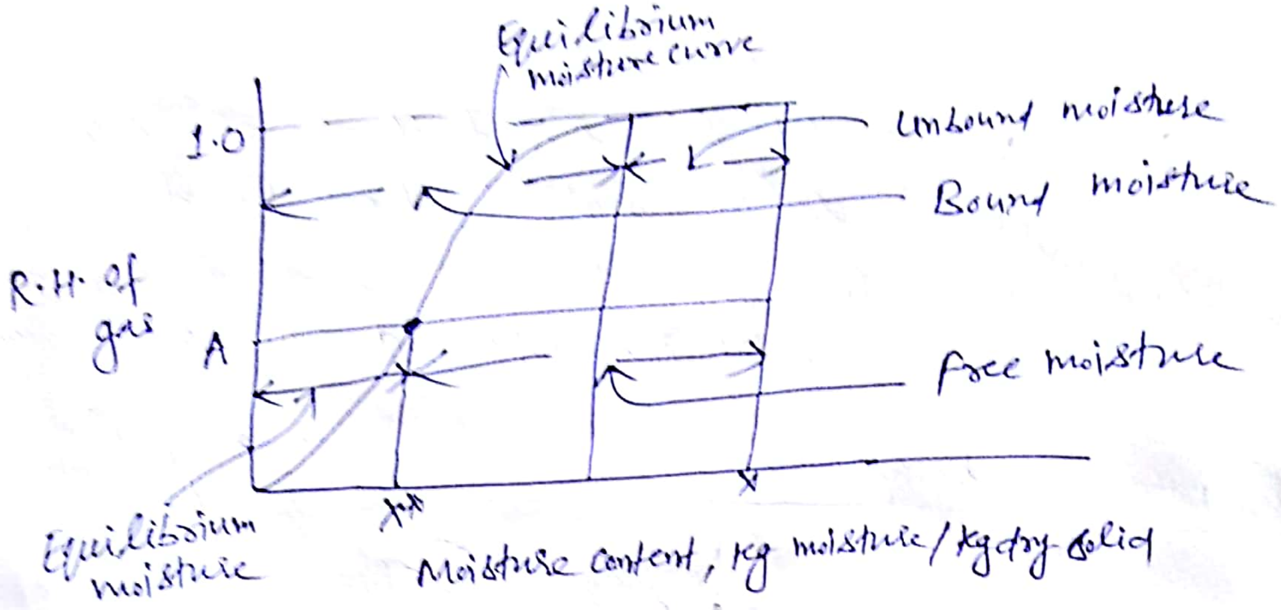
percentage moisture, dry basis = 100 X

Equilibrium moisture (X^*):- This is the moisture content of a substance when at equilibrium with a given partial pressure of vapor.

Bound moisture:- This refers to the moisture contained by a substance which exerts an equilibrium vapor pressure less than that of the pure liquid at the same temperature.

Unbound moisture:- This refers to the moisture contained by the substance which exerts an equilibrium vapor pressure equal to that of the pure liquid at the same temperature.

Free moisture:- Free moisture is that moisture contained by a substance in excess of the equilibrium moisture: $X - X^*$. Only free moisture can be ~~eq~~ evaporated, and the free - moisture content of a solid depends upon the vapor concentration in the gas.



The rate of batch drying

In order to set up drying schedules and to determine the size of equipment, it is necessary to know the time required to dry a substance from one moisture content to another under specified conditions.

Drying tests:- The rate of drying can be determined for a sample of a substance by suspending it in a cabinet or duct, in a stream of air, from a balance. The weight of drying sample can then be measured as a function of time.

(For large scale operation or scale-up)

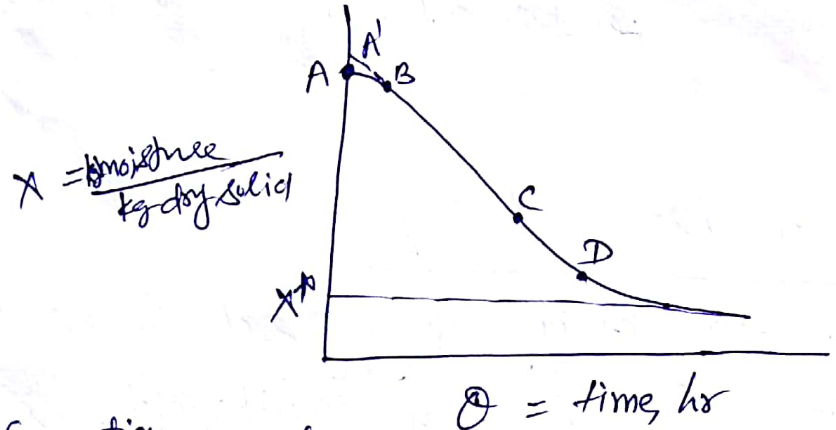
(a) the sample should be similarly supported in a tray or frame.

(b) It should have the same ratio of drying to non drying surface

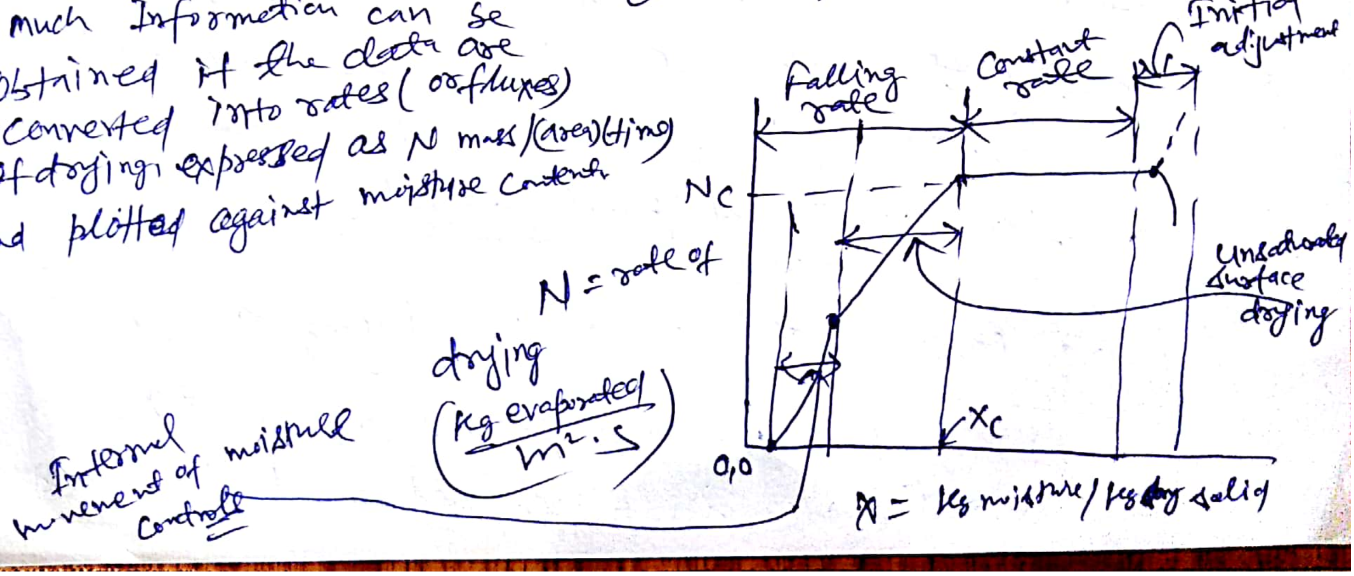
(C) It should be subjected to similar conditions of radiant heat transfer

(d) The air should have same temp., humidity, and velocity (speed and direction wrt sample).

Rate-of-drying curve



much Information can be obtained if the data are converted into rates (or fluxes) of drying, expressed as N mass/(area)(time) and plotted against moisture content.



$$N = \frac{-S_s \Delta X}{A \Delta \theta}$$ S_s = mass of dry solid.

Time of drying :-

The rate of drying is given by

$$N = -\frac{S_s\, dX}{A\, d\theta}$$

Rearranging and integrating over the time interval while the moisture content changes from its initial value X_1 to its final value X_2 gives

$$\theta = \int_0^\theta d\theta = \frac{S_s}{A}\int_{X_2}^{X_1}\frac{dX}{N}$$

① Constant rate period :-

$$\theta = \frac{S_s}{A}\int_{X_2}^{X_1}\frac{dX}{N_c}$$

$$\theta = \frac{S_s(X_1 - X_2)}{AN_c}$$

② Falling rate period

(a) general case : for any shape of falling rate curve, Can be integrated graphically by determining area under ~~the~~ a curve of $\frac{1}{N}$ as ordinate X as abscissa, the data for which can be obtained from the rate - of drying curve

(b) <u>Special case</u> : <u>N is linear in X</u>

$$N = mX + b$$

$$\theta = \frac{S_s}{A}\int_{X_2}^{X_1}\frac{dX}{mX+b} = \frac{S_s}{mA}\ln\left(\frac{mX_1+b}{mX_2+b}\right)$$

$\because$ $N_1 = mX_1 + b$, $N_2 = mX_2 + b$ and

$$m = (N_1 - N_2)/(X_1 - X_2)$$

$$\theta = \frac{S_s(X_1 - X_2)}{A(N_1 - N_2)}\ln\frac{N_1}{N_2}$$

$$\theta = \frac{S_s(X_1 - X_2)}{A N_m}$$

where N_m is the logarithmic average of rate N_1, at moisture content X_1, and N_2 at X_2.

Frequently the entire falling curve can be taken as a straight line, then

$$N = m(X - X^*) = \frac{N_c(X - X^*)}{X_c - X^*}$$

$$\theta = \frac{S_s(X_c - X^*)}{N_c A}\ln\frac{X_1 - X^*}{X_2 - X^*}$$

$\boxed{12.18\ 12.3}$ — Treybal

DRYING

Reference

Treybal, McCabe, Geankoplis

- **Module-5** DRYING: Introduction to drying, Rate of drying, Batch drying mechanism, the mechanism of moisture movement during drying, classification and design of dryer. (5)
- CRYSTALLIZATION: Introduction to crystallization, Theory of Crystallization, Formation and growth of crystals, crystal yield, Rate of crystallization

Classification of Dryers

- Batch or continuous
- Isothermal or Adiabatic
- For solids or slurry or solution

Classification – Batch or Continuous

- Batch

  - Direct Dryers
    - Try dryer
    - Truck dryer
    - Through circulation dryer

  - Indirect dryers
    - Vacuum shelf dryer
    - Agitated pan dryer
    - Freeze dryer

- Continuous
  - Tunnel dryer
  - Drum dryer
  - Turbo rotating shelf dryer
  - Through circulation screw dryer
  - Rotary dryer,
  - Through circulation rotary dryer
  - Spray Dryer
  - Fluidized bed dryer
  - Spouted bed dryer
  - Pneumatic dryer

Classification of dryers- material handled

- Solids and paste
  - Tray
  - Screen conveyer
  - Tower/Rotary shelf
  - Rotary dryer
  - Screw conveyer
  - Fluidized bed
  - Flash dryer
- Slurry solution
  - Spray
  - Thin Film
  - Drum Dryer

Solid Gas contact in adiabatic dryer

- Cross circulation
- Through circulation
- Shower
- Fluidized bed
- Continuous fluidization
- Drops suspended in gaseous phase as in Spray dryer

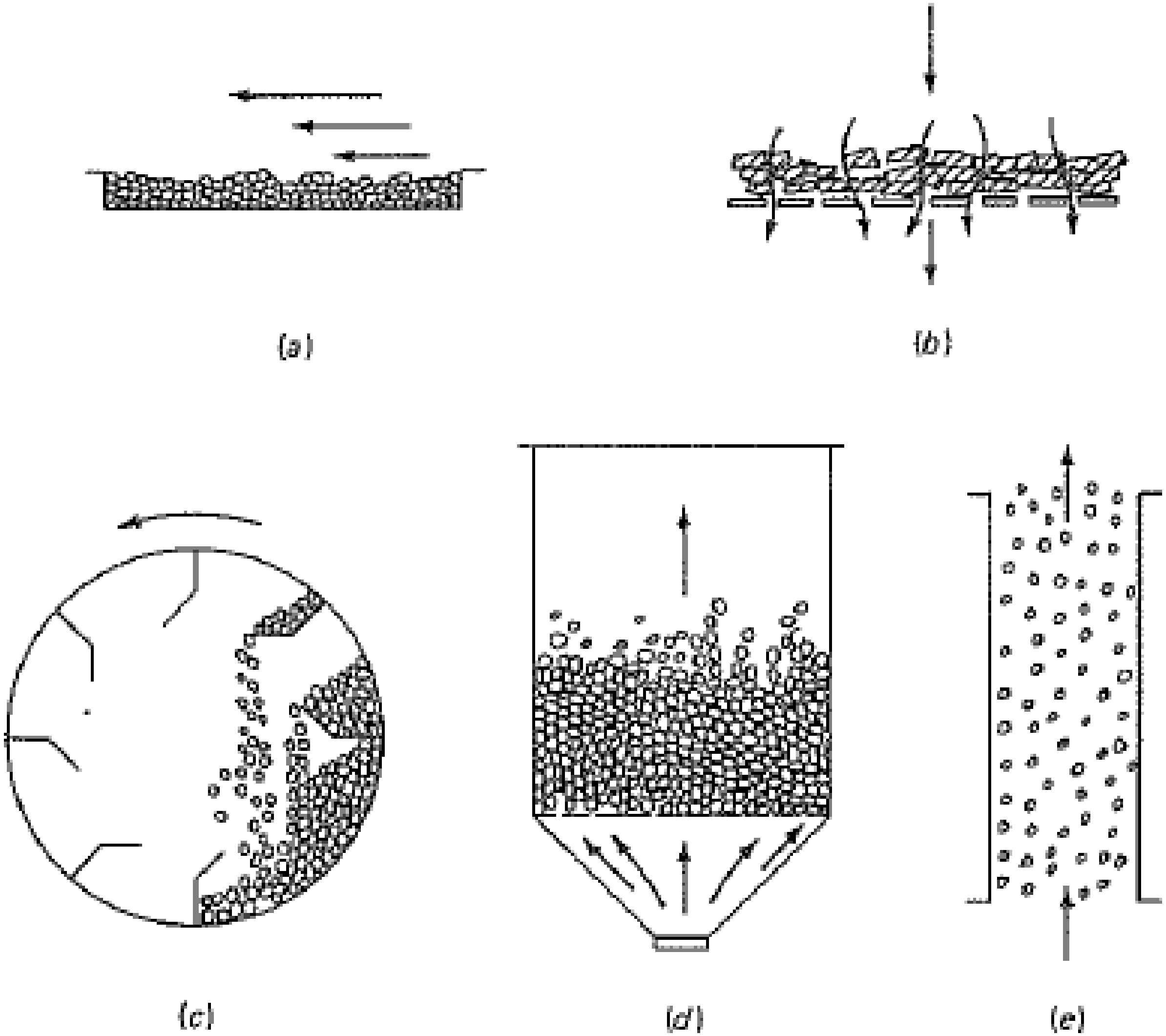
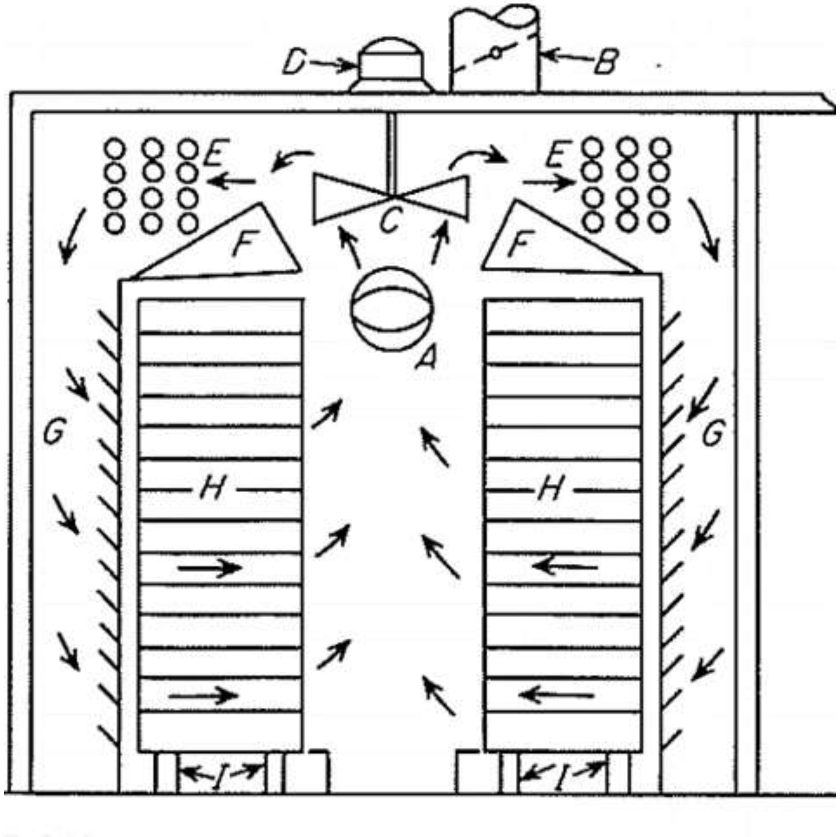


FIGURE 24.1
Patterns of gas-solid interaction in dryers: (*a*) gas flow across a static bed of solids; (*b*) gas passing through a bed of preformed solids; (*c*) showering action in a rotary dryer; (*d*) fluidized solids bed; (*e*) cocurrent gas-solid flow in a pneumatic-conveyor flash dryer.

TRAY/ TRUCK DRYER

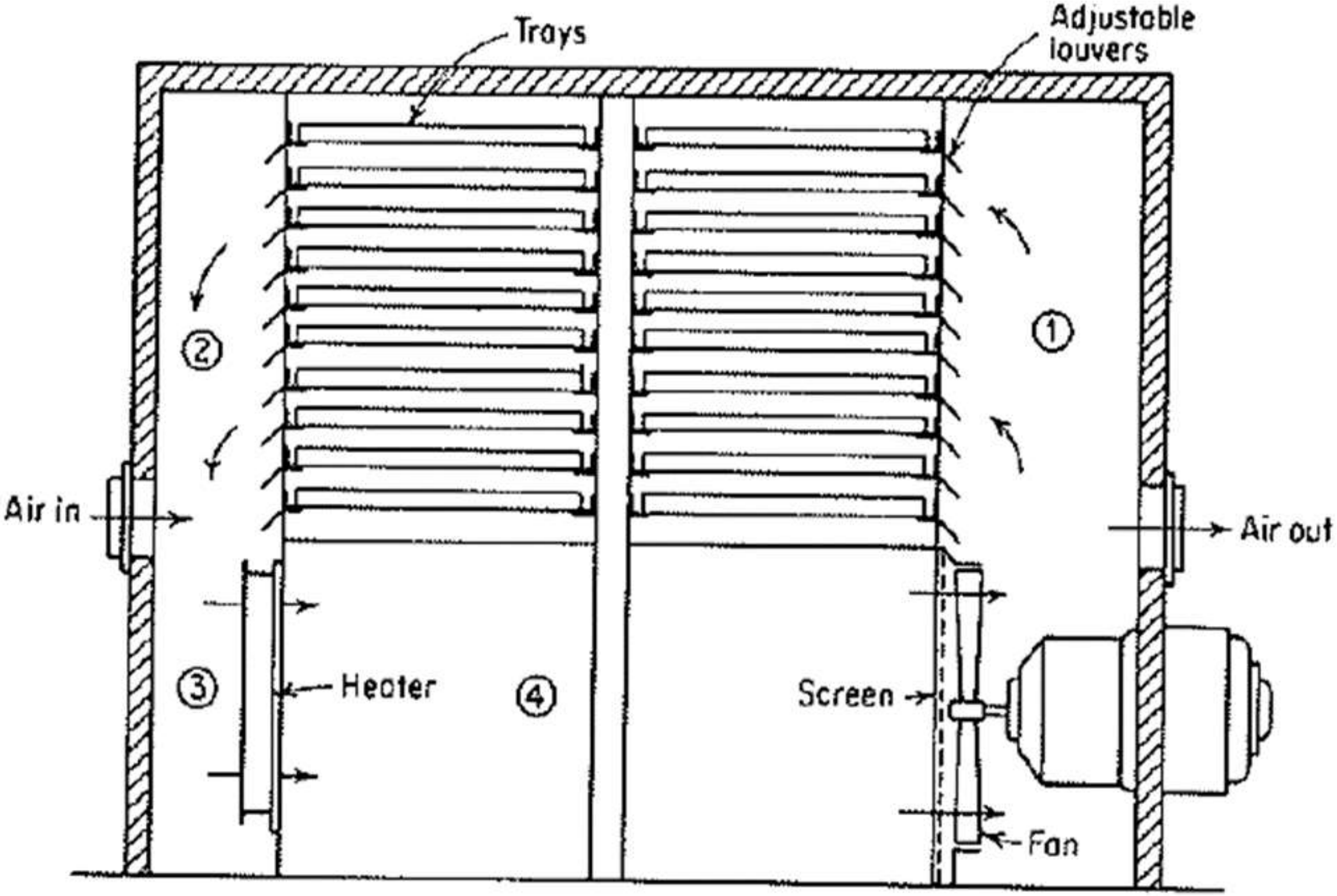
- Batch Dryer, which can be classified as:
- Direct
- Indirect – Vacuum shelf
- Truck or Tray Dryer
- Vacuum –indirect/N2 flow

- Bed depth – 5 to 15cm
- Velocity – 2-5m/s
- Time – 3-48 hours.



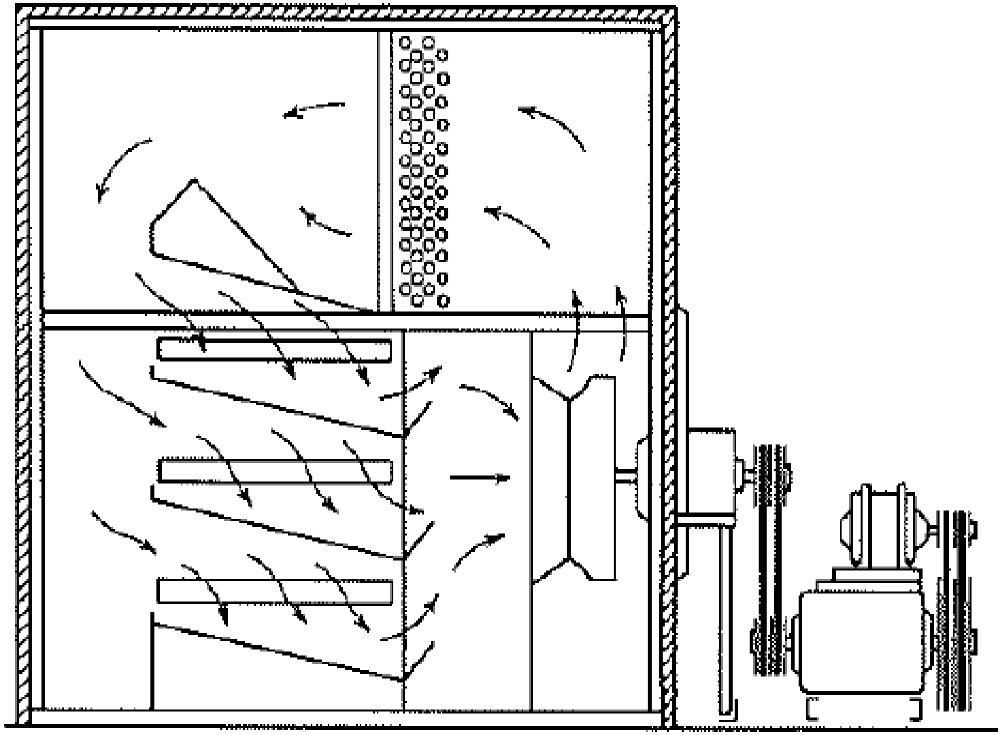
- A=Fresh air inlet; B= Exhaust
- C= Fan; D= Motor
- E= Heater; F= Deflector
- G= Baffles; H= Racks
- I= truck wheels

Cross Circulation Tray Dryer

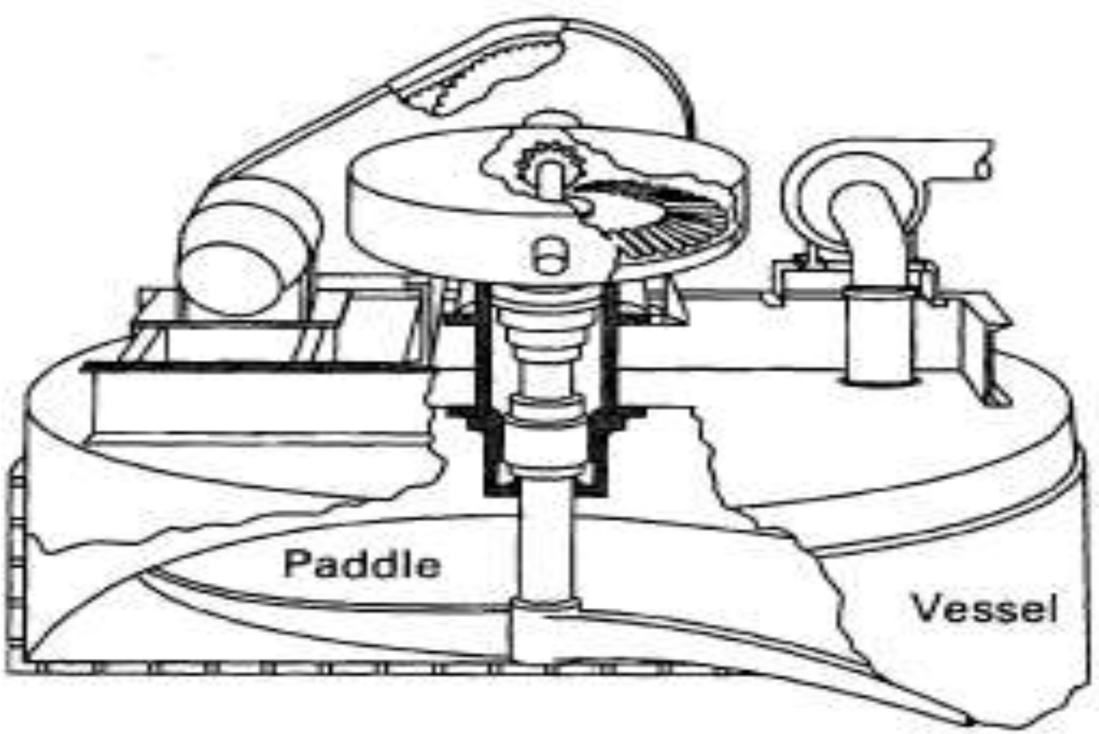


Through circulation
Tray Tower

- Through circulation dryer
- Coarse, granular flaky materials
- Sticky material by Preforming
  - Nodules by Extrusion
  - Granulation by screens
  - Briquetting

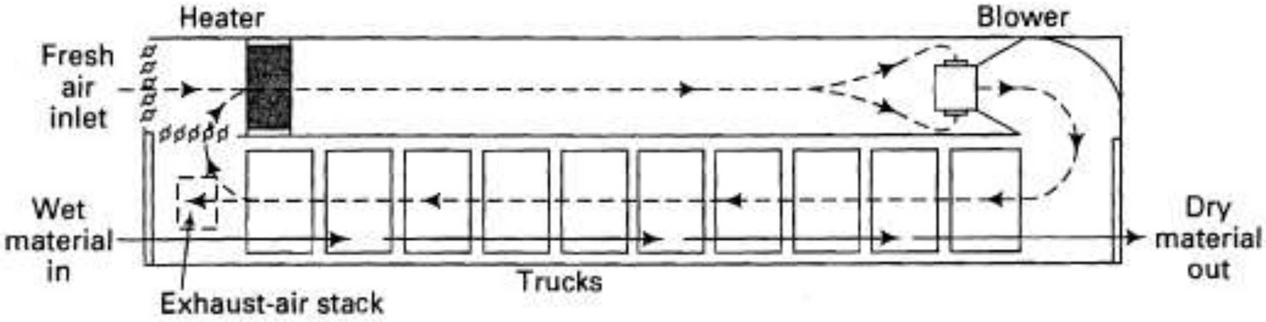


BATCH - AGITATED DRYER

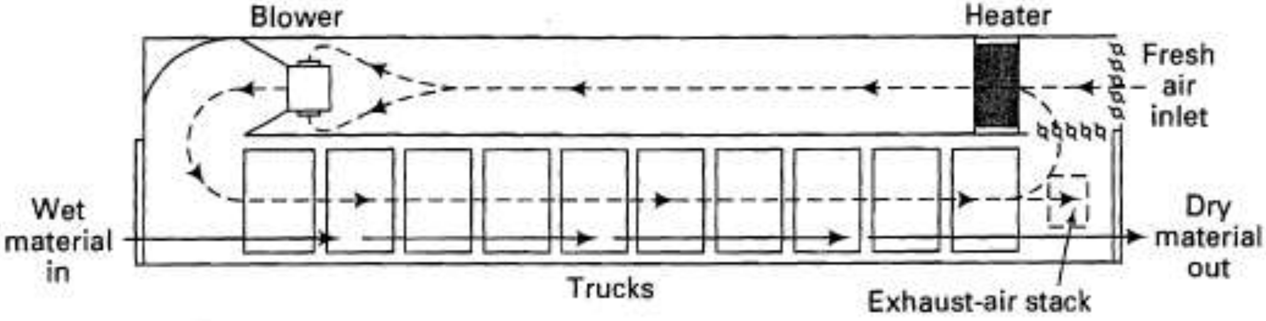


(a) Atmospheric pan dryer

Continuous – Tunnel Dryer

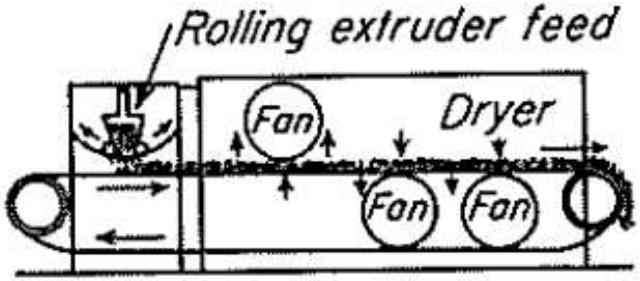


(a) Countercurrent flow

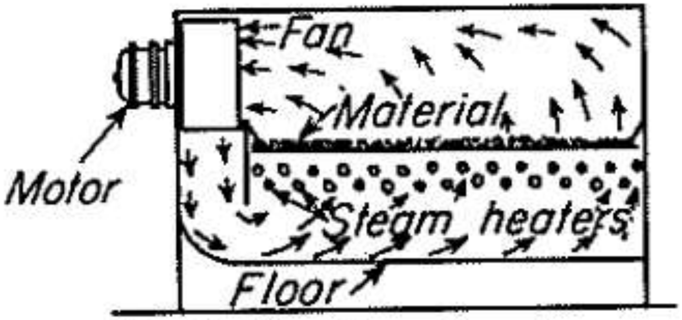


(b) Cocurrent flow

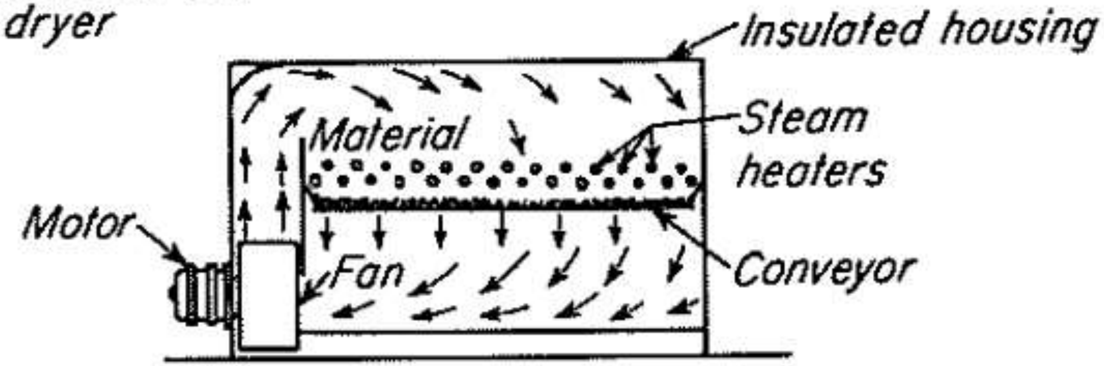
Through circulation screen dryer



(a) Path of travel of permeable bed through a 3-unit through-circulation dryer



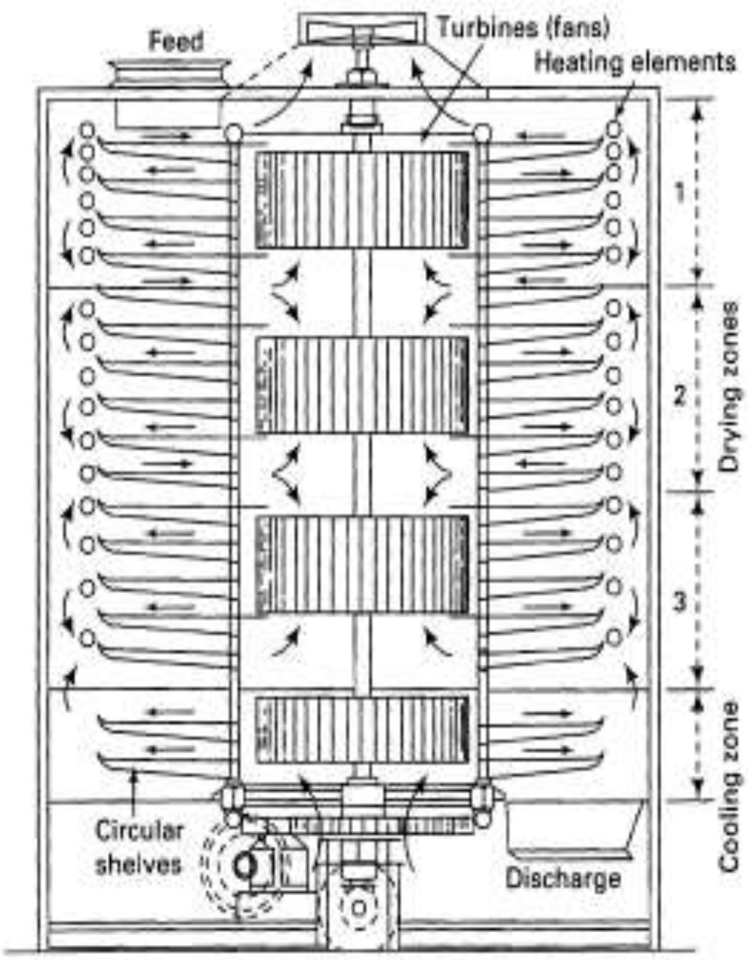
(b) Air flow in wet end



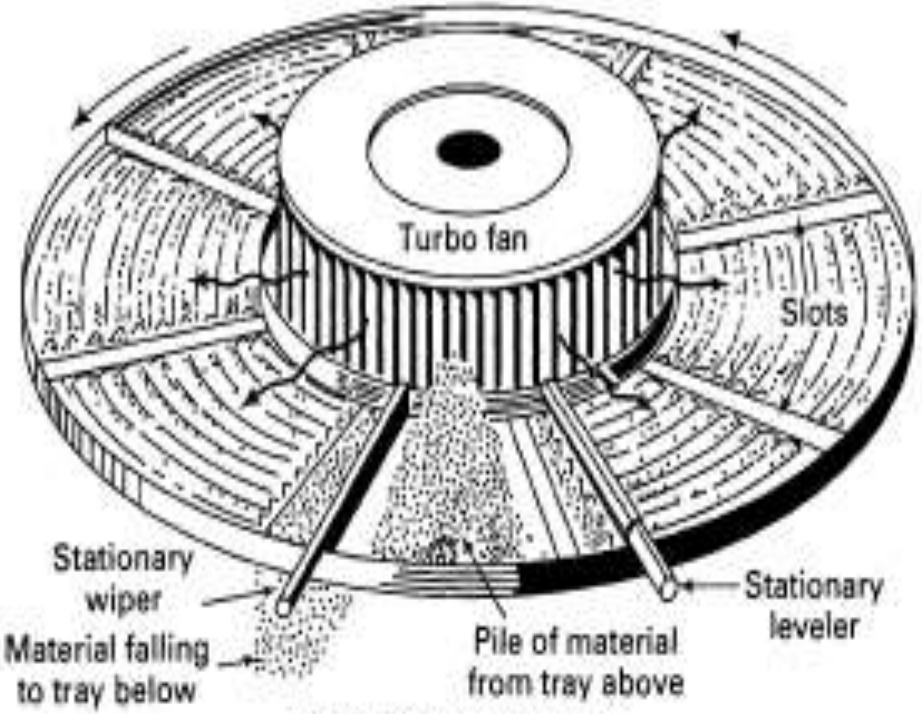
(c) Air flow in dry end

- 25 to 150mm thick bed; 2 m wide, 4 to 50m length
- 5 to 120min residence time
- Coarse, granular, flaky or fibrous material,
- Preformed sticky material

Continuous- rotating shelf dryer TOWER DRYER/TURBODRYER



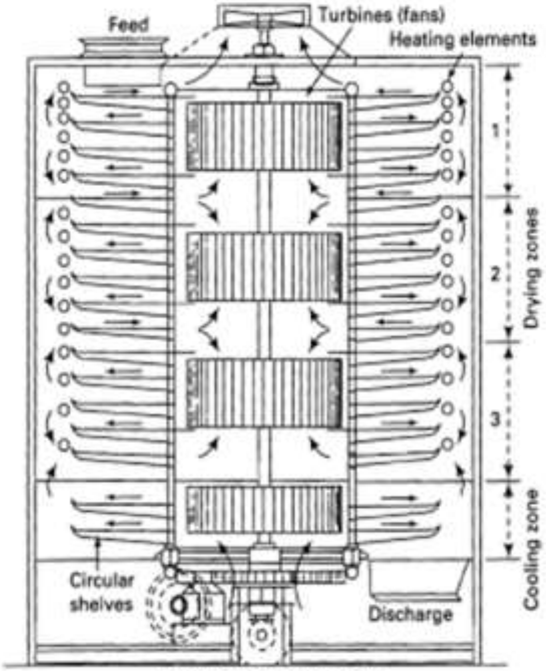
(a) Turbo-tray tower dryer



(b) Detail of annular shelf

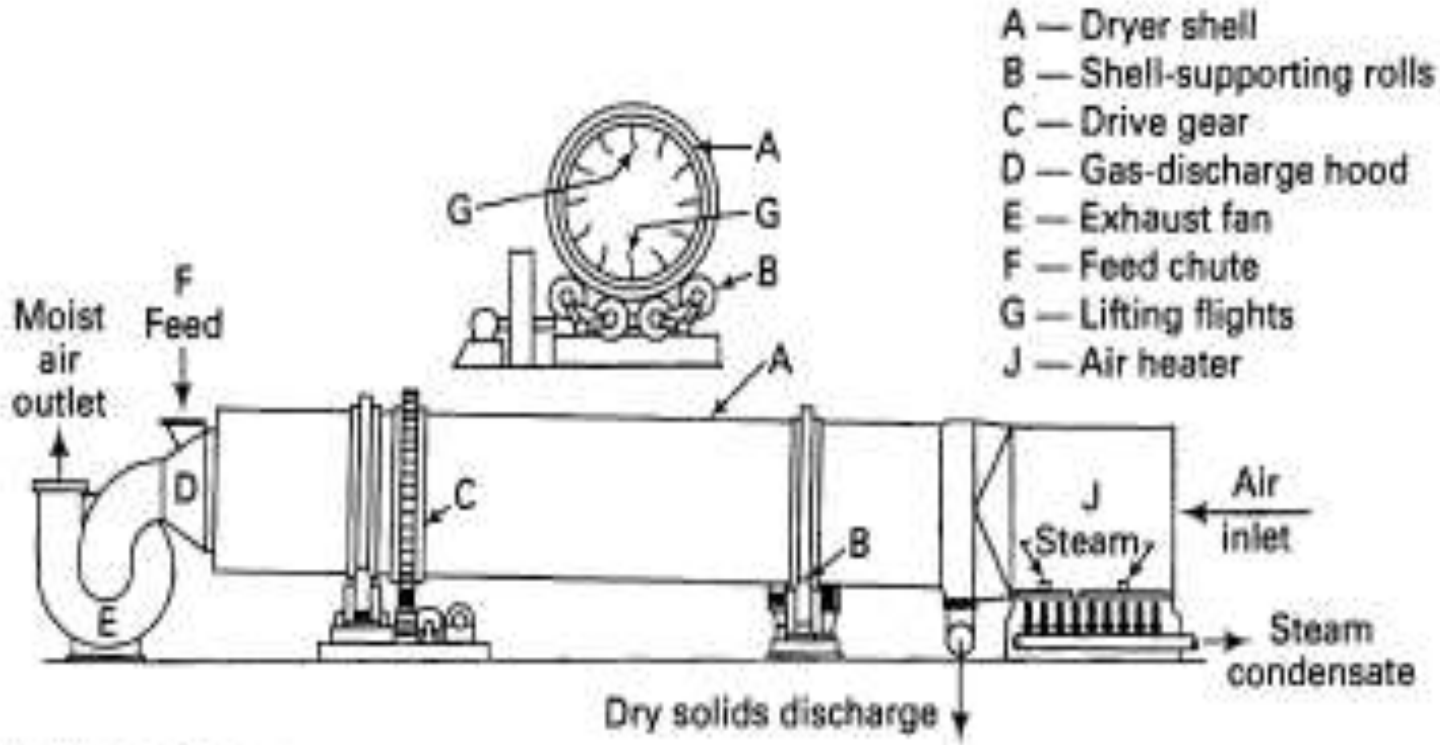
Continuous- rotating shelf dryer TOWER DRYER/TURBO DRYER

- Series of circular trays
- Solid feed dropped on the topmost tray, and exposed to hot air/gas as cross circulation
- Air is heated by heating elements all around and circulated by turbofans
- The solids are then scraped off and dropped to the tray below.
- Cross circulation and shower
- Gas velocity 0.6 to 2.4m/s
- Bottom trays are for cooling

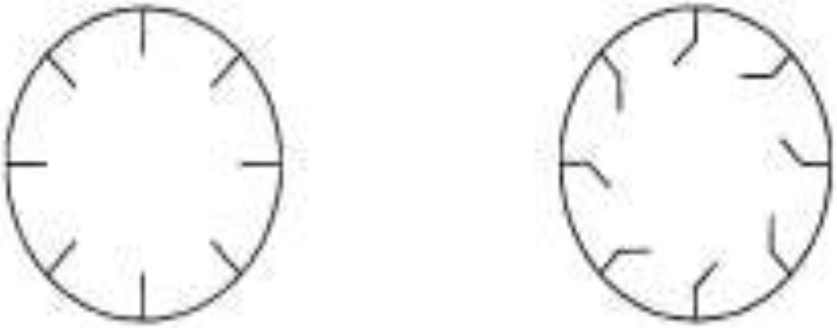


(a) Turbo-tray tower dryer

ROTARY DRYER



(a) Rotary dryer



Radial flights

45° lip flights

(b) Lifting flights

ROTARY DRYER

- Revolving cylindrical shell slightly inclined1-3 m dia, peripheral speed 20-25m/min
- Feed entered at the elevated end and flows towards the exit as the shell rotates the material are lifted by lifting flights, and then showers to the shell base.
- Hot air flows co current or counter current
- Direct or indirect
- Mass velocity of gas 2000-25000 kg/m2h
- 120-175 oC steam heated air/550-800for flue gas

DESIGNING OF ROTARY DRYER

Hold up in Rotary Dryer for zero air flow,

- $X = \frac{2.5F\prime}{SN^{0.9}D}$
- X = hold up in % dryer volume
- D =diameter, m
- N = Hz
- S = slope m/m
- F = feed rate m3/sm2

Hold up with air flow:

- $X_a = X \pm KG'$

Volumetric Heat transfer coefficient In rotary dryer

- $U_a = KG^n/D$
- U_a = volumetric HTC in W/m3K
- G in kg/m2s, D in m
- n= 0.67
- K=f(number of flights)
- Using SI units
- $K = 20(n_f - 1)$
- $U_a = 20(n_f - 1)G^{0.67}/D$

ROTARY DRYER – Design data

- Diameter of rotary dryer – 1 to several meters
- Length
  - 5 to 8D
  - Rotolouvres 2 to 4D
- Slope from free end to product end
  - 0 to -5 degrees
  - Cocurrent drying of light material +ve slope maybe used
- Peripheral speed
  - 0.1 to 0.5 m/s, 0.35 to0.4 m/s is common
- Number of flights per circle
  - 2.4 to 3D [D in feet]
- Flight depth
  - ${}^{1}/_{12}\ to\ {}^{1}/_{8}\ D$

ROTARY DRYER-Design Data

- Air inlet temperature - varies between 100 to 800oC, [200oc for heat sensitive material]
- Air outlet temperature varies between 50 and 150oC. Generally 100oC.
- Gas velocity – selected by considering the possible entrainment of solids typically 0.5 to 2.5m/s [check terminal velocities of particles]
- G, Air mass velocity 0.5 to 5.0kg/m2 s. typically 1.4kg/m2s
- Residence time : 15 minutes to 1 hour
- For most economic operation Nt is between 1.5 to 2.5.

Rotary dryers

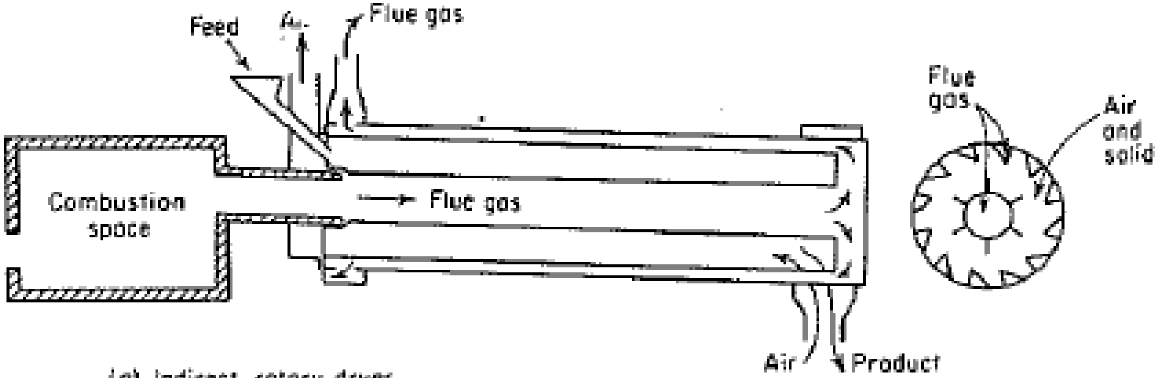
a.Indirect

b.Indirect

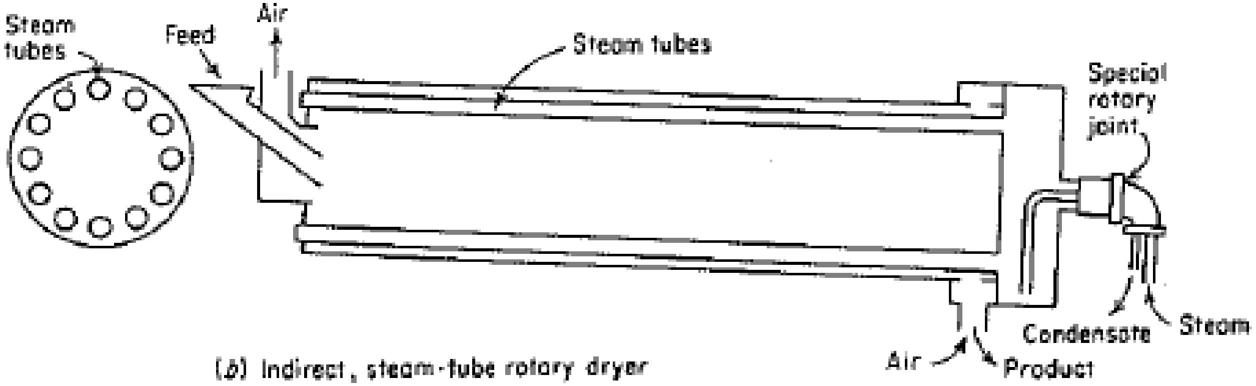
 -steam tube

c.Indirect

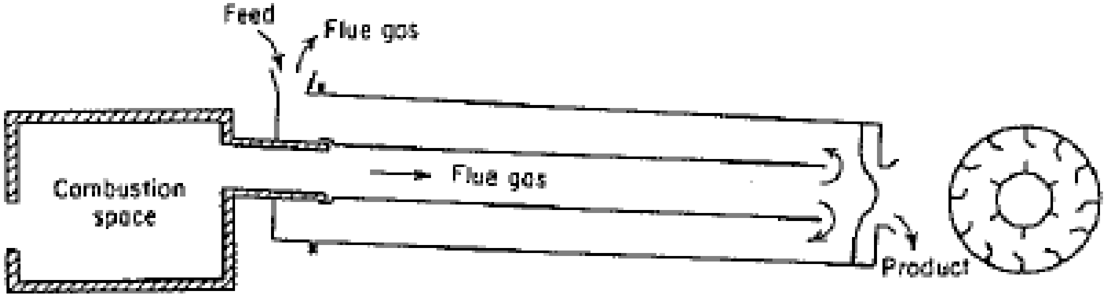
   -Direct



(a) Indirect rotary dryer



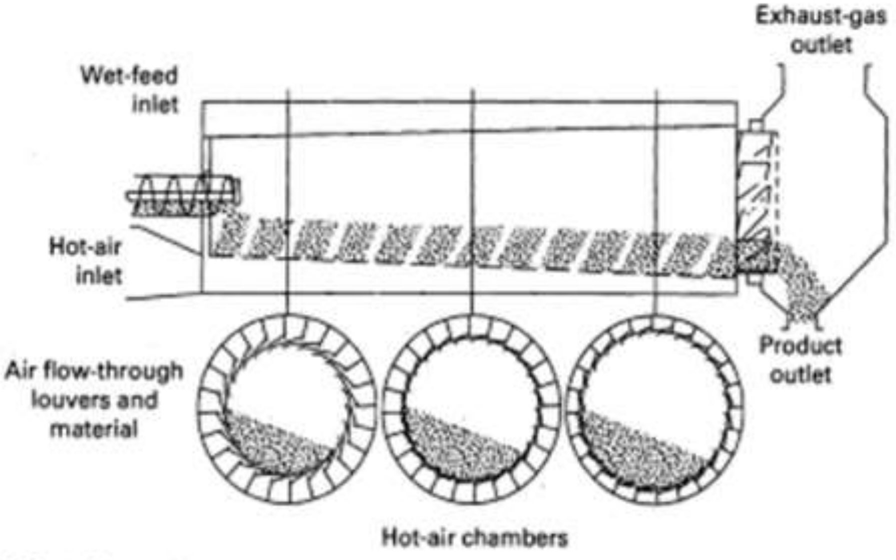
(b) Indirect, steam-tube rotary dryer



(c) Indirect-direct rotary dryer

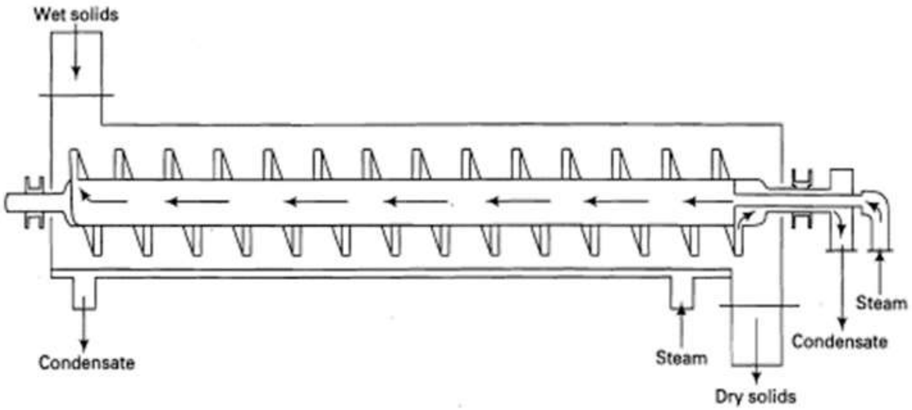
ROTOLOUVER THROUGH CIRCULATION ROTARY DRYER

- Slowly rotating taper drum fitted with louvers to support the solids
- Drying hot air is passed though the louver beneath the solid.
- No dusting as the material is not showered



(c) Roto-louvre dryer

Screw Conveyer dryer



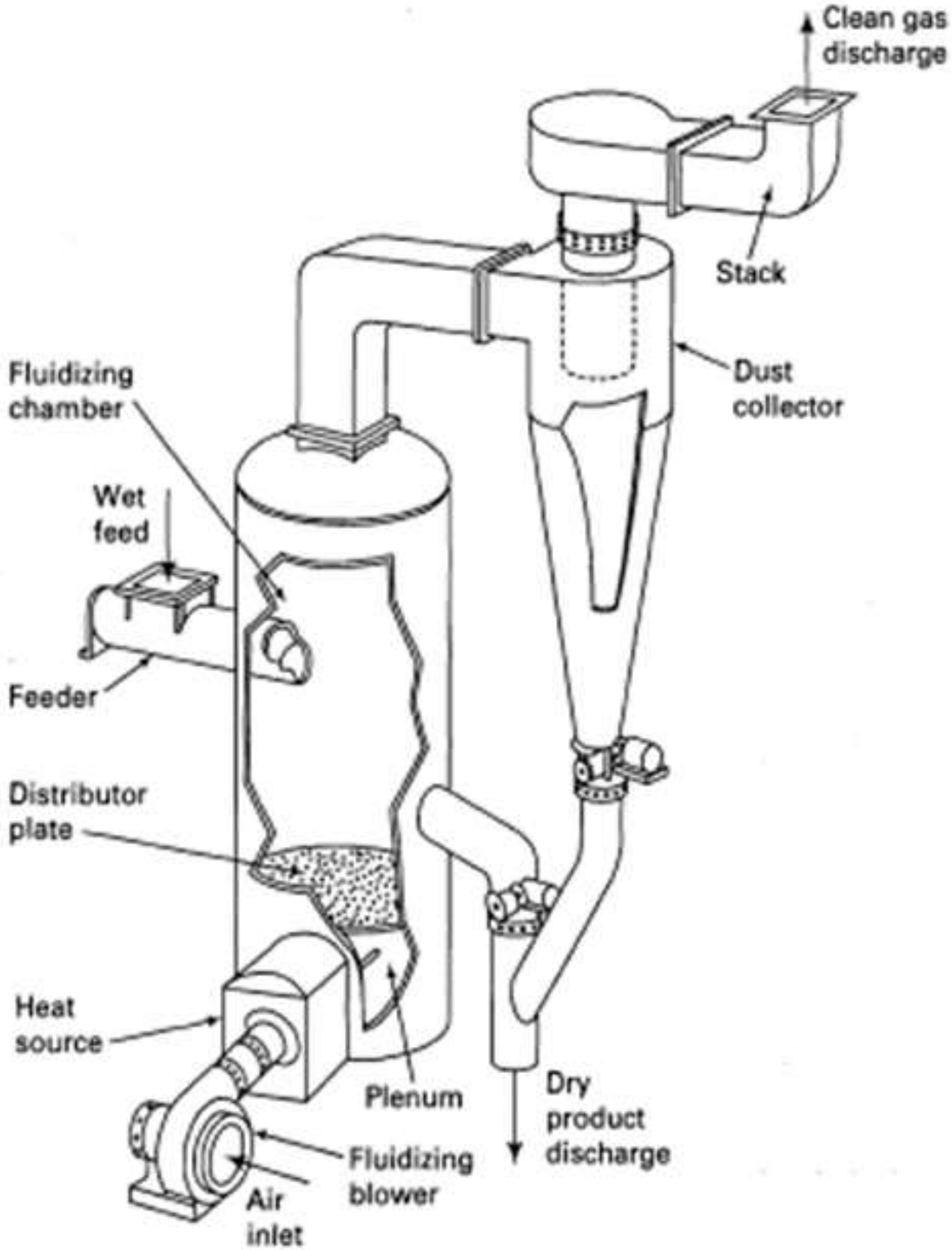
- 75 to 600 mm shell up to 6m long
- 2 to 30 rpm
- Shell 10 to 60% full
- Handles material too fine and too sticky for rotary dryer.
- Solvent recovery possible.

Fluidized bed dryer

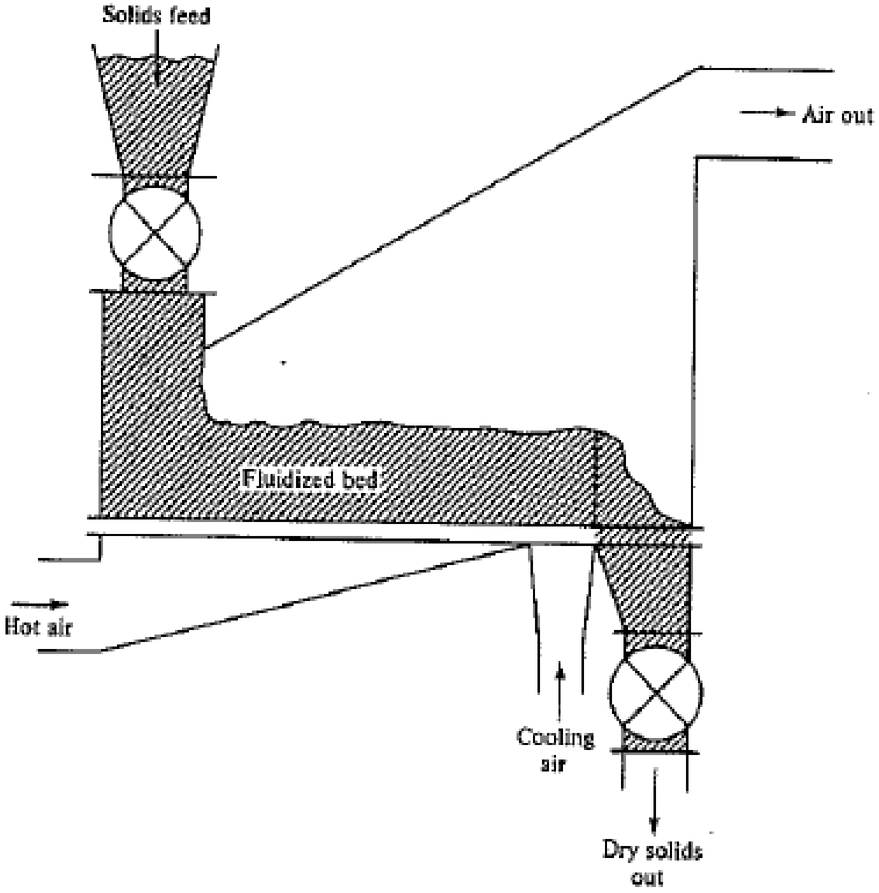
- Drying time-

  30 to 120 for surface drying

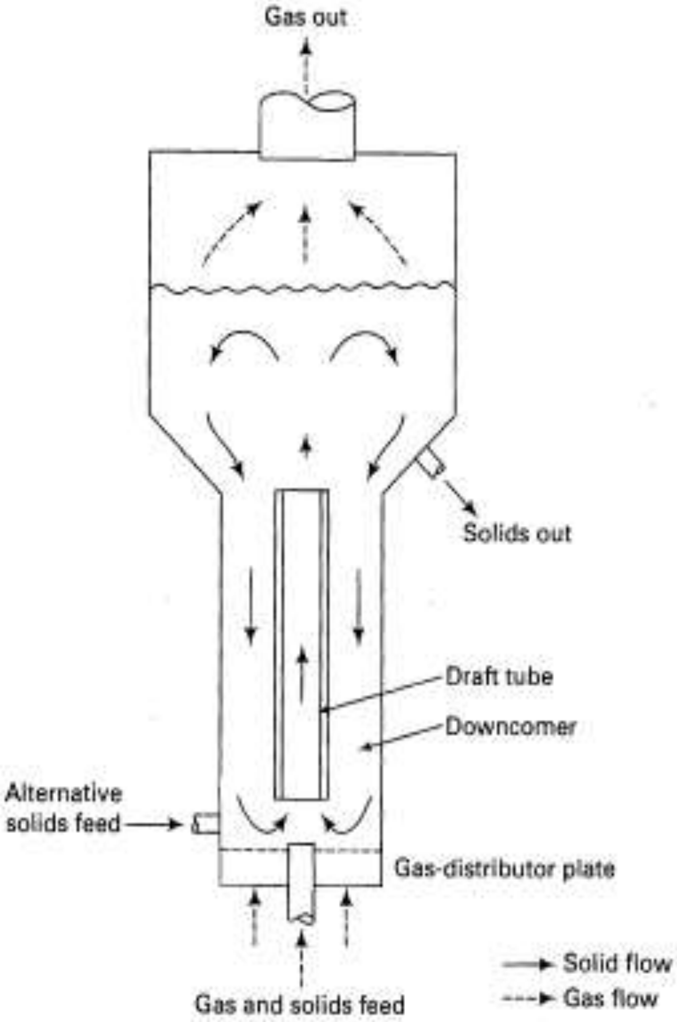
  15 to 30 minutes for internal diffusion
- Particles heated exit dry bulb temperature of gas so heat sensitive material the gas should be cool.
- Design
  - Circular cross section – Batch, replaces tray dryer
  - Rectangular – Plug flow



RECTANGULAR FLUIDIZED BED DRYER

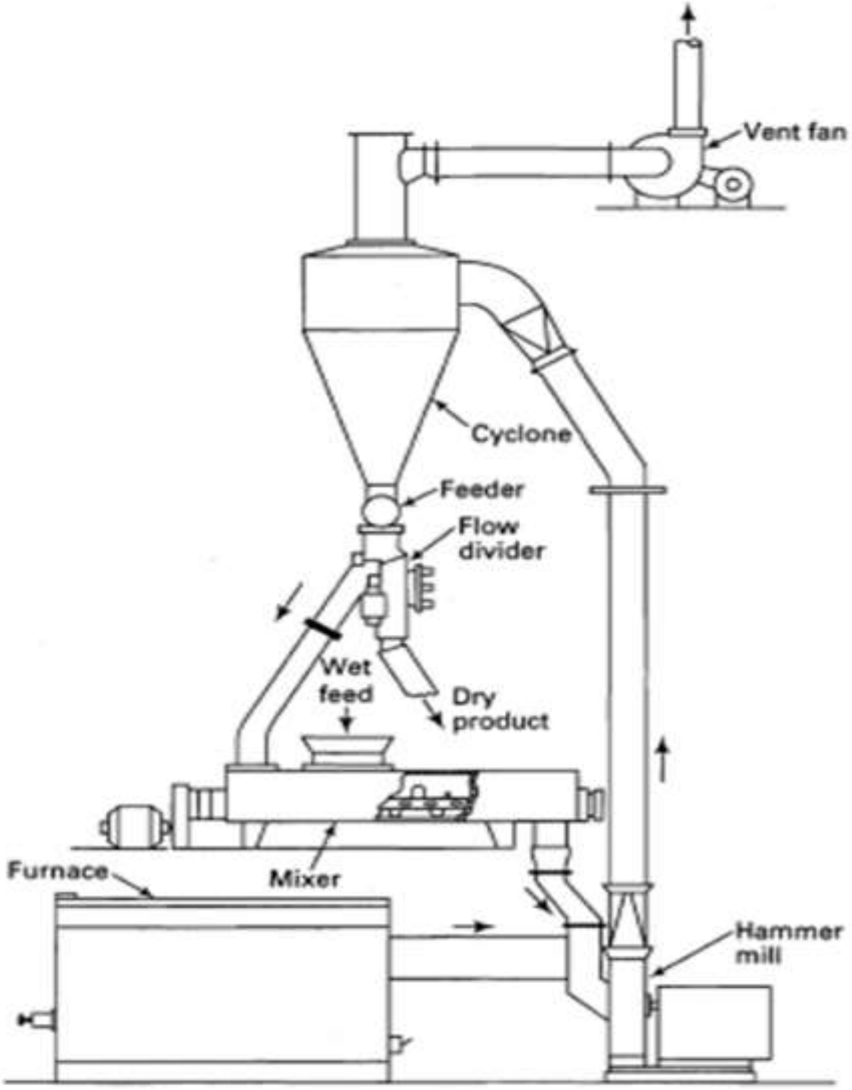


SPOUTED BED DRYER

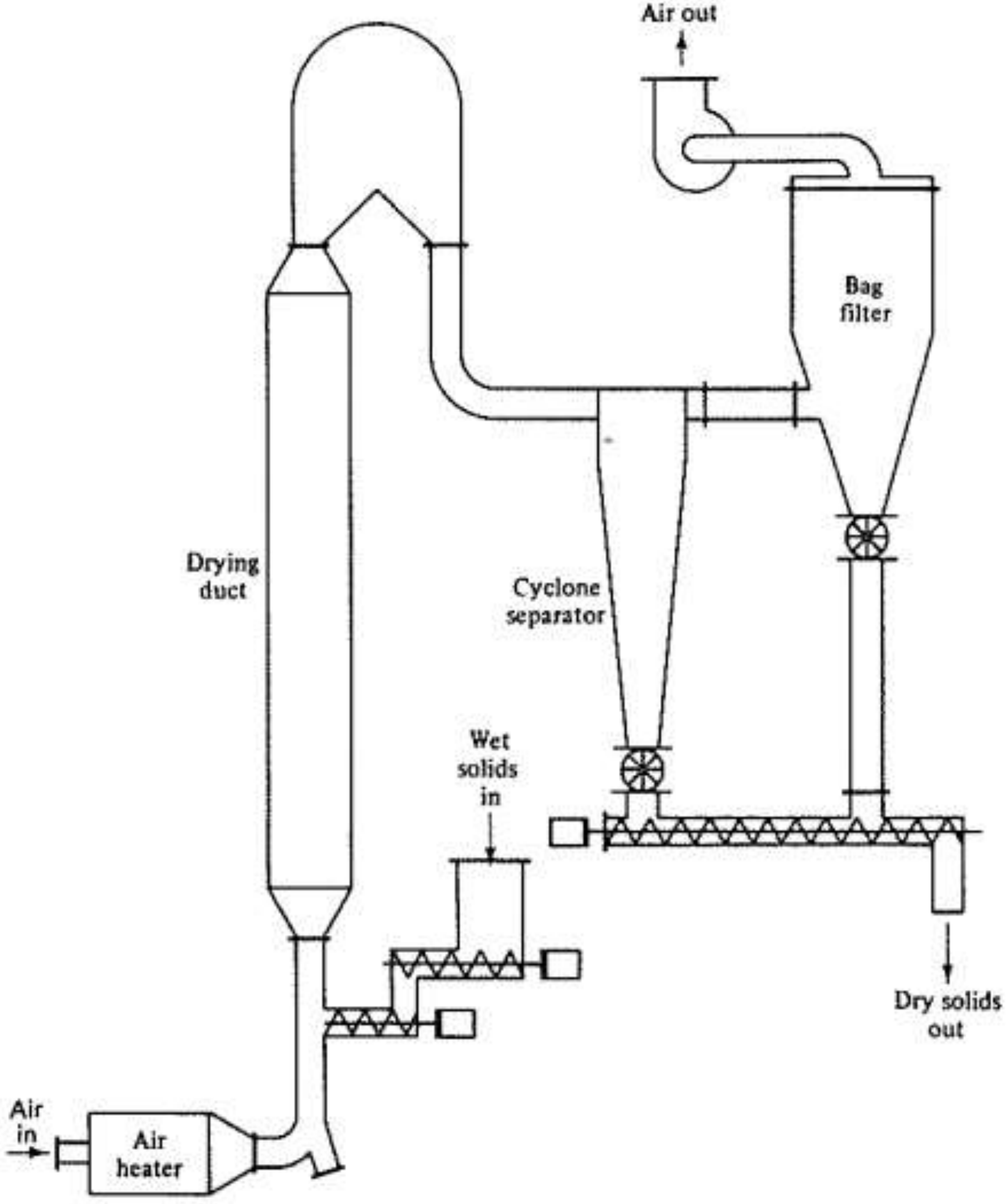


PNEUMATIC CONVEYER /FLASH DRYER

- Drying takes place during transportation
- Time 3-4 s
- Temperature of gas is high 650oC
- Heat sensitive materia
- Pulverizer incorporated for simultaneous size reduction and drying

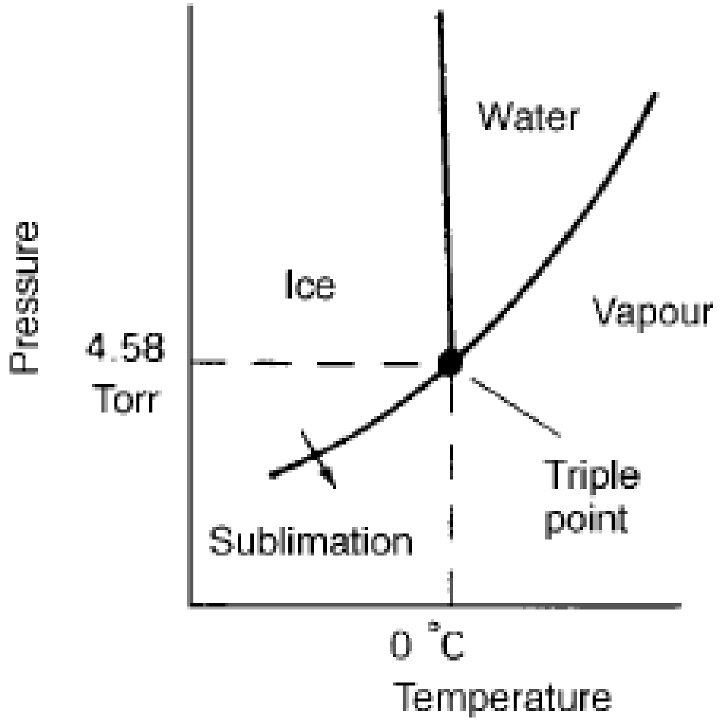


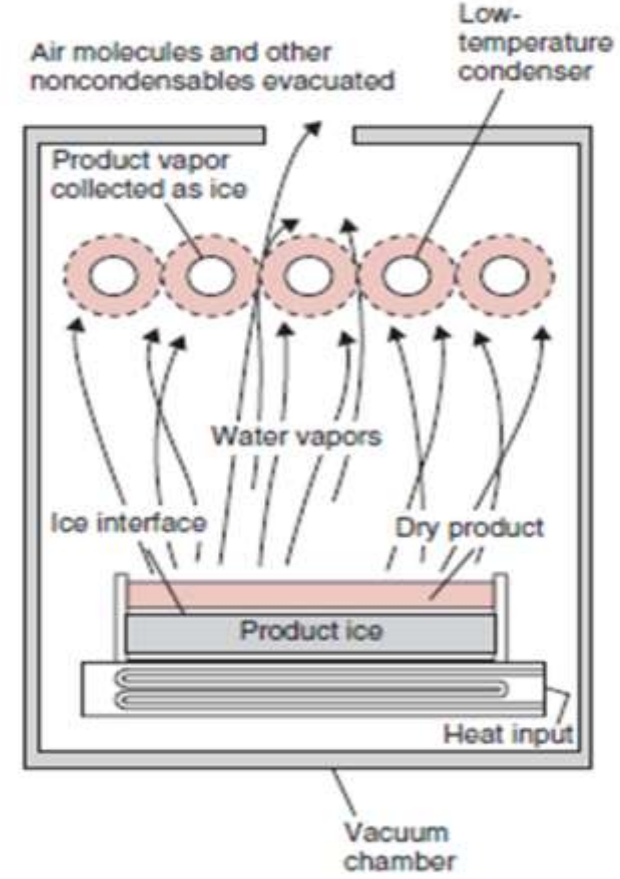
- Pneumatic Dryer



FREEZE DRYING

- Freeze-drying is accomplished by reducing the product temperature so that most of the product moisture is in a solid state, and by decreasing the pressure around the product, sublimation of ice can be achieved. When product quality is an important factor for consumer acceptance, freeze-drying provides an alternative approach for moisture removal.
- The heat- and mass-transfer processes during freeze-drying are unique. Depending on the configuration of the drying system , heat transfer can occur through a frozen product layer or through a dry product layer. Obviously, heat transfer through the frozen layer will be rapid and not rate-limiting. Heat transfer through the dry product layer will be at a slow rate due to the low thermal conductivity of the highly porous structure in a vacuum. In both situations, the mass transfer will occur in the dry product layer. The diffusion of water vapor would be expected to be the rate-limiting process because of the low rates of molecular diffusion in a vacuum.
- The advantages of the freeze-drying process are superior product quality resulting from low temperature during sublimation and the maintenance of product structure. These advantages are balanced against the energy-intensive aspects of the product freezing and vacuum requirements.





- If the water vapour pressure of a food is held below 4.58 Torr (610.5 Pa) and the water is frozen, when the food is heated the solid ice sublimes directly to vapour without melting . The water vapour is continuously removed from the food by keeping the pressure in the freeze drier cabinet below the vapour pressure at the surface of the ice, removing vapour with a vacuum pump and condensing it on refrigeration coils. As drying proceeds a sublimation front moves into the frozen food, leaving partly dried food behind it.

PROCESS PARAMETERS: Pressure and Condenser temperature

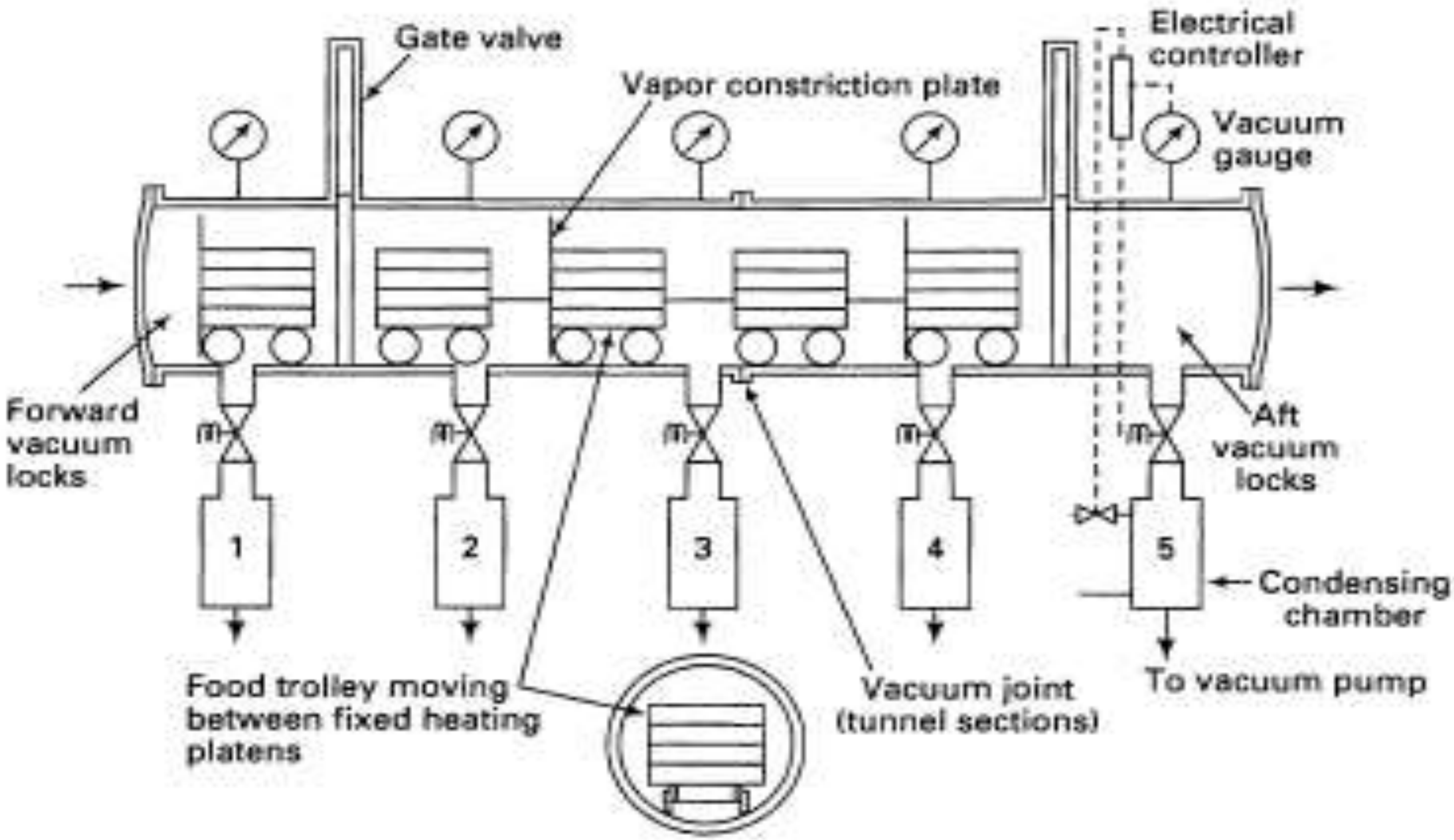
The factors that control the water vapour pressure gradient are:

- ➢ • the pressure in the drying chamber
- ➢ • the temperature of the vapour condenser, both of which should be as low as economically possible
- ➢ • the temperature of ice at the sublimation front, which should be as high as possible, without melting.
- In practice, the lowest economical chamber pressure is approximately 13 Pa and the lowest condenser temperature is approximately 35ºC.

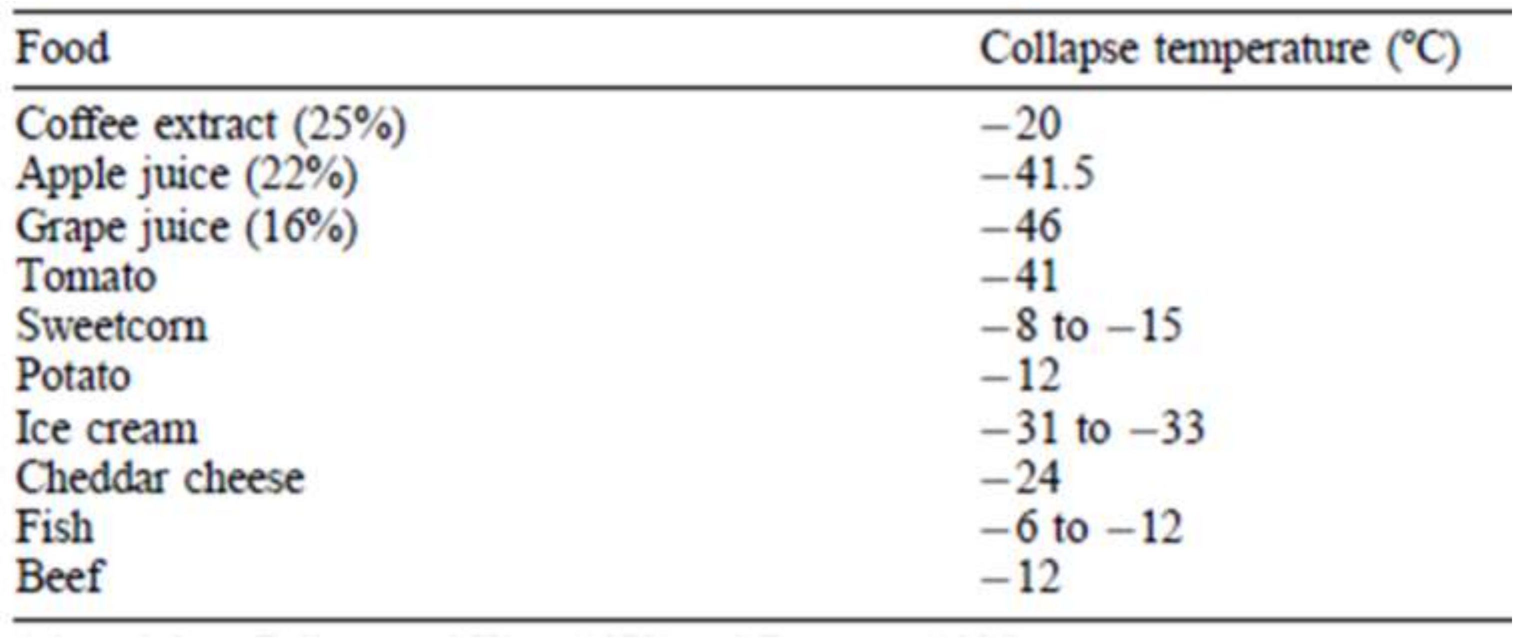
METHOD OF SUPPLYING HEAT

- Radiant Heating
- Contact heating by heating from shelves, opposite to the side from where evaporation takes place
- Microwave and dielectric heating.
- For granular material, hot air

Tunnel freeze dryer



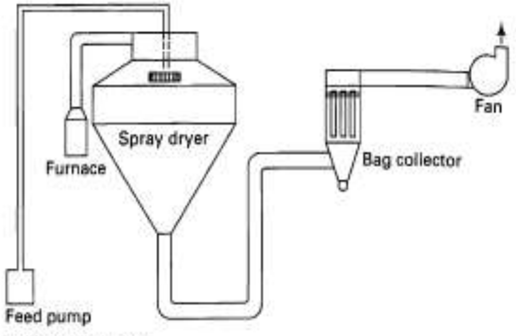
COLLAPSE TEMPERATURE



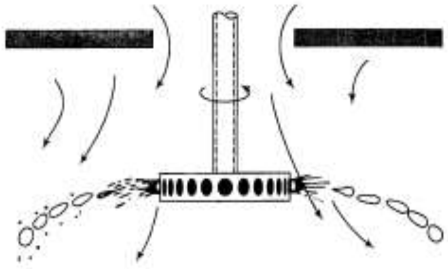
Food	Collapse temperature (°C)
Coffee extract (25%)	–20
Apple juice (22%)	–41.5
Grape juice (16%)	–46
Tomato	–41
Sweetcorn	–8 to –15
Potato	–12
Ice cream	–31 to –33
Cheddar cheese	–24
Fish	–6 to –12
Beef	–12

- Theoretically the temperature of the ice could be raised to just below the freezing point. However, above a certain critical *collapse temperature* the concentrated solutes in the food are sufficiently mobile to flow under the forces operating within the food structure. When this occurs, there is an instantaneous irreversible collapse of the food structure, which restricts the rate of vapour transfer and effectively ends the drying operation..

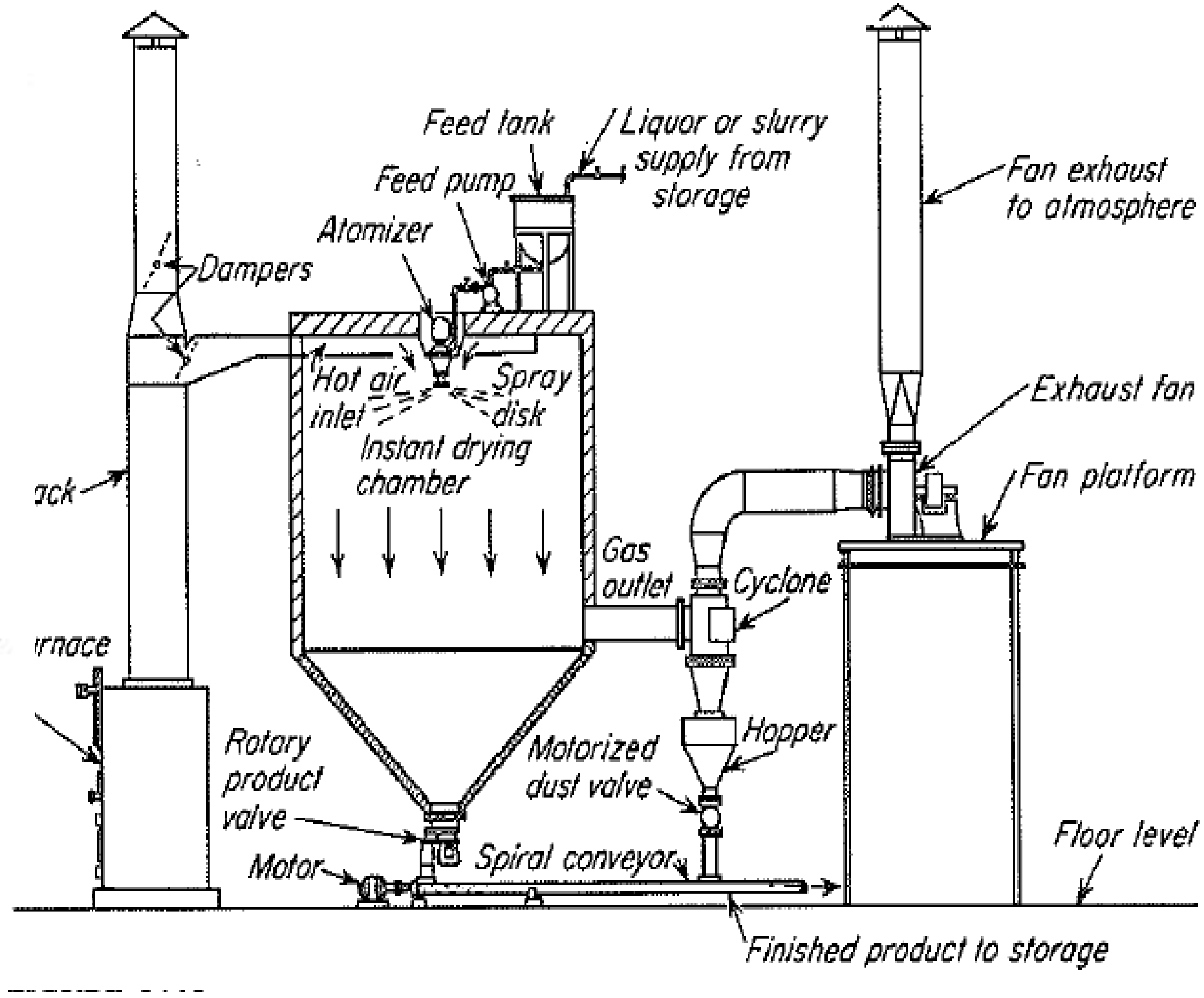
SPRAY DRYER



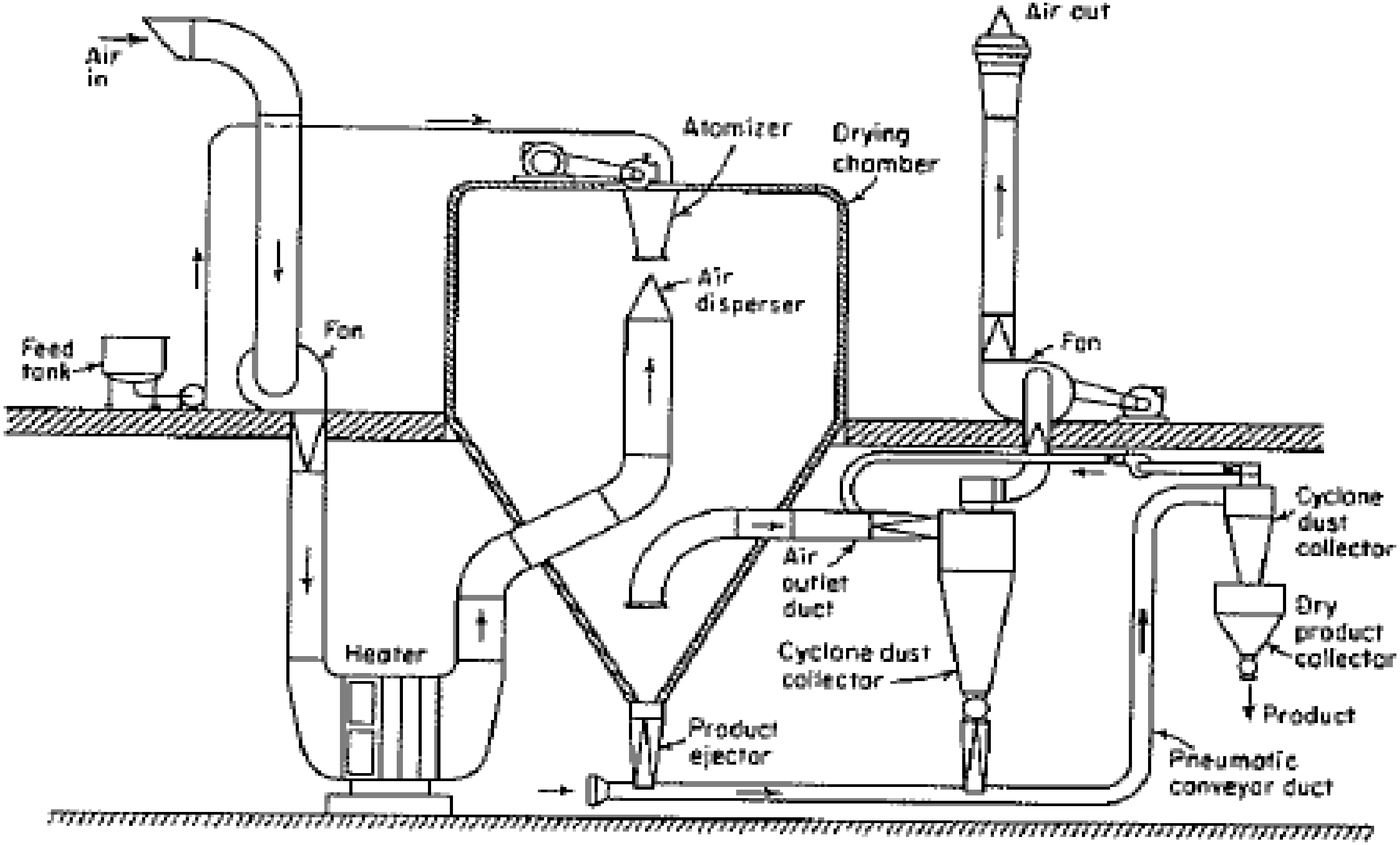
(a) Process system



(b) Centrifugal disk atomizer



SPRAY DRYER


Air in
Air out
Atomizer
Drying chamber
Air disperser
Feed tank
Fan
Fan
Heater
Air outlet duct
Cyclone dust collector
Cyclone dust collector
Dry product collector
Product
Product ejector
Pneumatic conveyor duct

SPRAY DRYER

- Large diameter to prevent the droplets from touching the walls – 2.5 to 9 m diameter Height 25 m
- Hot air 80 to 760oC[cold air near the wall so that they do not stick to wall]
- Average drop diameter 20 micron disk atomizer to 180 micronspray nozzle.
- Residence time – 36 seconds in cocurrent, and 25 to 30 seconds in countercurrrent.

SPRAY DRYER

The advantages of spray dried products:

- Very short drying time, so heat sensitive material can be handled
- Products are hollow and porous, making the product easily reconstituted.
- Products can be made free flowing, bulk density, appearance, flow properties.
- It can yield dry products directly from slurry, solution
- Can combine various steps – evaporator, crystalizer, dryer, size reduction, size classification.

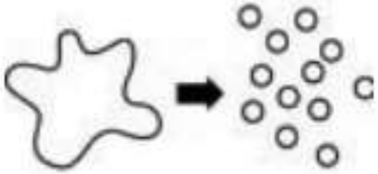
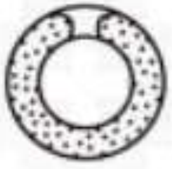
Major limitations are :

- Bulky
- Poor in thermal efficiency as a large volume of hot gas is discharged.

APPLICATIONS –

- Chemical Industry :Calcium carbonate, aluminium chloride, zeolite etc’:
- General Industry: detergent, latex, dyes, aromatics, perfumes
- Medical and pharmaceuticals : blood plasma, vaccinations albumin, plant extracts
- Food : milk, baby food, coffee, egg, fruit juice etc.
- Microencapsulation - spray drying of prepared emulsions consisted of water solution of modified cellulose and fish oil.
- Englobing

APPLICATION: SPRAY DRYING, MICRONIZATION, MICROENCAPSULATION, ENCLOBING

Application	Goal / use	Practicalapplication
Spray drying 	Drying of inorganic and organic products	corn starch pigments dried milk
Micronization 	Reduction of a product's par- ticle size	salt dyes
Micro encapsulation 	A liquid product is embedded in a solid matrix	perfumes strawberry aroma peach oil
Englobing 	A solid product is embedded in another solid or a mixture of solids	carotenoids in gelatins

SPRAY DRYER

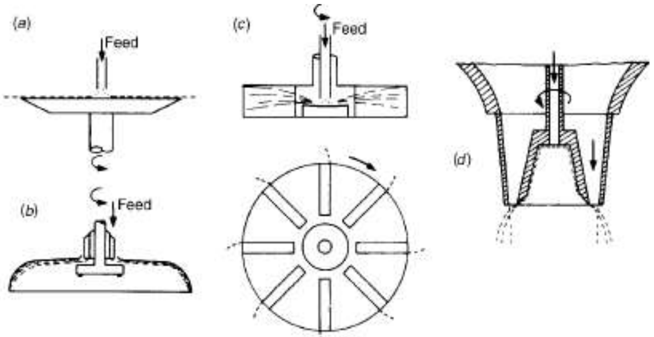
- Drying of drops:
- Evaporation rate depends on contact time , which is dependent on the terminal velocity of particle and height of dryer.
- Two main periods of evaporation are:
  1. Initial period of high velocity
  2. Free fall region after decelerated to terminal velocity
- Drops attaining terminal velocity the rate of evaporation can be determined by approximation equation for evaporation of pure liquid.

$$t = \frac{\rho\lambda\,(d_o{}^2 - d_t{}^2)}{8\,k_f \Delta T}$$

$t = time\ of\ drying$, d_o = initial diameter, d_t = dia at time t, ρ= density k_f= thermal conductivity of fluid, ΔT = Temperature difference, λ = *latent heat*

- Then solid deposition commences, a crust or solid film is rapidly formed which increases the resistance to transfer

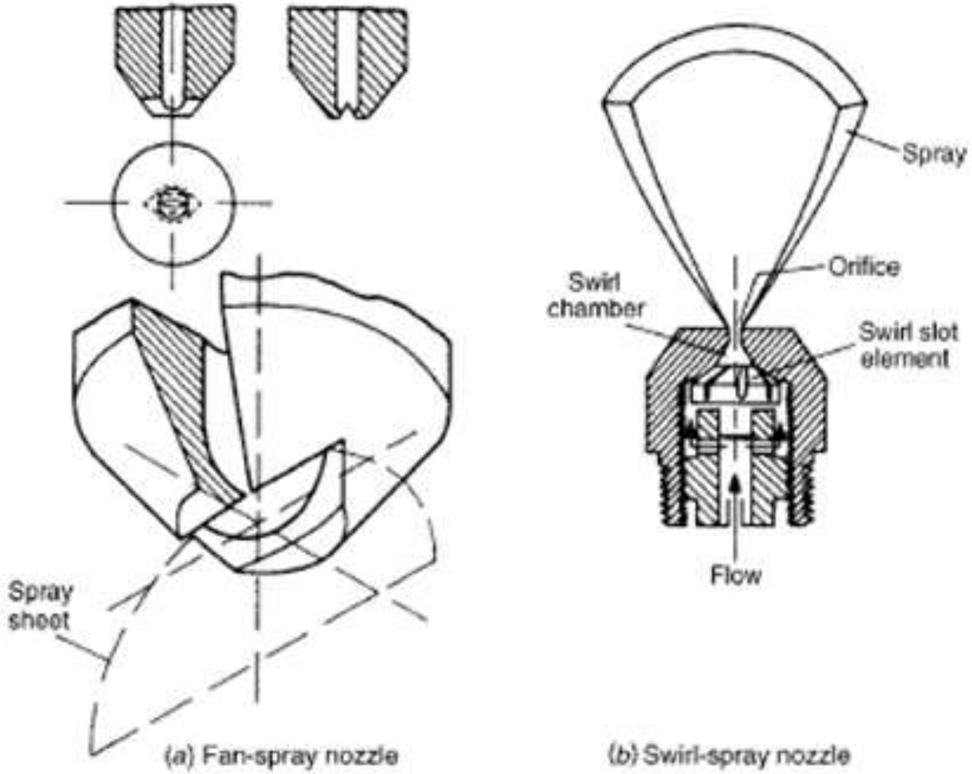
SPRAY DRYER:
The types of atomizer



(i) high pressure nozzle- genrally may be fan type and swirl type,

(ii) high speed disk atomizer – for very large capacity. The diameter of discis range between 25 to 450mm.The rotational speed – 200Hz – 1000Hz

(iii) Gaseous energy – two fluid atomizer- with high speed gas stream impinges [velocity between 50m/s to sonic velocity] on a liquid jet or film. This gives droplets of 20 micron, finer than other types of atomizer



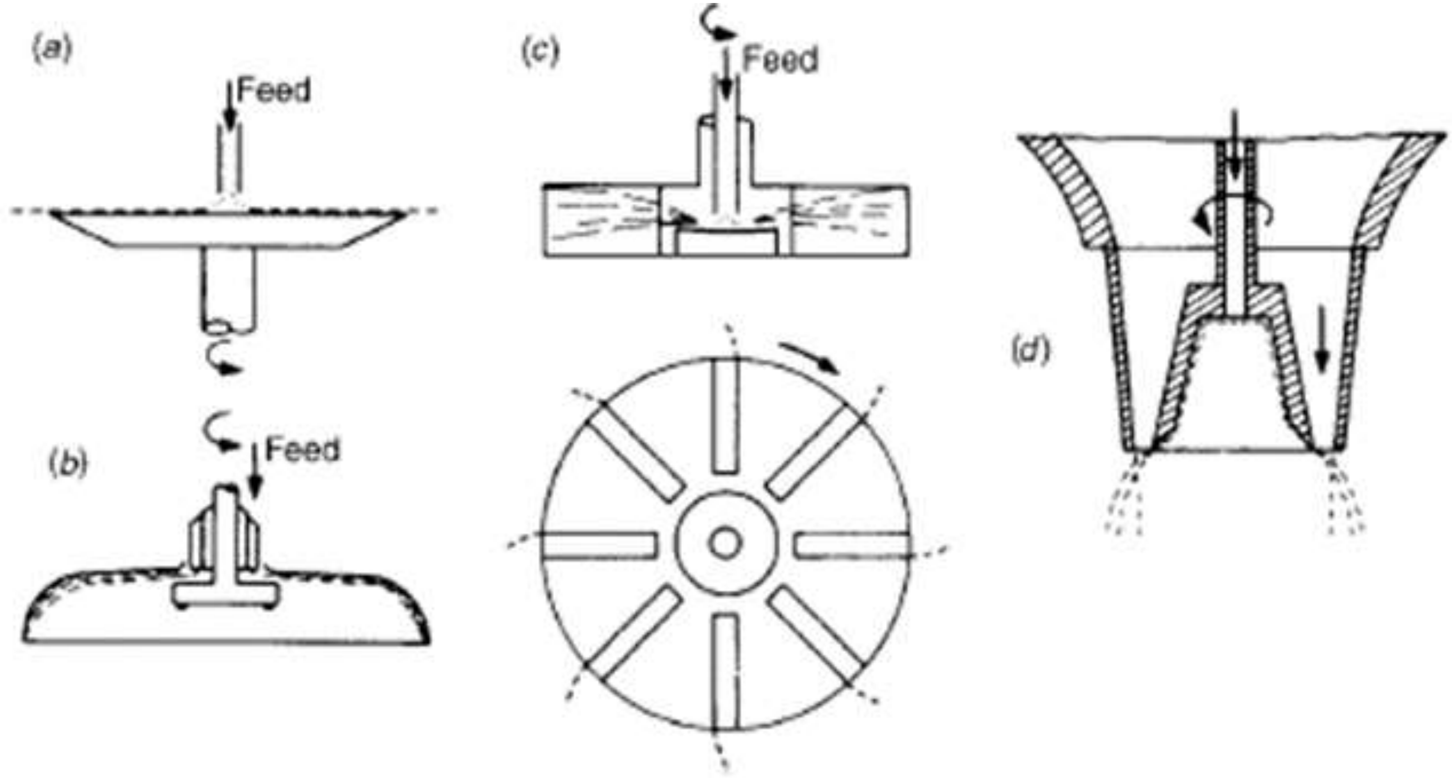
(a) Fan-spray nozzle

(b) Swirl-spray nozzle

Pressure atomizer

SPRAY DRYER: DISC ATOMIZER

(a)Sharp edged flat disc (b)bowl (c)Vane-disk (d)Air Blast



SPRAY DRYER :DISK ATOMIZER

- DD$\frac{\overline{D_S}}{r} = 0.4\left(\frac{X}{\rho_L n r^2}\right)^{0.6}\left(\frac{\mu}{X}\right)^{0.2}\left(\frac{\sigma \rho_L L_p}{X^2}\right)^{0.1}$

- $\overline{D_S}$= Average drop diameter
- r= disk radius
- X= spray mass rate per unit length of disk periphery
- ρ_L=Density of liquid
- $\rho_L n r^2$= disk rotational speed
- μ= Viscosity of liquid
- $\sigma \rho_L L_p$
- $\sigma \rho_L L_p$= disk periphery$2\pi r$

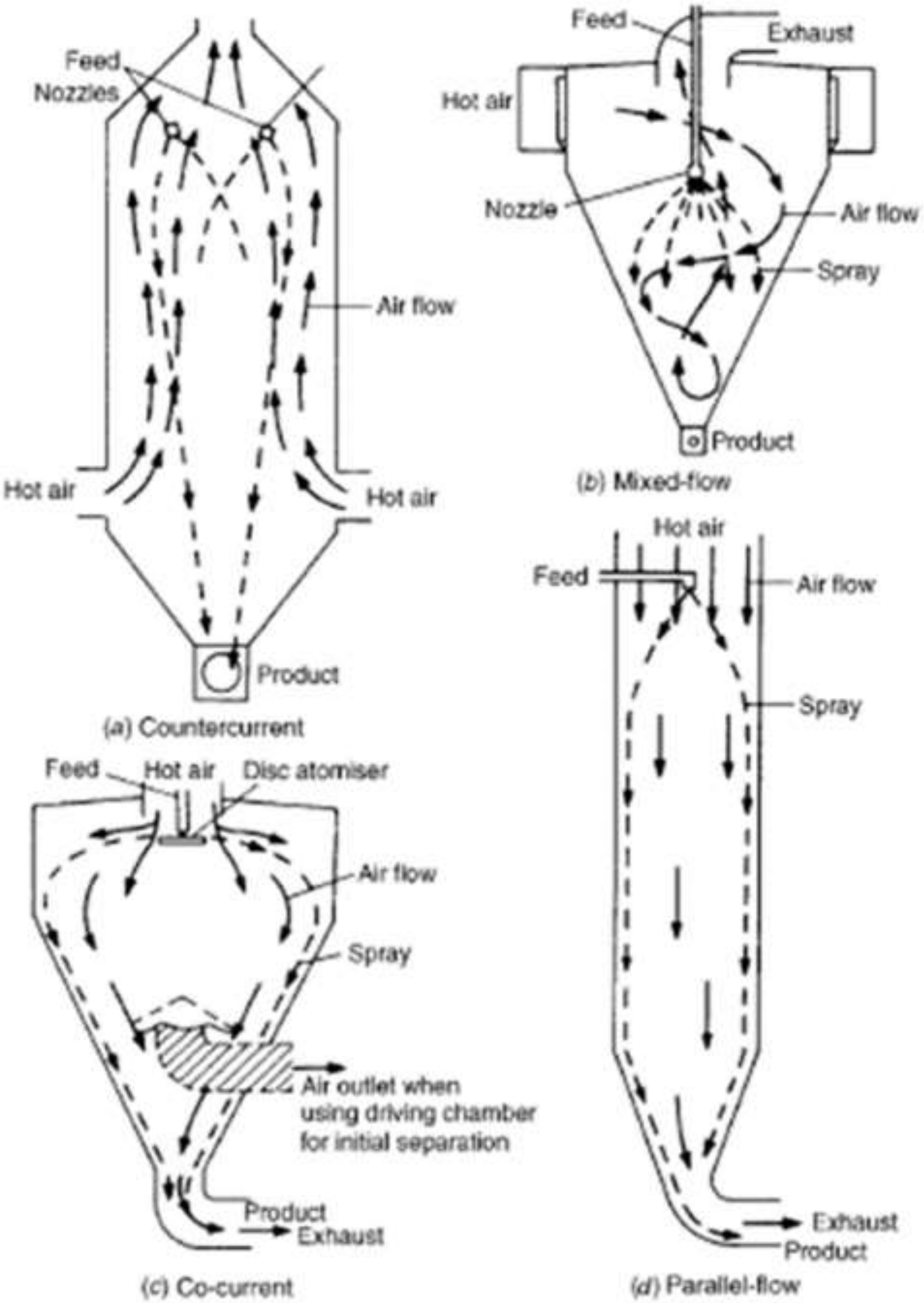
TYPES OF CONTACT GAS SOLID in SPRAY DRYER

(a) Counter current

(b) Mixed Flow

(c) Co current

(d) Parallel flow



(a) Countercurrent

(b) Mixed-flow

(c) Co-current

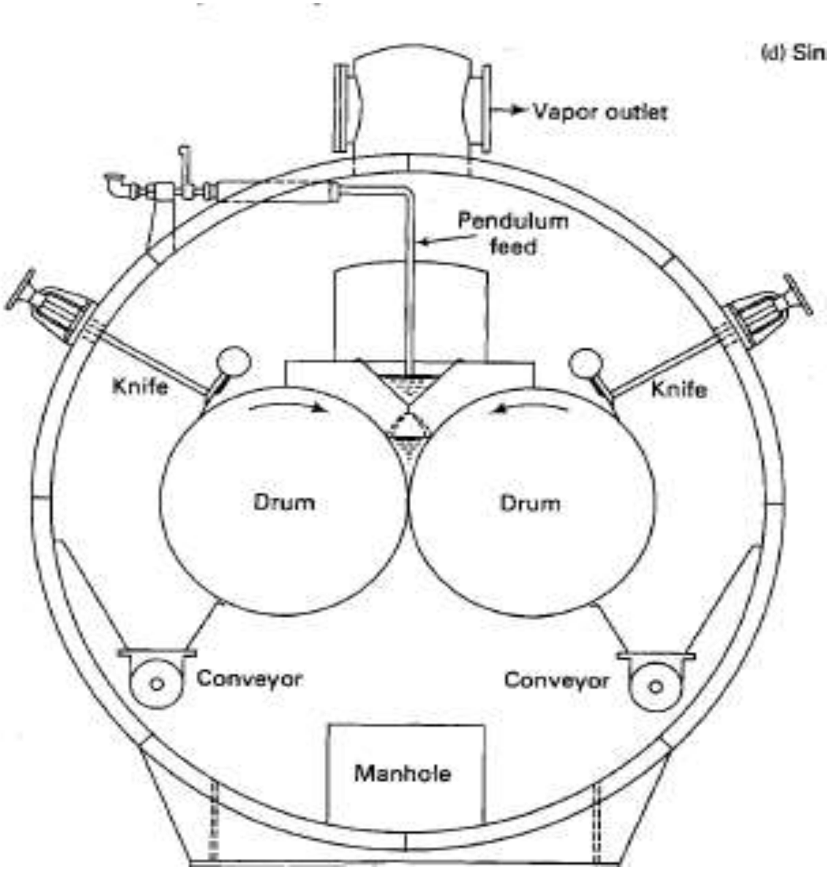
(d) Parallel-flow

DRUM DRYER

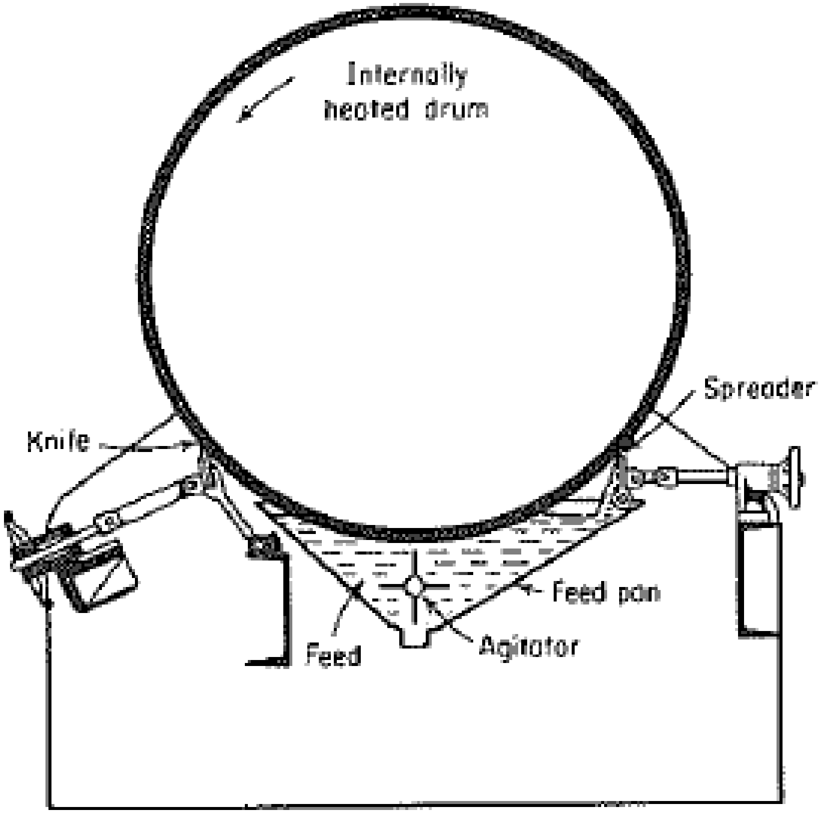
- Slowly revolving internally steam heat metal drum dips into a trough containing the slurry or solution
- Thickness controlled by spreader knife
- From solution : Liquid evaporates, solid precipitates from solution, at constant temperature,
- From slurry : the solvent evaporates at constant temperature till the solids are just dry
- the dried product are heated to the surface temperature of drum
- solid scraped off from the drub by another knife.
- Each drum limited to 35m2
- Rate of evaporated 0.003-0.02 kg/m2s
- Contact time – 6-15 s, Heat transfer coefficient 1-2kW/m2K.
- Vacuum drum drying for lower temperature.

drum dryer

VACUUM DOUBLE DRUM

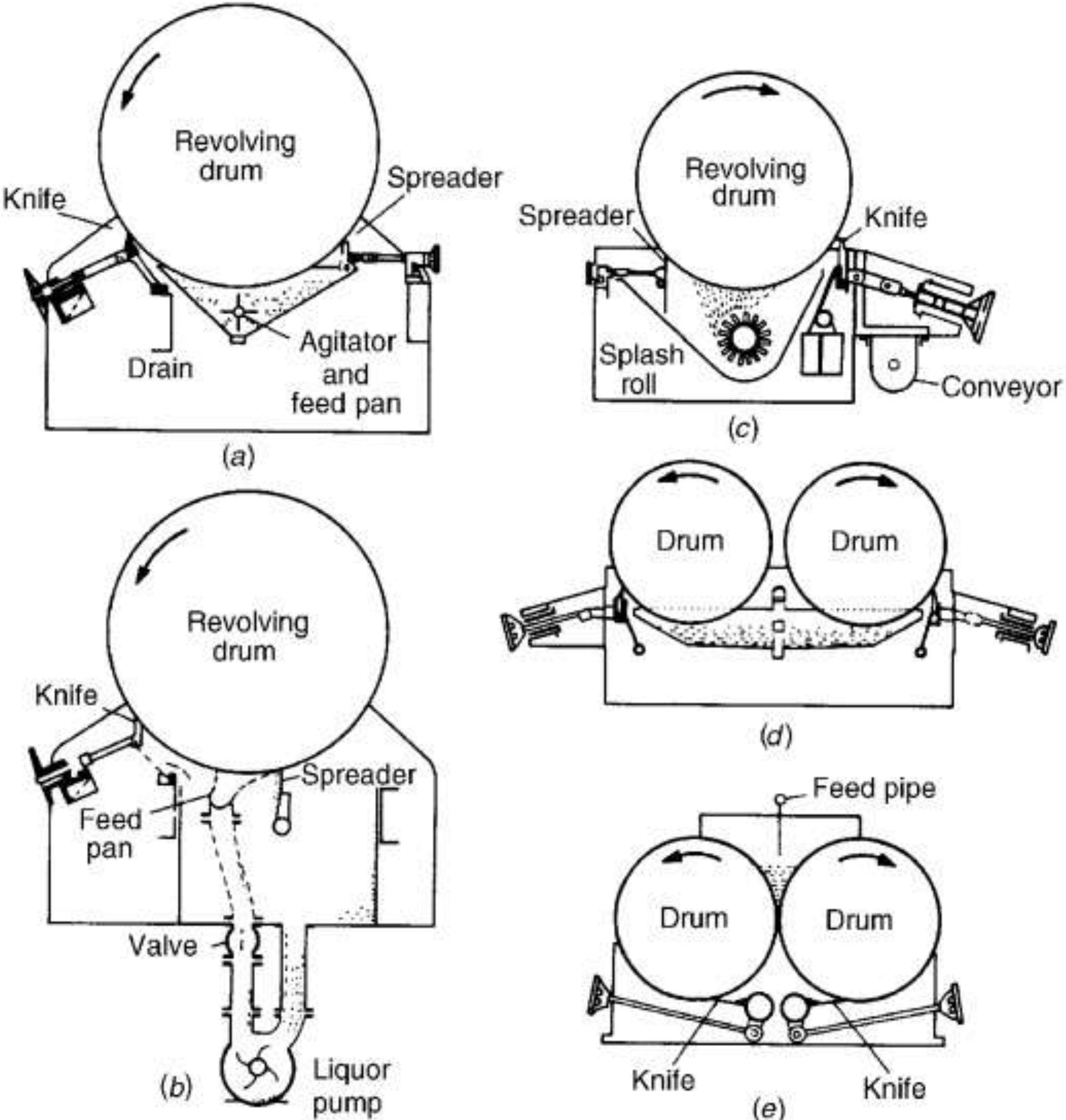


SINGLE DRUM

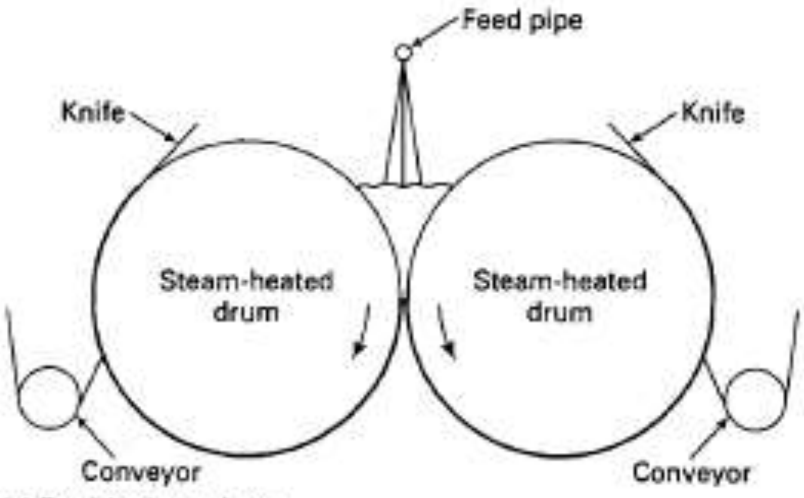


TYPE OF FEEDING DRUM DRYERS

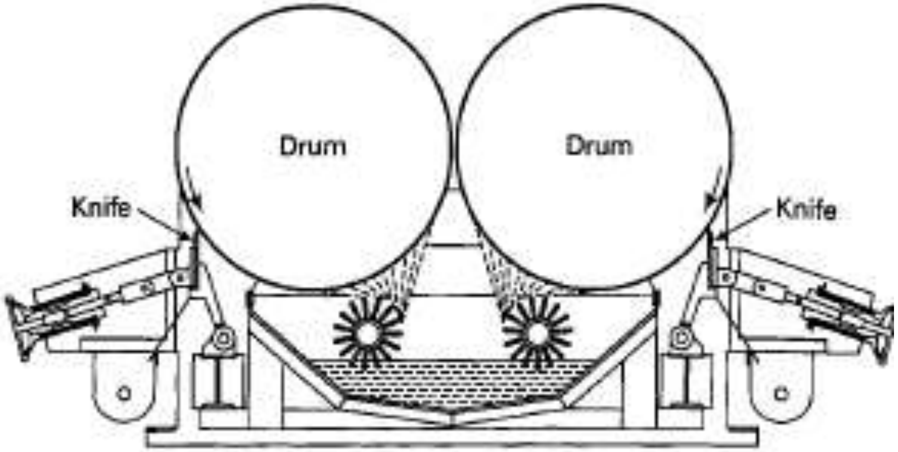
(a) Single drum dip feed
(b) Single drum pan feed
(c) Single drum splash feed
(d) Double drum, dip feed
(e) Double drum, top feed



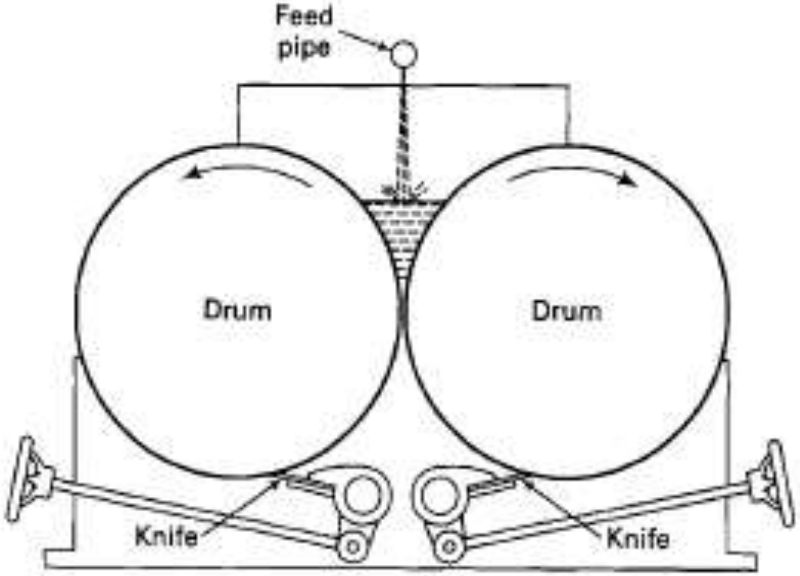
Drum dryers



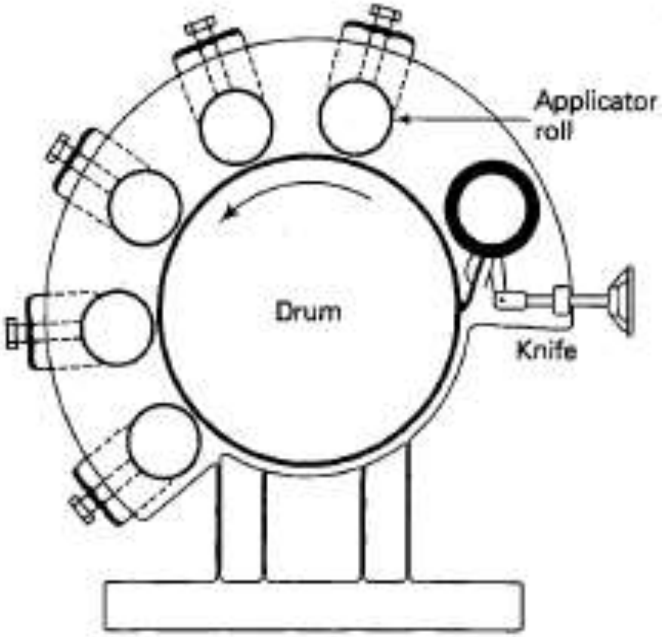
(a) Double-drum dryer



(c) Twin-drum dryer with splash feed



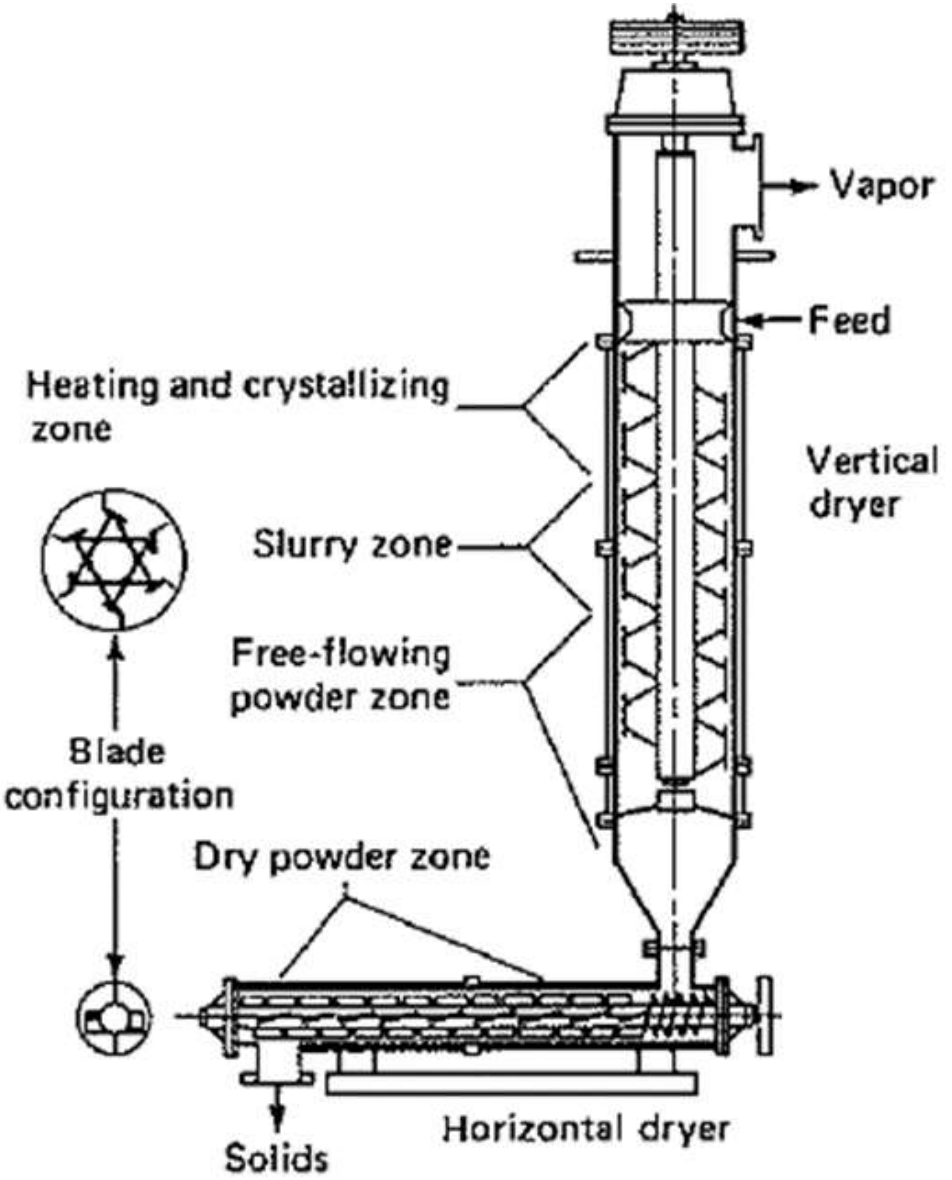
(b) Twin-drum dryer with top feed



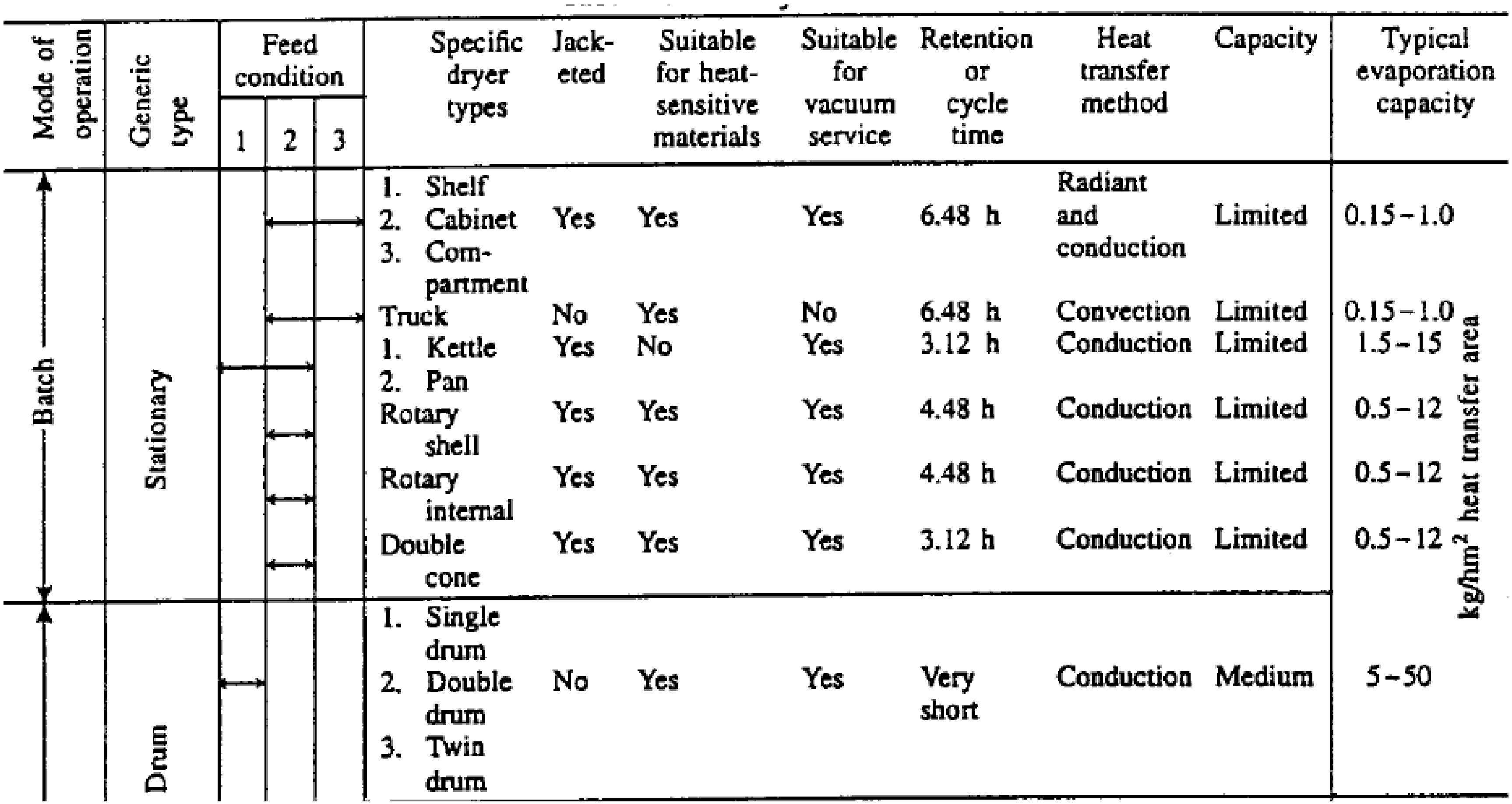
(d) Single-drum dryer with applicator feed

Thin film dryer

- Dry free flowing product from slurry or solution
- Top section - Vertical agitated evaporator dryer
- Bottom section – removal of moisture from the wet solid
- 100-200 kg/m2 hour.
- High thermal efficiency as no hot air is used
- Recovery of solvent possible.
- Expensive and limited HTA.



Dryer Selection



Mode of operation	Generic type	Feed condition 1	Feed condition 2	Feed condition 3	Specific dryer types	Jack-eted	Suitable for heat-sensitive materials	Suitable for vacuum service	Retention or cycle time	Heat transfer method	Capacity	Typical evaporation capacity kg/hm^2 heat transfer area
Batch	Stationary		↔	↔	1. Shelf 2. Cabinet 3. Com-partment	Yes	Yes	Yes	6.48 h	Radiant and conduction	Limited	0.15 – 1.0
			↔	↔	Truck	No	Yes	No	6.48 h	Convection	Limited	0.15 – 1.0
		↔	↔		1. Kettle 2. Pan	Yes	No	Yes	3.12 h	Conduction	Limited	1.5 – 15
			↔		Rotary shell	Yes	Yes	Yes	4.48 h	Conduction	Limited	0.5 – 12
			↔		Rotary internal	Yes	Yes	Yes	4.48 h	Conduction	Limited	0.5 – 12
			↔		Double cone	Yes	Yes	Yes	3.12 h	Conduction	Limited	0.5 – 12
	Drum	↔			1. Single drum 2. Double drum 3. Twin drum	No	Yes	Yes	Very short	Conduction	Medium	5 – 50

Mode of operation	Generic type	Feed condition 1	Feed condition 2	Feed condition 3	Specific dryer types	Jacketed	Suitable for heat-sensitive materials	Suitable for vacuum service	Retention or cycle time	Heat transfer method	Capacity	Typical evaporation capacity	
Continuous	Drum	⟷			1. Single drum 2. Double drum 3. Twin drum	No	Yes	Yes	Very short	Conduction	Medium	5–50	k
	Rotary		⟷		Rotary direct heat	No	No	No	Long	Convection	High	3–110	kg/hm³ dryer volume
			⟷		Rotary, indirect heat	No	No	No	Long	Conduction	Medium	15–200	
			⟷		Rotary, steam tube	No	Depends on material	No	Long	Conduction	High	15–200	
			⟷		Rotary, direct-indirect heat	No	No	No	Long	Conduction Convection	High	50–150	
			⟷		Louver	No	Depends on material	No	Long	Convection	High	5–240	
	Conveyor		⟷	⟷	Tunnel belt, screen	No	Yes	No	Long	Convection	Medium	1.5–35	
			⟷		Rotary shelf	Yes	Depends on material	No	Medium	Conduction Convection	Medium	0.5–10	kg/hm²
			⟷		Trough	Yes	Depends on material	Yes	Varies	Conduction	Medium	0.5–15	
			⟷		Vibrating	Yes	Depends on material	No	Medium	Convection Conduction	Medium	0.5–100	
			⟷		Turbo	No	Depends on material	No	Medium	Convection	Medium	1–10	
	Suspended particle	⟷			Spray	No	Yes	No	Short	Convection	High	1.5–50	kg/hm³
			⟷		Flash	No	Yes	No	Short	Convection	High	–	
			⟷		Fluid bed	No	Yes	No	Short	Convection	Medium	–	

⟷ = applicable to feed conditions noted

Key to feed conditions:

1. Solutions, colloidal suspensions and emulsions, pumpable solids suspensions, pastes and sludges.
2. Free-flowing powders, granular, crystalline or fibrous solids that can withstand mechanical handling.
3. Solids incapable of withstanding mechanical handling.

Definitions

For convenient reference, certain terms used to describe the moisture content of substances are summarized below:

Moisture content, wet basis. The moisture content of a solid or solution is usually described in terms of weight percent moisture, and unless otherwise qualified this is ordinarily understood to be expressed on the wet basis, i.e., as (kg moisture/kg wet solid)100 = [kg moisture/(kg dry solid + kg moisture)]100 $= 100X/(1 + X)$.

Moisture content, dry basis. This is expressed as kg moisture/kg dry solid $= X$. Percentage moisture, dry basis $= 100X$.

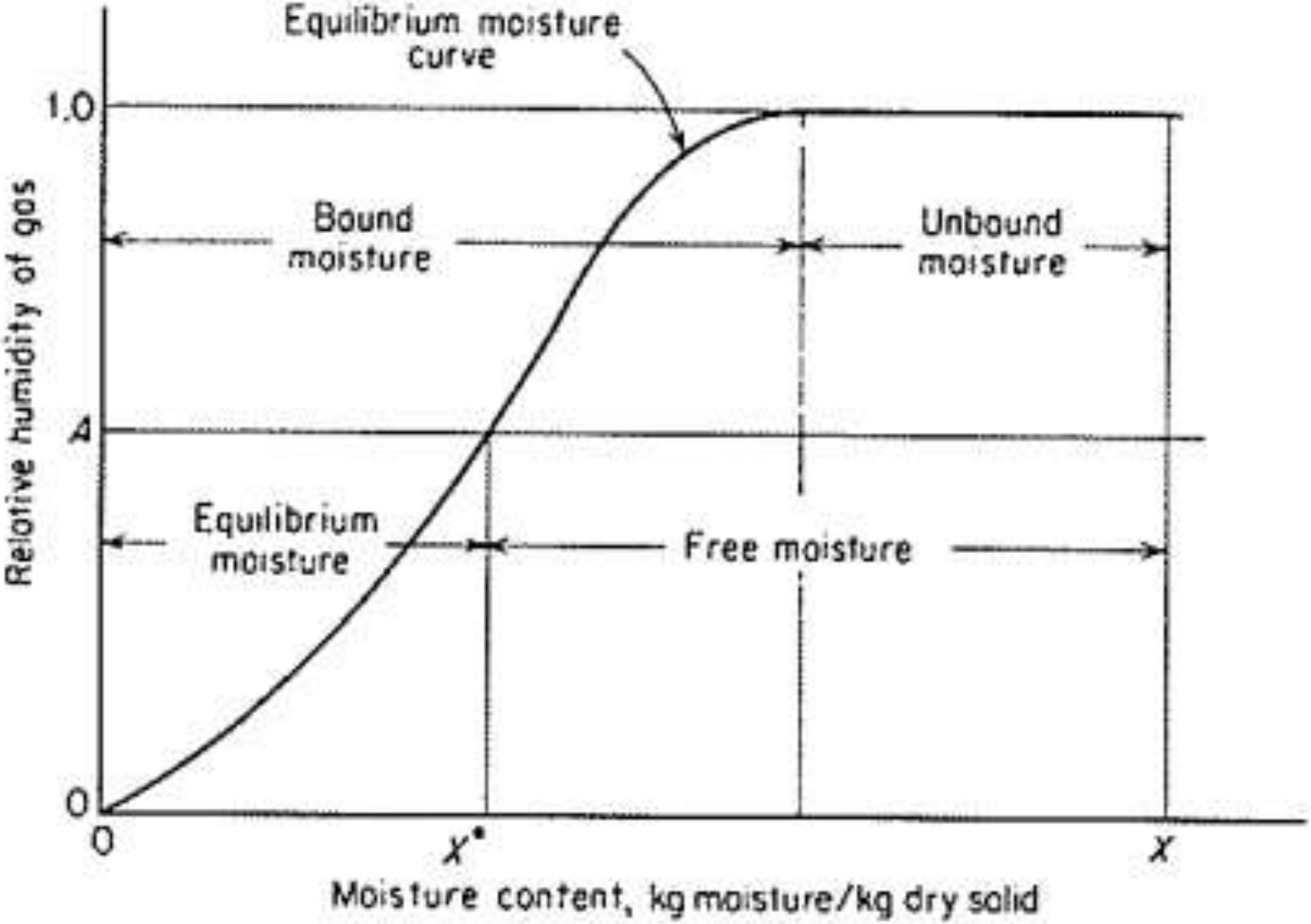
Equilibrium moisture X^*. This is the moisture content of a substance when at equilibrium with a given partial pressure of the vapor.

Bound moisture. This refers to the moisture contained by a substance which exerts an equilibrium vapor pressure less than that of the pure liquid at the same temperature.

Unbound moisture. This refers to the moisture contained by a substance which exerts an equilibrium vapor pressure equal to that of the pure liquid at the same temperature.

Free moisture. Free moisture is that moisture contained by a substance in excess of the equilibrium moisture: $X - X^*$. Only free moisture can be evaporated, and the free-moisture content of a solid depends upon the vapor concentration in the gas.

These relations are shown graphically in Fig. 12.5 for a solid of moisture content X exposed to a gas of relative humidity A.


Equilibrium moisture curve
1.0
A
0
Bound moisture
Unbound moisture
Equilibrium moisture
Free moisture
Relative humidity of gas
0
X^*
X
Moisture content, kg moisture/kg dry solid

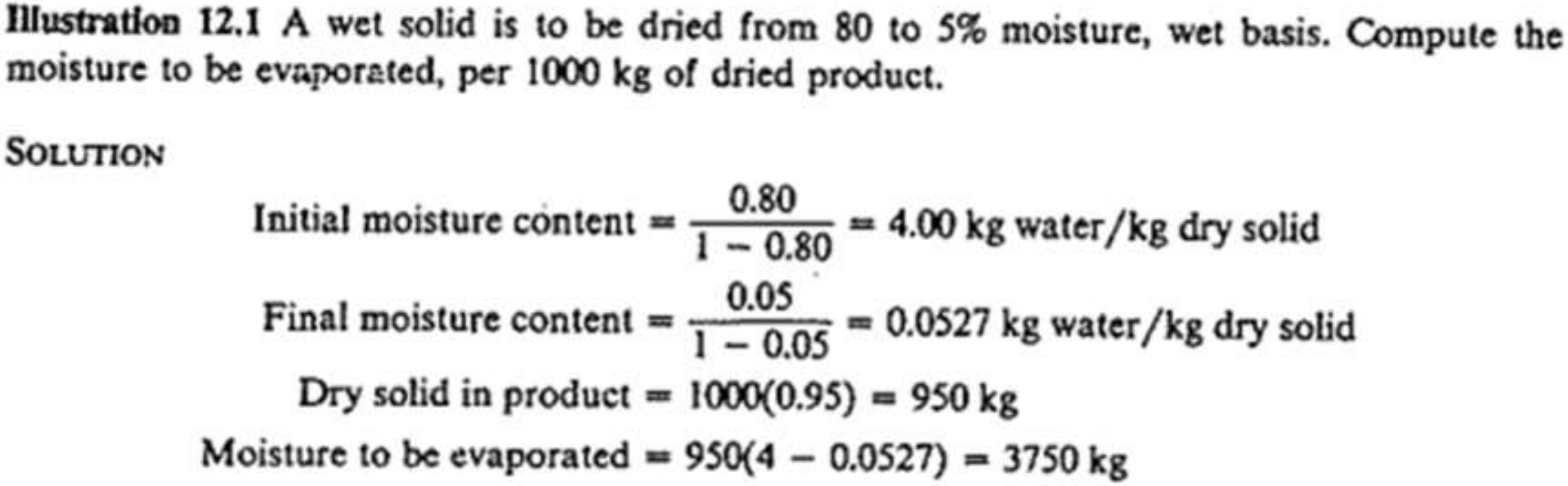


Illustration 12.1 A wet solid is to be dried from 80 to 5% moisture, wet basis. Compute the moisture to be evaporated, per 1000 kg of dried product.

SOLUTION

$$\text{Initial moisture content} = \frac{0.80}{1-0.80} = 4.00 \text{ kg water/kg dry solid}$$

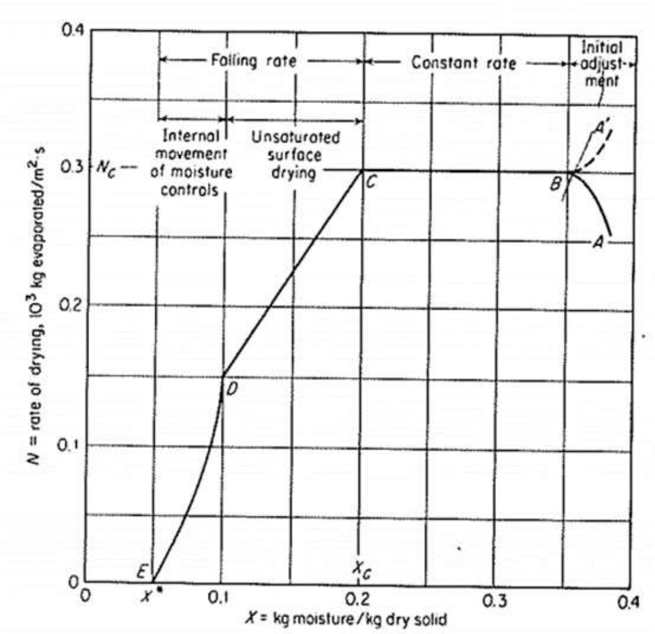
$$\text{Final moisture content} = \frac{0.05}{1-0.05} = 0.0527 \text{ kg water/kg dry solid}$$

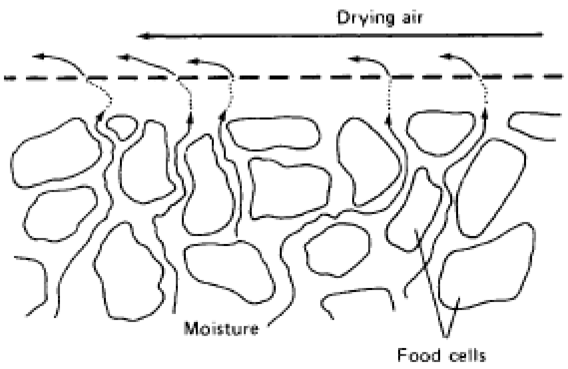
$$\text{Dry solid in product} = 1000(0.95) = 950 \text{ kg}$$

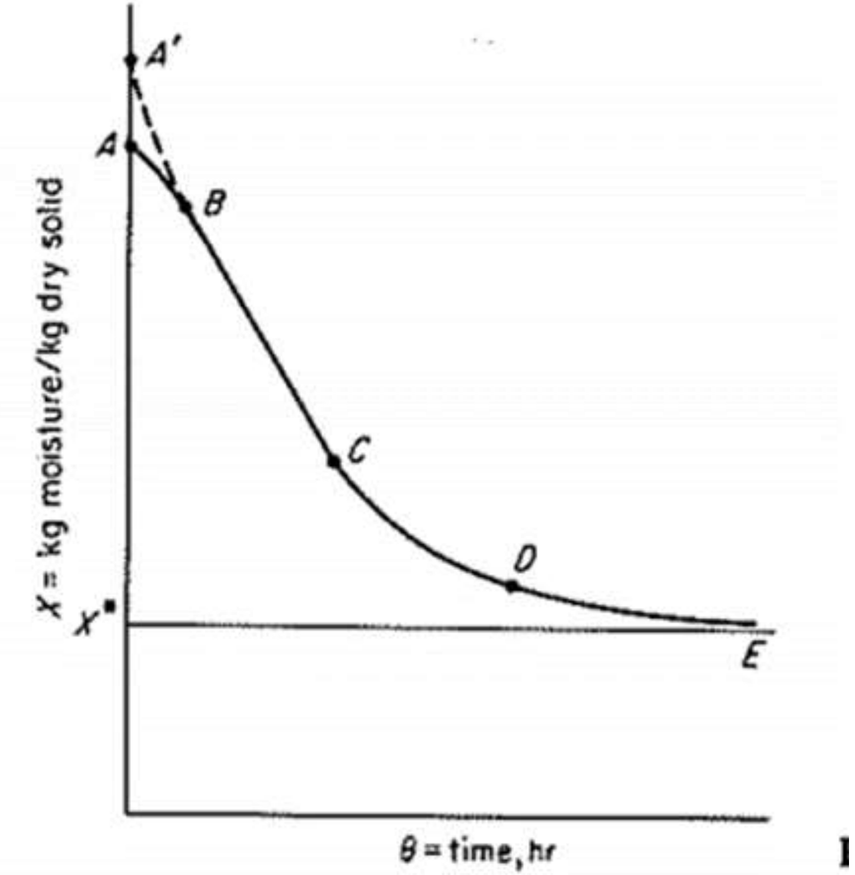
$$\text{Moisture to be evaporated} = 950(4 - 0.0527) = 3750 \text{ kg}$$

- Repeat the numerical if 80 to 5% are dry basis

Drying Rate Curve



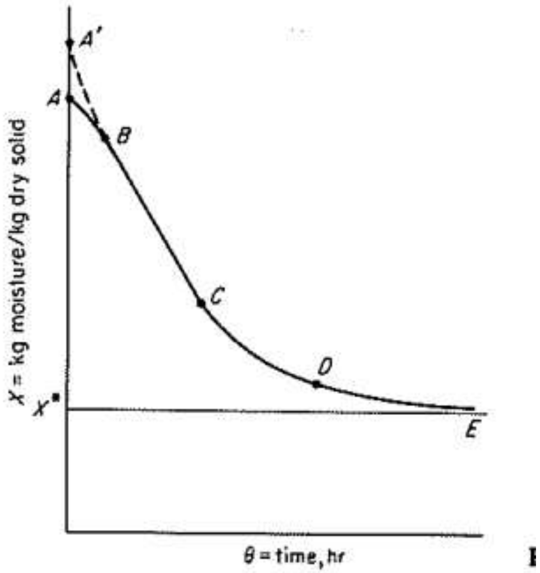


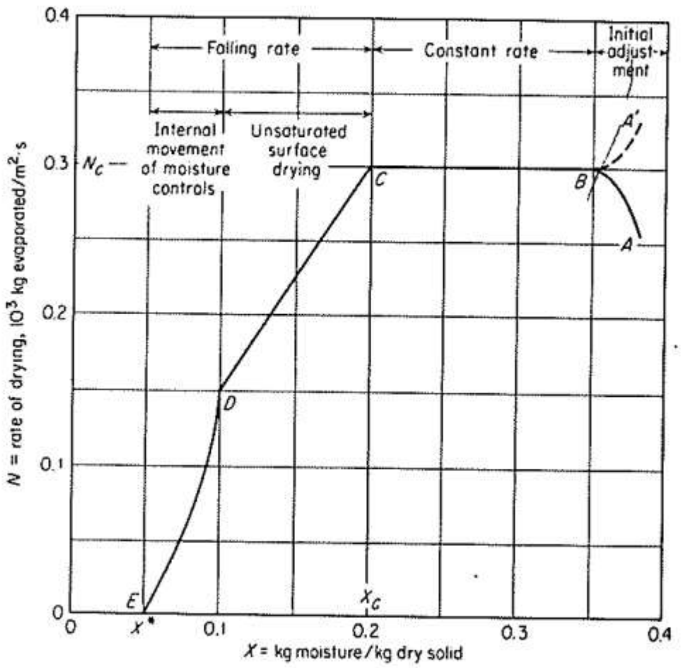


- Flow of moisture through food
- Moisture content vs time
- Drying rate
- Kg moisture removed/cm2 hour.

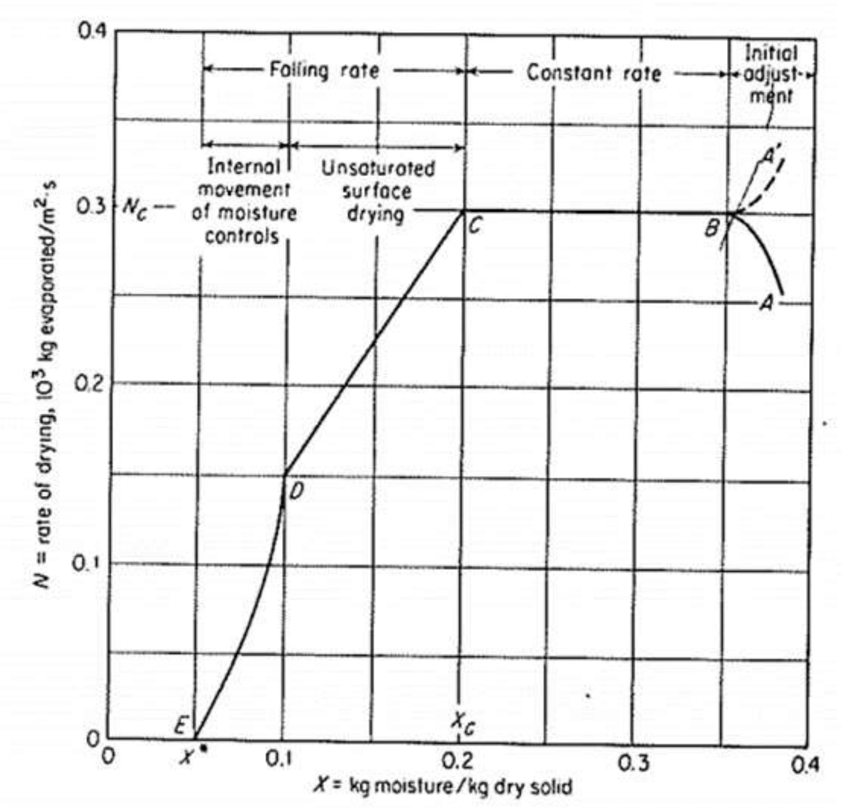
DRYING RATE CURVE

- A’-B= Initial adjustment period
- B-C = constant drying rate period, when the surface is completely covered with water,
- C-D First falling rate period,
- Dry patches appear on the surface, water supplied to the surface by diffusion, void spaced has water in continuous phase and air in dispersed phase
- D-E Second falling rate period-same as C-D, but air in continuous phase and water in dispersed phase, hence rate reduces faster
- C= first critical free moisture content
- D= second critical free moisture content





Drying rate curve



- Let W_S= weight of dry solid
- W= weight of wet solid
- $X = \frac{W - W_S}{W_S}, \frac{kg\ of\ moisure}{kg\ of\ dry\ solid}$
- Rate of drying:
- $R = -\frac{W_S}{A}\frac{dX}{dt}, kg\ water\ per\ unit\ area, unit\ time$

Time required for drying

- $R = -\frac{W_S}{A}\frac{dX}{dt}$
- $t = \int_0^t dt = \frac{W_S}{A}\int_{X_2}^{X_1}\frac{1}{R}dX$
- For constant rate period:
- $t = \frac{W_S}{AR_c}(X_1 - X_2)$
- Where, R_c= rate at constant rate period
- For straight falling rate period,
- $R = aX + b$
- $t = \int_0^t dt = \frac{W_S}{A}\int_{X_2}^{X_1}\frac{1}{aX+b}dX$
- $t = \frac{W_S}{aA}ln\frac{aX_1+b}{aX_2+b} = \frac{W_S}{aA}ln\frac{R_1}{R_2} = \frac{W_S\,(X_1-X_2)}{A(R_1-R_2)}ln\frac{R_1}{R_2}$

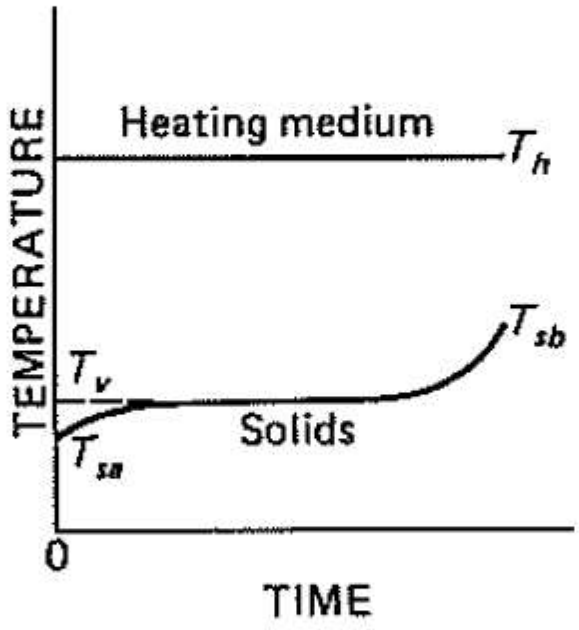
DRYING CHARACTERISTICS

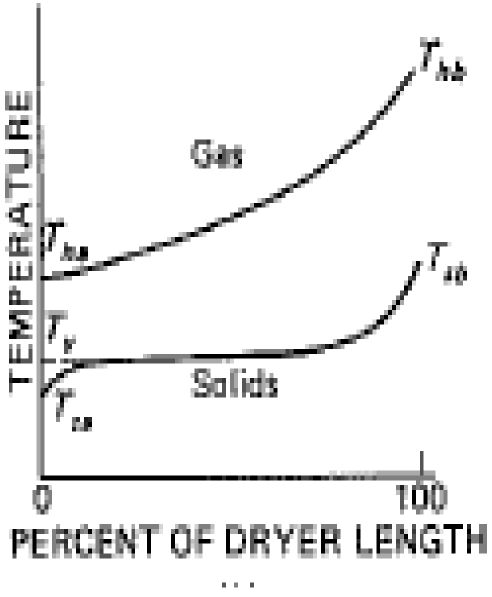
- Water moves from the interior of the MATERIAL to the surface by the following mechanisms:
- ➢ liquid movement by capillary forces, particularly in porous material
  - ➢ diffusion of liquids, caused by differences in the concentration of solutes at the surface and in the interior of the material
  - ➢ diffusion of liquids which are adsorbed in layers at the surfaces of material
  - ➢ water vapour diffusion in air spaces within the material caused by vapour pressure gradients.
- The three characteristics of air that are necessary for successful drying when the food is moist are:
  - 1. moderately high dry-bulb temperature
  - 2. low RH, percentage saturation
  - 3. high air velocity

Temperature patterns in dryers

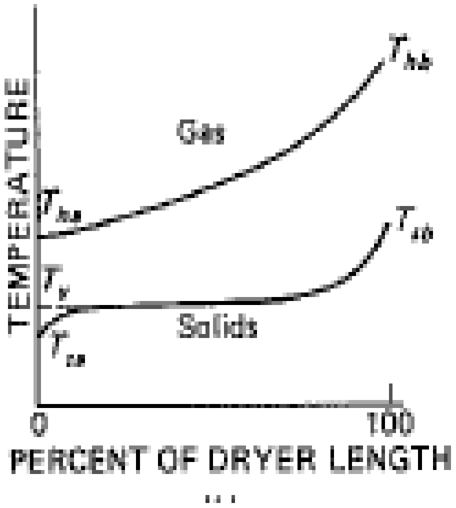
Batch Dryer

Continuous Countercurrent and adiabatic dryer





Calculation of heat load



- $\frac{q_T}{\dot{m}_s} = c_{ps}(T_{sb} - T_{sa}) + X_a c_{pL}(T_v - T_{sa}) + (X_a - X_b)\lambda + X_b c_{pL}(T_{sb} - T_v) + (X_a -$

- Heat feed (solid+liq.) to vapourization temperature
- Latent heat to convert liquid to vapor
- Head solid to final temperature
- Heat vapour to final temperature
- Heat air or other gasses to final temperature

Heat transfer coefficient in dryers

- In dryers heat transfer coefficients vary from section to section – preheat, vaporizaion , solids heating, for any section :

$$q = U A\overline{\Delta T}$$

- ***Volumetric Heat Transfer coefficient***: Heat transfer area is surface area of the solids. In some dryers like
  Rotary dryer, screw conveyor dryer, it is difficult to determine hence a volumetric heat transfer coefficient is used Ua, Watt/m3K
- $q_T = U_a V\overline{\Delta T}$

Heat-transfer unit

- Some adiabatic dryer, specially ROTARY DRYER, are rated in terms of Heat transfer units.

- $N_t = \int_{T_{ha}}^{T_{hb}} \frac{dT_h}{T_h - T_s}$
- $N_t = \frac{T_{hb} - T_{ha}}{\overline{\Delta T}}$

When initial liquid content is very high and most of the heat transferred is for vaporization, LMTD between dry bulb and wet bulb temperature can be taken for ΔT

- $\Delta T = \frac{T_{hb} - T_{wb} - (T_{ha} - T_{wa})}{ln[(T_{hb} - T_{wb})/(T_{ha} - T_{wa})]}$
- For water air system: $T_{wa} = T_{wb}$, and if $T_v = T_{wb}$
- $N_t = ln \frac{T_{hb} - T_{wb}}{T_{ha} - T_{wb}}$

CROSS CIRCULATION DRYING

- $\dot{m}_v = \frac{M_v k_y (y_i - y\ )A}{\overline{(1-y)_L}}$
- $\dot{m}_v = \frac{h_y (T - T_i)A}{\boldsymbol{\lambda}_i}$
- $\dot{m}_v =$ Rate of evaporation   A= Area of drying
- $M_v = Mol\ wt\ of\ vaipourk_y$
- h_y = heat transfer coefficient
- k_y = Mass transfer coefficient
- T= Temp of gas T_i= Temperature at interface
- y= mole fraction of vapour in gas
- y_i = mole fraction of vapour at interface
- $\boldsymbol{\lambda}_i =$ latent heat at T_i

Cross Circulation drying

- Turbulent flow in tray dryer:
- $Nu = \frac{h_y D_e}{k} = 0.037\, Re^{0.8} Pr^{0.33}$

OR

Dittus Boelter Equation

$Nu = 0.023 Re^{0.8} Pr^{\,n}$, where n is 0.4 for fluid being heated and 0.3 for fluid being cooled.

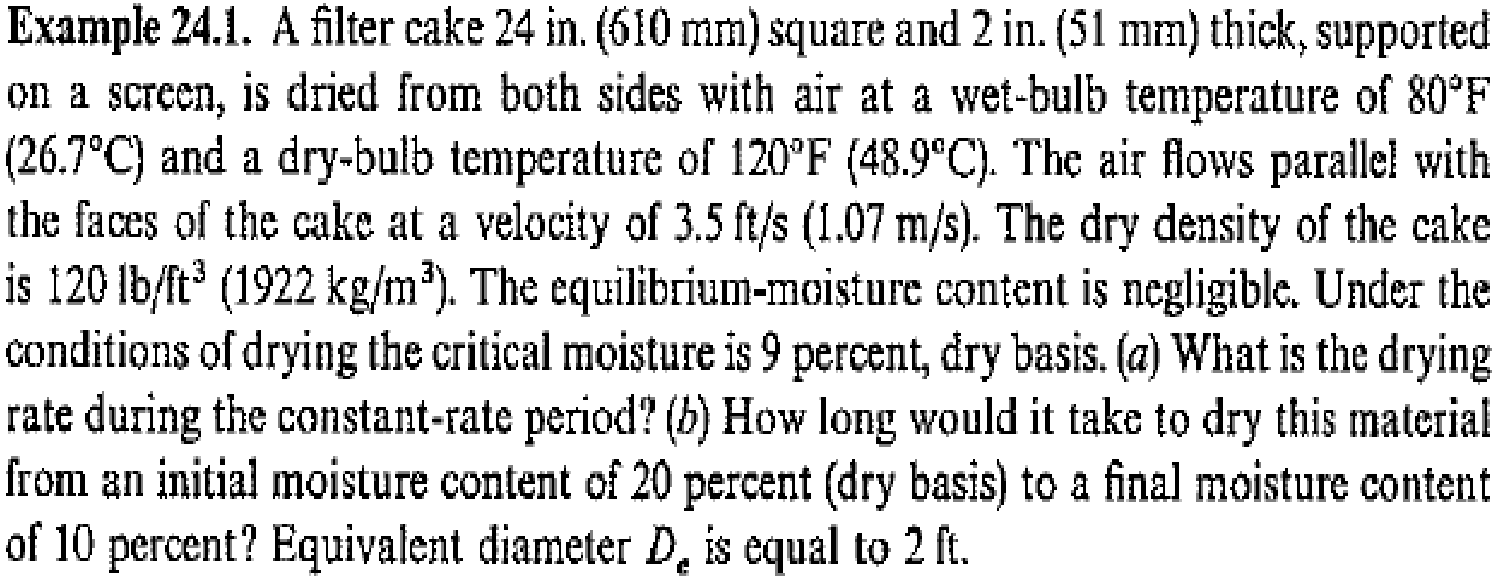
- Correction for entrance effect:

$$\frac{h_i}{h_\infty} = 1 + \left(\frac{D}{L}\right)^{0.7}$$

- L/D in tray dryers only 2 to 4 Equivalent diameter to be used for D. [for other driers L/D>50 it can be neglected
- Constant drying rate equation:

$$R_c = \frac{\dot{m}_v}{A} = \frac{h_y (T - T_i)}{\lambda_i}$$

Design of tray dryer – cross circulation
Reference: McCabe Smith

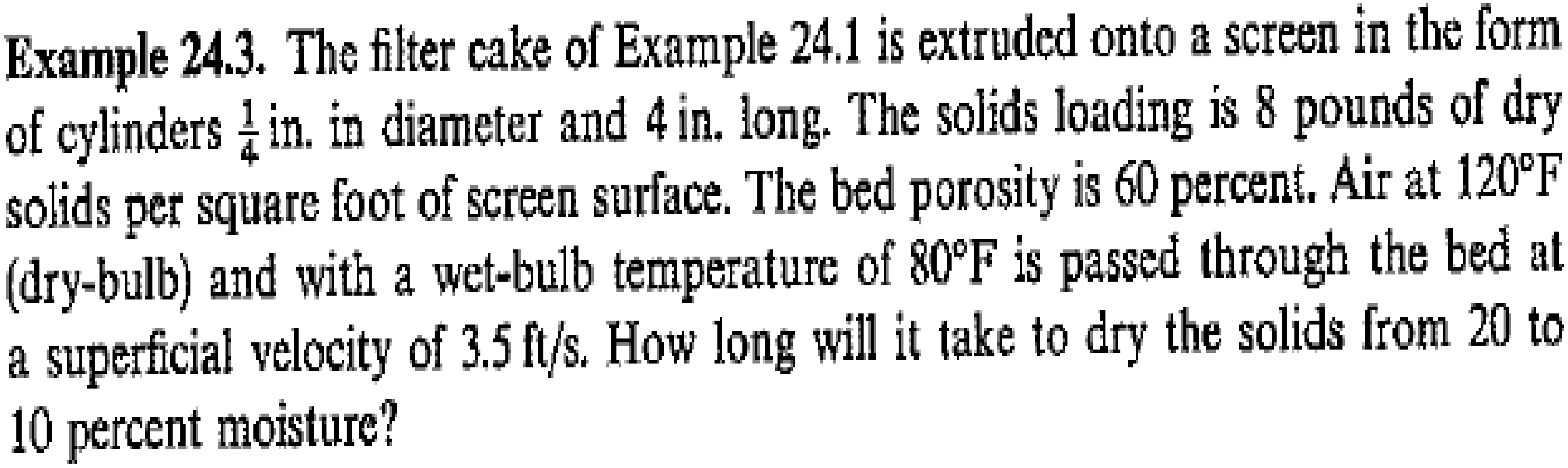


Example 24.1. A filter cake 24 in. (610 mm) square and 2 in. (51 mm) thick, supported on a screen, is dried from both sides with air at a wet-bulb temperature of 80°F (26.7°C) and a dry-bulb temperature of 120°F (48.9°C). The air flows parallel with the faces of the cake at a velocity of 3.5 ft/s (1.07 m/s). The dry density of the cake is 120 lb/ft^3 (1922 kg/m^3). The equilibrium-moisture content is negligible. Under the conditions of drying the critical moisture is 9 percent, dry basis. (*a*) What is the drying rate during the constant-rate period? (*b*) How long would it take to dry this material from an initial moisture content of 20 percent (dry basis) to a final moisture content of 10 percent? Equivalent diameter D_e is equal to 2 ft.

Through Circulation drying

- $\frac{hD}{k} = 1.17Re^{0.585}Pr^{1/3}$
- $Re = \frac{D_p v\rho}{\mu}$
- Heat transferred from the gas to a thin section of bed:
- $-\dot{m}_g c_s dT_h = hdA(T_h - T_w)$
- $ln\frac{T_{hb}-T_w}{T_{ha}-T_w} = \frac{hA}{\dot{m}_g c_s}$

Designing of through circulation tray dryer
Ref: McCabe Smith



Example 24.3. The filter cake of Example 24.1 is extruded onto a screen in the form of cylinders $\frac{1}{4}$ in. in diameter and 4 in. long. The solids loading is 8 pounds of dry solids per square foot of screen surface. The bed porosity is 60 percent. Air at 120°F (dry-bulb) and with a wet-bulb temperature of 80°F is passed through the bed at a superficial velocity of 3.5 ft/s. How long will it take to dry the solids from 20 to 10 percent moisture?

Thermal efficiency

- Thermal efficiency is the percentage of the energy supplied that is used in evaporating the water or solvent.

- Energy loss =
- sensible heat of warm moist air that is vented
- +Sensible heat of the discharged solid
- + heat loss to the surrounding

Heat and Mass balance in a cross flow dryer

- $\dot{m}_F = \dot{m_{vent}}$ and $\dot{m}_g = \dot{m}_F + \dot{m}_R$
- $\dot{m}_g H_b = \dot{m}_F H_F + \dot{m}_R H_R$
- $q_1 = hA\left(\frac{T_b+T_a}{2} - T_{wb}\right)$ [Heat for vapourization]
- $q_2 = \dot{m_{vent}}\ (T_a - T_F)c_s$ [Heat loss with vent]
- $q_3 = \dot{m}_F\ (T_b - T_F)c_s + \dot{m}_R\ (T_b - T_a)c_s$
- $q_3 = c_S\left(\dot{m}_g\ T_b - (\dot{m}_F\ T_F + \dot{m}_R\ T_a)\right)$[supplied]
- $\dot{m}_v = q_1/\lambda$ and $T_b - T_a = q_1/\dot{m}_g c_s$
- $H_a - H_b = \dot{m}_v/\dot{m}_g$
- $H_a - H_F = \dot{m}_v/\dot{m_{vent}}$

CRYSTALLIZATION

Reference

McCabe Smith

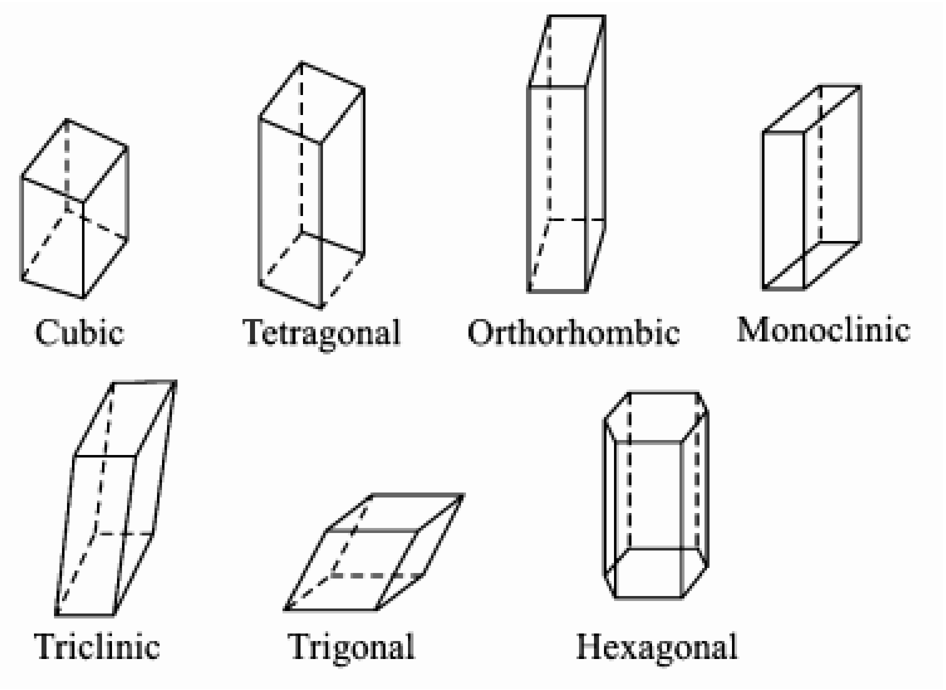
Coulson & Richardson

- **Module-5** DRYING: Introduction to drying, Rate of drying, Batch drying mechanism, the mechanism of moisture movement during drying, classification and design of dryer. (5)
- CRYSTALLIZATION: Introduction to crystallization, Theory of Crystallization, Formation and growth of crystals, crystal yield, Rate of crystallization. (5)

CRYSTAL AND CRYSTALLIZATION

- A Crystal is a solid body with plane faces i which the atoms are arranged in an orderly repetitive array
- Crystallization is formation or production of crystallization from a solution or a melt. It may be:
- Solution crystallization
- Melt crystallization

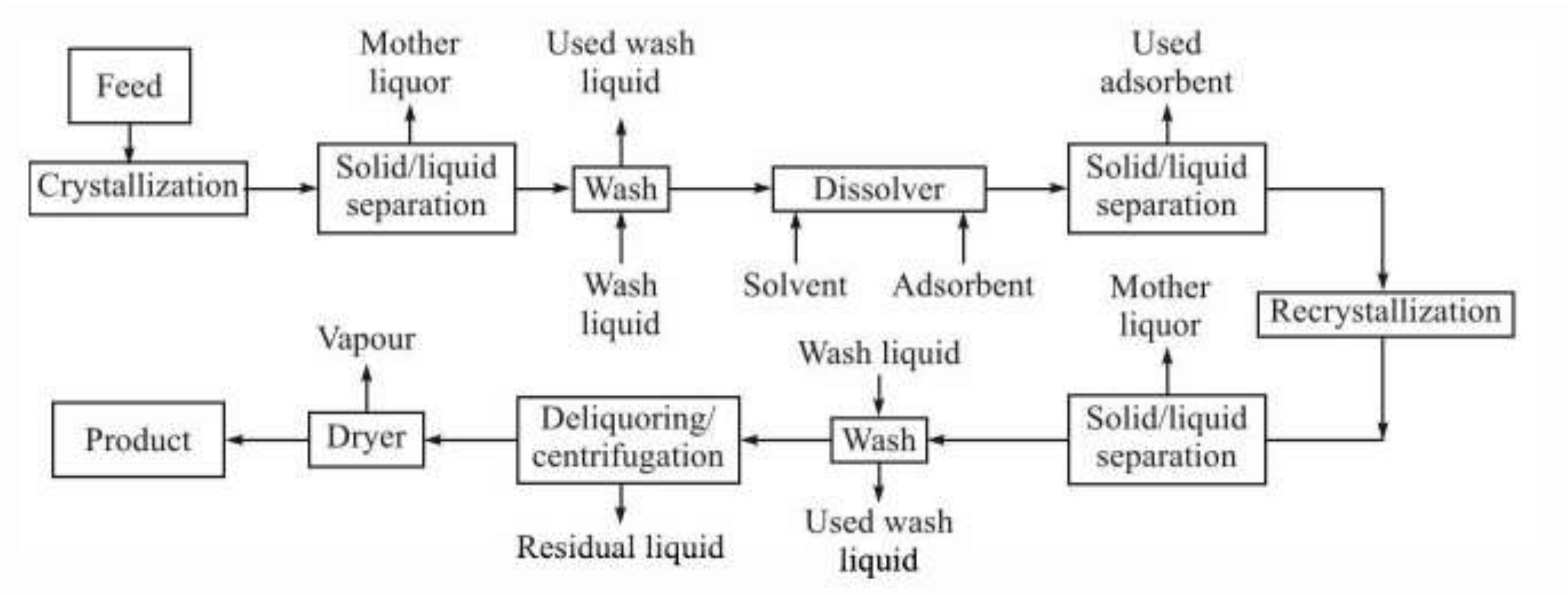
- .Crystals can be classified according to seven general crystal system



Industrial Crystallizer

- Industrial crystallization from solution, crystals are formed by creating supersaturation either by cooling or evaporation
- The crystals are recovered from **magma**, [mixture of crystallizer and the mother liquor].
- Objectives in crystallization:
- ➢ Good yield
- ➢ High purity
- ➢ Proper crystal size and
- ➢ crystal size crystallization [CSD}
- **Filtration and centrifugation** to remove Mother liquor separated from the crystals
- **Washing of crystal** to reduce amount of mother liquor waste.
- **Drying and Air tight packaging** of crystals to avoid caking of the crystals [cementing of crystals during storage]

TYPICAL CRYSTALLIZATION PROCESS

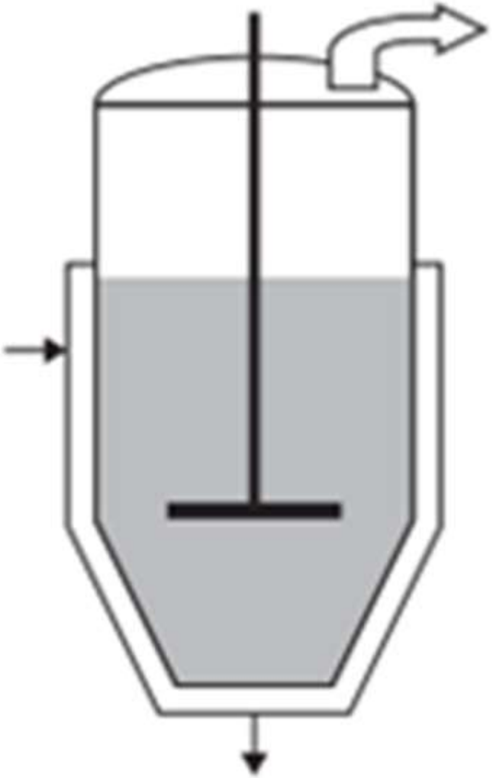


Classification of crystallizers

- Batch or Continuous.
- Basis of method of creation of supersaturation
  - Cooling with negligible evaporation
    - When solubility decreases markedly with temperature eg;
  - Evaporation with little or no cooling- Evaporator Crystallizer
    - When solubility independent of temperature eg NaCl
  - Cooling and evaporation in adiabatic evaporator-vacuum evaporator
-

- Basis of method of suspending the growing product crystals
  - Circulating liquid
  - Circulating magma
- Crystals for product size control
  - Remove bigger particles allowing smaller to grow
  - Mixed Suspension mixed product removal MSMPR
- Crystallizers with nucleation control
  - Dissolve small crystals, allowing only the big ones to grow

Batch Open Tank Crystallizer

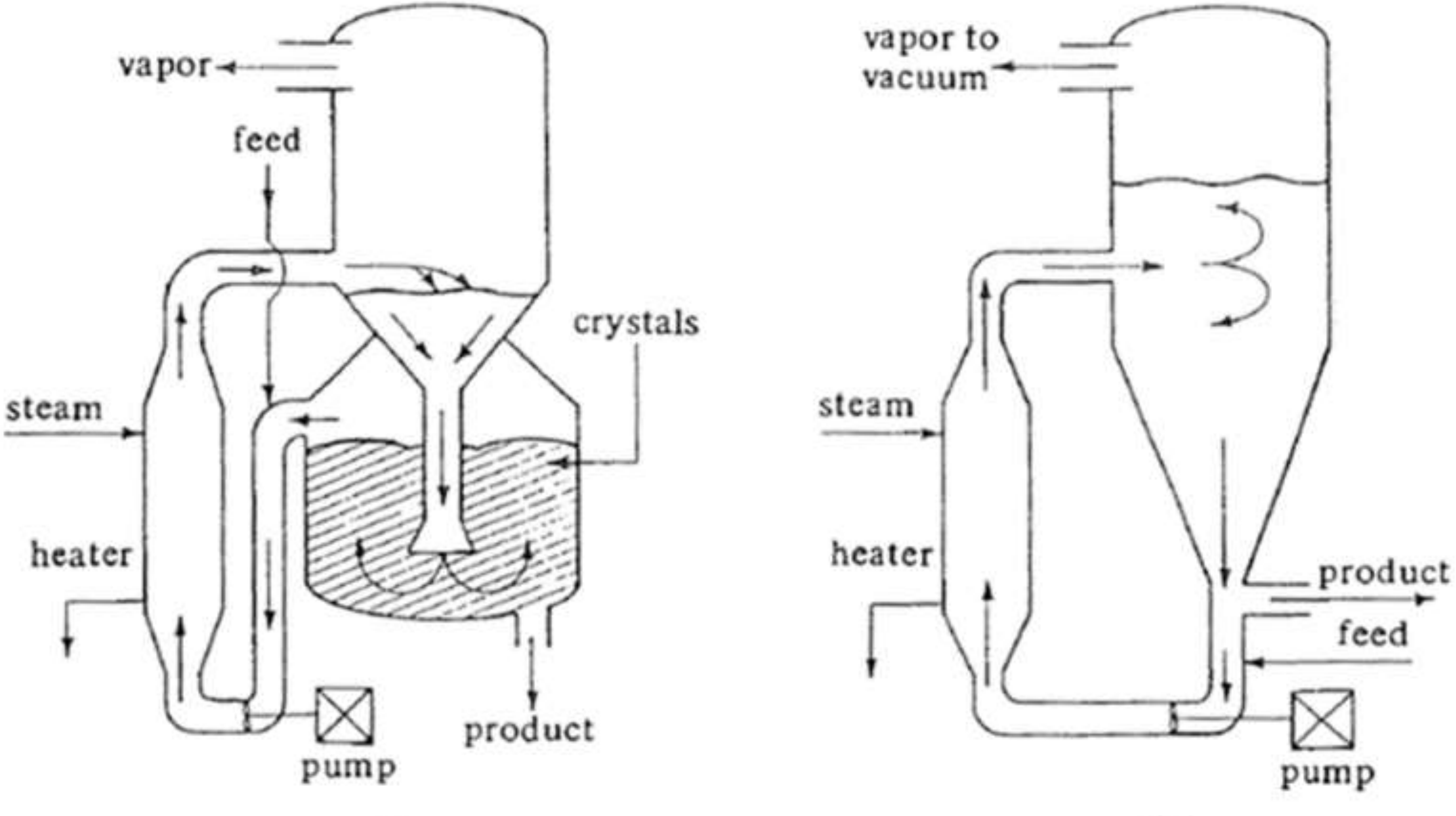


- Tank crystallisers
   - ➢ vary from shallow pans to large cylindrical tanks.
   - ➢ Non Agitated or Agitated

SWENSON WALKER SCRAPED SURFACE CRYSTALLIZER

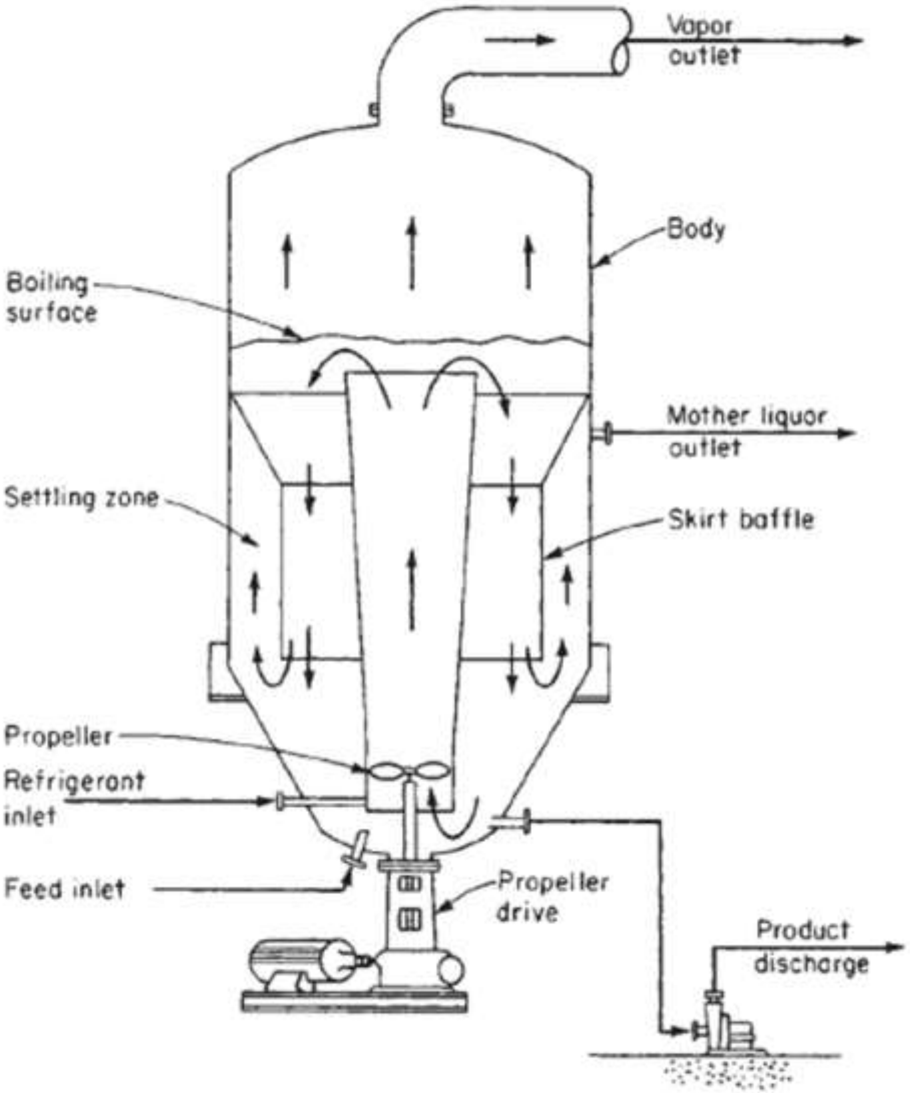
- The Swenson-Walker scraped-surface unit, which is used for processing inorganic salts that have a high temperature solubility coefficient with water, is a shallow semi-cylindrical trough, about 600 mm wide and 3–12 m long, fitted with a water-cooled jacket.
- A helical scraper rotating at 0.8–1.6 Hz, keeps the cooling surfaces clean and enhances growth of crystals by moving them through the solution which flows down the sloping trough.
- Several units may be connected in series and the capacity is determined by the heat transfer rate which should exceed 60 kWfor economic operation, with heat transfer coefficients in the range 50–150 W/m2 deg K.
- **Double pipe scraped surface crystallizer**: Cooling wter flows in the annulus. Internal agitated with spring loaded scrapers wipe the wall wipe the wall and provide High Heat Transfer coefficients and hence high production. Such units range from 75 to 600 mm in diameter and 0.3 to 3 m long.

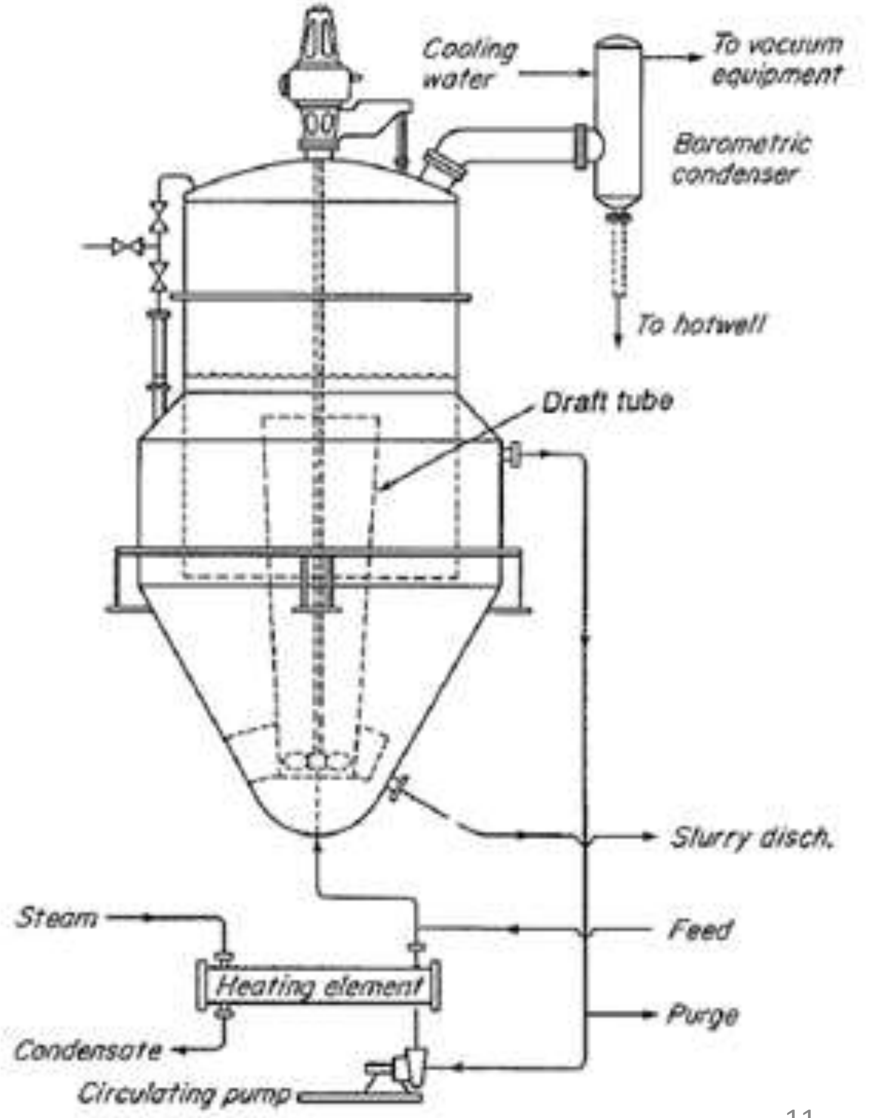
(a)CIRCULATING LIQUID AND (b) CIRCULATING MAGMA CRYSTALIZER



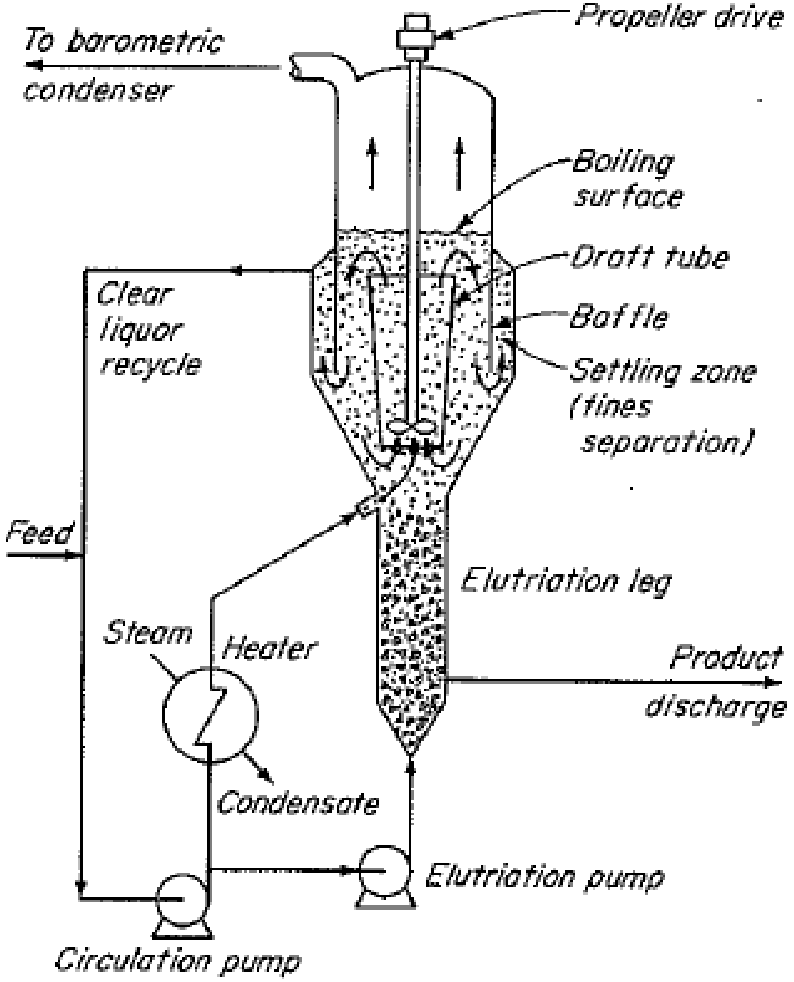
(a) (b)

VACUUM CRYSTALLIZER.





DRAFT TUBE BAFFLE CRYSTALLIZER



A slow-speed propellor agitator is located in a draught tube that extends to a small distance below the liquor level.

Hot, concentrated feed-stock, enters at the base of the draught tube, and the steady movement of magma and feed-stock to the surface of the liquor produces a gentle, uniform boiling action over the whole cross-sectional area of the crystalliser.

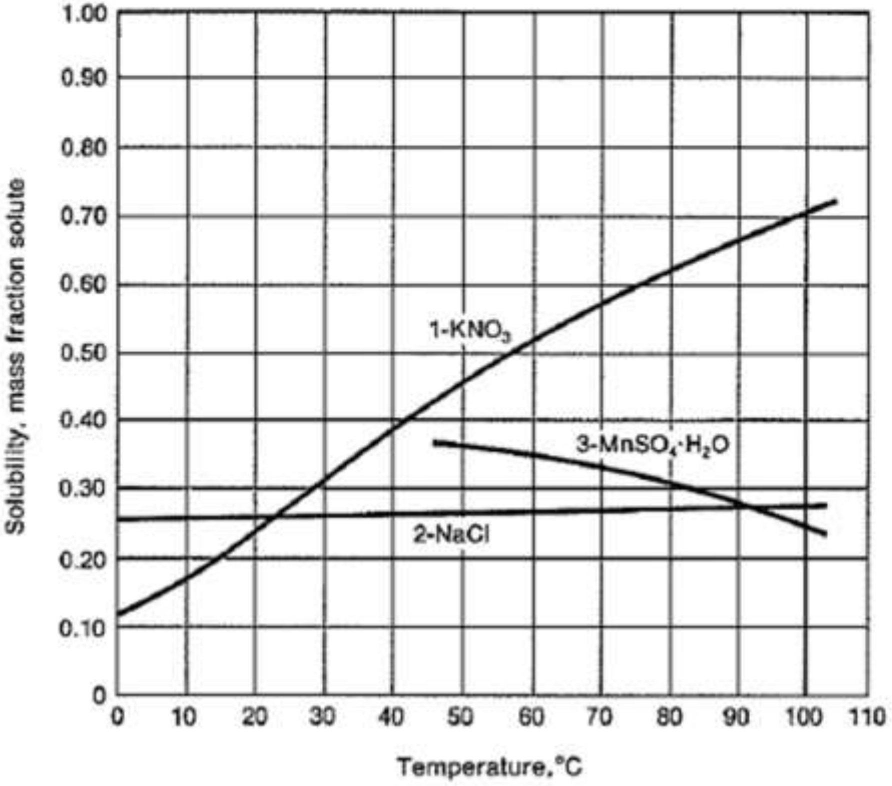
The degree of supercooling thus produced is less than 1 deg K and, in the absence of violent vapour flashing, both excessive nucleation and salt build-up on the inner walls are minimised.

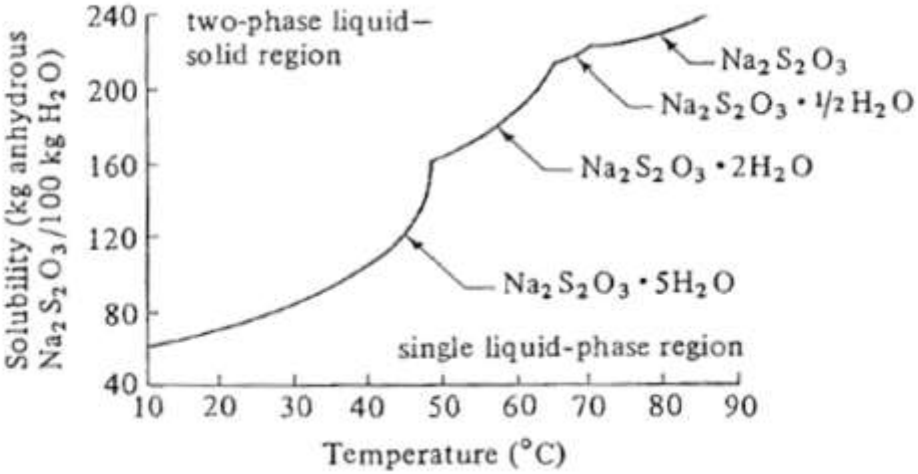
The internal baffle forms an annular space free of agitation and provides a settling zone for regulating the magma density and controlling the removal of excess nuclei.

An integral elutriating leg below the crystallisation zone to effect some degree of product classification.

EQUILIBRIUM IN CRYSTALLIZATION PROCESS

Examples of solubility curve





Sodium thiosulphate

3 types of solubility curves

1. Solubility increasing with temperature
2. Solubility not dependent on temperature
3. Inverted solubility curve: solubility decreasing with temperature

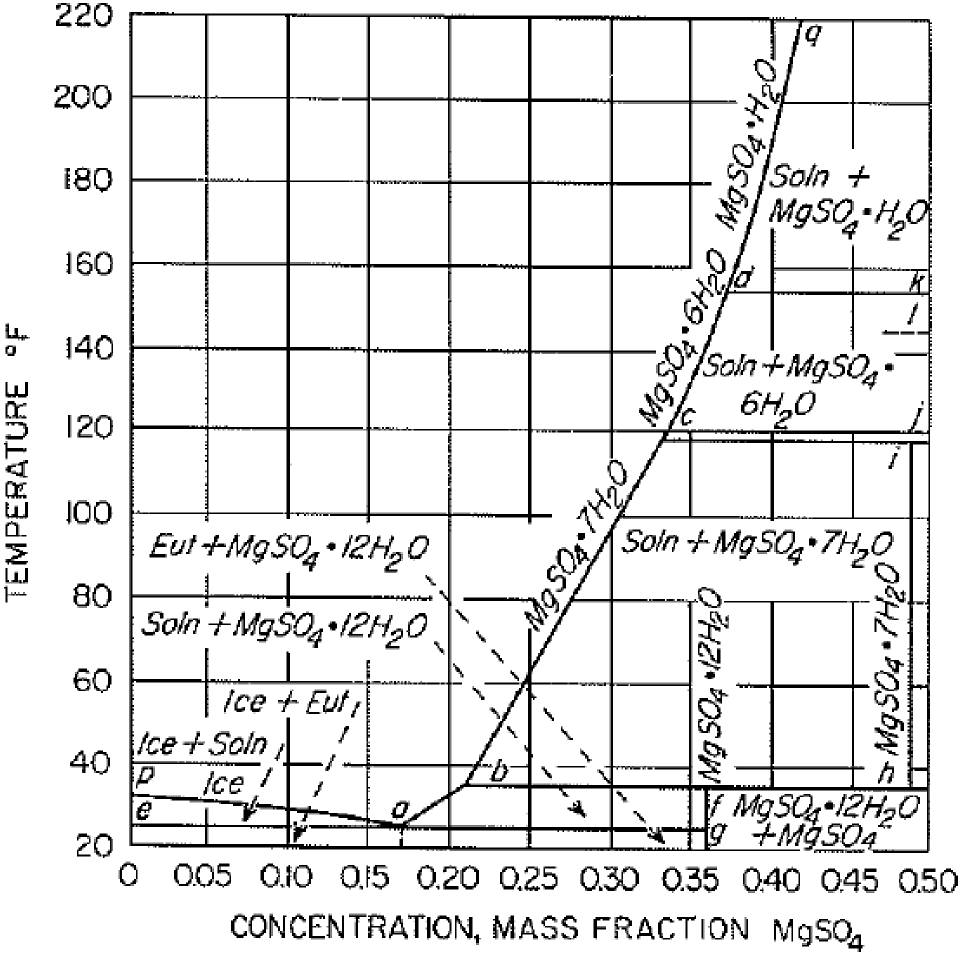
Phase equilibria for system with different hydrates . Example $\mathrm{Mg}SO_4$,

Line “eagfhij” Solidification line to form crystal from solution:

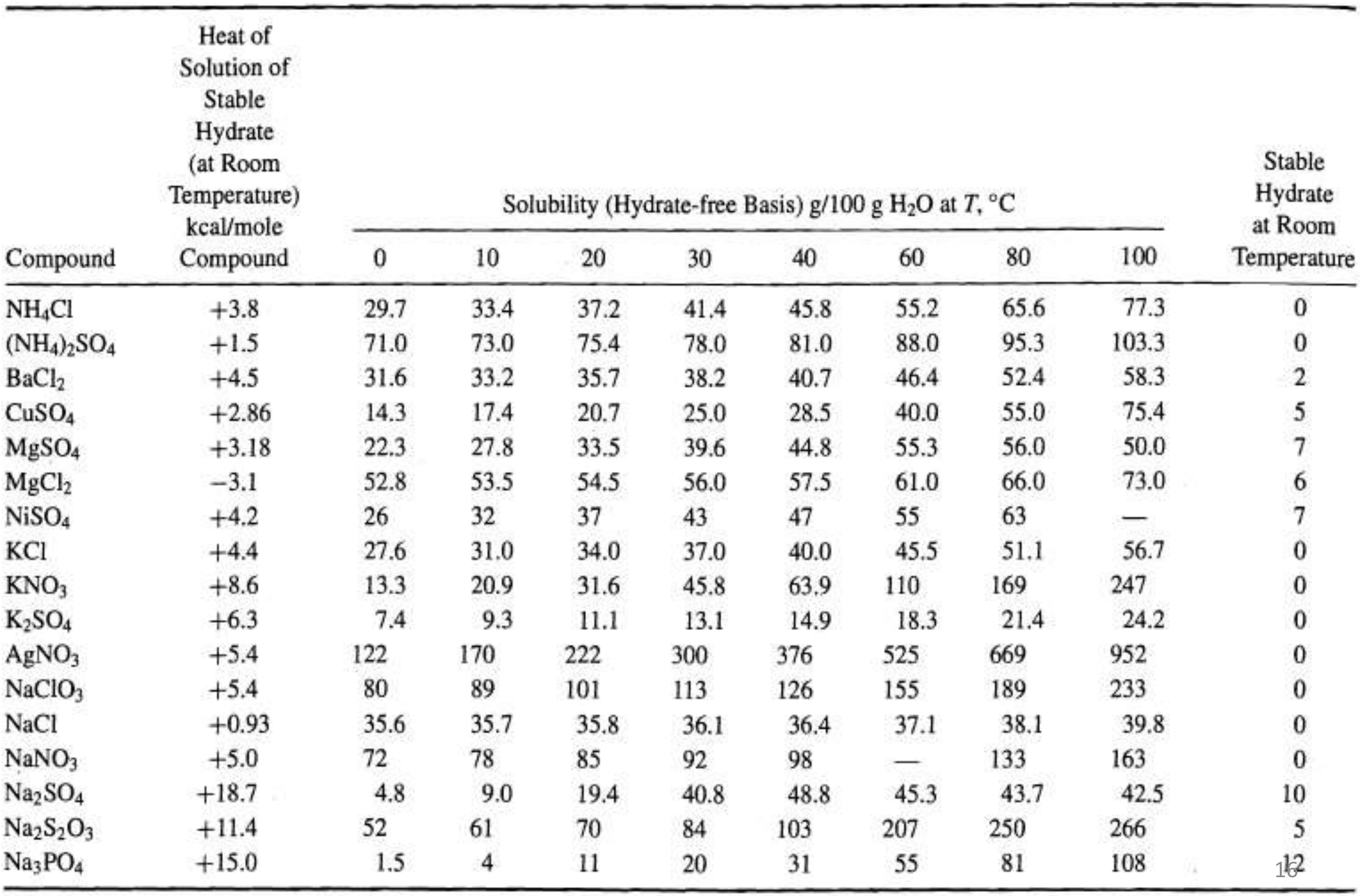
- “ab” $\mathrm{Mg}SO_4, 12H_2O$
- “bc” $\mathrm{Mg}SO_4, 7H_2O$
- “cd” $\mathrm{Mg}SO_4, 6H_2O$
- Above “d” $\mathrm{Mg}SO_4, H_2O$

Area“pae” Mixture of ice+ sat. soln,

Point “a” eutectic – Mechanical Mix of ice and $\mathrm{Mg}SO_4, 12H_2O$

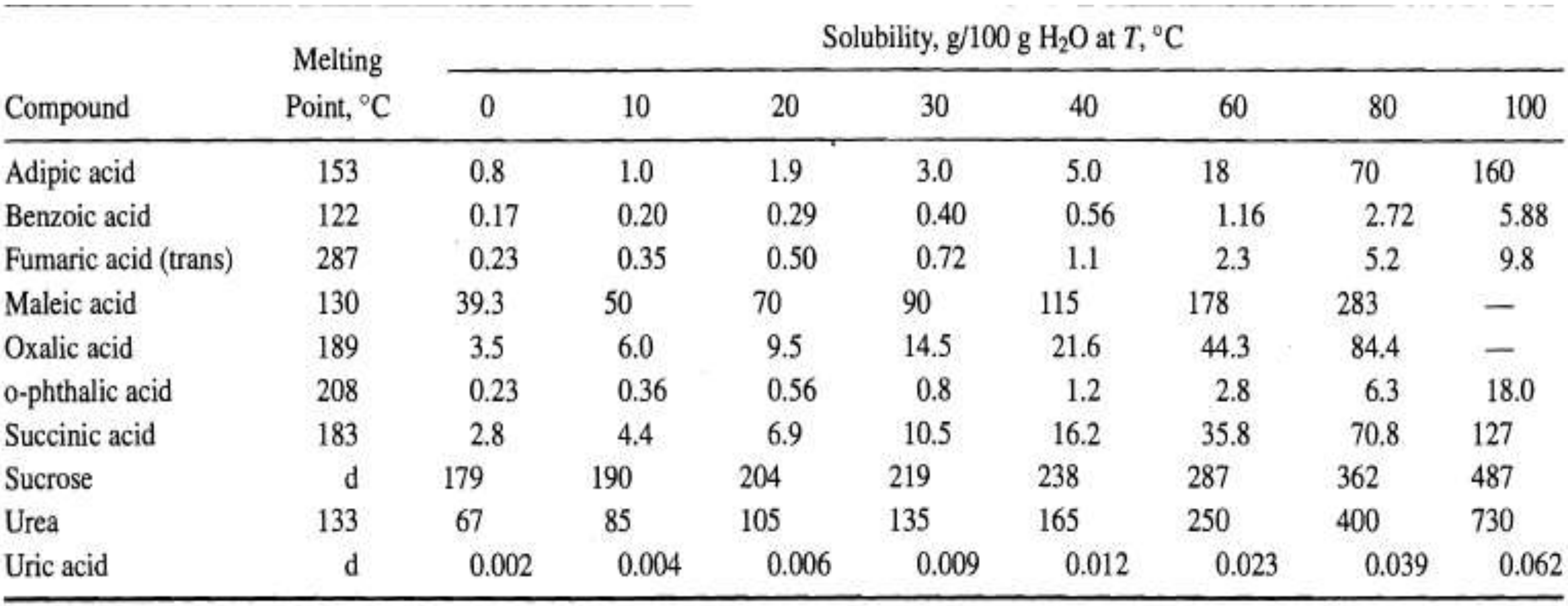


Solubility and Heat of solution at Infinite dilution of some inorganic compounds in water



Compound	Heat of Solution of Stable Hydrate (at Room Temperature) kcal/mole Compound	Solubility (Hydrate-free Basis) g/100 g H_2O at T, °C								Stable Hydrate at Room Temperature
		0	10	20	30	40	60	80	100	
NH_4Cl	+3.8	29.7	33.4	37.2	41.4	45.8	55.2	65.6	77.3	0
$(NH_4)_2SO_4$	+1.5	71.0	73.0	75.4	78.0	81.0	88.0	95.3	103.3	0
$BaCl_2$	+4.5	31.6	33.2	35.7	38.2	40.7	46.4	52.4	58.3	2
$CuSO_4$	+2.86	14.3	17.4	20.7	25.0	28.5	40.0	55.0	75.4	5
$MgSO_4$	+3.18	22.3	27.8	33.5	39.6	44.8	55.3	56.0	50.0	7
$MgCl_2$	−3.1	52.8	53.5	54.5	56.0	57.5	61.0	66.0	73.0	6
$NiSO_4$	+4.2	26	32	37	43	47	55	63	—	7
KCl	+4.4	27.6	31.0	34.0	37.0	40.0	45.5	51.1	56.7	0
KNO_3	+8.6	13.3	20.9	31.6	45.8	63.9	110	169	247	0
K_2SO_4	+6.3	7.4	9.3	11.1	13.1	14.9	18.3	21.4	24.2	0
$AgNO_3$	+5.4	122	170	222	300	376	525	669	952	0
$NaClO_3$	+5.4	80	89	101	113	126	155	189	233	0
NaCl	+0.93	35.6	35.7	35.8	36.1	36.4	37.1	38.1	39.8	0
$NaNO_3$	+5.0	72	78	85	92	98	—	133	163	0
Na_2SO_4	+18.7	4.8	9.0	19.4	40.8	48.8	45.3	43.7	42.5	10
$Na_2S_2O_3$	+11.4	52	61	70	84	103	207	250	266	5
Na_3PO_4	+15.0	1.5	4	11	20	31	55	81	108	12

Solubility and Melting point of some organic compounds in water



Compound	Melting Point, °C	Solubility, g/100 g H_2O at *T*, °C 0	10	20	30	40	60	80	100
Adipic acid	153	0.8	1.0	1.9	3.0	5.0	18	70	160
Benzoic acid	122	0.17	0.20	0.29	0.40	0.56	1.16	2.72	5.88
Fumaric acid (trans)	287	0.23	0.35	0.50	0.72	1.1	2.3	5.2	9.8
Maleic acid	130	39.3	50	70	90	115	178	283	—
Oxalic acid	189	3.5	6.0	9.5	14.5	21.6	44.3	84.4	—
o-phthalic acid	208	0.23	0.36	0.56	0.8	1.2	2.8	6.3	18.0
Succinic acid	183	2.8	4.4	6.9	10.5	16.2	35.8	70.8	127
Sucrose	d	179	190	204	219	238	287	362	487
Urea	133	67	85	105	135	165	250	400	730
Uric acid	d	0.002	0.004	0.006	0.009	0.012	0.023	0.039	0.062

CRYSTAL YIELD: Material balance in crystallizer

- $w_1 \; and \; w_2$ =initial and final masses of solvent in the liquor,
- $c = concentration = \frac{mass\ of\ anhydrous\ salt}{mass\ of\ solvent}$
- $c_1 and \; c_2$ =initial and final concentration of solution.
- y= crystal yield [mass of crystal formed]
- $R = \frac{Molecular\ mass\ of\ hydrate}{Molecular\ mass\ of\ anhydrous\ \ salt}$
- $E = \frac{Mass\ of\ solvent\ evaporated}{Mass\ of\ initial\ solvent}$
- s
- Initial water= water in final mother liquor+ water in water of crystallization, in crystal+ water evaporated.
- $w_1 = w_2 + y\frac{R-1}{R} + \; w_1E$
- Solute Balance:
- $w_1c_1 = w_2c_2 + y/R$
- $w_1c_1 = c_2\left[w_1(1-E) - y\frac{R-1}{R} + \right] + y/R$

Theoretical Crystal Yield

$$w_1 c_1 = c_2 \left[w_1 (1 - E) - y \frac{R-1}{R} + \right] + y/R$$

$$\boldsymbol{y} \left(\frac{\mathbf{1}}{\boldsymbol{R}} - \boldsymbol{c_2} \frac{R-1}{R} \right) = \boldsymbol{y} \frac{\mathbf{1} - \boldsymbol{c_2}(\boldsymbol{R} - \mathbf{1})}{\boldsymbol{R}} = \boldsymbol{w_1}[\boldsymbol{c_1} - \boldsymbol{c_2}(\mathbf{1} - \boldsymbol{E})]$$

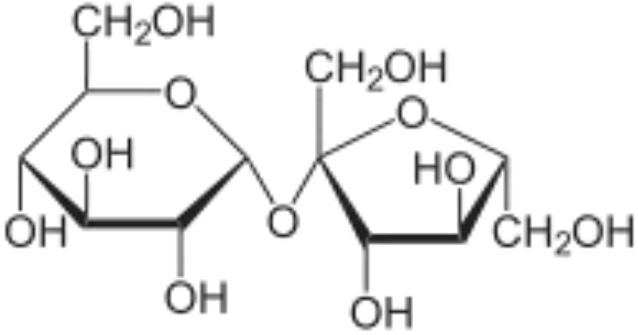
$$\boldsymbol{y = R w_1 \frac{c_1 - c_2(1 - E)}{1 - c_2(R - 1)}}$$

- R= Ratio of (molecular mass of hydrate/molecular mass of anhydrous salt)
- E= ratio (Mass of solvent evaporated/mass of solvent in the initial solution)
- w_1= Initial mass of solvent in the liquor
- w_2= final mass of solvent in liquor
- c_1 = initial concentration of solution expresses as mass of anhydrous salt/mass of solvent
- c_2= final concentration of solution expressed as mass of anhydrous salt/mass of solvent

Solubility of NaCl and Sucrose in gm/100g water

Temperature oC	NaCl	Sucrose
0	35.6	179
10	35.7	190
20	35.8	204
30	36.1	219
40	36.4	238
60	37.1	287
80	38.1	362
100	39.8	487

- Calculate crystal yield when a 100 kg hot saturated sucrose solution at 100oC is cooled to 20oC. [$C_{12}H_{22}O_{11}$]



- Calculate the crystal yield when a 100 kg of saturated salt solution at 25oC is evaporated to remove 50 % of the water.

HEAT BALANCE IN CRYSTALLIZER

- When an anhydrous solid compound, whose solubility increases with increasing temperature, dissolves isothermally in a solvent, heat is absorbed by the solution.
- This amount of heat per mole of compound in an infinite amount of solvent varies with temperature, is ***the heat of solution at infinite dilution,*** $(\Delta \boldsymbol{H}_{\boldsymbol{SOL}}^{\infty})$ **.**
- The solubility of anhydrous NaCl is seen to increase slowly with increasing temperature from 10 to100^0C. Correspondingly, the heat of solution at infinite dilution is modestly endothermic (+) at room temperature.
- In contrast, the solubility of anhydrous KNO3 increases more rapidly with increasing temperature, resulting in a higher endothermic heat of solution.
- For compounds that form hydrates, heat of solution at infinite dilution may be exothermic for the anhydrous form, but becomes less negative and often positive as higher hydrates are formed by

$$A.nH_2O = A_{(aq)} + nH_2O$$

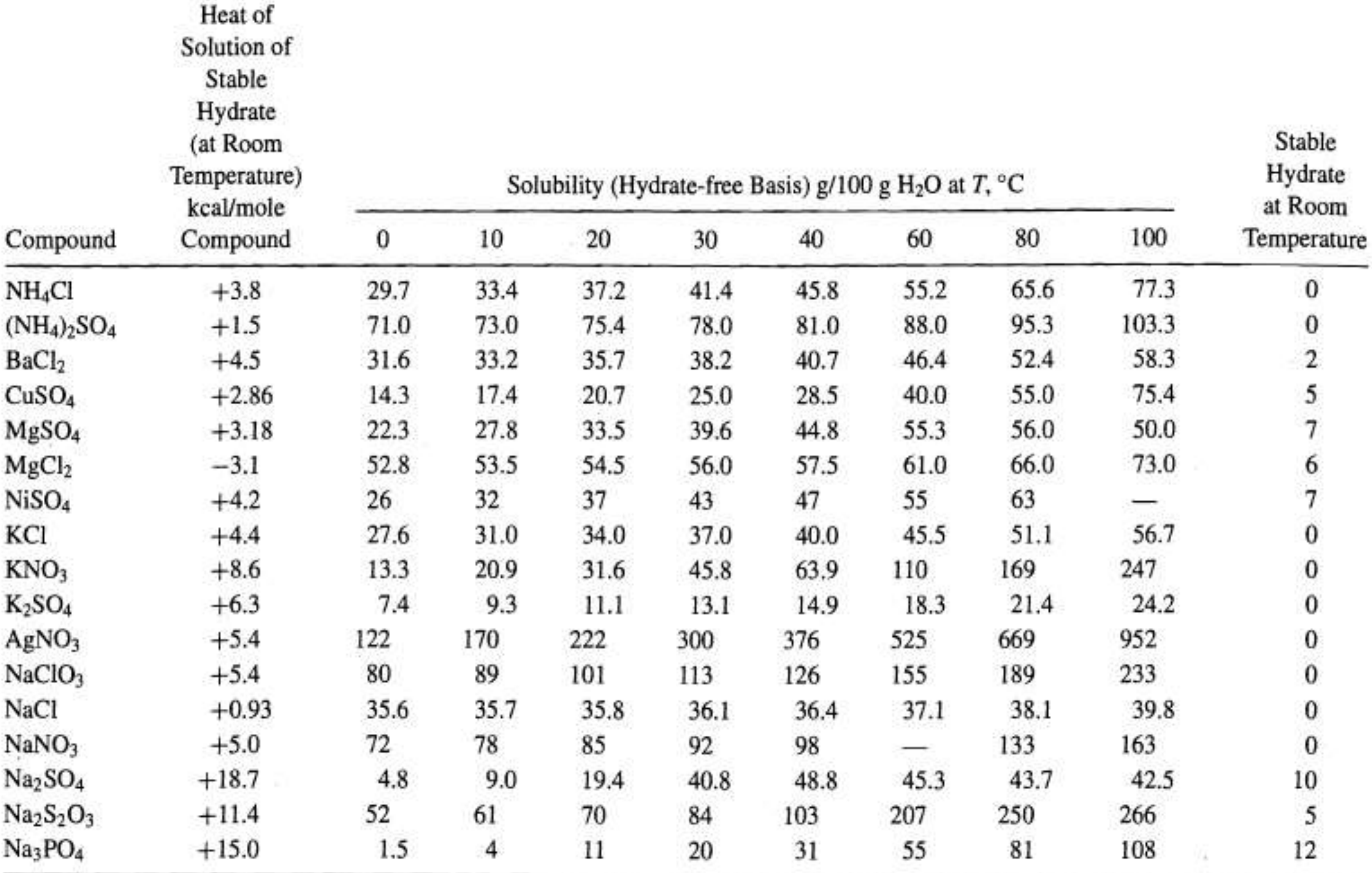
-

	$\boldsymbol{MgSO_4}$	$\boldsymbol{MgSO_4}H_2O$	$\boldsymbol{MgSO_4}6H_2O$	$\boldsymbol{MgSO_4}7H_2O$
ΔH_{SOL}^{∞},kj/mol	-88.3	-58.3	-2.3	+13.3

- Compounds whose solubility decreases with temperature, the dissolution is exothermic, +ve heat of solution
- For compounds whose solubility does not change with temperature, there is no heat evolution/absorption.
- At equilibrium heat of crystallization = (-Heat of solution)

- An energy balance calculation around a crystallizer is complex because in involves no only integral heat of solution but also the specific heats of solute and solvent and heat of vaporization of the solvent .
- The calculation is easy with enthalpy mass fraction diagram for the system including

Solubility and Heat of Solution at Infinite Dilution for some inorganic compoiunds in water (A +ve Heat of solution is Endothermic)



Compound	Heat of Solution of Stable Hydrate (at Room Temperature) kcal/mole Compound	Solubility (Hydrate-free Basis) g/100 g H_2O at T, °C								Stable Hydrate at Room Temperature
		0	10	20	30	40	60	80	100	
NH_4Cl	+3.8	29.7	33.4	37.2	41.4	45.8	55.2	65.6	77.3	0
$(NH_4)_2SO_4$	+1.5	71.0	73.0	75.4	78.0	81.0	88.0	95.3	103.3	0
$BaCl_2$	+4.5	31.6	33.2	35.7	38.2	40.7	46.4	52.4	58.3	2
$CuSO_4$	+2.86	14.3	17.4	20.7	25.0	28.5	40.0	55.0	75.4	5
$MgSO_4$	+3.18	22.3	27.8	33.5	39.6	44.8	55.3	56.0	50.0	7
$MgCl_2$	−3.1	52.8	53.5	54.5	56.0	57.5	61.0	66.0	73.0	6
$NiSO_4$	+4.2	26	32	37	43	47	55	63	—	7
KCl	+4.4	27.6	31.0	34.0	37.0	40.0	45.5	51.1	56.7	0
KNO_3	+8.6	13.3	20.9	31.6	45.8	63.9	110	169	247	0
K_2SO_4	+6.3	7.4	9.3	11.1	13.1	14.9	18.3	21.4	24.2	0
$AgNO_3$	+5.4	122	170	222	300	376	525	669	952	0
$NaClO_3$	+5.4	80	89	101	113	126	155	189	233	0
NaCl	+0.93	35.6	35.7	35.8	36.1	36.4	37.1	38.1	39.8	0
$NaNO_3$	+5.0	72	78	85	92	98	—	133	163	0
Na_2SO_4	+18.7	4.8	9.0	19.4	40.8	48.8	45.3	43.7	42.5	10
$Na_2S_2O_3$	+11.4	52	61	70	84	103	207	250	266	5
Na_3PO_4	+15.0	1.5	4	11	20	31	55	81	108	12

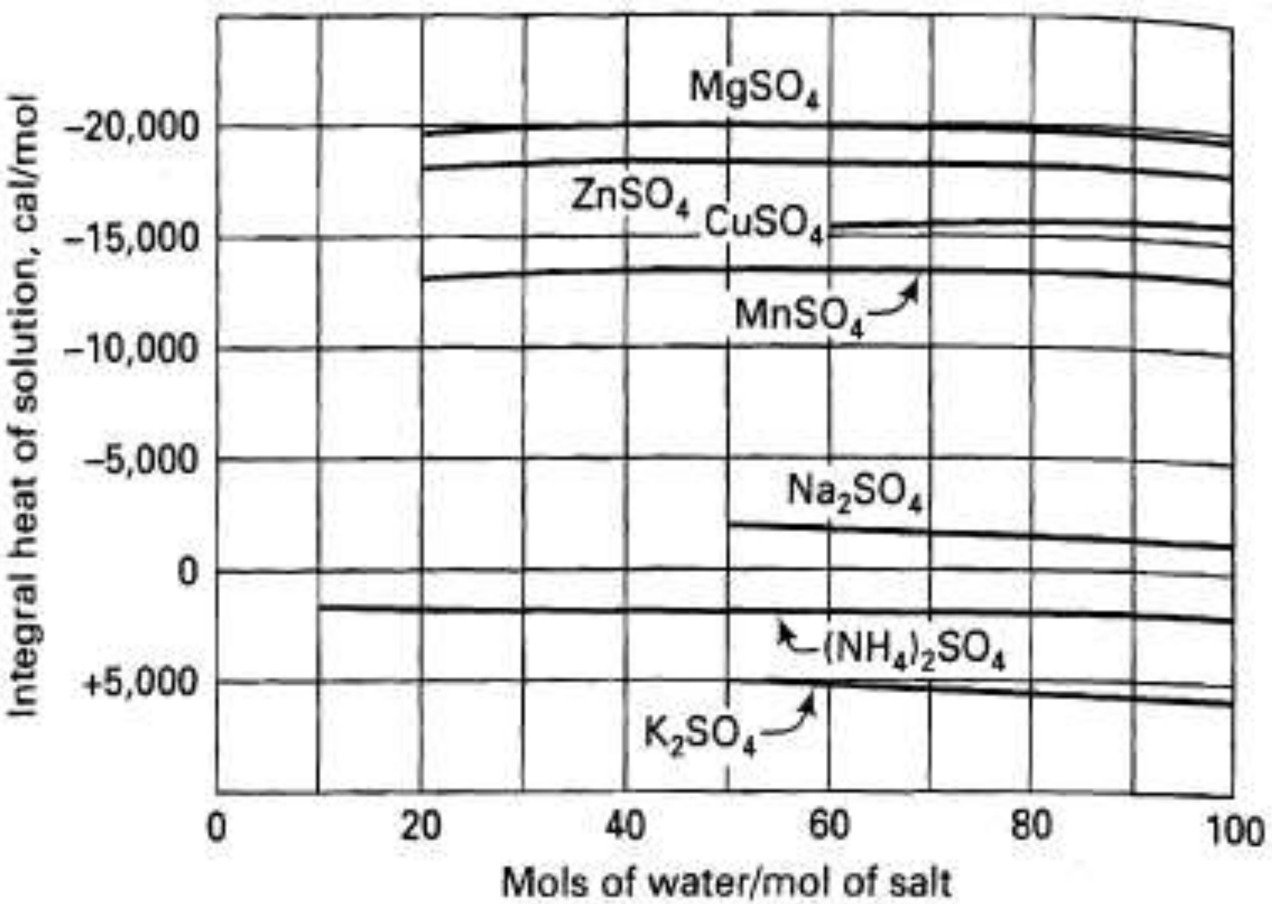
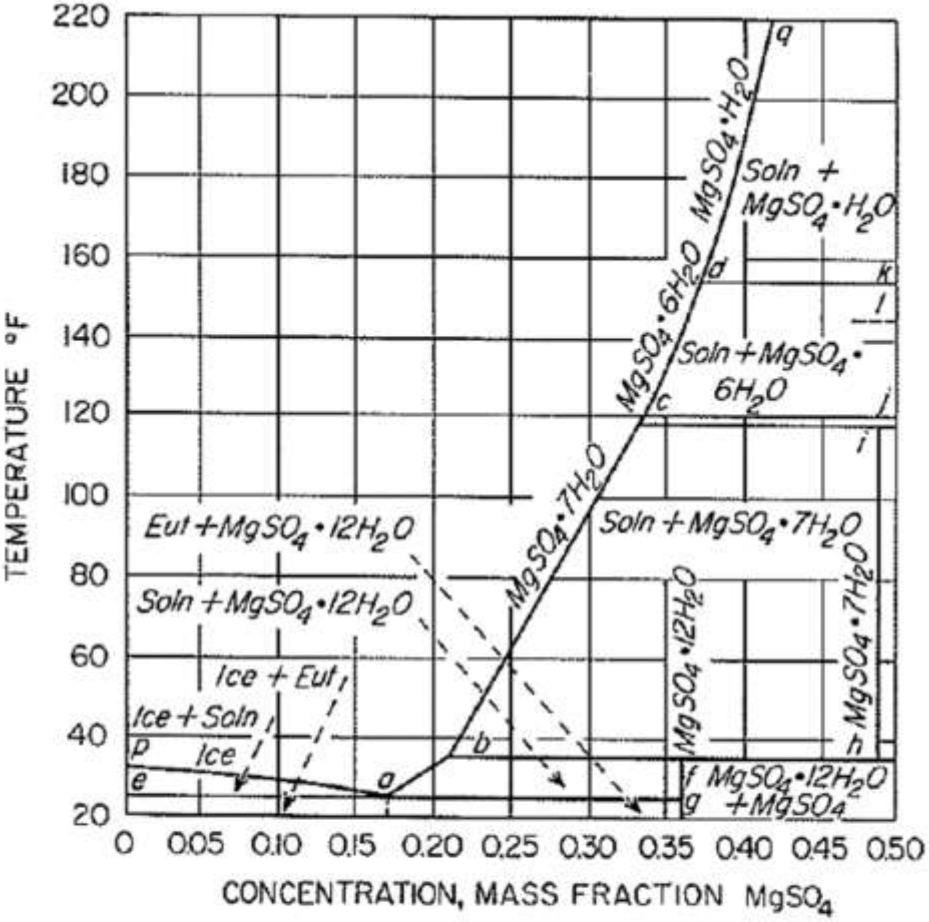
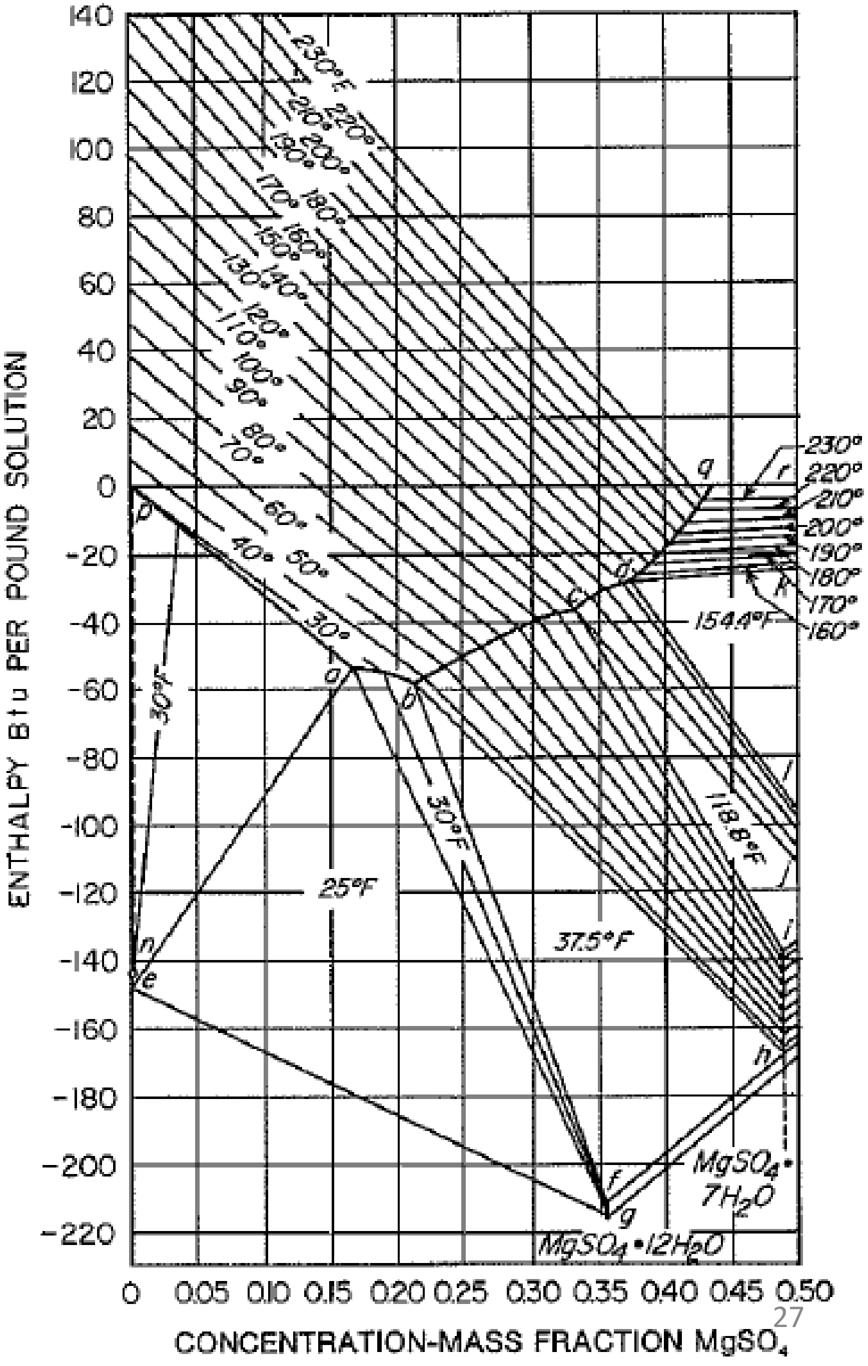


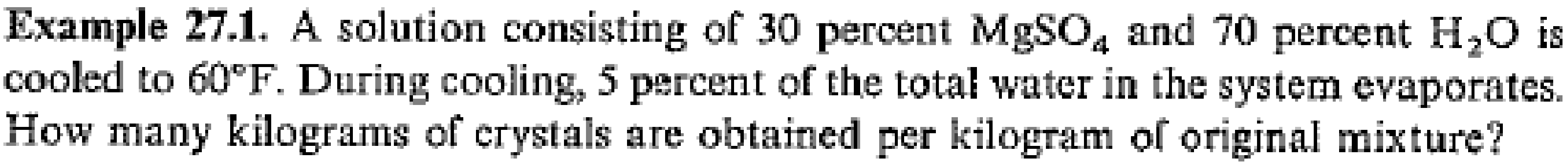
Figure 17.9 Integral heats of solution for sulfates in water at 25°C.

Phase and Enthalpy Concentration Diagram for $Mg\,SO_4$

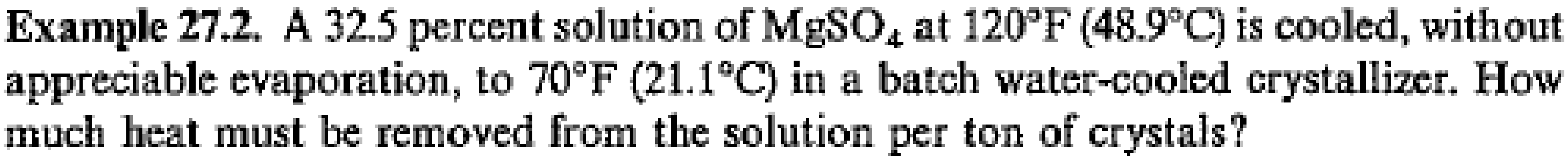




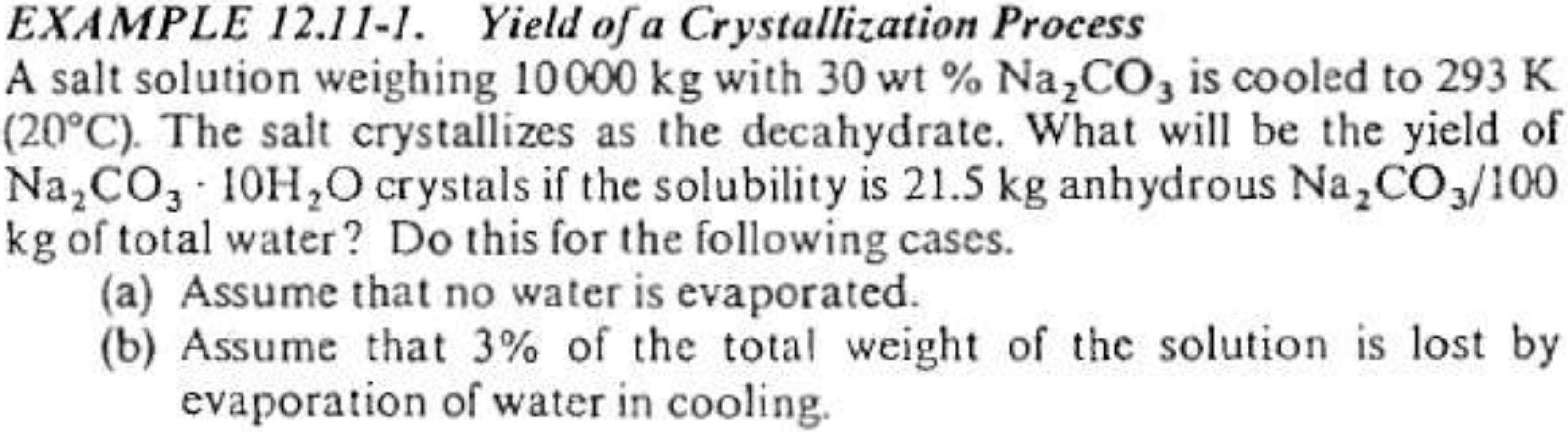
- A 32.5% solution of $MgSO_4$ at 120oF (48.9oC)is cooled without appreciable evaporation to 70oF (21.1oC) in a batch water cooled crystallizer. How much heat must be removed from the solution per 1000kg of crystals?
- Solubility at 70oF = 0.259 mass fraction $MgSO_4$
- Enthalpy:
- 120oF, 0.325 = -33Btu/lb
- 70oF, 0.325 = -78.4 Btu/lb.



Example 27.1. A solution consisting of 30 percent $MgSO_4$ and 70 percent H_2O is cooled to 60°F. During cooling, 5 percent of the total water in the system evaporates. How many kilograms of crystals are obtained per kilogram of original mixture?



Example 27.2. A 32.5 percent solution of $MgSO_4$ at 120°F (48.9°C) is cooled, without appreciable evaporation, to 70°F (21.1°C) in a batch water-cooled crystallizer. How much heat must be removed from the solution per ton of crystals?

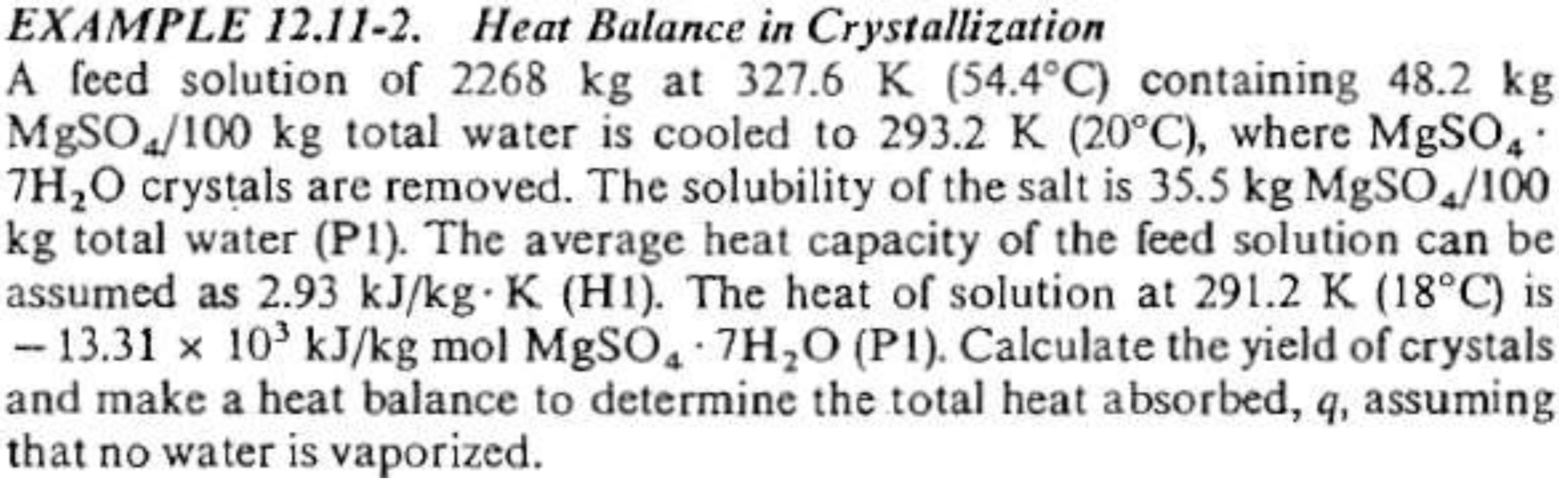


EXAMPLE 12.11-1. Yield of a Crystallization Process

A salt solution weighing 10000 kg with 30 wt % Na_2CO_3 is cooled to 293 K (20°C). The salt crystallizes as the decahydrate. What will be the yield of $Na_2CO_3 \cdot 10H_2O$ crystals if the solubility is 21.5 kg anhydrous Na_2CO_3/100 kg of total water? Do this for the following cases.

(a) Assume that no water is evaporated.

(b) Assume that 3% of the total weight of the solution is lost by evaporation of water in cooling.

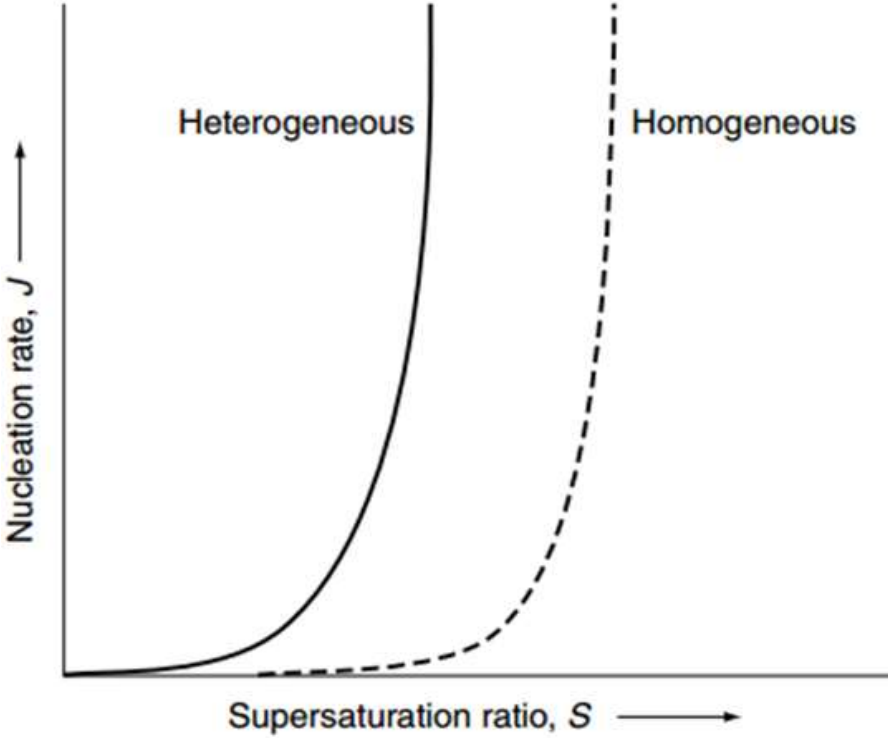


EXAMPLE 12.11-2. Heat Balance in Crystallization

A feed solution of 2268 kg at 327.6 K (54.4°C) containing 48.2 kg $MgSO_4$/100 kg total water is cooled to 293.2 K (20°C), where $MgSO_4 \cdot 7H_2O$ crystals are removed. The solubility of the salt is 35.5 kg $MgSO_4$/100 kg total water (P1). The average heat capacity of the feed solution can be assumed as 2.93 kJ/kg · K (H1). The heat of solution at 291.2 K (18°C) is -13.31×10^3 kJ/kg mol $MgSO_4 \cdot 7H_2O$ (P1). Calculate the yield of crystals and make a heat balance to determine the total heat absorbed, q, assuming that no water is vaporized.

CLASSIFICAITON OF NUCLEATION

- Primary Nucleation
  - – Homogeneous nucleation
  - – Heterogeneous nucleation
- Secondary Nucleation
  - – Fluid shear nucleation
  - – Contact nucleation



SUPERSATURATION

Supersaturation, mole fraction of solute:$\Delta y = y - y_s$

- Where y, ys= mole fraction of solute in super satu soln. and saturated solution

Molar super-saturation, moles/unit volume:$\Delta c = c - c_s$

- Where c, cs = molar conc of solute in supersaturated and solution and saturated solution

- **Fractional Super saturation,** $s = \frac{\Delta c}{c_s} = \frac{\Delta y}{y_s}$
- **Concentration Ratio,** $\alpha = \frac{y}{y_s} = \frac{c}{c_s}$

$$\alpha = 1 + s$$

At 293 K, a supersaturated solution of sucrose contains 2.45 kg sucrose/kg water. If the equilibrium saturation value is 2.04 kg/kg water, what is the supersaturation ratio in terms of kg/kg water and kg/kg solution?

Solution

For concentrations in kg sucrose/kg water:

$$c = 2.45 \text{ kg/kg}, \; c^* = 2.04 \text{ kg/kg}$$

and:

$$S = c/c^* = (2.45/2.04) = \underline{\underline{1.20}}$$

For concentrations in kg sucrose/kg solution:

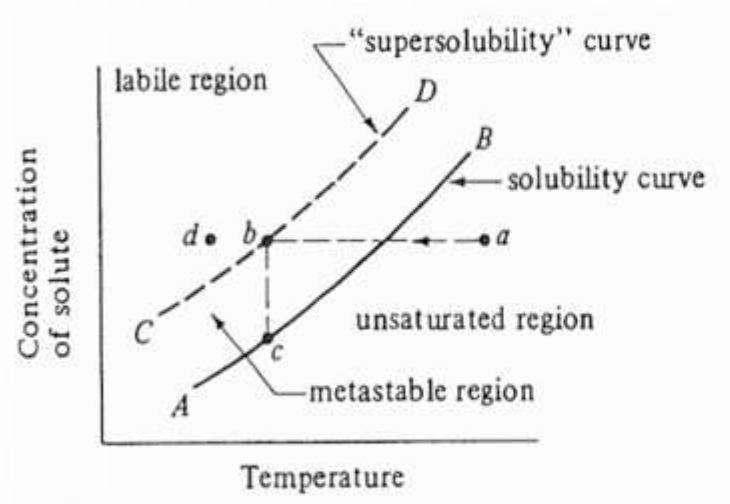
$$c = 2.45/(2.45 + 1.0) = 0.710 \text{ kg/kg solution,}$$

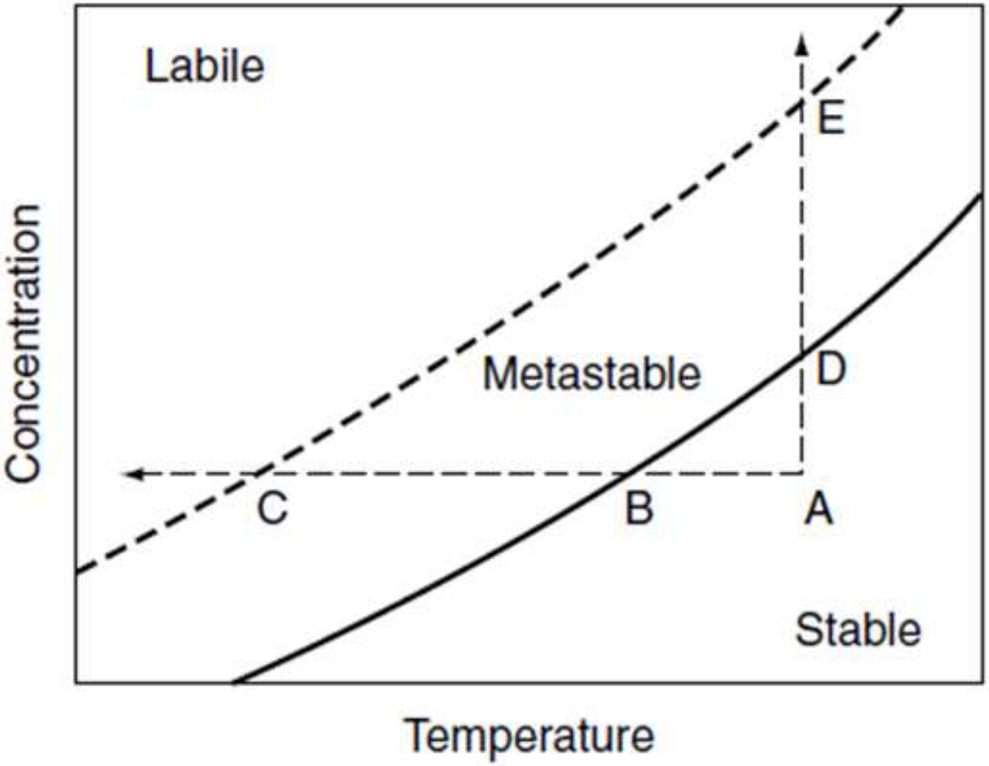
$$c^* = 2.04/(2.04 + 1.0) = 0.671 \text{ kg/kg solution}$$

and:

$$S = (0.710/0.671) = \underline{\underline{1.06}}$$

Miers Theory
SOLUBILITY
SUPER SOLUBILITY
CURVE





The driving force for crystallization is the thermodynamic super saturation. Labile and Metastable super saturation conditions describe conditions, under which spontaneous (primary nucleation) would or would not occur. Metastable zone can be represented by means of solubility, super solubility diagram.

- Whilst the (continuous) solubility curve can be determined accurately, the position of the (broken) supersolubility curve is less certain as it is influenced by factors such as the rate at which the supersaturation is generated, the degree of agitation and the presence of crystals or impurities. In the stable unsaturated zone, crystallisation is impossible. In the metastable supersaturated zone, spontaneous nucleation is improbable although a crystal would grow, and in the unstable or labile saturated zone, spontaneous nucleation is probable but not inevitable.
- If a solution at A is cooled without loss of solvent along ABC, spontaneous nucleation cannot occur until C is reached. Although the tendency to nucleate increases once the labile zone is reached, some solutions become too viscous to permit nucleation and set to a glass.
- Supersaturation can also be achieved by removing solvent and ADE represents such an operation carried out at constant temperature. Because the solution near the evaporating surface is more highly supersaturated than the bulk solution, penetration into the labile zone rarely occurs and crystals at the surface fall into the solution and induce nucleation, often before bulk conditions at E have been reached. Industrial crystallisers often combine cooling and evaporation.

HOMOGENEOUS NUCLEATION

- **Unit of crystals: molecules, atoms or ions**
- **The units are at random motion. They can momentarily join to form a cluster – a loose aggregate.. Occasionally they may grow to an embryo which is the beginning of a lattice arrangement and the formation of new and separate phase. , if supersaturation is large enough a thermodynamic equilibrium is reached a nucleus is formed which grow to form crystals.**
- $\boldsymbol{Cluster} \rightarrow \boldsymbol{embryo} \rightarrow \boldsymbol{nucleus} \rightarrow$
  $\rightarrow \boldsymbol{crystal};$

HOMOGENEOUS NUCLEATION:EQUILIBRIUM BY KELVIN EQUATION

- OSTWALD RIPENING: Smaller crystal due to higher surface energy per unit mass has higher solubility than a bigger crystal. A small crystal can be in equilibrium with a supersaturated solution. If a large crystal is also present, the smaller crystal dissolve and the larger one grow till the smaller one disappears

- KELVIN EQUATION {Solubility as a function of particle size}:

$$ln\alpha = \frac{4V_M\sigma}{\vartheta RTL}$$

- ➢ L= crystal size; V_M = molar volume of crystal
- ➢ α= ratio of concentration of supersaturated and saturated solution
- ➢ σ= average interfacial tension between solid and liquid
- ➢ ϑ =number of ions per molecule of solute(=1 for molecular crystals)

HOMOGENEOUS NUCLEATION: RATE OF NUCLEATION

- From theory of chemical kinetics:
- $B^0 = Cexp\left[-\frac{16\pi\sigma^3 V_M^2 N_o}{3\,\vartheta^2 (RT)^3 (ln\alpha)^2}\right]$
- B^0 = nucleation rate number/cm3.s
- C= frequency factor, statistical measure of the rate of formation of embryo that reach the critical size.
- V_M = molar volume of crystal
- N_o = Avogadro Number 6.0222 $x\ 10^{23}$ molecules/gmol
- ➢ α= ratio of concentration of supersaturated and saturated solution
- ➢ σ= average interfacial tension between solid and liquid
- ➢ ϑ =number of ions per molecule of solute (=1 for molecular crystals)
- ➢ R= gas constant, 8.3143 $x10^7$ergs/g mol.K

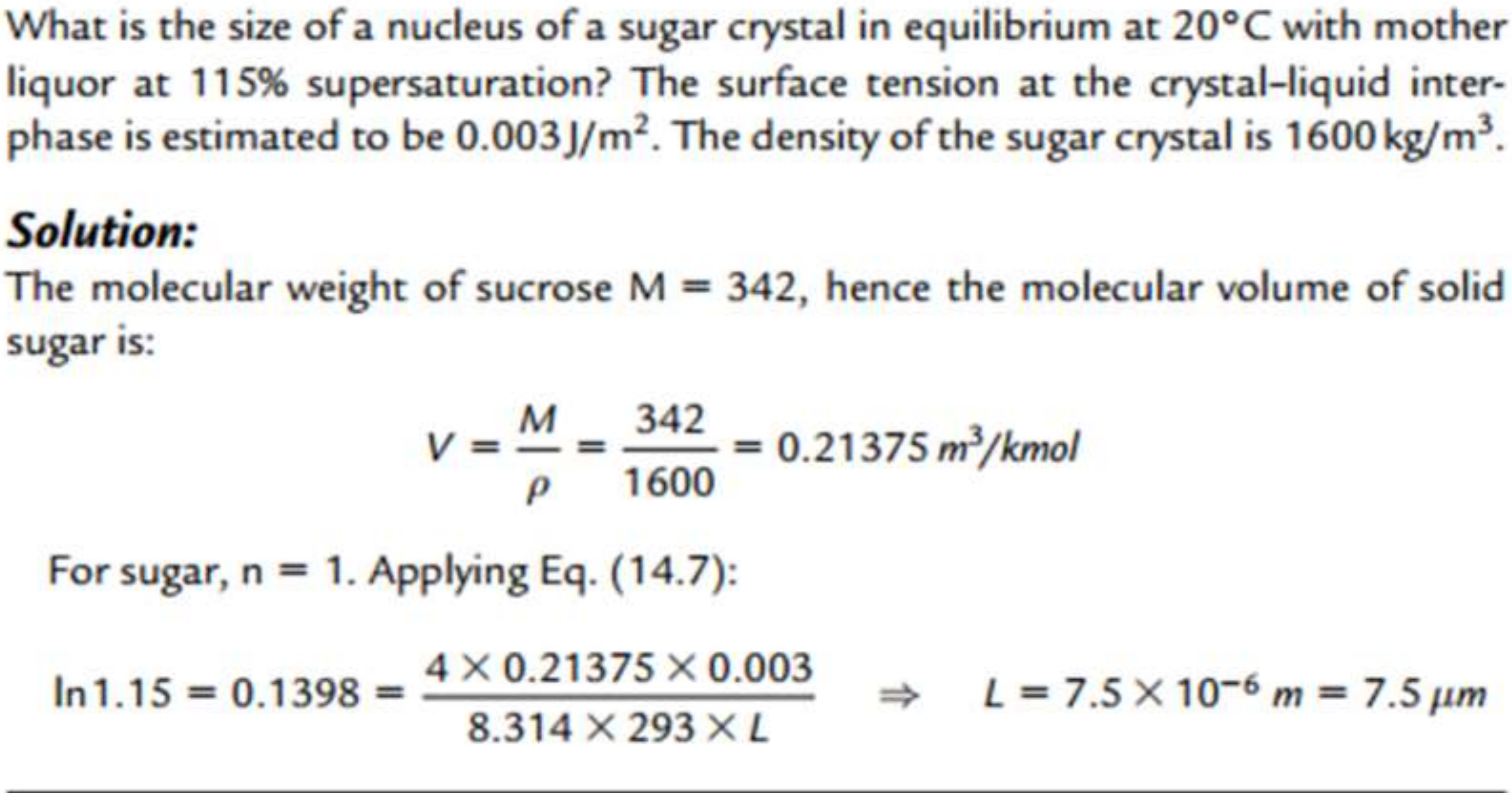
HETEROGENEOUS NUCLEATION

- **The catalytic effect of solid particles on nucleation rate : reduces the energy required for nucleation.**

- C= frequency factor, statistical measure of the rate of formation of embryo that reach the critical size=10^7
- $\boldsymbol{ln\alpha = \alpha - 1 = s}$

$$B^o = 10^{25}\ exp\left[-\frac{16\pi V_M{}^2 N_o \sigma_o{}^3}{3\vartheta^2 (RT)^3 s^2}\right]$$

- B^0 = nucleation rate number/cm3.s
- V_M = molar volume of crystal
- N_o = Avogadro Number 6.0222 $x\ 10^{23}$ molecules/gmol
- α= ratio of concentration of supersaturated and saturated solution
- σ= average interfacial tension between solid and liquid
- ϑ =number of ions per molecule of solute (=1 for molecular crystals)
- R= gas constant, 8.3143 $x10^7$ergs/g mol.K



What is the size of a nucleus of a sugar crystal in equilibrium at 20°C with mother liquor at 115% supersaturation? The surface tension at the crystal-liquid interphase is estimated to be 0.003 J/m². The density of the sugar crystal is 1600 kg/m³.

Solution:

The molecular weight of sucrose M = 342, hence the molecular volume of solid sugar is:

$$V = \frac{M}{\rho} = \frac{342}{1600} = 0.21375\, m^3/kmol$$

For sugar, n = 1. Applying Eq. (14.7):

$$\ln 1.15 = 0.1398 = \frac{4 \times 0.21375 \times 0.003}{8.314 \times 293 \times L} \quad \Rightarrow \quad L = 7.5 \times 10^{-6}\, m = 7.5\, \mu m$$

- $ln\alpha = \frac{4V_M\sigma}{\vartheta RTL}$ R= 8.314 m3Pa/kgmol

- Assuming that the rate of heterogeneous nucleation of potassium chloride is consistent with an apparent interfacial tension of 2.5ergs/cm2, Plot the nucleation rate as a function of s at a temperature of 300K.

[Crystal Density = 1.988gm/cm3]

- What would be the size of nucleus in equilibrium with a super saturation of 0.29 when the growth rate is 1 /cm3s

[Use Kelvin Equation]

SECONDARY NUCLEATION

- Formation of nuclei due to te influence of existing macroscopic crystals in magma.
- FLUID SHEAR
- CONTACT- contact with one another or with the walls of the crystallizer and impellor

NUCLEATION RATE IN COMMERCIAL CRYSTALLIZER

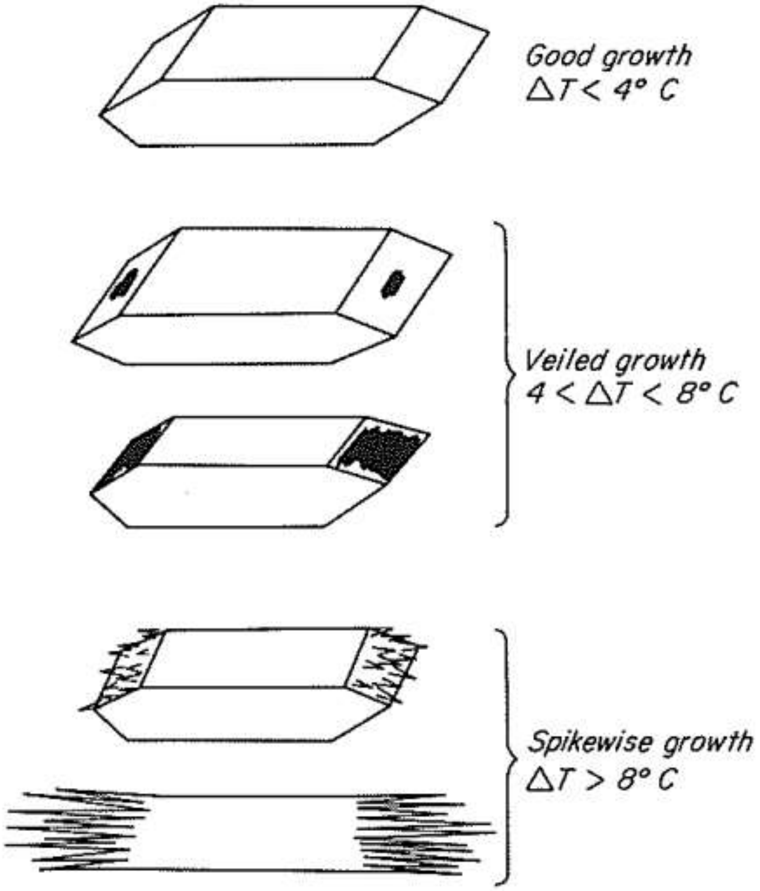
- Overall rate of Nucleation in a commercial crystallizer

$$B^0 = B_{ss} + B_{ci} + B_{cc}$$

- B_{ss}= rate of nucleation due to supersaturation
- $B_{ci} =$ rate due to contact with impeller
- $B_{cc} =$ rate due to crystal – crystal contact

Undesired Nucleation

- **<u>Initial breeding</u>**: During addition of seed crystals, many small crystals formed during drying and storage wash off and form nucleus
- **<u>Growth related spurious nucleation</u>** due to very large value of supersaturation
  - ➢ Needle breeding
  - ➢ Veiled growth



CRYSTAL GROWTH

- The growth of crystal:
  1. Crystal units diffuses from the solution to the surface of crystal
  2. The molecules or ions must be accepted by the crystal and organized into the space lattice.
- The mass transfer equation:

$$N_A = \frac{\dot{m}}{s_p} = k_y(y - y')$$

- N_A = molar flux, moles per unit time per unit area
- $\dot{m}$ = rate of mass transfer, mol / h
- s_p = surface area of crystal
- k_y = mass transfer coefficient
- y = conc. In the bulk y' = conc. at interface
- y_s = saturated conc.
- k_s = surface reaction coefficient K= overall rate coefficient
- Equation for surface reaction rate:

$$\frac{\dot{m}}{s_p} = k_s(y' - y_s)$$

$$\frac{\dot{m}}{s_p} = K(y - y_s)$$

$$K = \frac{1}{\left(1/k_y\right) + (1/k_s)}$$

CRYSTAL GROWTH RATE, G

- Volume of the crystal=v_p
- $characteristic\ length = L$

$$v_p \propto L^3$$

$$v_p = aL^3$$

- Mass of the particle
- $m = v_p \rho_M = aL^3 \rho_M$
- $\dot{m} = \frac{dm}{dt} = 3aL^2 \rho_M \frac{dL}{dt}$

$$\frac{dL}{dt} = \mathrm{G} = \text{Growth rate}$$

- $\dot{m} = 3aL^2 \rho_M G$
- $\frac{\dot{m}}{s_p} = K(y - y_s)$
- Assuming crystal to have sphericity =1[$\varphi = 1$]
- $s_p = 6v_p/L = 6aL^2$;
- $\dot{m} = 6aL^2\ K(y - y_s)$

$$3aL^2 \rho_M G = 6aL^2\ K(y - y_s)$$

$$G = \frac{2K(y - y_s)}{\rho_M}$$

ΔL law of crystal growth

- *If all crystals in magma grow in a uniform supersaturation field and at the same temperature and if all crystals grow from birth at a rate governed by the supersaturation, then all crystals are not only invariant but also have the same growth rate that is independent of size.*

$$G \neq f(L)$$
$$\Delta L = G\Delta t$$

- ΔL= growth of each crystal in magma
- Δt= time interval
- G=dL /dt= growth rate

$$G = \frac{2K(y - y_s)}{\rho_M}$$

K= overall mass transfer coefficient

$K = \frac{1}{1/k_y + 1/k_s}$ where ky= mtc in liquid, ks=surface reaction coefficient

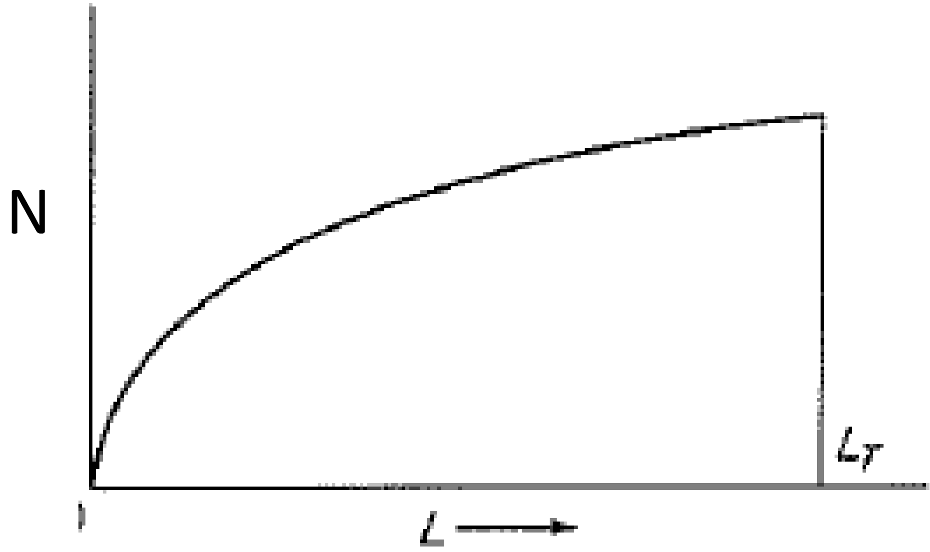
- ρ_M =molar density

Designing of MSMPR(Mixed Suspension Mixed Product Removal) Crystallizer

- Steady state
- Suspension completely mixed
- Super-saturation uniform
- No crystal in feed
- ΔL law applies
- Ideal mixed – CSTR
- Product magma leaves the crystallizer at equilibrium
- No Crystal breakage

Crystal population density function n

- N =total cumulative number of crystals per unit volume of suspension of size L and smaller
- n= **crystal population density** = slope of N vs L curve
- $n = \frac{dN}{dL}$
- n=number of crystals/Lmm
- n characterizes nuclear growth rate in a crystallizer



n as a function of L can be obtained from screen analysis curve

-Mesh	+Mesh	L min	L max	L avg	Vp=a Lavg3	Wt fraction	ΔL=Lmax-Lmin	ΔN=m/densityx volume	n =ΔN/ΔL

- a = crystal shape factor.
- vp= volume of a particle
- $\Delta N = \frac{m}{density\ x\ volume}$
- $n = \frac{\Delta N}{\Delta L} = \frac{\left(conc\ in \frac{g}{L}\right) Wt\ fraction}{mass\ of\ 1\ crystal\ x\ \Delta L} = \frac{\left(conc\ in \frac{g}{L}\right) Wt\ fraction}{\rho(aL^3)\Delta L}$

Population material balance

- Basis : timeΔt
- Amount of crystals withdrawn =Δn x ΔL
- Amount of out flow = Q L/hr
- Composition of out flow = composition of magma in crystallizer
- $\frac{n\Delta L}{V} = -\frac{\Delta n\ \Delta L}{Q\ \Delta t} = -\frac{\Delta n\ G\Delta t}{Q\ \Delta t} = -\frac{\Delta n\ G}{Q}$

  $-\frac{\Delta n}{n} = \frac{\Delta L\ Q}{V\ G} = \frac{\Delta L}{G\tau}$ or $\int_{n^0}^{n} \frac{dn}{n} = -\frac{1}{G\tau} \int_0^L dL$
- $ln\, n = -\frac{L}{G\tau} + ln\, n^0$
- From plot of ln n vs L no and G can be obtained

Design equations

- Average size in mm of mass distribution

$$L_{avg} = 3.67G\tau$$

- Predominant particle size

$$L_p = 3.00G\tau$$

- Nucleation rate:

$$B^0 = Gn^0$$

- Prediction of cumulative weight fraction obtained:

$$\left(1 - W_f\right) = e^{-x}(1 + x + x^2/2 + x^3/6)$$

- $\left(1 - W_f\right)$=cumulative wt fraction at opening L mm
- x= L/Gτ

- Calculate Population density and nucleation growth rates for crystal samples of urea from screen analysis. The slurry density (g of crystals) is 450gm/lit, the crystal shape factor a is 1.00 the crystal density is 1.335 g/cm3, residence time is 3.38 hours The screen analysis from the reference is as follows:

Mesh	Wt %
-14 + 20	4.4
-20+28	14.4
-28+35	24.2
-35+48	31.6
-48+65	15.5
-65+100	7.4
-100	2.5

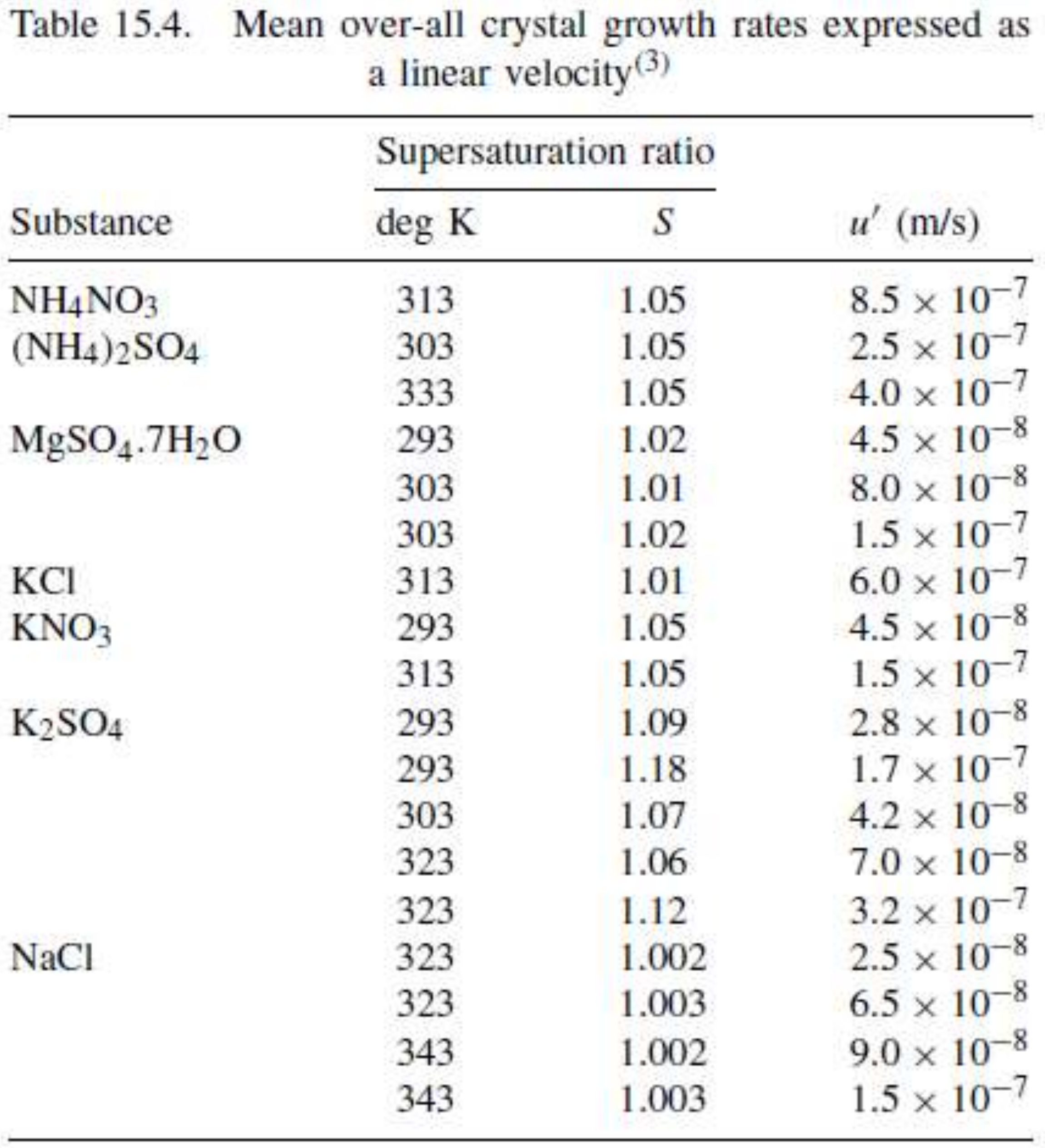


Table 15.4. Mean over-all crystal growth rates expressed as a linear velocity(3)

	Supersaturation ratio		
Substance	deg K	S	u' (m/s)
NH_4NO_3	313	1.05	8.5×10^{-7}
$(NH_4)_2SO_4$	303	1.05	2.5×10^{-7}
	333	1.05	4.0×10^{-7}
$MgSO_4.7H_2O$	293	1.02	4.5×10^{-8}
	303	1.01	8.0×10^{-8}
	303	1.02	1.5×10^{-7}
KCl	313	1.01	6.0×10^{-7}
KNO_3	293	1.05	4.5×10^{-8}
	313	1.05	1.5×10^{-7}
K_2SO_4	293	1.09	2.8×10^{-8}
	293	1.18	1.7×10^{-7}
	303	1.07	4.2×10^{-8}
	323	1.06	7.0×10^{-8}
	323	1.12	3.2×10^{-7}
NaCl	323	1.002	2.5×10^{-8}
	323	1.003	6.5×10^{-8}
	343	1.002	9.0×10^{-8}
	343	1.003	1.5×10^{-7}