Extraction of Non-Ferrous metals

Basic principles-1

Standard free energies of formation of oxides $(-\Delta G^\circ = -RT \ln p_{O_2})$: kilojoules/mole O_2
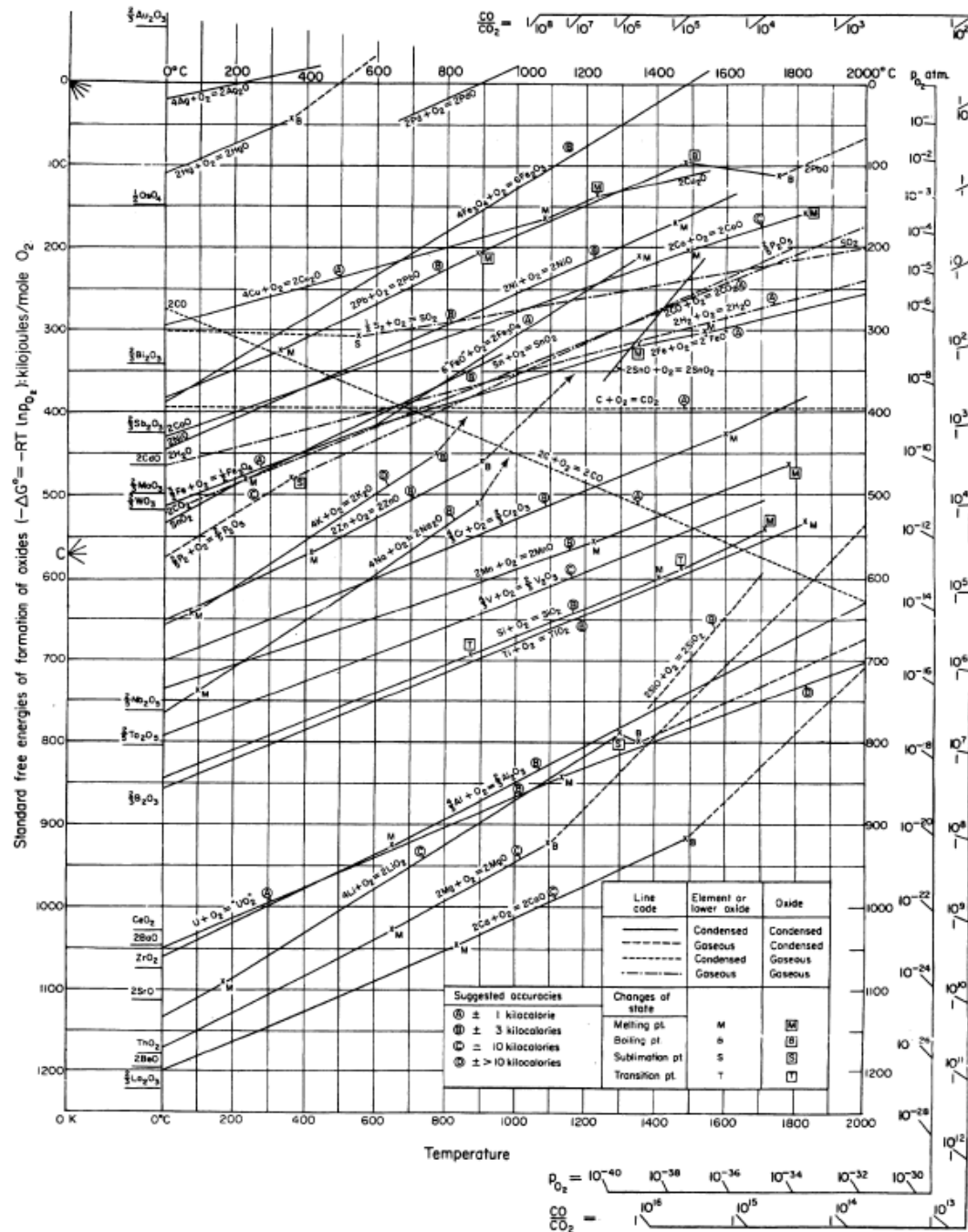
$$\Delta G = \Delta H - T\Delta S$$

It is a plot of $\Delta G \; vs. \, T$

$\Delta H \; and \; \Delta S$ are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept.

The slope of the line changes when any of the materials involved *melt or vaporize*.

The *oxygen partial pressure* is taken as *1 atmosphere*, and all of the reactions are normalized to consume *one mole of O_2*.

The *majority of the lines slope upwards*, because both the metal and the oxide are present as condensed phases (solid or liquid). The reactions are therefore reacting a gas with a condensed phase to make another condensed phase, which reduces the entropy. *A notable exception to this is the oxidation of solid carbon*. The line for the reaction:

$C+O_2 ==> CO_2$
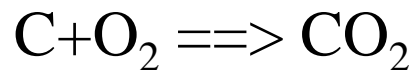
It is a solid reacting with a mole of gas to produce a mole of gas, and so there is *little change in entropy and the line is nearly horizontal*.

For the reaction

$2C+O_2 ==> 2CO$
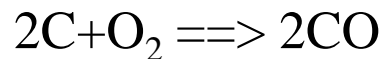
we have a solid reacting with a gas to produce two moles of gas, and so there is a *substantial increase in entropy and the line slopes rather sharply downward*.

Similar behavior can be seen in parts of the lines for lead and lithium, both of which have oxides that boil at slightly lower temperatures than the metal does.

There are three main uses of the Ellingham diagram:

➢Determine the *relative ease* of reducing a given metallic oxide to metal;

➢Determine the *partial pressure of oxygen* that is in equilibrium with a metal oxide at a given temperature; and

➢Determine *the ratio of* carbon monoxide to carbon dioxide that will be able to reduce the oxide to metal at a given temperature.

Ease of Reduction:

The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature.

Reactions closer to the top of the diagram are the most "noble" metals (for example, gold and platinum), and their oxides are unstable and easily reduced. As we move down toward the bottom of the diagram, the metals become progressively more reactive and their oxides become harder to reduce.

A given metal can reduce the oxides of all other metals whose lines lie above theirs on the diagram. For example, the $2Mg + O_2 ==> 2MgO$ line lies below the $Ti + O_2 ==> TiO_2$ line, and so metallic magnesium can reduce titanium oxide to metallic titanium.

Since the $2C + O_2 ==> 2CO$ line is downward-sloping, it cuts across the lines for many of the other metals. This makes carbon unusually useful as a reducing agent, because as soon as the carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to metal. So, for example, solid carbon can reduce chromium oxide once the temperature exceeds approximately 1225°C, and can even reduce highly-stable compounds like silicon dioxide and titanium dioxide at temperatures above about 1620°C and 1650°C, respectively. For less stable oxides, carbon monoxide is often an adequate reducing agent.

Equilibrium Partial Pressure of Oxygen:

The scale on the right side of the diagram labelled "p_{o2}" is used to determine what partial pressure of oxygen will be in equilibrium with the metal and metal oxide at a given temperature. The significance of this is that, if the oxygen partial pressure is higher than the equilibrium value, the metal will be oxidized, and if it is lower than the equilibrium value then the oxide will be reduced.

To use this scale, you will need a straightedge. First, find the temperature you are interested in, and find the point where the oxidation line of interest crosses that temperature. Then, line up the straightedge with both that point, and with the point labelled "0" that is marked with short radiating lines (upper left corner of the diagram). Now, with the straightedge running through these two points, read off the oxygen partial pressure (in atmospheres) where the straightedge crosses the "Po_2" scale, and this is the equilibrium partial pressure.

It is possible to reach the equilibrium oxygen partial pressure by use of a hard vacuum, by purging with an inert gas to displace the oxygen, or by using a scavenger chemical to consume the oxygen.

Ratio of CO/CO$_2$ Needed for Reduction:

When using carbon as a reducing agent, there will be a minimum ratio of CO to CO$_2$ that will be able to reduce a given oxide. The harder the oxide is to reduce, the greater the proportion of CO needed in the gases.

To determine the CO/CO$_2$ ratio to reduce a metal oxide at a particular temperature, use the same procedure as for determining the equilibrium pressure of oxygen, except line up the straightedge with the point marked "C" (center of the left side of the diagram), and read the ratio off of the scale marked "CO/CO$_2$".

Calcination

Calcination is a thermal treatment process and applied to ores and other solid materials to bring about:

1. Thermal decomposition

2. Phase transition

3. Removal of volatile fraction such as CO_2, H_2O.

Temperature: Below the melting point

Product of the calcination: Calcine

Furnace: Rotary kiln, Fluidized bed reactor, Multiple hearth furnaces etc. (Done in Solid state)

Fuel (source of energy): Fossil fuel

Secondary fuel (e.g. producer gas)

Applications:

1. To produce cement from $CaCO_3$.

2. Decomposition of hydrated minerals (e.g. calcination of bauxite to produce refractory grade Al_2O_3)

3. To produce anhydrous Al_2O_3 for electrolysis in Hall-Heroult call.

4. Decomposition of volatile matter contained in the petroleum coke.

5. Heat treatment to effect phase trans formation (e.g. devitrification of glass materials).

Roasting

- Roasting of an ore or concentrate is to convert it into another chemical form.

- An oxide is more easily reduced to metal than a sulphide and leaching is easier if the metal is present as sulphate, chloride or oxide.

- Some typical roasting operations are:

1. **Oxidizing Roasting:** Metal sulphide → Metal oxide.

2. **Volatilizing Roasting:** Elimination of volatile oxides such as As_2O_3, Sb_2O_3, ZnO from the ore.

3. **Chloridizing Roasting:** Metal compounds to chlorides under oxidizing or reducing conditions

$$2NaCl + MS + 2O_2 \rightarrow Na_2SO_4 + MCl_2$$

4. **Sulphatizing Roasting:** Sulphide ores to sulphates prior to leaching.

5. **Magnetic Roasting**:

Controlled reduction of hematite (Fe_2O_3) $\rightarrow$ magnetite (Fe_3O_4).

6. **Reduction Roasting**: Partial reduction of an oxide ore prior to actual reduction smelting.

7. **Blast Roasting or Sinter Roasting**: Partial oxidization as well as physical condition ore is changed

Calcination vs. Roasting

Calcination

- Used primarily for carbonate ores.
- Work in absence of air.
- CO_2 gas evolved/separated

Roasting

- Used primarily for sulphide ores.
- Work/done in presence of excess air
- Sulphur dioxide (SO_2) is a product.

Basic Steps in Roasting:

➢ Particles are heated.
➢ Reactive gas (air, oxygen, chlorine, etc.) contacts the particles.
➢ Particles react with the gas.
➢ Gaseous reaction product are carried away.

Since the particles do not melt, the reaction starts on the particle surface and gradually works in to the particle core, as shown in the *Shrinking-Core* reaction model.
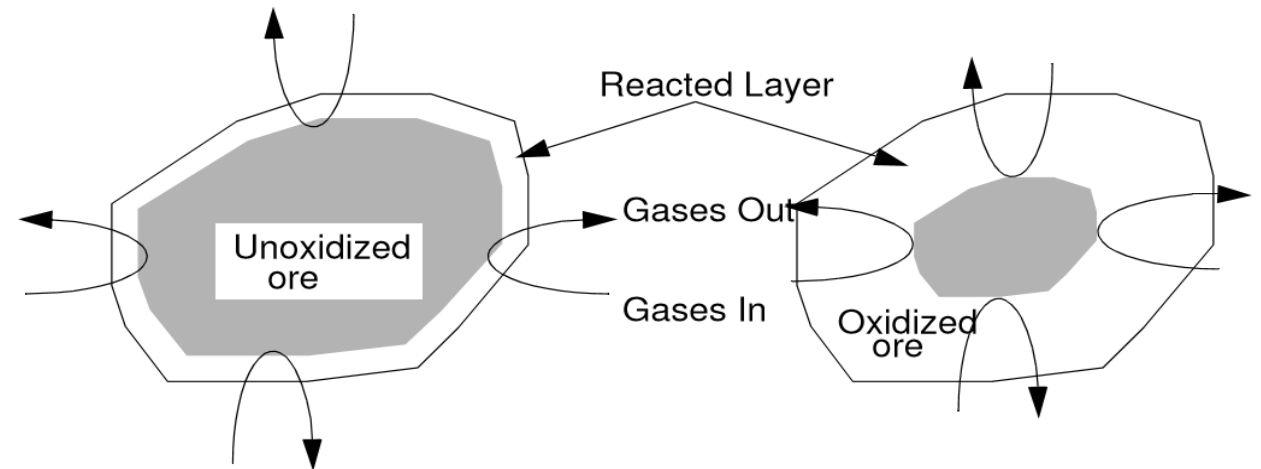
The Shrinking-Core model. As the shell of oxidized ore becomes thicker, it becomes more difficult for fresh gas to reach the unreacted ore, and so the roasting rate slows down. It is often difficult to react the last bit of material in the center of the particles

Basic Roasting Terms:

- Dead Roast: the ore is completely reacted, and leaves the process cold.
- Sweet Roast: the ore is completely reacted, but leaves the furnace still hot.
- Sour Roast: the roasting reaction is not run to completion.

Roasting depends on following factors:

1. Time

2. Temperature

3. Availability of O_2 or air

4. Physical condition

5. Nature of the mechanical device used

Criteria of selection of roasting process

1. **Physical condition of product**

➢ Blast furnace smelting – product should coarse or cellular.

➢ Reverberatory furnace – product should be fine.

➢ Leaching - product should be porous.

2. **Chemical composition of product**

➢ For copper – retain some Sulphur

➢ For Lead & Zinc - complete elimination of Sulphur

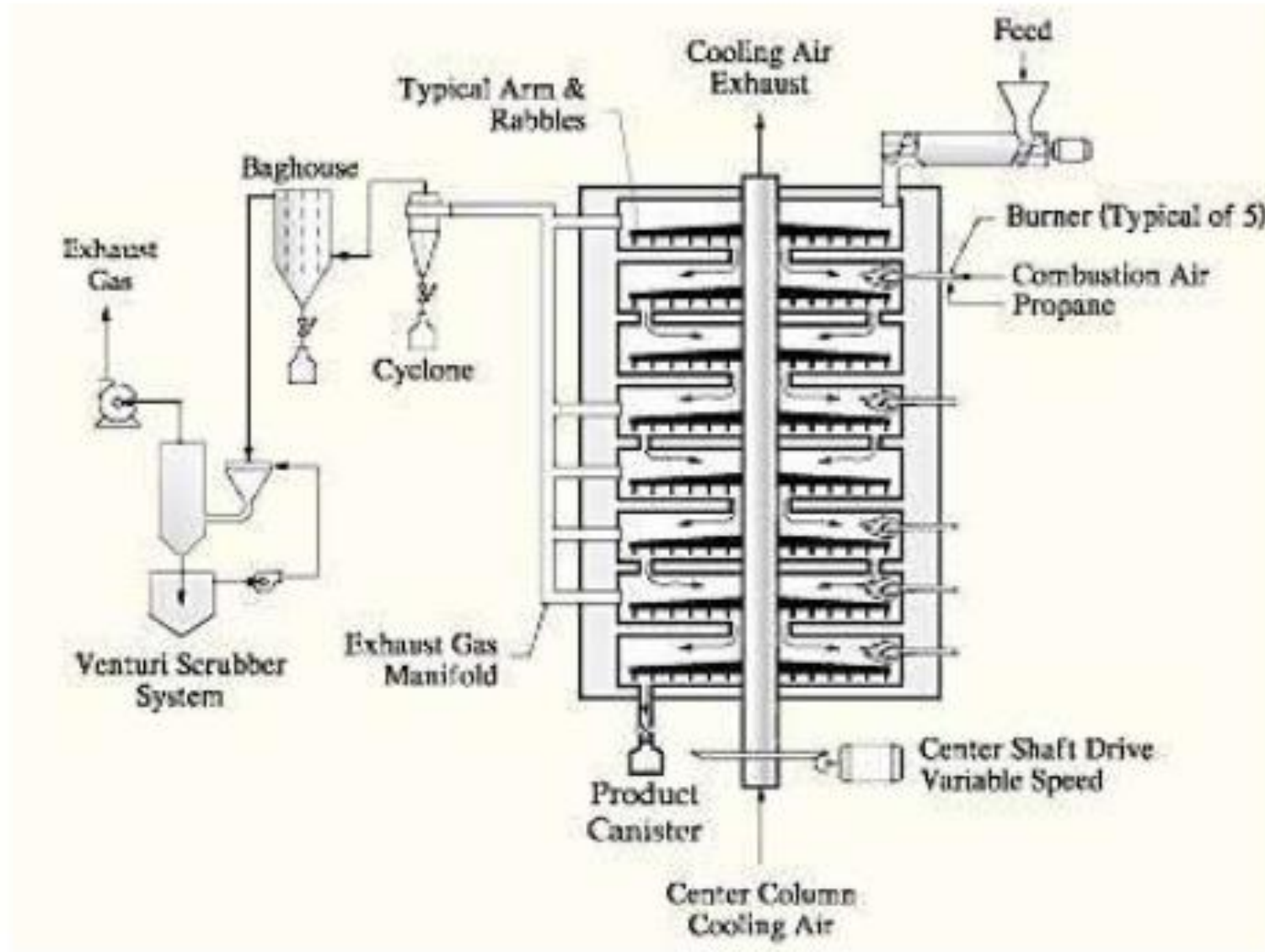# Multiple Hearth Roasting

MacDougall in England (19th Century)

Basic principle : Counter current flow of solid ore & the oxidizing gases.

Construction:

➢ It consists of several (about 10) circular brick hearths superimposed on each other.

➢ Cylindrical steel shell lined with brick.

➢ Revolving mechanical rabbles attached to arms move over the surface of each hearth to continuously shift the ore.

➢ Arms are attached to a rotating central shaft that passes through the center of the roaster.

Solids Flow

Hearths

Gas Flow
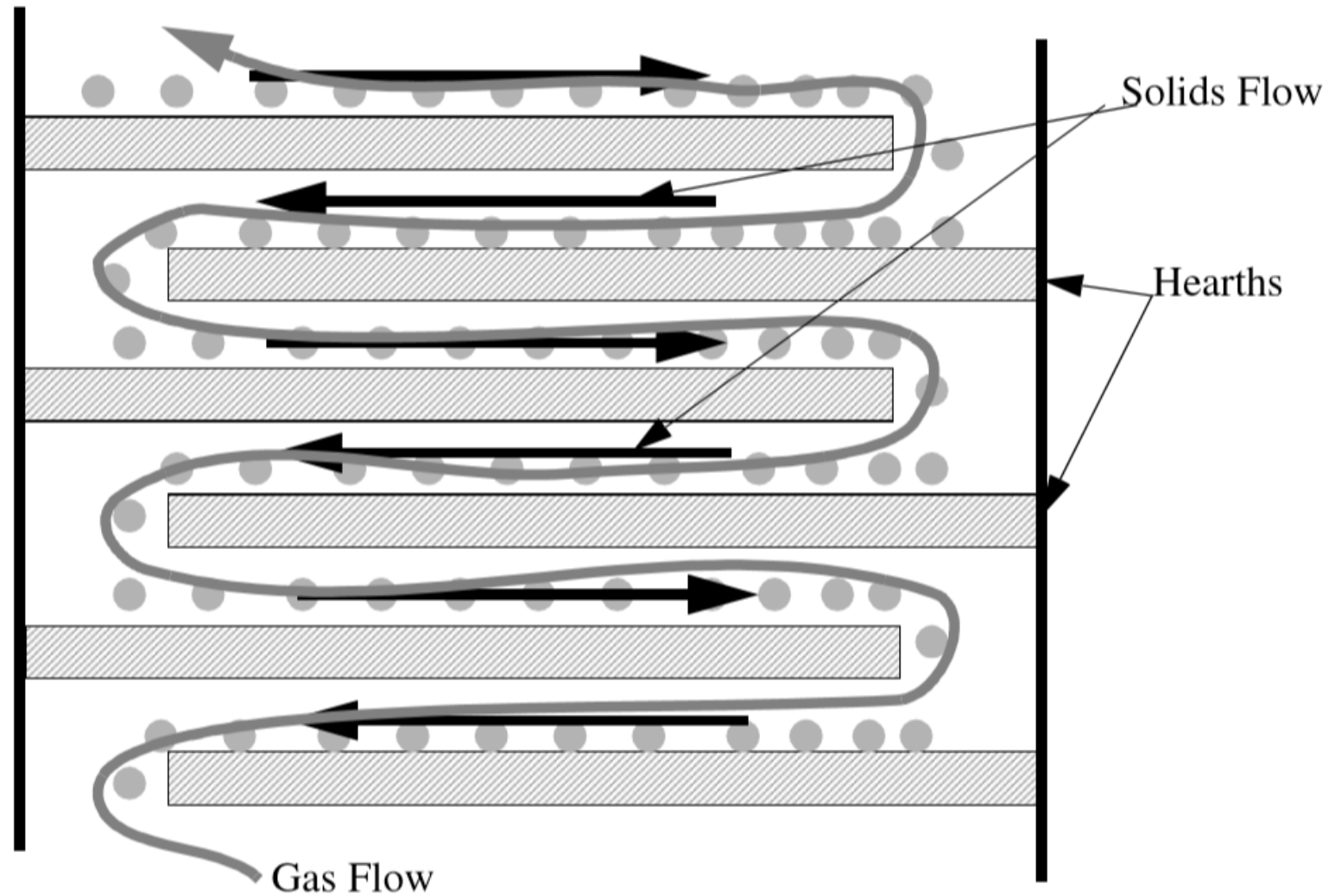
Working principle:

➢ The hearth at the top dry and heat the charge.

➢ Ore is discharged automatically at the top hearth.

➢ It gradually moves downwards through alternate passages around the shaft and periphery and finally emerges at the bottom.

➢ The oxidizing gases flow upwards.

➢ External heating of charge is unnecessary *except* when charge contain moisture.

Drawbacks:

➢ Roasting is slow.

➢ Gases are unsuitable for production of H_2SO_4 because they do not contain sufficient SO_2 and SO_3.

➢ Roasting is a high-temperature process that converts zinc sulfide concentrate to an impure zinc oxide called calcine.

➢ The following reactions occur during roasting:

$2ZnS + 3O_2 \rightarrow 2ZnO + SO_2$

$2SO_2 + O_2 \rightarrow 2SO_3$
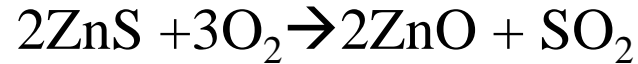
➢ In a multiple-hearth roaster, the concentrate drops through a series of 9 or more hearths stacked inside a brick-lined cylindrical column.

➢ As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine.

➢ Multiple hearth roasters are unpressurized and operate at about 690°C (1300°F). Operating time depends upon the composition of concentrate and the amount of the sulfur removal required. Multiple hearth roasters have the capability of producing a high-purity calcine.

➢Preheated ore particles are made to fall through body of hot air resulting in instantaneous oxidation or '*flashing*' of combustible constituents of the ore, mainly Sulphur. Hence called flash roasting.

➢Ore should be of fine size.

➢Capacity of flash roaster > hearth roaster.

➢Temp. of combustion zone = 900-950 °C
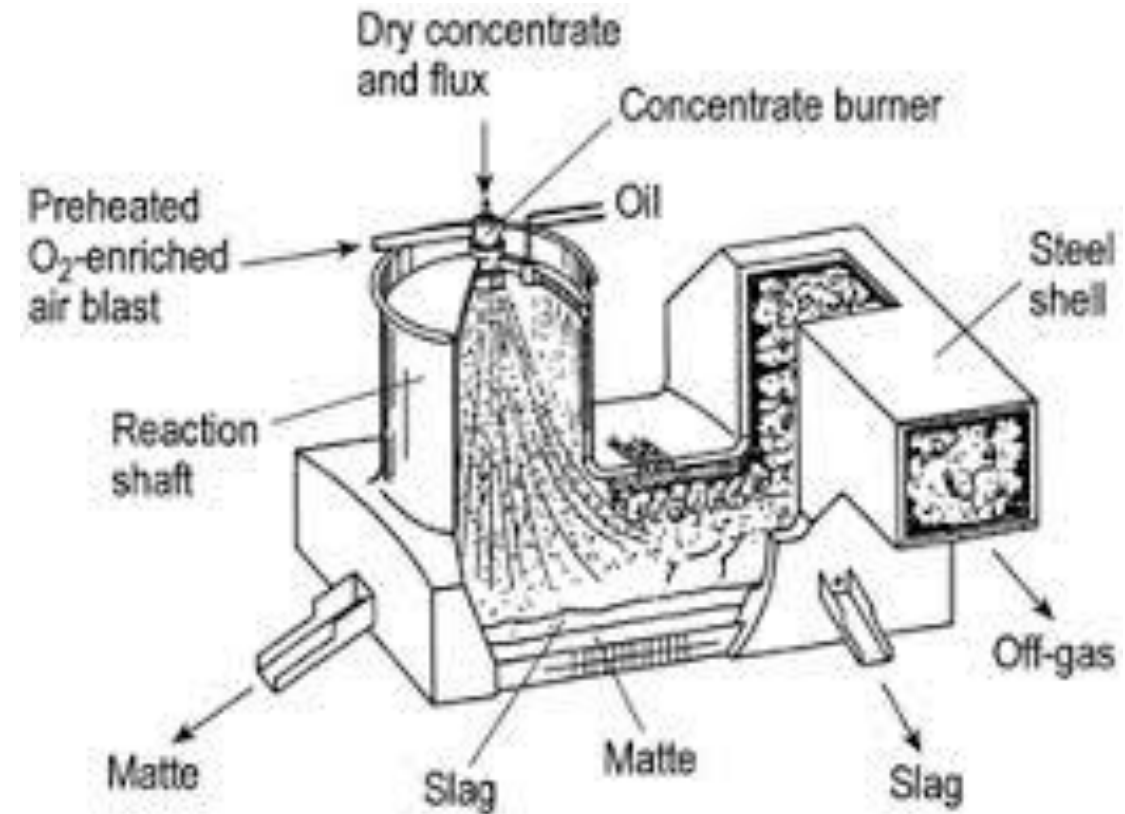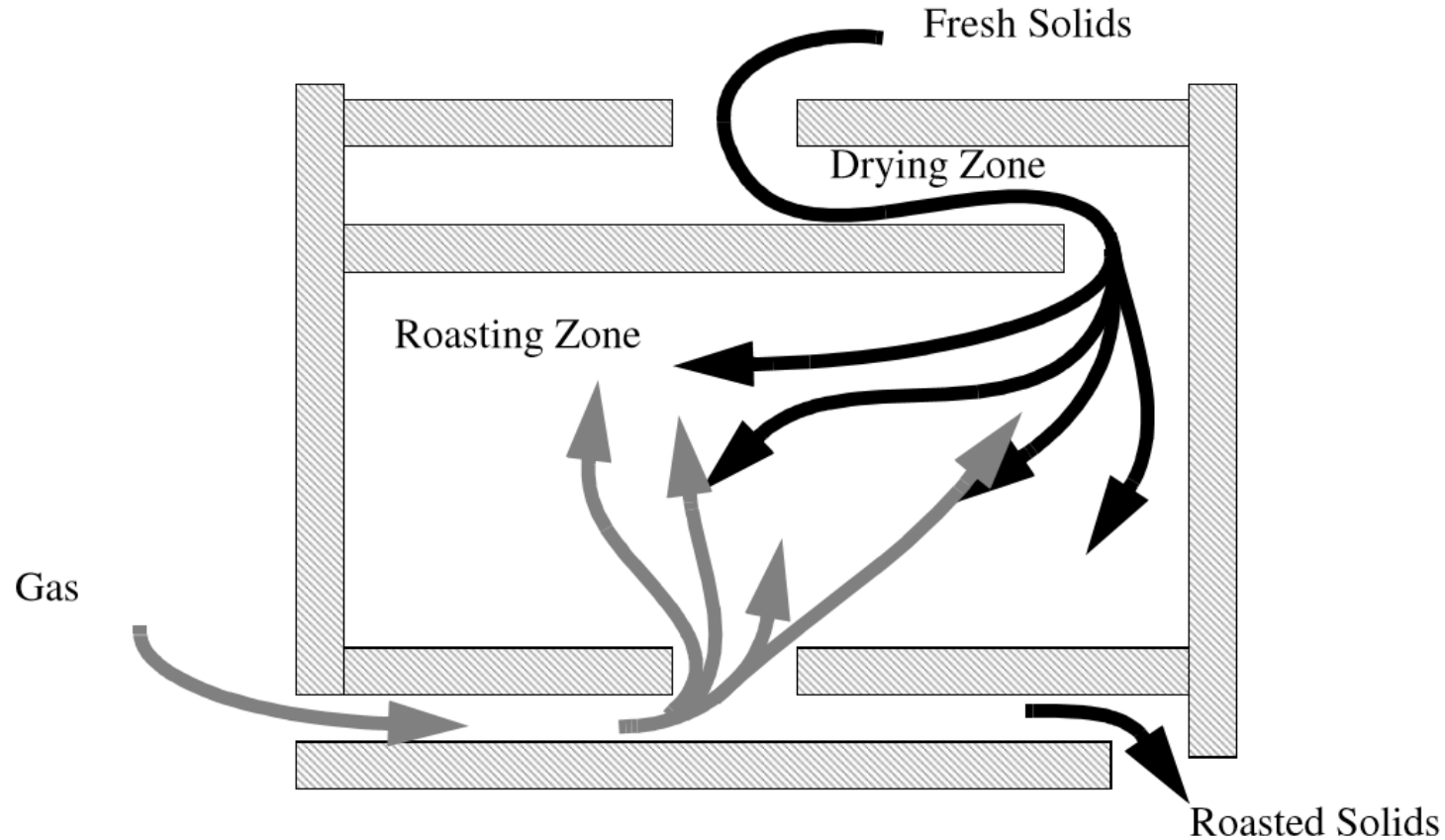
Flash Smelting. The heat produced by the roasting reaction is used to dry the incoming ore and bring it up to roasting temperature. If the reaction is sufficiently exothermic, the ore can even be melted.

Fluidized bed Roasting

➢The ore particles are roasted while suspended in an upward stream of gas.

➢Finely ground sulfide concentrates in size over the range 0.005 to 0.05 cm in diameter is used.

➢As in the suspension roaster, the reaction rates for desulfurization are more rapid than in the older multiple hearth processes.

➢Fluidized-bed roasters operate under a pressure slightly lower than atmospheric and at temperatures averaging 1000°C (1800°F).

➢In the fluidized-bed process, no additional fuel is required after ignition has been achieved.
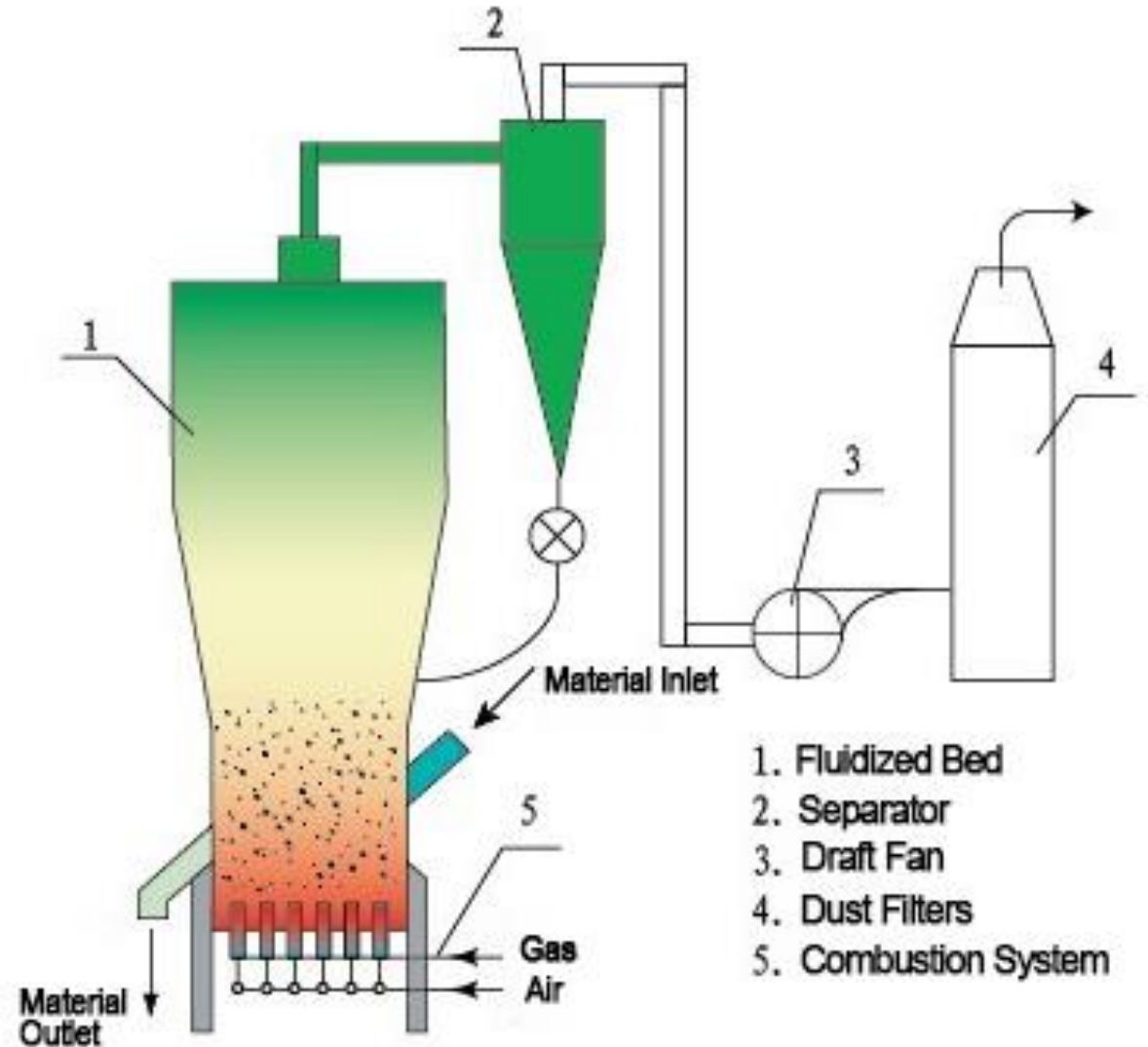
Fluidized Bed Reactor
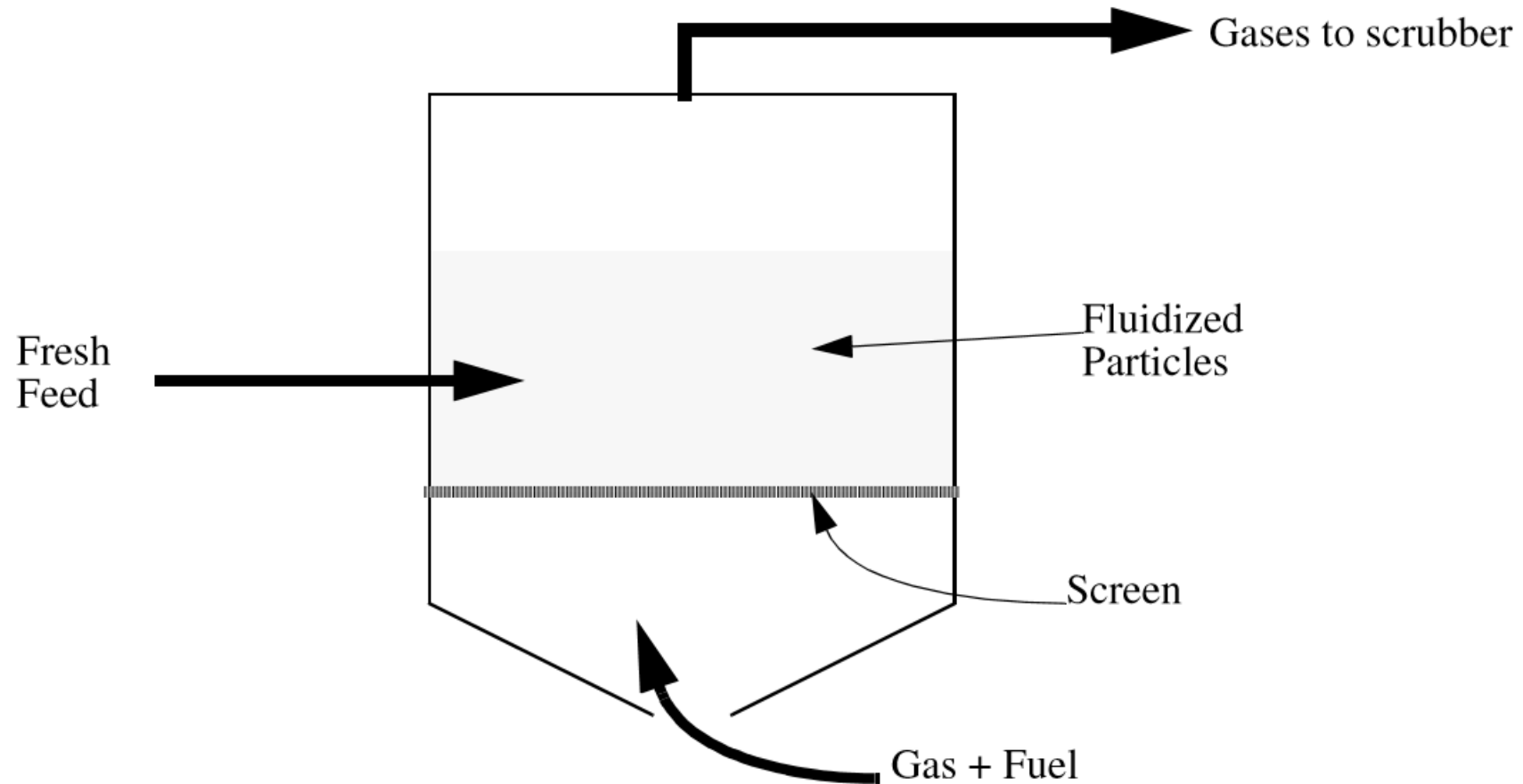
Principle:

➢ Ore particles are roasted while it is suspended in an upward stream of gases.

➢ Gas passes through bottom of the bed.

➢ Behavior of the bed depends on the velocity of gas.

1. Fluidized Bed
2. Separator
3. Draft Fan
4. Dust Filters
5. Combustion System

Stages observed during roasting process :

Stage-1

➢When the gas flow rate is very low, and the ore bed is porous, the gas permeates the bed without disturbing the ore particles.

➢Pressure drop across the bed is proportional to flow rate.

Stage-2

➢Gas velocity increases, the bed expands upwards due to the effect of the drag forces exerted by gas stream.

➢The pressure drop across the bed depends on the gas velocity.

Stage-3

➢When gas velocity further increases a stage is reached.

➢Pressure drop = wt. of the particle per unit area of the bed.

➢Particles remain individually suspended and offer less resistance to gas flow.

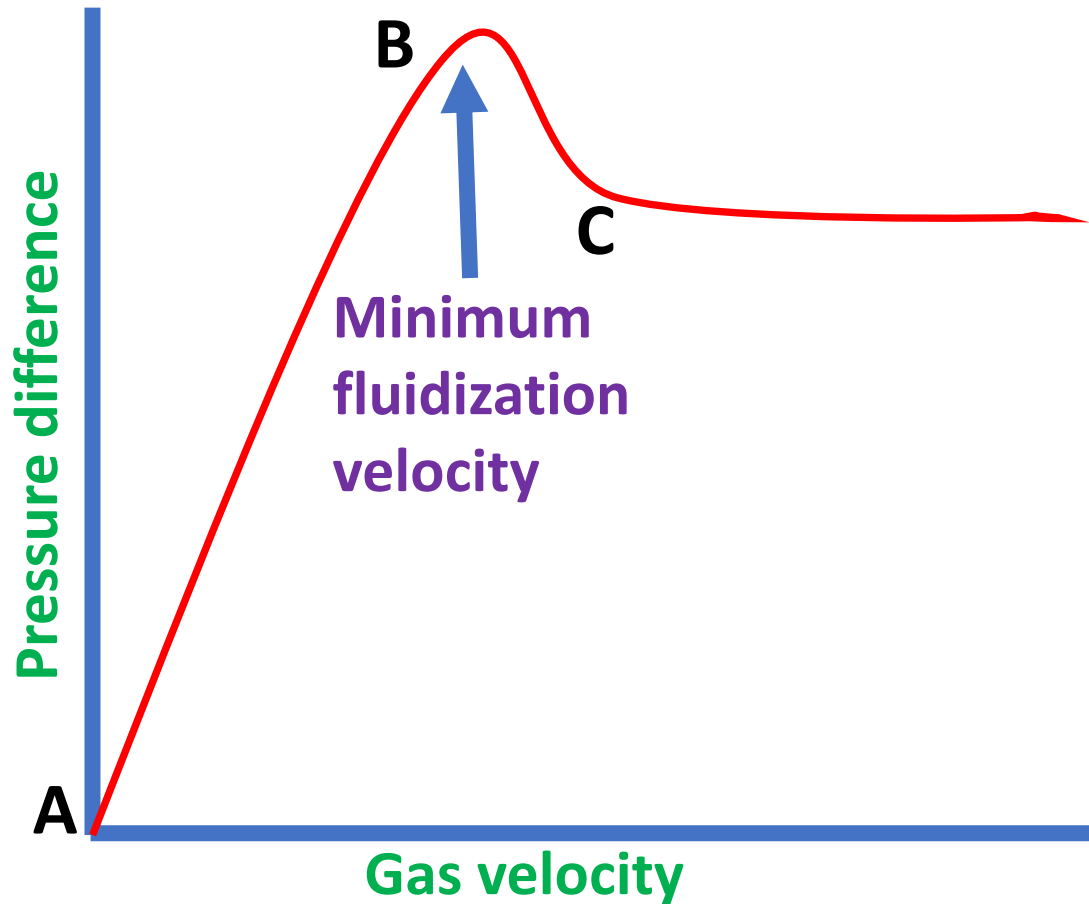**Stages observed during roasting process :**

Stage-4

➢Further increase in gas velocity lead to continued expansion of the bed.

➢Results in increase in interparticle distance.

➢Pressure drop across bed continues to decrease as the gas velocity increase.

Stage-5

➢Finally, the expansion of the bed is independent of gas velocity.

➢Outcoming gas stream appears in the form of bubbles bursting on the surface of the bed which looks like well stirred boiling liquid.

➢In this condition the bed is said to be fluidized.

➢The fluidized bed has an apparent density distinctly different from the density of the solid and is capable of flowing like a liquid.

Stages observed during roasting process :

Pressure difference

B

C

Minimum fluidization velocity

A

Gas velocity

Typical fluidization curve

AB = Pressure drop across the bed before fluidization.

BC = As pressure drop increases, bed is rearranged and cause minimum resistance to gas flow.

Point C = Maximum voidage of packed bed and minimum gas velocity required for fluidization.

Advantages:

➢ High energy efficiency because it can be autogenously operated.

➢ Useful in recovery of Sulphur because the gas that it produces has high SO_2 content.

➢ Ideal for roasting of oxide ores because the oxidizing reactions that take place during roasting is highly exothermic. e.g. Pyrite (FeS_2), Millerite (NiS) etc.

- Fine ore & concentrate have to be agglomerated before they can be charged in a blast furnace.
- Treatment of sulphide ore in a sintering machine where roasting and agglomeration take place simultaneously.
- Charge = (fine ore+ moisture) as layer of 15-50 cm thick on revolving belt.
- Combustion is done by burner.
- Speed is adjusted - roasting should be completed before it is discharged.
- Produce porous cinder called sinter.
- Cooled sinter is sized to give uniform product.

➢ PbS lead ore (Galena) is friable, brittle and fuses easily.

➢ For blast furnace smelting it should be in the form of hard, strong and porous. Hence sinter roasting is carried out in Dwight-Lloyd sintering machine.

➢ Roasting reacting:

$PbS + 3/2\ O_2 \rightarrow PbO + SO_2$ at 800°C