

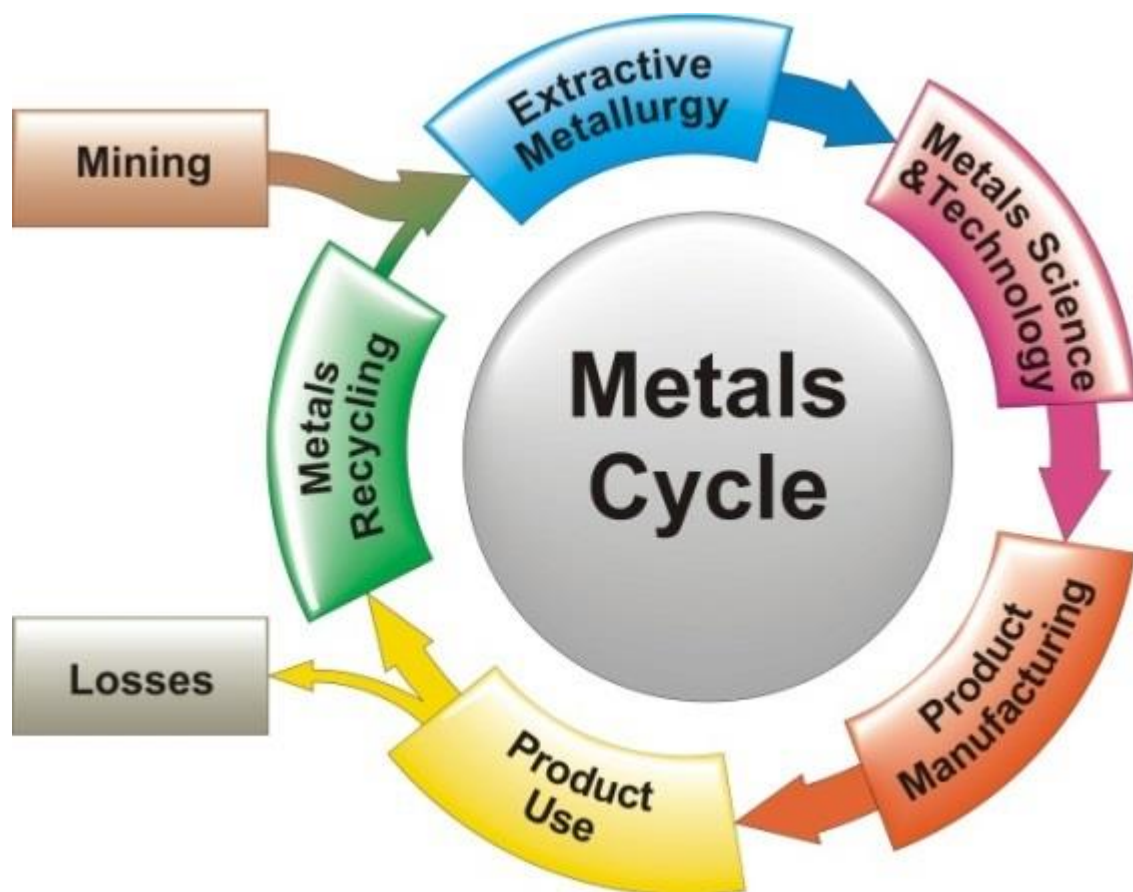
PRINCIPLE OF EXTRACTIVE METALLURGY

UNIT PROCESSES IN PYROMETALLURGY: DRYING, CALCINATION, ROASTING, PELLETIZING AND SINTERING



NATIONAL INSTITUTE OF TECHNOLOGY, JAMSHEDPUR

ASSIGNMENT



Team Members:

1. Rachel Anamika :2019UGMM020
2. Rachana Sabbavarapu :2019UGMM050

Extractive metallurgy is a branch of metallurgical engineering wherein process and methods of extraction of metals from their natural mineral deposits are studied. It is the practice of removing valuable metals from an ore and refining the extracted raw metals into a purer form. In order to convert a metal oxide or sulphide to a purer metal, the ore must be reduced physically, chemically, or electrolytically.

Based on the extraction processes of the ore, extractive metallurgy is classified into:

- Pyrometallurgy
- Hydrometallurgy
- Electrometallurgy

Pyrometallurgy, extraction and purification of metals by processes involving the application of heat. It consists of the thermal treatment of minerals and metallurgical ores and concentrates to bring about physical and chemical transformations in the materials to enable recovery of valuable metals. Pyrometallurgical treatment may produce products able to be sold such as pure metals, or intermediate compounds or alloys, suitable as feed for further processing.

Most pyrometallurgical processes require energy input to sustain the temperature at which the process takes place. The energy is usually provided in the form of combustion or from electrical heat. When sufficient material is present in the feed to sustain the process temperature solely by exothermic reaction (i.e., without the addition of fuel or electrical heat), the process is said to be "autogenous". Pyrometallurgical treatment may produce products able to be sold such as pure metals, or intermediate compounds or alloys, suitable as feed for further processing. Examples of elements extracted by pyrometallurgical processes include the oxides of less reactive elements like [iron](#), [copper](#), [zinc](#), [chromium](#), [tin](#), and [manganese](#).

In the following document we study about some of the **unit processes** under **pyrometallurgy**. The processes that involve a physical change are known as Unit Operations example: crushing, grinding, concentration etc. and the

processes that involve a chemical change are known as Unit Processes. For Example: Drying, calcination, roasting, pelletizing and sintering.

DRYING:

Drying is thermal removal of liquid moisture (not chemically bound) from a material. Drying is usually accomplished by contacting the moist solids with hot combustion gases generated by burning fossil fuels. In some cases, heat for drying can be provided by hot air or inert gas that has been indirectly heated. The amount of heat required for a given drying operation corresponds to the heat required to vaporize the liquid moisture, the heat required to raise the temperature of the products (dry solids and water vapor) to the final drying temperature, and heat required to offset radiant heat losses.

Usually, the drying temperature is set at a nominal value above the boiling point of water, often about 120°C. In special cases, such as in the drying of certain water-soluble salts, higher drying temperatures are required. In salt drying, the feed moisture is saturated with dissolved salts, which alters the boiling point and requires higher drying temperatures.

Drying of moist solids is carried out in several types of industrial dryers, including rotary dryers, fluidized bed dryers, and flash dryers.

ROTARY DRYERS:

The **rotary dryer** is a type of [industrial dryer](#) employed to reduce or minimize the liquid [moisture](#) content of the material it is handling by bringing it into direct contact with a heated gas.



Single Shell Rotary Drum Dryer

The dryer is made up of a large, rotating cylindrical tube, usually supported by [concrete](#) columns or [steel beams](#). The dryer is inclined to slopes slightly so that the discharge end is lower than the material feed end in order to convey the material through the dryer under [gravity](#). Material to be dried enters the dryer, and as the dryer rotates, the material is lifted up by a series of internal fins lining the inner wall of the dryer. When the material gets high enough to roll back off the fins, it falls back down to the bottom of the dryer, passing through the hot gas stream as it falls. This gas stream can either be moving toward the discharge end from the feed end (known as co-current flow), or toward the feed end from the discharge end (known as counter-current flow). The gas stream can be made up of a mixture of air and combustion gases from a burner, in which case the dryer is called a direct heated dryer. Alternatively, the gas stream may consist of air or another (sometimes inert) gas that is preheated. When the gas stream is preheated by some means where burner combustion gases do not enter the dryer, the dryer known as an indirect-heated type. Often, indirect heated dryers are used when product contamination is a concern. In some cases, a combination of direct-indirect heated rotary dryers is also available to improve the overall efficiency.

A rotary dryer is suitable to dry metallic and non-metallic mineral, clay in cement industrial and coal slime in coal mine, etc. Rotary dryers can be widely used to dry various materials, and are simple to operate.

FLUIDIZED BED DRYER:

Fluidized bed dryer (also called fluid bed dryer) is a kind of equipment used extensively in the pharmaceutical industries to reduce the moisture content of pharmaceutical powder and granules. The equipment works on a principle of fluidization of the feed materials.

In fluidization process, hot air is introduced at high pressure through a perforated bed of moist solid particulate. The wet solids are lifted from the bottom and suspended in a stream of air (fluidized state). Heat transfer is accomplished by direct contact between the wet solid and hot gases. The vaporized liquid is carried away by the drying gasses. Sometimes to save energy, the exit gas is partially recycled.

Advantages of Fluidized-bed Dryers:

1. High rates of moisture removal due to excellent gas-particle constant which results in high heat and mass transfer rates.
2. High thermal efficiency is usually achieved if part of the thermal energy for drying is supplied by the internal heat exchanger
3. Lower capital and maintenance cost
4. Reduced contact time for drying.
5. Ease of control.

FLASH DRYERS:

Wet material is dispersed into a stream of heated air (or gas) which conveys it through a drying duct. Using the heat from the airstream, the material dries as it is conveyed. Product is separated using cyclones, and/or bag filters. Typically, cyclones are followed by scrubbers or bag filters for final cleaning of the exhaust gases to meet current emission requirements.

For even greater thermal efficiency and where inertization is required, recycling of exhaust gases can be used. This partial gas recycle (PGR) configuration can be implemented on all our airstream drying systems as well as retrofitted on customer's existing drying operations.

Flash dryers have been used to dry products in many industries including agrifood, chemical, mineral. A broad range of feed materials including powders, cakes, granules, flakes, pastes, gels, and slurries can be processed. For slurries, pastes, or sticky materials, back-mixing of the wet feed with a portion of dry product to produce a suitable conditioned material is required.

• Benefits of Flash Dryers:

- *Promotes product quality*
- *Flexibility to work with different dewatering systems and to enable use with friable and non-friable wet feeds*
- *Enables energy savings and system integration*
- *Suitable for operation with solvent and recovery thereof*

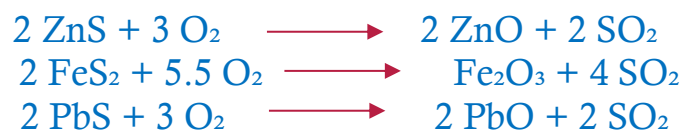
- *Cost effective and reliable with low maintenance and cleaning requirements - good for regular grade changes*

Another type of drying, called **spray drying**, is carried out when the material to be dried is completely dissolved in aqueous solution. The solution is sprayed (usually through a specially designed nozzle) into a heated chamber and as the water is evaporated, solids crystallize. The water vapor is exhausted from the dryer, and dry solids are collected, usually in a conical section of the dryer. Solid material produced from a spray dryer often has special particle size and shape characteristics, which may be controlled by the concentration of dissolved material in the solution, and the design of the atomizing spray nozzle.

ROASTING

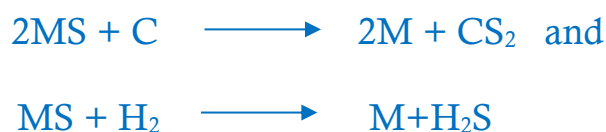
Roasting is the oxidation of metal sulphides to give metal oxides and Sulphur dioxide. It is an exothermic reaction. Roasting is essentially a surface reaction where the oxide layer is formed first and continues to remain as a porous layer through which oxygen can pass into the still unreacted inner sulfide portion of the particle and the SO₂ gas formed comes out.

The underlying chemical equations depicts the process of roasting.



Heat helps to keep the roaster at the required roasting temperature so that the process can continue with little extra heat supplied by the burning fuel. Hence, sulfide roasting is an autogenous process, that is, where no extra fuel is supplied.

Sulfides are not reduced with the most widely used reducing agents, carbon and hydrogen, because the free energy change for the reactions

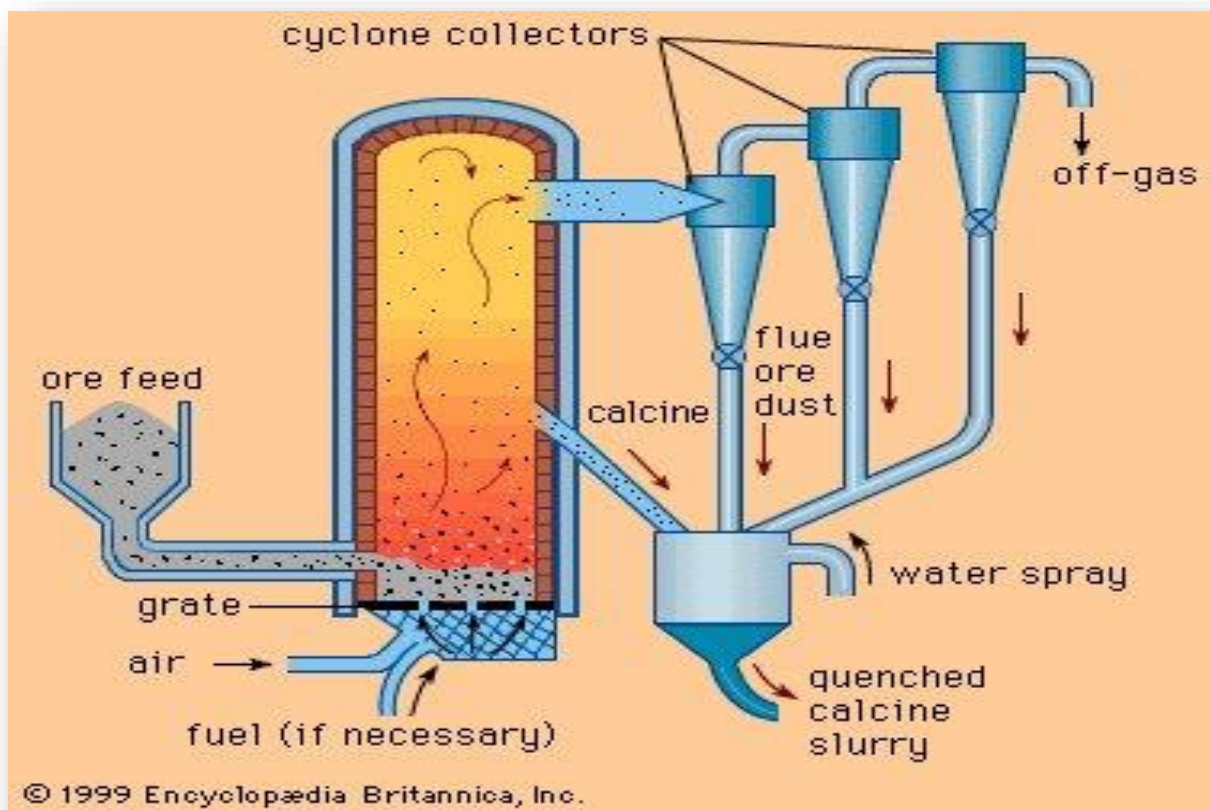


is positive due to the lesser stability of CS₂ and H₂S, compared to most sulfides. Reduction of sulfides with metals is not economical.

The roasting is also eliminated in the production of lead from galena concentrate by the Ausmelt process

HOW ROASTING IS TAKING PLACE

In roasting, air in large amounts, sometimes enriched with oxygen, is brought into contact with the sulfide mineral concentrate. This is done at elevated temperatures when oxygen combines with sulfur to form sulfur dioxide and with the metal to form oxides, sulphates and so on. The oxidation must be done without melting the charge in order to prevent reduction of particle surface–oxidizing gas contact area. Stirring of the charge in some manner also ensures exposure of all particle surfaces to the oxidizing gas.



ROASTING PROCESS

METHODS OF ROASTING

There are several commercial roasters used on the industrial scale. The multiple hearth roaster that consists of a number of horizontal circular refractory hearths placed one above the other in a steel shell for the purpose of charging the feed on the top hearth as well as for discharging the roasted calcine from the bottom hearth, has been virtually replaced by the flash or

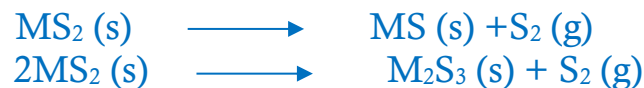
suspension roaster that has only the top and bottom hearths. The capacity of such roasters is three times larger than that of multiple hearth roasters. In flash roasting, the preheated ore is injected through a burner. This process is most appropriate for the roasting of sulfides, which oxidize exothermally and require no additional fuel. In flash roasting, the benefits of a counter flow operation are partially lost.

FACTORS AFFECTING ROASTING:

- Time (duration)
- Availability of oxygen or air
- Temperature
- Physical condition of the ore
- Nature of the mechanical device used

CHEMISTRY OF ROASTING

1. Decomposition of higher sulfides to lower sulfides, for example,



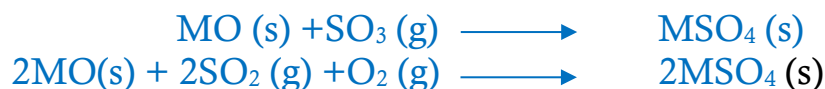
2. Oxidation of sulfides to form oxides or sulphates



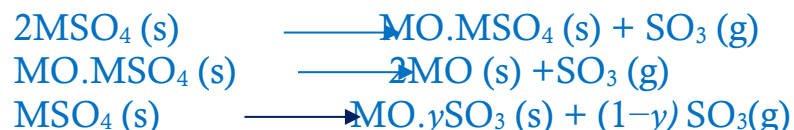
3. Burn-up of sulfur to form its oxides



4. Sulfation of metal oxides



5. Decomposition of sulphates to basic (oxy) sulphates



6. Sulfide–sulphate interaction



7. Sulfide–oxide interaction



TYPES OF ROASTING

- Oxidation Roasting
- Salt Roasting
- Chlorination Roasting
- Reduction Roasting
- Volatilizing Roasting
- Sinter Roasting

• Oxidation Roasting

It is the process of converting metallic compounds in waste materials into oxides using oxidants. Oxide is obtained to facilitate next step of smelting. Used in sulfide ore smelting. use to remove Sulphur ore, arsenic, antimony & other harmful impurities in ore.

• Salt Roasting

Main aim of this process is to convert metallic sulfides or oxides in the material into soluble salts dissolved in water or dilute acids under controlled conditions. Sulfuric acid roasting & chlorination roasting are typical examples of salt roasting.

The main control conditions of sulfuric acid roasting are temperature & air volume. Sulfuric acid roasting is applied to the treatment of Cu concentrate & low grade metal material.

• CHLORINATION ROASTING

It produces chloride by the action of some components & chlorinated agent in the material. Chlorinated materials may be oxides, carbides, sulfides &

metals or alloys. Chlorinated agents are Cl, HCl, CCl₄, CaCl₂, NaCl, MgCl₂ & FeCl₃. Examples are high titanium slag chlorination (TiCl₄).

- **REDUCTION ROASTING**

It is the lowering of oxygen content of ore by heating in reducing atmosphere using CO. The CO is supplied by mixing carbonaceous material like coke or coal with the ore.

- **VOLATILIZING ROASTING**

It involves careful oxidation at elevated temperatures of the ores, to eliminate impurity elements in the form of their volatile oxides. Examples of such volatile oxides are As₂O₃, Sb₂O₃, ZnO & sulfur oxides. Excessive oxidation forms non volatile oxides hence control on oxygen content is necessary.

- **SINTER ROASTING**

It involves heating the fine ores at high temperatures, where simultaneous oxidation & agglomeration of the ores take place. For example: lead sulfide(PbS) ores are subjected to sinter roasting in a continuous process after froth floatation to convert the fine ores to workable agglomerates for further smelting operations.

CALCINATION

Calcination refers to heating a solid to high temperatures in absence of air or oxygen, generally for the purpose of removing impurities or volatile substances. However, calcination is also used to mean a thermal treatment process in the absence or limited supply of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition. As the most decomposition reaction is endothermic, so the temperature of calcination is generally depends on the transfer of heat into the particle.

- **Calcination of zinc carbonate**

- zinc carbonate is heated at 400 degree Celsius and it gives zinc oxide and carbon dioxide as result.



- 2 molecules of Mercury sulphide are heated in the presence of air and it gives it two molecules of mercuric oxide and two molecules of Sulphur dioxide.

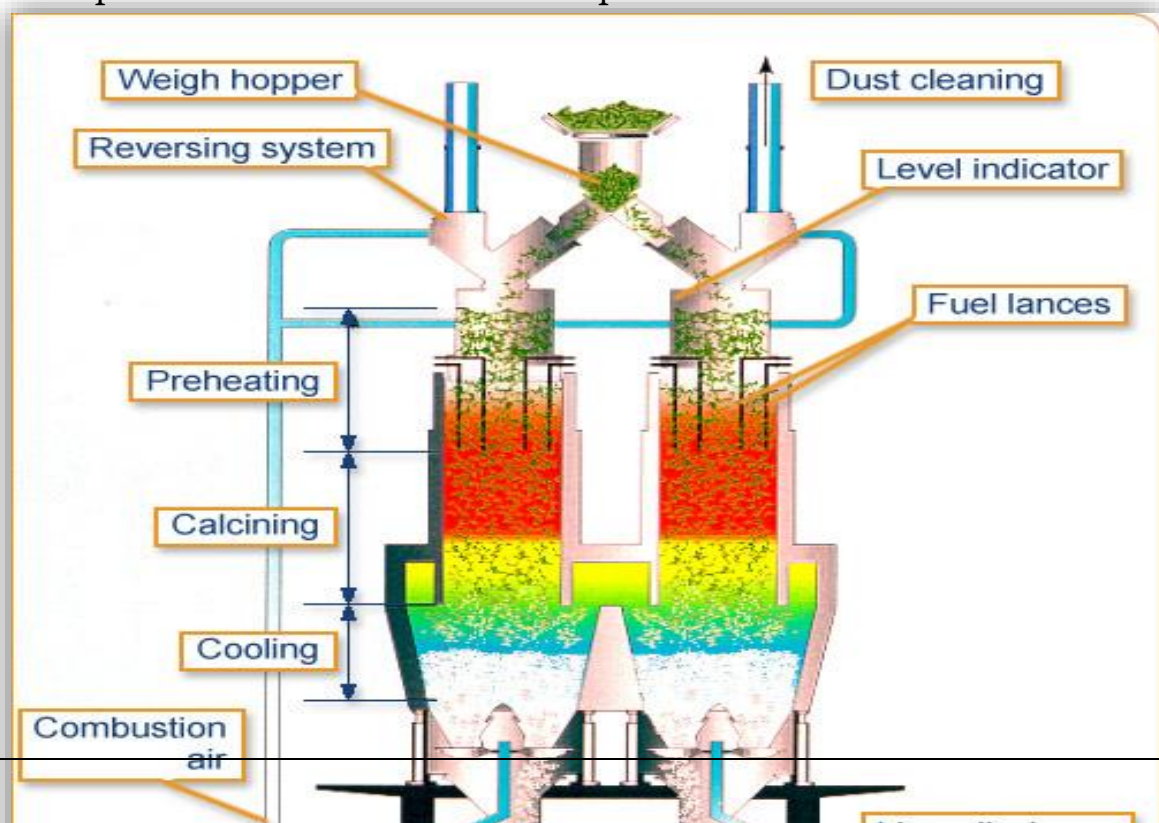


- The aluminum takes the oxygen from the manganese dioxide and reduces the manganese dioxide to metallic manganese and creates aluminum oxide and a lot of heat.



- **Calcination of lime stone**

- Calcination of limestone takes places essentially at about 1000 °C. The reaction is highly endothermic and consumes large amount of thermal energy that comes from the burning of coke.
- Furthermore, limestone decomposition releases CO₂ gas, and the CO₂ gas will react further with coke through Boudouard reaction, leading to extra solution loss of carbon.
- For every 100-kg limestone charged to the blast furnace, the coke rate increases by approximately 25–35 kg/THM.
- Therefore, fluxing of the iron ore (using prefluxed sinters and pellets) and calcination of limestone outside the blast furnace is preferred to avoid extra consumption of coke.



CALCINATION PROCESS

APPLICATION OF CALCINATION

- To produce cement from CaCO_3
- To cause decomposition of hydrated minerals as in calcination of bauxite to produce refractory grade Al_2O_3 .
- To cause decomposition of volatile matter contained in petroleum coke.
- To heat treat to effect phase transformation as in devitrification of glass materials
- To produce anhydrous Al_2O_3 for electrolysis of Al_2O_3 to Al in Hall-Heroult cell.

Before moving on to sintering and pelletizing, I would like to give a bit description about agglomeration process.

What is Agglomeration?

It is the process of converting separate particles into mass or cluster.

An enormous number of fines (40-50%) is generated during mining and ore dressing operations. Fines cannot be used directly in the blast furnace; therefore, it is necessary to agglomerate them into lumps, pellets and briquettes. This process is used for changing the size of concentrate

particles, when the particle size of an ore is too small for the use in latter stage of treatment in the blast furnace. It must be reformed to lumps of appropriate size and strength.

Agglomeration techniques include **sintering, pelletizing, briquetting** and **nodulizing**.

In this presentation we'll be discussing about sintering and pelletizing.

SINTERING

Sintering or frittage is the process of compacting and forming a solid mass of material by heat or pressure at a temperature below the melting point (mixture of iron ore, fluxes and coke in the **sinter plant**). It is the agglomeration of fine mineral particles into a porous and lumpy mass by incipient fusion caused by heat produced by combustion of solid fuel within the mass itself. The atoms in the material diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece.

In other words, **sintering** is a heat treatment commonly used to increase the strength and structural integrity of a given material.

Powder metallurgy processes also use **sintering** to convert metal powders and other unique materials into end use parts.

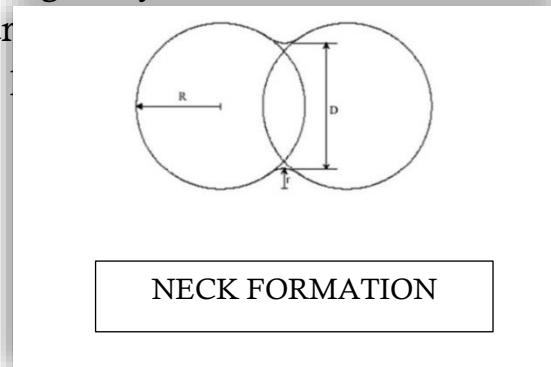
WHY DO WE NEED SINTERING?

- To utilize the fines generated during the beneficiation process.
- To form strong and porous agglomerate.
- These fines cannot be charged into blast furnace because it lowers permeability of charge bed. So, **sinter** is made from these fines to be used as a charging material.
- Used as charging material in blast furnace to increase the productivity and lower the fuel rate.
- To utilize different additives like mil scale, hearth slag, etc. in an integrated steel plant.

STAGES OF SINTERING-

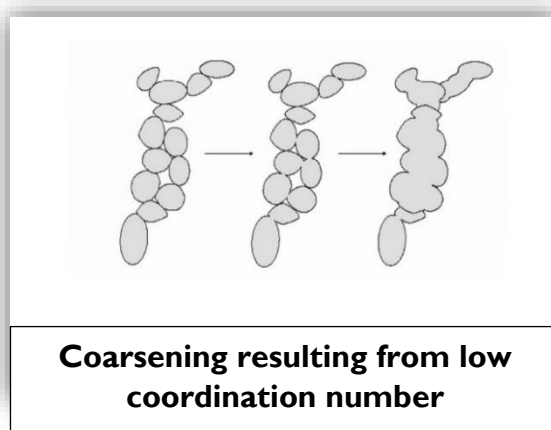
1. First stage:

Initial neck growth- Sintering causes the particles that are in contact to form grain boundaries at the point of contact through **diffusion**. This is the point contact stage and does not result in any dimensional change. Greater will be the particle contact more will be the degree of coherency in the material. In this stage only **neck** formation starts between the adjacent particles and is driven by the difference in the curvatures of the



2. Second stage:

Intermediate stage sintering- It begins when the adjacent necks begin to impinge upon each other. **Densification** and **grain growth** occur during this stage. Pore channel gets closed because of neck formation and also due to creation of new contact points by pore shrinkage within the pore itself. At the beginning of this stage the pores form a network of interconnected cylindrical pores broken up by necks. By the end, pores are smoother and begin to pinch off and become isolated from each other.

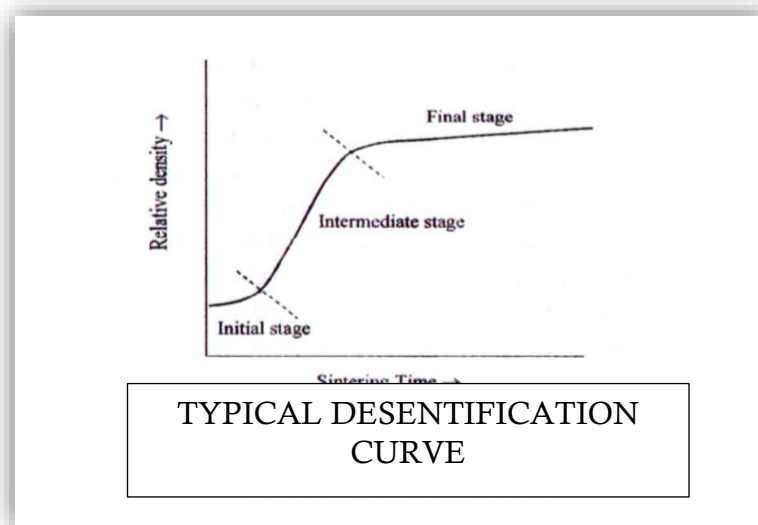


3. Third stage:

Final stage sintering- This stage begins when most of the pores are closed. As sintering proceeds networked formed pores become isolated from each other. This is the slowest stage. As grain size increases, the pores tend to

break away (**pore shrinkage**) from the grain boundaries and become **spherical**. And for this to occur solids must be transported into the pores and a means must exist by which the gas in the pores can escape to the surface. The resultant effect is to decrease the volume of the sintering mass.

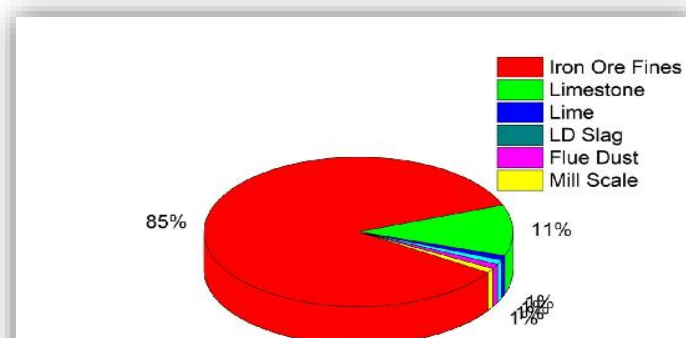
DENSIFICATION CURVE-



The density-time curve in the figure is composed of three distinct portions. The first portion reflects the initial stage where densification is due to only neck growth. The densification in the intermediate stage is due to concurrent grain growth and reduced number of interconnected pores. When the pores is completely in the closed form, the rate of densification is reduced in the final stage.

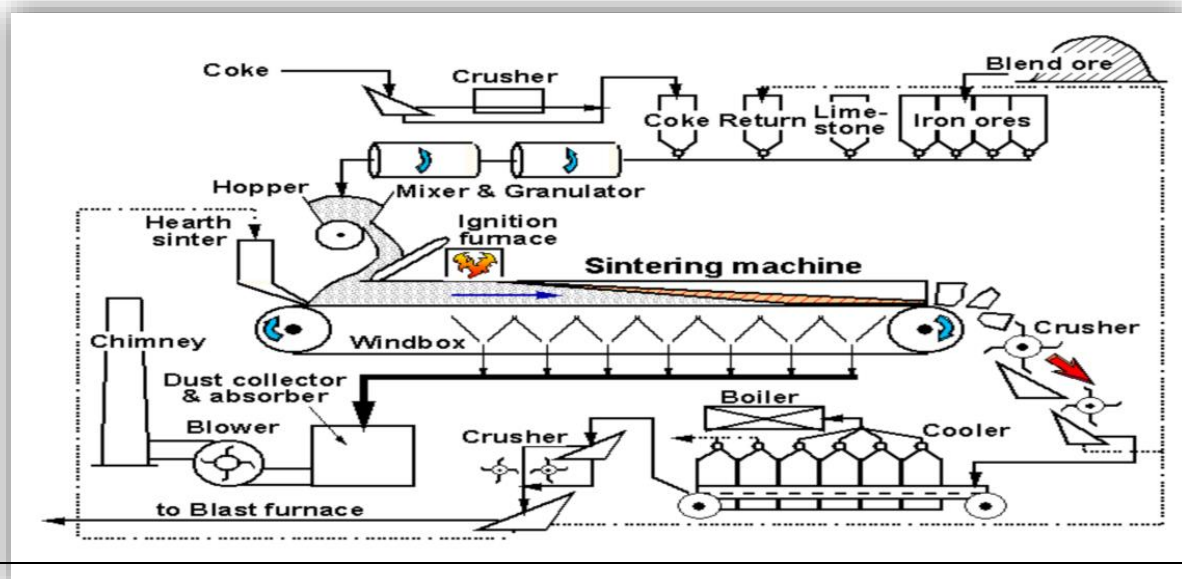
RAW MATERIAL USED-

Iron ore fines, flux (limestone and dolomite), coke breeze, waste materials (flue dust, mill scale, L.D. slag, lime dust), sinter return (own generation).



PRINCIPLE STEPS FOR SINTERING PROCESS-

1. The iron ore fines, limestone fines, dolomite fines, lime dust, metallurgical wastes and coke breeze are taken proportionately based on charge calculations. Then this mixture is mixed and balled in mixing and balling drums with the addition of water and then loaded over a traveling grate in form of permeable bed.
2. The top layer of this sinter bed is heated to the sintering temperature (1200°C - 1300°C) inside an Ignition Hood furnace. In the ignition hood the air is drawn downwards, through the grate with the help of exhaust blowers (Waste Gas Fan) connected by means of Waste gas main.
3. The narrow combustion zone developed initially at the top layer by layer to the sintering level. The cold blast drawn through the bed cools the already sintered layer the thereby gets itself heated.
4. The heat contained in the blast is utilized in drying and preheating the lower layers in the bed.
5. In advance of combustion therefore each layer gets dried and preheated by the heat transferred from the upper combustion zones. The lower portion of the bed absorbs much of the heat in the gases. In the combustion zone, bonding takes place between the grains and a strong and porous aggregate is formed.
6. The process is over when the combustion zone has reached the lowest layer of the bed. The sinter cake is thus tipped from the grate in hot condition. It is then broken, cooled in sinter cooler cold sized and sent to the Blast furnace.



ADVANTAGES OF SINTER-

- Agglomerated fines are hard, strong and irregular porous lumps gives better bed permeability.
- Iron ore fines are easily available at much cheaper rate than lump ore.
- Sinter is pre-fluxed. So, reducibility of sinter is better than lump ores
- Size of sinter is narrower so heat zone distribution inside furnace is better and stable.
- Blast furnace operation becomes smoother and more stable with sinter.
- Eliminates moisture, hydrated water or any volatile on strand with a cheaper fuel.
- Use of sinter increases the permeability, hence reduction and heating rate or burden increases. Thus, productivity increases.

DISADVANTAGE OF SINTER-

- 100% sintered (iron ore) cannot be charged in the blast furnace.
- By sintering one cannot create uniform sizes.

PELLETIZATION

Pelletizing is a process which involves mixing of very finely ground particles of iron ore fines having a size which is less than 200 mesh (0.074 mm) with additives like bentonite and then shaping them into near oval/spherical balls having size in the range of 8 mm to 16 mm in diameter by a pelletizer and hardening the balls by firing with a fuel. This is the process of converting iron ore fines into 'uniformed sized iron ore pellets' which can be charged directly into a blast furnace or into a vertical furnace or rotary kiln normally used for the production of direct reduced iron (DRI).

Typically, limestone, dolomite and olivine are added and Bentonite is used as binder. This process generates iron ore cake which needs to be pelletized so that it can be used in an **iron making process**.

Pelletization is the process or the only way to preserve our precious iron ore and use it wisely.

MANUFACTURING OF PELLETS-

Manufacturing:

1. Pellets are formed from the raw materials – fine ores and additives of < 0.05 mm - into 9-16 mm spheres using very high temperatures and this is mainly carried on at the site of the mine or its shipping port.
2. The pelletization process consists of grinding and drying or dewatering, balling and induration, followed by screening and handling.

Transport & Storage:

1. Transport on site takes place by conveyor belt or truck. Storage techniques used are either open air stockpiles or in (covered) bunkers.
2. Transport to the final customer can take place by truck, rail and ship. The loading and unloading of pellets can be done by crane, wheel loader, shovel, conveyor belt, etc.

Charging the blast furnace/ BOS plant:

1. Pellets are primarily used in blast furnaces. Occasionally pellets are used in the steel process.
2. The mixture of iron bearing materials (iron ore rubble, sinter and/or pellets) and additives (flux material) are known collectively as the "burden".

Other activities:

Cleaning operations in the pellet plant (floors and walls) take place by using brushes and shovels, bobcats and suction (vacuum removal). Occasional cleaning of machinery takes place before maintenance activities.

Maintenance Planned or unplanned maintenance can take place in all the above- mentioned areas. Sampling is carried out at several places in the manufacturing process.

PRINCIPLE STEPS FOR PELLETIZATION PROCESS-

Grinding and drying/de-watering-

In the wet process, additives (olivine, dolomite and/or limestone depending on the end product) are ground and then added to the ore slurry, typically at a level of 3 to 3.5%, before de-watering. In the other process after hot grinding, the material is re-wetted in paddle-type mixers and combined with additives. In both cases the moisture content is adjusted to 8–9%.

Green ball preparation-

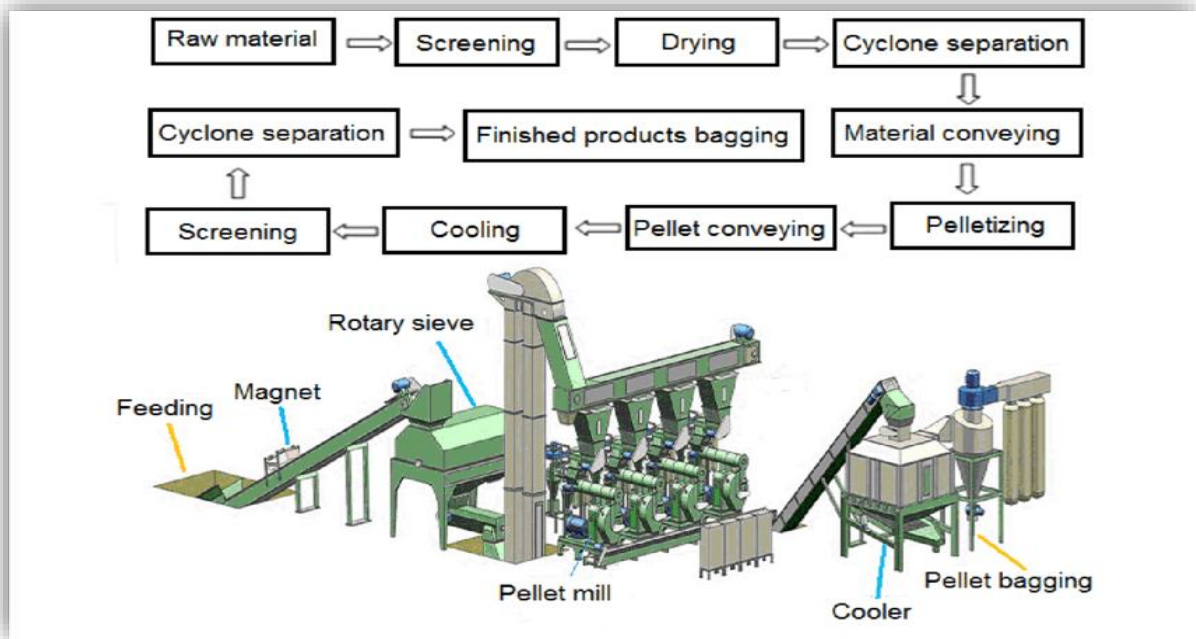
This is typically equipped with 4 to 6 balling circuits consisting of a feed bin, balling drum, roller screens and conveyors for circulating the materials. The balling drum is inclined 6° to 8° to the horizontal plane.

Induration-

Induration, which means thermal treatment, consisting of drying, hard and cooling. It can be carried out by using two different systems; in 'straight grate' or 'grate kiln' systems. During thermal treatment magnetite is almost completely oxidized to hematite.

Handling & Screening-

At the end of the induration strand, the pellets are screened. Undersize or broken pellets can be recycled.



ADVANTAGES OF PELLETS-

- Pellets are uniformly sized, with purity of 63%-68% contributing to faster reduction and metallization rates.
- Pellets with their high, uniform mechanical strength and high abrasive strength increase production of sponge iron by 25% to 30% with same amount of fuel.
- Standardization- Uniform size range, generally within a range of 9-16mm.
- Purity- 63% to 68% iron, mainly Fe_2O_3 .
- Cost effectiveness- There is no loss of handling iron ore, as pellets will not break during transport or handling. Reduces coal consumption in sponge iron making with lower fines generation. Maintenance cost is low as there is no need for crushing and screening of iron ore lumps.
- Productivity- A wholesome 20-25% increase in sponge iron making. A perceptible improvement in productivity of iron making through blast furnace route due to the uniformity of pellets which results in better permeability.

DISADVANTAGE OF PELLETS-

The main disadvantage of using pellets to heat your home is **they rely on electricity to operate some of the components**. The amount of electricity

they use is minimal, but this can become a problem where an electrical supply is not available, or in a power outage.

ENVIRONMENTAL IMPACT ASSESSMENT AND ITS MANAGEMENT AT PELLETIZATION REFERENCES PLANTS-

1. Presently general environmental norms are being compiled by the operating pelletization units, but a guideline of best practices along with specific environmental standard is quite essential for better regulation of these industries.
2. It is proposed that a detailed study on the various aspects of Iron Ore Pelletization process and best practices adopted nationally/worldwide may be undertaken by Central Pollution Control Board (CPCB).

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