UNIT PROCESSES IN PYROMETALLURGY

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Under the Guidance of
Outline of Presentation

• Introduction
• Drying
• Calcination
• Roasting
• Pelletising
• Sintering
PYROMETALLURGY

- Principle means of metal extraction despite of rapid development in hydro and electro metallurgy.
- Extraction and refining carried at elevated temperature where physical and chemical changes occur at 500-2000°C.
- Significance of pyrometallurgy over hydro and electro metallurgy.
- Since it is a high temperature process so it is cheaper and more versatile.
Drying

- Drying is a mass transfer process consisting of the removal of water or another solvent by evaporation from a solid, semi-solid or liquid. ... A source of heat and an agent to remove the vapor produced by the process are often involved. Moisture that is bound chemically cannot be removed by drying.

- The purpose of drying is to retain the physio-chemical properties of materials, to ensure, in many cases, the preservation of materials over prolonged periods, and to eliminate excess weight in shipping.
Subsequent to the forming, drying is usually necessary, before the shaped bodies can be debindered in the furnace. The moisture content must thereby be reduced from 10 to 50% by volume to approximately 1% by volume.

At higher moisture contents, the rapid heating of the shaped bodies during the removal process would lead to the boiling of the liquid component and to damage to the mouldings.

Forming processes that usually require drying are slip casting, film casting, wet pressing and plastic moulding processes, such as extrusion. Organic solvents such as alcohols and increasingly water is used as liquids.

Even with slower drying, mechanical or thermal stresses are created as a result of the dry shrinkage, which can lead to the deformation of the mould parts or to cracks.

A gentle and even drying process takes a lot of time, sometimes many weeks, and correspondingly lots of space.

The aim is to identify drying parameters which do not yet cause damage to the moulded parts but which enable the most economical drying.
Drying Parameters

- Depending on the degree of drying - are the relative humidity of the surrounding atmosphere.
- The temperature and the gas convection on the surface of the moulded body.
- The drying rate and the forming stresses also depend on the vapor pressure of the solvent.
- The solvent concentration at the liquid / gas interface and capillary effects, and the geometry of the drying material. Drying parameters therefore must be optimized for each product.
Rotary dryer

- Rotary Dryer is a simple, inexpensive unit for reducing the moisture content of flotation concentrates, as well as chemical and industrial products.
- Frequently the saving of shipping weight so effected will pay for the dryer in a few months. Difficulties from freezing while in transit are also eliminated.
- Many industrial projects are now using Dryers for control and production purposes on many materials.
Figure: Rotary Dryer
Conti…

- For evaporating moisture from concentrate or other products from plant operations, Rotary Dryers are designed and constructed for high efficiency and economy in fuel consumption.
- Whenever possible to apply heat direct to the material to be dried, Rotary Dryers of the Direct Heating Design are used.
- If it is not possible to apply heat direct to the material to be dried, Rotary Dryers of the Indirect Heating Design can be furnished so that the heated gases will not come in direct contact with the material.
Three main types of Rotary Dryers can be supplied. The direct heat unit is used when it is permissible for the drying gases to come in direct contact with the material being dried. Partition plates increase the heating surface. Drying may be by hot air or exhaust gases from other operations. If this drying gas has a deleterious effect on the product, then an indirect type of dryer can be supplied. A further derivation is the Tedrow Steam Dryer.
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.
Figure: Fluidized bed dryer
Working Principle

- The fluidized bed is divided into the upper and lower bed body, air distributor, the inlet and outlet 2 ports, etc., and the wet material entering the fluidized bed is in contact with the hot air above the air distribution plate, and the material particles are suspended in the air flow to form a fluidized state.
- The material and the hot air are heat-exchanged and dried, and the finished product is discharged from the discharge port of the fluidized bed, and the dust-containing gas is purified by the dust collecting device and then discharged into the atmosphere by the induced draft fan.
Spray dryers or Flash dryers

- Spray drying is a well-known method of particle production which comprises the transformation of a fluid material into dried particles, taking advantage of a gaseous hot drying medium, with clear advantages for the fabrication of medical devices.
- In fact, it is quite common the production of microspheres and microcapsules designed for drug delivery systems.
Spray Drying Process Overview

Closed-cycle system shown with organic solvent recovery, inert drying gas (N₂) loop and non-atomizing liquid feed.
This diagram describes the different stages of the mechanism of the spray-drying process: atomization, droplet-to-particle conversion and particle collection.

In particular, this work addresses the diversity of available atomizers, the drying kinetics and the importance of the configuration of the drying chamber, and the efficiency of the collection devices.

The final properties of the dried products are influenced by a variety of factors, namely the spray dryer design, the feed characteristics and the processing parameters.

The impact of those variables in optimizing both the spray-drying process and the synthesis of dried particles with desirable characteristics is discussed.

The scalability of this manufacturing process in obtaining dried particles in submicron-to-micron scale favors a variety of applications within the food, chemical, polymeric, pharmaceutical, biotechnology and medical industries.
Calcination

- Calcination (also referred to as calcining) is a thermal treatment process, in presence of air or oxygen, applied to ores and other solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction.

- The calcination process normally takes place at temperatures below the melting point of the product materials.

- One of the most common applications is as a step in the production of Portland cement, in which calcium carbonate (limestone) is calcined at around 850°C to produce calcium oxide (quicklime) and carbon dioxide.

- A typical example is the manufacture of lime from limestone. In this process the limestone is brought to a temperature high enough to expel the carbon dioxide, producing the lime in a highly friable or easily powdered condition. Calcination in special cases may be carried on in furnaces designed to exclude air, for which an inert gas may be substituted.
Calcination of Limestone

- 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 CO$_2$ gas, and the CO$_2$ gas will react further with coke through Boudouard reaction, leading to extra solution loss of carbon.

\[
\begin{align*}
\text{CaCO}_3(s) &= \text{CaO}(s) + \text{CO}_2(g) \\
\Delta G_{298 \text{K}} &= 130.423 \text{ kJ}, \quad \Delta G_{1273 \text{K}} \\
\Delta H_{298 \text{K}} &= 178.175 \text{ kJ}, \quad \Delta H_{1273 \text{K}} \\
\text{C} + \text{CO}_2(g) &= 2 \text{CO}(g) \\
\Delta G_{298 \text{K}} &= 120.004 \text{ kJ}, \quad \Delta G_{127} \\
\Delta H_{298 \text{K}} &= 172.422 \text{ kJ}, \quad \Delta H_{127}
\end{align*}
\]
Figure: Calcination of limestone
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.
Other Examples of calcination processes include the following

- Decomposition of carbonate ores, as in the calcination of limestone to drive off carbon dioxide
- Decomposition of hydrated minerals, as in the calcination of bauxite and gypsum, to remove water of crystallization as water vapor
- Decomposition of volatile matter contained in raw petroleum coke
- Removal of ammonium ions in the synthesis of zeolites
- Defluorination of uranyl fluoride to create uranium dioxide and hydrofluoric acid gas.
Roasting is the oxidation of metal sulphides to give metal oxides and sulphur dioxide.

The underlying chemical equations depict the process of roasting.

\[
\begin{align*}
2 \text{ZnS} + 3 \text{O}_2 &= 2 \text{ZnO} + 2 \text{SO}_2 \\
2 \text{FeS}_2 + 5.5 \text{O}_2 &= \text{Fe}_2\text{O}_3 + 4 \text{SO}_2 \\
2 \text{PbS} + 3 \text{O}_2 &= 2 \text{PbO} + 2 \text{SO}_2
\end{align*}
\]
Roasting Process
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.
• USES:-
  1) Used in sulfide ore smelting.
  2) Used 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.
➢ Typical 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.
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 As$_2$O$_3$, Sb$_2$O$_3$, 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.
Pelletising

- The formation of raw iron ore pellets, also known as pelletizing, has the objective of producing pellets in an appropriate band of sizes and with mechanical properties high usefulness during the stresses of transference, transport, and use.

- Both mechanical force and thermal processes are used to produce the correct pellet properties. From an equipment point of view, there are two alternatives for industrial production of iron ore pellets: the drum and the pelletizing disk.
Manufacturing of Pellets

- **Manufacturing of Pellets**
- Pellets are formed from the raw materials – fine ores and additives of $< 0.05 \text{ mm}$ - 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.
- The pelletisation process consists of grinding and drying or de-watering, balling and induration, followed by screening and handling.
Pellet Plant
Process

(1) 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%.

(2) 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.
(3) 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.

(4) Handling & Screening

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

- **Transport & Storage**

  Transport on site takes place by conveyor belt or truck. Storage techniques used are either open air stockpiles or in (covered) bunkers.

  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**

  Pellets are primarily used in blast furnaces. Occasionally pellets are used in the steel process.

  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

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

Sampling is carried out at several places in the manufacturing process.
Features of Pellet Production Technology
Sintering

• Sintering is a thermal process (1300-1400°C) by which a mixture of iron ore, return fines, recycled products of the iron and steel industry, slagforming elements, fluxes and coke are agglomerated in a sinter plant with the purpose of manufacturing a sintered product of a suitable chemical composition, quality (physically) and granulometry to be fed into the blast furnace, ensuring a homogenous and stable operation in the blast furnace.

• This describes the sintering process, but prior to sintering there is an important process called granulation. Granulation is the homogenization of the iron ore mixture in a rotatory drum with 7-8% water having as objective the obtaining of a pre-agglomerated product, which is then delivered as a layer over a continuously moving grate or “strand” (Dwight-Lloyd machine) to obtain the sintered product.
Sinter quality indices

- **Softening melting test**
  This test was developed to simulate the behavior of iron ore materials in the cohesive zone of the blast furnace.

- **Tumbler Index (TI)**
  This test was developed with the purpose of knowing the cold strength of the sinter. (TI % > 6.3 mm) (min. 63, max. 79, typical > 74)

- **Low temperature degradation tests**
  Low Temperature Breakdown Test was developed with the purpose of evaluating the abrasion resistance of iron bearing materials under reducing conditions
● **Reducibility index (RI)**

This test informs about the ability of the sintered products for transferring oxygen during the indirect reduction process in the blast furnace stack. (RI min. 49, max. 78)

● **Reduction Degradation Index (RDI)**

This test gives a measure of the sinter strength after the partial reduction of the material. (RDI % < 3 mm) (min. 27, max. 33, typical < 33)

● **Coke consumption**

It was developed in an attempt of reducing CO₂, NOx and SOx as coke breeze has 0.42-1% S and 1.06-1.23% N and for that reason it is necessary to guarantee the coal for coking production. (min. 39 kg t⁻¹ sinter, max. 54 kg t⁻¹ sinter)
● **Fe total**

Iron ore market is mainly composed by hematite (Fe$_2$O$_3$), goethite (α- FeOOH) and magnetite (Fe$_3$O$_4$), with low impurities content (alkalis, sulfur and phosphorus) and iron average content of 60-65% in 2016 (around 40% in 1940). However, the depletion of rich iron ore mines will lead to exploitation of complex chemistry ores and low-grade iron ore mines, considering in some cases the bioprocessing. (Fe % min. 51, max. 61, typical > 56)

● **Basicity index**

Basicity index has importance in the hardness and reducibility of the sinter as expresses the relation CaO/SiO$_2$. (Basicity Index is typically 1.70)
Environmental impacts due to Pellet and Sinter plants
Environmental impact assessment and its management at pelletization plants

- 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.
- 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).
Measures to Enhance Air Quality
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THANK YOU