CHAPTER - II

EXTRACTIVE METALLURGY

Dr. P. N. CHAUDHARY

2.1 INTRODUCTION

Metal is extracted from ores. The main factors which determine whether a particular mineral is an ore of the metal are a) the percentage metal content a) the cost of extraction b) the market price.

Broadly, the ore consists of mainly two parts: Metal and Gangue (impurities). The metal is usually reduced from their oxides (ores). The separation of the metal from their impurities is carried out in the extraction the metal. The entire process is known as extractive metallurgy. The metal can be extracted by different methods. They are classified into the following categories:

a) Pyro metlallurgy
b) Hydrometallurgy and
c) Electrometallurgy

The choice of the process depends mainly on two factors- i) the chemical strength of the bond to be broken up, and ii) economic considerations.

Pyro metallurgical processes are carried out at high temperatures. These processes are usually suited for large scale production. They are employed to extract metals like iron zinc, magnesium, lead, aluminium, copper, sodium, antimony etc. i.e. mostly inexpensive metals. The process consists of smelting the ore in a furnace in the presence of the reducing substances like carbon. The separation of metals by carbon reduction of oxides is possible only when the desired metals is nobler than the metal whose oxides constitute the gangue e.g., aluminium oxide contained in an iron ore is not reduced by carbon during smelting. Some metals, which form stable oxides, can also be used as reducing agents (Fig.1). The reactions, which are not possible at low temperatures, become feasible at high temperatures in the pyrometallurgical operation (Fig.2). The reduced metal due to its high density collects at the bottom of the furnace in a liquid state and is tapped off. The gangue is usually treated with the flux and forms slag which being lighter floats on the top. The difference in the density of the liquid metal and slag causes to separate in layers so that they may be tapped out of the furnace at different levels. In pyro metallurgy all reduced element join the metal and oxidized ones go to form a slag.

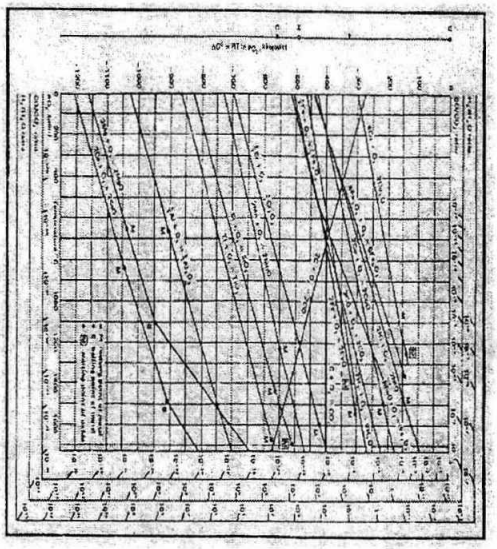
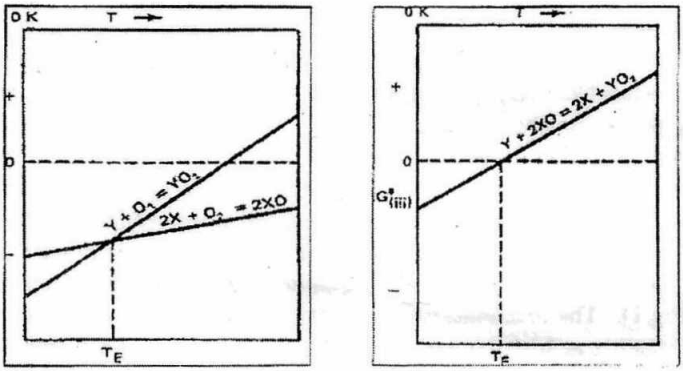


Fig.1: Ellingham Diagram for Metallurgically Important Oxides



IF PURE X WERE TO BE USED AS A REDUCING AGENT TO REDUCE PURE YO_2 TO FORM Y AND PURE XO, THEN THE REQUIRED REDUCTION COULD ONLY BE EFFECTED AT TEMPERATURES IN EXCESS OF T_E

Fig. 2

2.2 PYROMETALLURGY

Pyro processing is required to make the ore suitable for their extraction. The different methods of pyro processing are as follows:

Drying

Drying is a removal of water from substances (ores) by evaporation. In this process vapour pressure of water in the substance should be more than the vapour .pressure of the surrounding atmosphere. By heating the substance above the normal boiling point of water at atmospheric pressure the locked moisture in the ore is removed.

Calcining

Calcining is a process of removing a volatile constituent of a compound at a temperature below fusion, without otherwise affecting the resultant product chemically. Most hydrates give up their water below 300 degree C and carbonates at about 800 degree C. This is a endothermic process i.e. heat is required to complete the process The limestone, dolomite and Magnesite are calcined to drive off carbon dioxide before using them in the smelting furnace for pyrometallurgical operations. I

Roasting

Roasting is defined as heating to an elevated temperature without fusion of metal or metallic compounds in contact with Oxygen water vapour carbon sulphur and chlorine in order to effect a chemical change and thereby eliminate some component by volatilization. The examples are

$2PbS + 3O_2 = 2PbO + 2SO_2$ (Oxidising Roasting)

$ZnS + 2O_2 = ZnSO4$ (Sulphate Roasting)

$3Fe_2O_3 + C = 2Fe_3O_4 + CO$ (Reduction Roasting)

$TiO_2 + C + 2Cl_2 = TiCl + 3\ (g) + CO_3$ (Cholorodizing Roasting)

Agglomeration

The aim of agglomeration is to utilize the ore fines generated at the mines site for extraction of metals. For pyrometallurgical operations, normally lump ores are used for extraction of metals but during sizing operations lot of fines are generated. These fines are agglomerated in different forms such as Sinter, Pellets and briquettes depending on their mesh size and intended applications to make them suitable for charging into the furnace. The requirement of particle size for sintering is much coarser (upto 10 mm) then that of pelletising (<0.1mm)..

The metals are extracted using a suitable reducing agent. These reducing agents could be

1. Carbon
2. Metal (Al,Mg, Ca, Na etc.)
3. Gases (H_2 Carbonaceous gases)

The selection of a suitable reducing agent depends on several factors. One of them is the energy requirement, which is known from the standard value of free energy formation of compound vs. temperature diagram known as Ellingham Diagram (Fig.1). The Ellingham diagram provides the comparative stabilities of different compounds w.r.t temperatures.. The salient points of this diagram are given below:

a) The more stable oxides appear on the lower part of the diagram in the order FeO, P_4O_{10}, Cr_2O_3, MnO, SiO_2, Al_2O_3 , MgO and CaO. Thus, if conditions are made favourable for the reduction of MnO, then the oxides of iron, phosphorus and chromium will also be reduced.

b) For a given oxide mineral, the oxides below it on the Ellingham diagram are stabler and therefore, the elements of the latter (such as Al, Si and Ca) could readily act as reducing agents. This principle is utilized in metallothermic reduction processes.

c) Whereas most lines in the Ellingham diagram slope upward, the CO line slopes downward because of entropy considerations. Thus, there is temperature above which CO is more stable than the oxide mineral to be reduced. However, the actual operation may have to be conducted at temperatures higher than the temperature of intersection between MO and CO lines in order to enhance the reaction rates and facilitate metal slag separation.

d) All the lines plotted in the Ellingham diagram correspond to standard states (pure condensed substances). For impure oxides, the line would rotate clockwise (with respect to zero temperature) indicating greater ease of formation: conversely for impure elements, the lines would rotate anti clockwise

The typical reduction reaction could be shown as:

$$MO + C = M + CO \quad \text{----- direct}$$

$$MO + CO = M + CO_2 \quad \text{----- Indirect}$$

The indirect reduction is more exothermic relative to the direct reduction. Consequently, the energy efficiency of a process could be

significantly enhanced by utilizing the CO formed by direct reduction for subsequent indirect reduction as accomplished in the iron making blast furnace (Fig.2). However the latter calls for a long stack and elaborate burden preparation so that descending charge could be preheated and reduced indirectly by the upward having hot gases before getting directly reduced.

2.3 HYDROMETALLURGY

Hydrometallurgical process involves separation of metal in aqueous solution from the rest of the ore followed by precipitation in a metallic form. The separation is by means of a solvent. The electrolysis is used to reduce and precipitate some metals from solution. The technique is applied to extract number of metals such as gold, silver,copper,zinc cadmium etc.

Advantages:

1. It is possible to extract higher percentage of the valuable metal
2. It requires very less fuel
3. The process is particularly suited to lean ores.
4. The equipment needed is very simple compared to pyrometallurgical process
5. It may be possible to regenerate the solvent

UNIT OPERATIONS INVOLVED IN HYDROMETALLURGY

- Feed preparation
- Leaching (selective dissolution of metal values in an appropriate solvent)
  Water
  Acid
  Alkali
  Salts
- Solid/Liquid separation
- Solution purification
- Recovery of metal values
  - Chemical precipitation
  - Cementation
  - Ion Exchange
  - Solvent Extraction
  - Electro winning

Feed Preparation

Ore to be leached must be crushed and ground to such a size so that solvent can readily act on soluble minerals. Gold ore requires fine grinding. Material to be leached is roasted due to following reasons:

1. to convert the metal into soluble form
2. to volatalize certain soluble impurities that could contaminate the solution
3. to make the metallic compounds porous so that they are readily attacked by the solvent

Leaching

Leaching is a process of dissolving the desired mineral by the chosen solvent. In leaching, metallic portion of the ore must be soluble in the reagent used and the gangue should be insoluble.

Types of leaching

Heap leaching

In this process the broken the ore is heaped up and oxidized by roasting and water is then applied to dissolve metallic content.

Sand leaching

This is practiced when the ore is coarse enough to permit free passage of the solvent through the voids. It is essentially a batch process. Sand leaching is most suitable for low grade ores.

Slime leaching

Slimes are ore products that are so finely ground that they tend to pack the container andprevent the free circulation of the solvent through interstices of the bed of the ore. Therefore, the slime and the leach solution are agitated until the ore is completely dissolved.

Bacterial Leaching

The value of the bacterial leaching as a metal recovery process is widely recognized. The process is particularly suited for treating low grade or waste material.

When the dissolution of ore is completed, the liquid is separated from the solid material so that metal may be precipitated from liquid by following methods and the tailings discarded.

Chemical Precipitation

The basis of chemical precipitation is the solubility product. Solid compounds may dissolve in aqueous solutions by reactions such as

$NaCl(s) = Na+ _ + Cl^-$

$AgCl(s) = Ag^+ + Cl^-$

$Al(OH)\ (s) = Al^{3+} + 3(OH)^-$

Each of these reaction is characterized by an equilibrium constant. For equilibrium between solid NaCl and the solution.

$a_{Na+} + a_{Ca-} = K$

This is solubility product of NaCl

Cementation:

The most important type of chemical precipitation is cementation, in which a metal is displaced from solution by a less noble metal. This method is less costly but precipitate produced is usually impure.

$CuSO_4 + Fe$ —— $FeSO_4 + Cu$

Ion exchange: exchange of ions between an ion exchanger (an organic resin) and aqueous solution containing metal ions.

Ex: Absorption of uranyl sulphate complex by an anion resin

$4R^+ X^- + U O_2 (SO_4)_3\ 4- = (R^+)_4\ U O_2 (SO_4)_3\ 4- + 4 X^-$

R resin cation; X- anoion like Cl or NO_3

Once the resign is loaded with U, it is stripped by means of a strong acidified chloride or nitrate solution

Solvent extraction: In principle similar to IE but instead of an organic resin an organic solvent is used for exchange of ions

At Anode (if inert)

$H_2O + SO4 = H_2SO_4 + ½\ O_2 + 2\ e^-$ (Oxidation)

At cathode

$Cu^{++} + 2\ e^- = Cu$ (Reduction)

$Cu^{++} + SO_4^{--} + H_2O = H_2SO_4 + ½\ O_2$(anode) + Cu (Cathode)

(Overall reaction)

2.4 ELECTROMETALLURGY

The alkali and alkaline metals are usually extracted by electro metallurgical methods. These metals are not reduced by common reductant such as carbon. The only draw back of thee methods are that they require

electrical power which is costly in our country. The common metals which are extracted by these methods are, Aluminium, Sodium, Lithium, Magnesium, Chromium, Cadmium, Zinc, Copper, Nickel etc. In addition, several other metals such as Be,Ta, Nb, R.E. metals, Ca, Ti, Tl, In, Zr, Hf, B etc are also obtained by electrolysis, amongst other methods.

2.5 OVERVIEW OF IRON AND STEEL MAKING

At present, per capita steel consumption in India is 39 kg against world average of 174 kg. The total production of steel was 38.385 million tonnes in 2004-05 out of which integrated steel plant produced about 28 million tonnes, 6 m tonnes came from secondary sector and 4 m tonnes from mini steel plant (Induction Furnace). The total consumption was 35 million tonnes and 3 million tonnes were exported. As per steel policy decided in 2005, India aims to achieve100 miilion tonnes production by 2020 which has been revised now to 160 million tonnes.

Steelmaking technology has greatly changed during the last two decades under the pressure of increased demand, new specifications and the need to reduce energy and material consumption. Production efficiency has been improved by increasing the melt capacity of furnaces, implementing on-line computer control modules, and introducing new technologies, such as the combined blowing process for LD (Linz Donawitz) converters, the Ultra High Power (UHP) electric furnace, the ladle steelmaking processes and continuous casting.

Steel is produced by two process routes (Figure 3):

- The Blast Furnace-Basic Oxygen Converter (BOF)
- The Electrical Arc Furnace (EAF)

In both routes the process consists of producing refined iron to which the required alloying elements are added to produce the finished steel specification.

Their respective shares in crude steel production are 70% (BOF) and 30% (EAF). High production rates and low impurity steel production give a dominant role to the first process route. Low energy costs and an ample supply of recycled scrap ensure a competitive market share for the second process route, especially when using the UHP furnace.

Before casting, the steel can be refined in the ladle by various processes according to the specification with respect to its deoxidation state, inclusion content and level of phosphorus, sulphur, nitrogen and hydrogen. At the same time, its content of carbon, manganese and microalloying elements such as niobium, vanadium and titanium can be adjusted. This process step is generally referred to as Secondary or Ladle steelmaking.

During the last step of steelmaking, the steel is cast either into slabs, blooms or billets on a continuous casting machine or into ingots, depending on the final product. Flat products and light shapes are normally produced from continuous cast feedstock; whereas heavy beams and plates are more likely to follow the ingot route.

The major activities of steel plant is Iron making, Steel making and rolling mill.

2.6 IRON MAKING

Iron making is mainly based on reduction of iron oxide bearing materials through solid-gas reaction.

Raw materials

Iron ore	:	Beneficiated and sized Hematite and magnetite ore
Coke	:	Metallugical coke
Fluxes	:	Lime stone, Dolomite, quartzite, Mn-ore
Sinter	:	Under sized iron ore is agglomerated by partial fusion

Ore Reserve

- Inferred : 23, 000 million tonnes (85% Hematite, 8% magnetite)
- Proven Deposit: 13,200 million tonnes
- 43% of total iron ore reserve of India is in Jharkhand and Orissa. Rest of the reserve are in M.P, Mysore, Maharastra and Andhra.

Blast Furnace

It has not been possible to replace blast furnace for high level of production of iron. The sketch of blast furnace is shown in Fig. 3. This is an extremely efficient counter current reactor where more than 99%) iron recovery is possible. A high level of Productivity 2-3 t/m^3/day can be achieved.

The blast-furnace is a shaft type furnace (Fig. 3) operating by the counterflow technique: the descending burden of sinter and coke, charged from the top of the furnace, is heated and reduced by the combustion gases ascending from the tuyere zone where a hot air blast is injected to burn C to CO. The air blast is compressed by a blower and heated in special stoves to 1100°C by combustion of the cleaned furnace exhaust gases.

The iron oxides (FeO, Fe_2O_3) and some of the elements present in the gangue of the sinter are reduced by CO gases to produce hot metal.

The blast furnace flue dust containing about 40% Fe is recycled by the sinter process.

The high permeability of the sinter and the even distribution of the charge produced by revolving chutes help to improve productivity of the blast furnace. Coke consumption can be reduced to 470 kg/t of hot metal. The use of tuyere injectant such as powdered fuel (120 kg/t) or oil (60 kg/t) further reduces the coke consumption of the furnace and so the cost.

At higher temperatures softening-melting of iron ore takes place in the cohesive zone. Iron droplets trickle through dripping zone.

Below the tuyere zone, where the temperature is highest, the molten material collects on the furnace hearth where the liquid iron (pig iron) separates from the slag by difference in density. The slag and liquid pig iron are tapped from separate tapholes. The tapped slag is granulated by water jets and removed for use in other products including road construction materials, fertilizers, etc. The liquid pig iron (hot metal) is tapped into ladles or torpedo cars (capacity: 300 - 400 t) and conveyed to the steel plant for refinement and conversion into steel.

A typical analysis of the hot metal produced at a temperature of 1400°C is:

4,7% carbon (C); 0,5% manganese (Mn); 0,4% silicon (Si); 0,1% phosphorus (P) and 0,04 % sulphur (S), the remainder being iron (Fe).

Sulphur removal from the melt needs low oxygen activities. Desulphurization is therefore achieved in the hot metal by injection of calcium carbide fluxes to form calcium sulphide (CaS) or fluxes containing metallic magnesium to form MgS and CaS.

The current research activities of NML for BF

NML is executing a comprehensive research programme in collaboration SAIL and Tata Steel to create a knowledge base on the process dynamics of blast furnace through

a) rigorous process models

b) experimental investigations

c) real time process simulator

The knowledge base generated is being implemented in the plant (BF-5, BSL) to assist the operator to further improve the furnace performance.

Major testing facilities available for iron making

- RI, RDI, TDI, Shatter, trumbler properties of ore
- Softening melting characteristic of ore
- Ash fusion furnace
- High temperature viscometer etc

Iron Blast Furnace

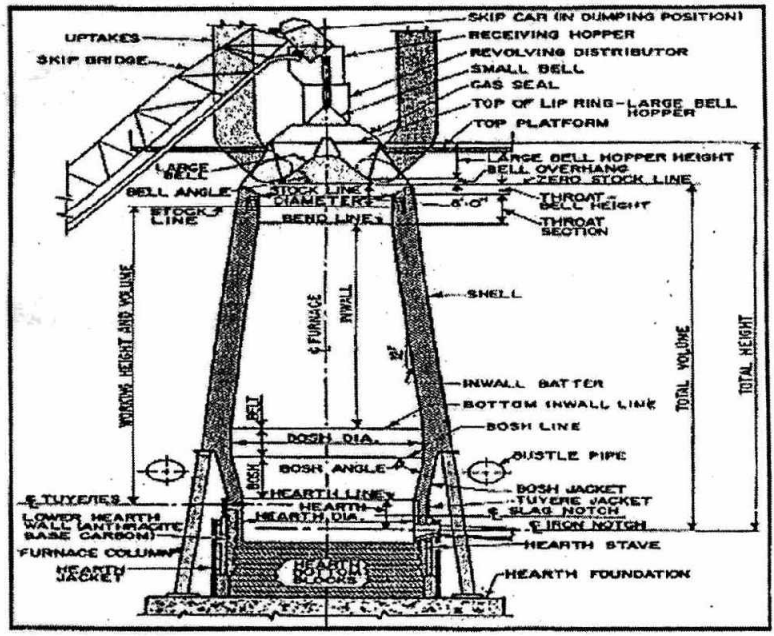


Fig. 3

2.7 STEEL MAKING

Steelmaking is a selective oxidation of impurities present in pig iron. Amongst the impurities, carbon is the major element (>4%) present in the hot metal. Steelmaking is governed by carbon elimination reaction. The duration of carbon removal fixes the duration of steelmaking. The aim of the development has been mainly to increase the rate of carbon removal and decrease the heat time. The sequence is given below

Bessemer Process (1861) :

In this process air was used for oxidising impurities. The process was fast but contained high nitrogen content. The process was types depending upon the input materials

a) **Acid Bessemer process** (1867):

The process was suitable for input material with low P&S (,0.05%) Product contained high nitrogen content making it unfit for drawing purpose

b) **Basic Bessemer process (1878):**

It requires metal with 1.5% phosphorus to generate sufficient heat for achieving steelmaking temeratures (>1500^{0}C) which is also called Thomas Prpcess. This process was not suitable for Indian pig iron, which contained 0.2-0.3%P.

- **Open Hearth Process (1878):**

  With the development of regenerative principle by Simon brother, it was possible to achieve steelmaking temperatures for making alloy steels. This process was very useful for melting scrap. It had ability to accept wide variations of charge materials but the process was very slow. It took 12-16 hours to make one heat.

- **Electric Arc Process (1899):**

  Paul Herault used direct electric arc furnace for making steel. It produces clean steel as no solid/gaseous fuel is used. All types of steel can be produced through this method. Nature of slag can be controlled to achieve desired composition. It offers better option to basic open hearth for production of alloy steel.

- **Induction Furnace (1927):**

  Suitable for foundry for melting scrap. Some adjustment in composition is also possible

- **LD Process (1952):**

  Pure oxygen is used for refining of impurities. The formation of metal-slag-gas emulsion increases the interfacial area many fold making the process highly efficient. The oxidation of phosphorus starts from the beginning of the blow when the carbon content is still high which was not possible in the processes discussed above.. It is possible to remove about 30% sulphur present in HM. The nitrogen content can be controlled within desirable limits.

  Amongst the processes mentioned above, some of processes currently being used are described below:

The basic oxygen furnace or LD converter (originating from the Linz-Donawitz process started in 1956) is based on oxygen injection by a lance into the melt of hot metal. Scrap and lime are charged into the converter to cool the melt and remove phosphorus, silicon and manganese.

The converter is lined with dolomite or magnesite refractory which best resists erosion by slag and heat during oxygen blowing. The life of a converter lining is about 800 to 1400 heats.

The oxygen burns out the carbon as carbon monoxide CO and carbon dioxide CO_2 gas which is collected in the chimney stack and cleaned of its dust (Fe_2O_3, and lime particles, etc.). The elements Mn, Si and P are oxidized and combine with lime (CaO) and FeO formed by the oxidation of Fe to form a molten slag.

As these oxidation reactions are highly exothermic, the process needs cooling in order to control the temperature of the melt. This cooling is done by charging scrap (recycled plant and mill scrap) and by adding iron ore during the blowing process.

The oxygen blowing takes 15 to 20 minutes, regardless of the size of the converter (70 to 400 t) because the oxygen flow rate of the lance is adjusted to the melt weight. The charging and discharging of steel and slag, including sampling for temperature and analysis of the melt, extends the tap to tap time of a converter to 40 - 60 minutes. The process is characterized by high productivity and steel of low impurity content.

The steel is tapped to the ladle through a taphole by tilting the furnace. During this operation ferro-alloys for control of the steel composition are added to the ladle. The oxidized slag containing 12 to 16% of Fe is poured into a cast iron slag pot after the tapping and is disposed of in a slag yard.

Electric Arc Furnace

In the electric arc furnace process, the cold metallic charge, mainly scrap, is melted by the energy of electric arcs generated between the tips of graphite electrodes and the conductive metallic charge.

The three electrodes and the furnace roof are raised and swung away from the furnace shell to allow the charging of scrap. The electrodes maintain the arc in accordance with the voltage and current level selected to produce the desired power input at the desired arc length for melting and refining. As the noise generated by the arcs is high during the melt-in-period, with levels up to 120 dBA, special protection is provided to the operators cabin and the furnace has a special enclosure.

The three phase alternating current is supplied by the low voltage side (300 - 700V) of a high power transformer. The nominal transformer rating, expressed as KVA/t, extends from 300 to 500 KVA/t for high power furnaces and from 500 KVA/t upwards for Ultra High Power (UHP) furnaces. These furnaces have an inner diameter of 6 to 9 metres with a capacity of 100 to 200 tons of steel. The tap-to-tap time for these furnaces is 90 to 110 minutes.

The traditional role of the EAF process is producing alloy, tool and carbon steels, and it has been extended by the UHP furnace to mass steel production. Thus, the concept of the Mini-Mill was born. As the size and

productivity of the furnace increased, the operation of continuous casting for billet and bloom production became possible. Flat products specification, however, require low residual impurity levels and even higher production rates which cannot be satisfied by the UHP-furnace.

The share of steel production produced by electric arc furnace is about 30%, at which level it seems to be stabilized as scrap of acceptable quality becomes more scarce. Pellets and sponge iron of higher price have to be used for critical steel grades to control the level of injurious elements, i.e. copper, nickel, tin, etc..

Metallurgy

The traditional high power furnace produces high quality carbon and alloy steels by the two slag technique. After melt down of the scrap charge, a first oxidizing slag removes the elements P and Si and reduces carbon to the required level. After deslagging, a second basic reducing slag is formed to lower the sulphur and oxygen contents and the steel composition is adjusted by ferro alloy additions.

The UHP furnace operates with only a lime based oxidizing slag. The melt down of the scrap charge is accelerated by the use of oxy-fuel burners positioned to reach the cold spots of the large hearth furnace. Oxygen lancing and carbon additions are used to make a foaming slag which yields better energy input from the arcs and improves dephosphorization. After this period, the melt is discharged by a taphole. Deoxidation and refining under reducing slag takes place in the steel ladle (secondary steelmaking). The 100% scrap charge makes the process more vulnerable to injurious "tramp elements", such as copper, nickel and tin which cannot be removed by the process, their stability being higher than that of iron. To control these "tramp elements", it is of great importance to identify the sources of the incoming scrap and to make provision to keep the different qualities separate.

Secondary or Ladle Steelmaking

Achieving the required properties of steel often requires a high degree of control over carbon, phosphorus, sulphur, nitrogen, hydrogen and oxygen contents. Individually or in combination, these elements mainly determine material properties such as formability, strength, toughness, weldability, and corrosion behaviour.

There are limits to the metallurgical treatments that can be given to molten metal in high performance melting units, such as converters or electric arc furnaces. The nitrogen and phosphorus content can be reduced to low levels in the converter but very low carbon, sulphur, oxygen and hydrogen contents (< 2 ppm) can only be obtained by subsequent ladle treatment. To

ensure appropriate conditioning of steel before the casting process, the alloying of steel to target analysis and special refining treatments are carried out at the ladle metallurgy stand.

The objectives of ladle steelmaking can be summarized as follows:

- refining and deoxidation
- removal of deoxidation products (Mn0, SiO_2, Al_2O_3)
- desulphurization to very low levels (< 0,008%)
- homogenisation of steel composition
- temperature adjustment for casting, if necessary by reheating (ladle furnace)
- hydrogen removal to very low levels by vacuum treatment.

The high oxygen content of the converter steel would result in large blow-hole formation during solidification. Removal of the excess oxygen ("killing") is therefore vital before subsequent casting of the steel. Steels treated in this way are described as killed steels. All secondary steelmaking processes allow deoxidising agents to be added to the ladle so that deoxidation in the converter vessel is not necessary.

Deoxidation can be performed by the following elements classified by increasing deoxidation capacity; carbon - manganese - silicon - aluminium - titanium. The most popular are silicon and aluminium.

After addition, time must be allowed for the reaction to occur and for homogeneity to be achieved before determination of the final oxygen content using EMF probes (electro-chemical probe for soluble oxygen content).

As most of these deoxidation agents form insoluble oxides, which would result in detrimental inclusions in the solid steel, they have to be removed by one of the following processes during the subsequent refining stage:

1. Argon stirring and/or injection of reactants (CaSi, and/or lime based fluxes) achieves:
   - homogeneous steel composition and temperature
   - removal of deoxidation products
   - desulphurization of aluminium-killed steel grades
   - sulphide inclusion shape control.
2. Ladle furnace
   Stirring of the melt by argon or by an inductive stirring equipment and arc heating of the melt (low electric power, typical 200 KVA/t) allows:

- long treatment times

- high ferro-alloy additions
- high degree of removal of deoxidation products due to long treatment under optimized conditions
- homogeneous steel composition and temperature
- desulphurization, if vigorous stirring by argon.

Vacuum-Treatment: RH process (Ruhrstahl-Heraeus) and tank degassing unit.

In the RH process the steel is sucked from the ladle by gas injection into one leg of the vacuum chamber and the treated steel flows back to the ladle through the second leg. In the tank degasser process, the steel ladle is placed in a vacuum tank and the steel melt is vigorously stirred by argon injected through porous plugs in the bottom of the ladle.

Vacuum treatment achieves:

- reduction of the hydrogen content to less than 2 ppm
- considerable decarburization of steel to less than 30 ppm when oxygen is blown by a lance (RH - OB)
- alloying under vacuum
- homogeneous steel composition, high degree of cleanness from deoxidation products

High temperature losses (50 - 100°C) are a disadvantage, therefore high superheat of the melt prior to this process is essential.

For most secondary steelmaking techniques it is either desirable or essential to stir the liquid steel. Gentle stirring is sufficient for inclusion removal; non-metallic inclusions are brought into contact with liquid slag on top of the melt where they can be fixed. For degassing and desulphurization however, violent stirring is necessary to increase the surface of steel exposed to vacuum (H-removal) or to mix the steel and slag for good desulphurization efficiency.

Casting and Solidification

For solidification, steel is cast into moulds either of cast iron for the ingot casting route or into copper moulds for the continuous casting process.

The heat of liquid steel is extracted by the cold mould surface so that crystals can form and grow. A solid shell is formed and solidification progresses by maintaining the cooling.

During solidification, the density of metals rises and causes shrinkage. This favours the stripping of the cast from the mould. However, this

contraction also causes internal shrinkage which tends to leave a hollow core in the cast product. In continuous casting this is prevented by the continuous flow of molten metal to the mould. For ingot casting an adequate liquid metal pool has to be maintained at the head of the mould by the provision of exothermic material (hot-top).

A second concern during the solidification process is segregation due to the fact that some solute elements have a much lower solubility in the solid than in the liquid phase. The segregation tendency is most pronounced for sulphur, phosphorus, oxygen and hydrogen. As has been described, these elements can be controlled to sufficiently low levels by the metallurgical process steps. The manganese content of steel also combines with sulphur to form manganese sulphide inclusions which are elongated during rolling and become detrimental to steel properties if significant stresses are applied perpendicular to the rolling direction. For such applications, shape and content of the sulphide inclusions have to be controlled closely during the refining stage.

The casting of ingots is a discontinuous process in which the ingot moulds are filled individually by top pouring or in batches by a central feeder through runners in the base plate. This up-hill teeming technique is characterized by a low rising speed of the steel in the mould, which reduces cracks and surface defects when casting critical steel grades.

The teeming operation is done directly from the steel ladle through a sliding gate valve at the bottom that regulates the steel flow, and a nozzle that gives a concentric steel jet.

The ingot weights and sections are fixed by the capacity of the primary rolling mill. The ingot size may vary from 4 to 30 t, or even higher for forging.

The ingot remains in the mould until solidification is complete. Then the mould is stripped off by crane and left to cool in the mould yard. The ingot is charged into the soaking pit furnace to equalize and raise the temperature for the rolling process (» 1300°C).

The solidification of an ingot progresses from the bottom (cooled by the base plate and the mould) to the top of the ingot.

In the case of a fully killed (Si + Al) steel melt, with a low free oxygen content, the solidification shrinkage is concentrated at the upper centre of the ingot. To minimise the development of shrinkage porosity in this region, the top of the ingot is insulated (hot top) to provide a reservoir of liquid metal to fill up the hollow core. The hot top is subsequently cropped. This scrap amounts to approximately 12% of the ingot weight.

By deoxidation with silicon alone, the free oxygen content of the melt

can be set to a well defined level so that towards the end of solidification it will react with the carbon of the melt to form CO gas. The formation of these small gas bubbles, or blow holes, compensates for the shrinkage of steel and top crop losses are small (» 2%). The blow-holes are eliminated during primary rolling. Such steels are referred to as 'balanced' steels.

Ingot casting is very flexible as regards product specifications and the production of small orders on relatively short delivery terms. It is also indispensable for the forming of heavy shaped profiles like beams, heavy plate or heavy forging pieces.

2.8 FERRO ALLOYS

In all steel making processes ferroalloys are used for the purpose of deoxidizing and alloying the steel. Ferromanganese and ferrosilicon are extensively used in the steel plant.

When silicon and manganese are required to be added together, it may be added in the form of silicomanganese. Because of high melting points of Chromium, Tungsten, Molybdenum, they are added in the form of ferroalloys for the purpose of alloying.

2.9 CONTINUOUS CASTING

Conventionally ingot (3 ton to 25 ton) is made from liquid steel. Different shapes (Blooms, Billets and Slabs)are given after reheating and hot rolling

Continuous casting technique allows molten steel from the ladle to be cast directly into the basic shapes (blooms, billets & slabs). In addition to more rapid freezing, continuous casting differs from ingot casting in following ways:

1. Pouring is continuous.
2. Heat transfer is essentially in the transverse direction hence there is no end effect as found in ingot casting.
3. It requires very controlled pouring so that it matches with the withdrawl speed of the ingot
4. The depth of liquid metal pool is several meters long which suppresses the blowhole formation.

The continuous casting process has become the major casting technology for steel plants. The reasons are:

- yield improvement
- energy conservation (direct production of semi-finished products)
- savings in manpower

The ratio of continuous cast steel has reached 80 - 90% of total raw steel production in the Western World. The advent and rapid growth of mini-mills could not have occurred without continuous billet casting technology. The essential feature of the continuous casting process is the oscillating water-cooled copper mould. The main function of this mould is to form a solidified steel shell having sufficient strength to prevent breakouts below the mould. This is achieved by the high heat extraction in the mould system. The mould walls are tapered to accommodate the strand shrinkage over the mould length of 700 mm and to maintain a high heat flux.

The oscillation creates a relative movement between strand and mould, and prevents metal sticking to the mould surface. Stripping is facilitated by providing an adequate lubricant (casting powders or oil) at the steel meniscus. This lubricant is also essential to maintain a high heat extraction and prevent breakouts.

On leaving the mould, the strand is cooled by water sprays and is supported by rolls to prevent bulging until solidification is complete. Strand sections cover the range of semi-finished products, such as billets, blooms or slabs, for the hot finishing mills. Depending on the section to be cast, a continuous caster is laid out with two (slab), four (bloom or round caster) or six strands (for billets below 180 mm^2 in size).

Modern casters are curved type machines which are cheaper and easier to accommodate in the plant than the original vertical machines. The curved strand is straightened by rollers after complete solidification and cut to the required length for further processing in the rolling mills.

Continuous casting technology makes the process continuous so that a number of molten steel batches are cast in sequence. To achieve a continuous supply of steel to the mould, the steel in the ladle is first cast into a tundish, which acts as a reservoir during ladle changing and distributes the steel to the different moulds of the machine. Tundishes are equipped with stoppers or sliding gates to regulate the flow rate to the casting speed of the strand. To prevent oxidation by air exposure, the ladle and tundish streams are shrouded by refractory tubes.

2.10 SPONGE IRON

The story of sponge iron also known as Direct Reduced Iron (DRI) industry is very interesting as far as India goes. The three-decade old this industry came into existence all on a sudden when mini steel plants were looking out raw materials randomly. Since, India has adequate coal deposits, its utilisation for steel plants was considered of prime importance. Production of coal based sponge iron in the beginning was taken as a viable option. Sponge iron industry grew at very slow speed till the mid of 1980 due to government's restrictive licensing. The 1985 proved as a historical year for

the industry in general and the steel industry in particular. In this year the DRI production was delicensed and since then the industry started growing rapidly to reach today's level. DRI is a high quality metallic product obtained from iron ore, pellets etc. as a feedstock in the Electric Arc Furnaces (EAFs), blast furnace (BF) as well as other iron and steelmaking process. Hot briquatted iron (HBI) is a denser and compacted form of sponge iron. There are four main sources of metallics for steel making and they are scrap, hot metal from blast furnaces (BFs, including its variants) as well as from smelting reduction (SR) process, DRI/HBI (Hot briquatted iron) and iron carbide. Traditionally, scrap has been the main feed to electric arc furnaces (EAFs). With more and more continuous casting (CC) in use, the applications of scrap has reduced drastically. Even in a developing country like India, CC has been extensively used to enable steel to remain competitive. Today, steel industry is facing a situation of less generation of scrap accompanied by greater demand. Neverthless, it needs to be emphasized that scrap will continue to remain the major feed for EAFs. At the same time, the quality of scrap may at best remain at today's level, and pre-reduced material will gradually substitute more and more scrap in making high quality steels. Consequently, the supply of sponge iron is expected to grow to the level of 50MTPA in 2010 against 30 MTPA, today. Liquid hot metal and solid pig iron would also be used to larger extents. Chattisgarh is endowed with rich deposits of non coking coals suited to sponge iron manufacturing. Iron ore is also available in neighboring state of Orissa. As a result, several mini sponge iron plants have started in this region and many others are in pipeline.

The major raw materials required for production of sponge iron are oxides of iron in the form of lump iron, pellets, non-coking coal and fluxes (limestone and dolomite). Some precaution is necessary in selecting the iron oxide especially the phosphorus content and its reliability for easy reduction. Use of high purity of lump ore, pellets with low phosphorus at an economic price helps in the cost effective production of sponge iron. As far as chemical composition for sponge iron goes, for maximum yield, the metallic iron content should be at the highest possible level with sulfur and phosphorus as low as possible. The gauge content should preferably be within 2 per cent, and silica less than 3 per cent to ensure lower slag volume, less power consumption and for achieving higher productivity.

2.11 ENVIRONMENTAL CONSIDERATIONS AND WASTE UTILIZATION

The pollutants generated in the integrated steel plants are CO, CO_2, SO_2,NO_x, cyanides, volatile organic compounds (VOC), NH_3 etc and suspended particulate matters(SPM).The chemical pollutants are formed in

coke oven, sinter plant, blast furnace , BOF and other furnaces.Carbon dioxide is a green house gas. Since iron making uses coal as fuel, its contribution on the total carbon dioxide generation is significant. During recovery of by products coming out of coke oven, hazardous effluents and solid wastes are generated and a number of toxic chemicals also escape. The effluent contains both organic and inorganic toxic chemicals such as ammonia, cyanide, oil, grease, nitrate etc.The sintering plant is another source of pollutions in steel plants. The laddle furnaces and reheating furnaces are the other sources of gaseous pollutants in the steel plants.

SPM is a major pollutant from steel plants. The reduction of SPM is usually taken as a direct measure of effectiveness of pollution control. This problem is equally applicable to foundry sector of metallurgical industry. There are about 6000 foundries currently operating, mainly in clusters, at Ahmedabad, Agra, Batala, Coimbatore and Howrah and most of these are coke based.Normal stack emission from foundries ranges from 1000 to 2500 mg/ m^3 of SPM.whereas as per the norms of Central Pollution Control Board (CPCB)the SPM level must not be more than 150 mg/ m^3. Considering the enormity of problems from technical, economical and social angles,the National Metallurgical Laboratory (NML) developed a less expansive dry gas cleaning system of various modules/sizes to meet the requirements of Cupolas that ranges from 2t/hr to 25t/hr capacities. Each module of the gas cleaning system has less weight and fewer capital equipment. They consist of ducting to carry all the SPM in flue gas dischrged fromcupola high pressure cyclones, ID fans, chimney,dust disposal unit and rotary air lock discharger to give exhaust emmission less than150 mg/ m^3 through stack. The first demonstration unit was set up in M/S Crawley &ray, Howrah in 1995. The second demonstration unit was set up in M/S Uma foundry Pvt ltd. Liluah (Howrah) in 1996. Based on these developments, NML received a turnkey job from Kulti, IISCO. The system system installed by NML at Kulti Works are functioning effectively and have met the CPCB norms effectively.

A even better alternative was thought later . It was decided to replace coal, which is main source of pollution, by gas or oil. An existing conventional cupola of 1 t/hr was redesined to suit the new fuel.Several trials were carried out and follwing observations were made:

- No visible emission at the top of the shaft during the melting period.
- Closer control over the melting process than in conventional process
- low slag volume during the melting, leading to a greater efficiency
- No sulphur pick up by metal during melting

Effort is on to commercialize the process.

Waste Utilization

While the usage of blast furnace slag is well established in the area of cement making, recycling of steelmaking slag is still a challenging task. About 150-180 kg steelmaking slag is generated per ton of steel depending upon the quality of hot metal. At present less than 50% of the slag is used in road making, construction and sinter making, and the remainder is dumped. This slag may find application in refining of steel or iron making processes due to its high metal value and lime content provided phosphorus (P_2O_5=2-4 %) is removed from the slag. An effort has been made at NML to remove phosphorus from Steelmaking slag to make it recyclable.

Amongst the different methods tried for phosphorus removal, chemical process has been considered most suitable because it utilizes the energy content of the slag The results have shown 70-75% recovery of metallic values from slag whereas phosphorus removal varied in the range of 65-95%.