

SPONGE IRON & FERRO ALLOY

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Chapter1: Review of Sponge Iron Making Processes

Introduction:-

- During the past century, many efforts were made to develop processes for producing iron for steelmaking that could serve as alternatives and/or supplements to the conventional blast furnace.
- Many of these projects were stimulated by a desire or necessity to use lower grade ores and available fuels that are unsuitable for the blast furnace.
- Processes that produce iron by reduction of iron ore below the melting point of the iron produced are generally classified as direct reduction processes and the products referred to as direct reduced iron (DRI). The processes that produce a molten product, similar to blast furnace hot metal, directly from ore are classified as direct smelting processes.
- In some of the more ambitious projects, the objective is to produce liquid steel directly from ore and these processes are classified as direct steelmaking processes.
- These broad categories are clearly distinguished by the characteristics of their respective products, although all of these products may be further treated to produce special grades of steel in the same refining or steelmaking process.
- While the blast furnace is expected to remain the world's chief source of iron units for steelmaking as long as adequate supplies of suitable coking coals remain available at competitive cost, DRI contributes 3–4% of the world's total iron making capacity with approximately 42 million annual tons (Mt/y) of DRI capacity having been installed in the free world as of 1997.
- As of the end of 1996 there were 15.5 Mt/y of direct reduction capacity under construction, which is expected to increase world DRI production to 55 Mt/y by the year 2000 and 70 Mt/y by the year 2005. The major part of DRI production is used as a substitute for scrap in the electric arc steelmaking furnace (EAF). DRI derived from virgin iron units is a relatively pure material which dilutes contaminants in the scrap and improves the steel quality.
- The availability of low cost scrap and the high cost of energy restrict the use of DRI in most highly industrialized countries. Direct reduction processes are favored in those locations with abundant reserves of inexpensive natural gas, non-coking coals and/or hydroelectric power, and that have access to suitable iron ores or agglomerates.
- This chapter presents a review of the alternative processes that have achieved some measure of pilot or commercial success, with emphasis on those now in commercial operation.

Historical Development of Sponge Iron Making:

- Sponge iron provided the main source of iron for many centuries before the blast furnace was developed. In historic times, sponge iron was produced in shallow hearths, which used charcoal as reductant fuel.
- The product of these early smelting process was a sponge mass of coalesced granules of nearly pure iron intermixed with considerable slag.

Table 11.1 Classification of Processes	
<p>Direct Reduction Processes—Reducing Gas Generated Externally from the Reduction Furnace (Section 11.3)</p> <p>Gas-based Processes</p> <p>Shaft Processes</p> <p>Midrex HYL Process Purofer</p> <p>Fluidized Bed Processes</p> <p>Fior/FINMET Iron Carbide Circored</p>	<p>Direct Reduction Processes—Reducing Gas Generated from Hydrocarbons in the Reduction Furnace (Section 11.4)</p> <p>Coal-based Processes</p> <p>Rotary Kiln Processes</p> <p>Krupp-CODIR SL/RN DRC ACCAR/OSIL</p> <p>Shaft and Hearth Processes</p> <p>Kinglor-Metor Fastmet INMETCO</p>
<p>Reduction Smelting Processes (Section 11.5)</p> <p>COREX Direct Iron Ore Smelting (DIOS) AISI Direct Steelmaking HISMELT ROMELT Cyclone Converter Furnace (CCF)</p>	<p>Inactive Processes of Historical and Developmental Interest (Section 11.6)</p> <p>Höganäs Process^(a) Wiberg-Soderfors Process Sumitomo Dust Reduction Process (SDR) Sumitomo Pre-reduction Method Process (SPM) Kawasaki Process Armco Process Nippon Steel Process High Iron Briquette Process (HIB)</p>

- Usable articles of wrought iron were produced by hammering the sponge mass, while still hot, to expel most of the slag and compact the mass.
- By repeated heating and hammering, the iron was further freed of slag and forged into the desired shape.
- All of the methods through which low carbon wrought iron can be produced directly from the ore are referred to as direct reduction processes.
- After the development of the blast furnace, which produced high carbon pig iron, direct processes were nearly abandoned.
- However, direct reduction process is still used because of the ease with which iron ores are reduced making the processes appear enticingly simple, and primarily because the reduction takes place at relatively low temperature compared to Blast Furnace.
- Process that produce iron by reduction of iron ore, below the melting point of the iron produced, are called direct reduction processes, and the products referred to as Direct Reduced Iron (DRI), commonly called sponge iron.
- In modern times, sponge iron has found increasing use in the manufacture of wrought iron and as substitute of scrap during steel making.
- Sponge iron is chemically more active than steel or iron millings, turnings or wire strips.
- Sponge iron is produced as granular material or as sintered mass, depending upon the methods of treatment applied to hot material. In the granular form, it is commonly known as powdered iron and used in the manufacture of many useful articles by the techniques of powder metallurgy.
- Today the major portion of DRI is melted along with Hot Metal / Pig Iron/scrap in the Electric Arc Furnace (EAF) and Induction Furnace (IF) for steel making and producing steel castings (rounds/ slabs/ billets/ blooms).
- The attempts to develop large-scale DRI plants have embraced practically every known type of apparatus suitable for the purpose, including pot furnaces, shaft furnaces, reverberatory furnaces, regenerative furnace, rotary hearth furnace / rotary kilns, electric furnaces, fluidized bed furnaces and plasma reactors.
- Many different kinds of reducing agents, such as natural gas, coal, coke, graphite, charcoal, distillation residues, fuel oil, tar, producer gas, coal gas, and hydrogen have been tried.
- However, no effort has been made to evaluate or compare the different processes on either on economical or technical basis because in many cases, factors associated with location, capital cost and availability of ore and fluxes, availability of trained manpower, and proximity of markets, may be overriding.
- Over the past several decades, experiments were made to develop a low cost and simple to operate substitute of blast furnace.
- Many of these developments were targeted to use non-coking coal or natural gas as reductant.
- The processes that produce molten product (similar to blast- furnace hot metal) directly from ore are generally classified as direct smelting processes.
- In some of the more ambitious projects, the objective is to produce liquid steel directly from ore and these processes are generally classified as direct steel making process.

- These broad categories are clearly distinguished by the characteristics of their respective products, although all of these products may be further treated to produce special grades of steel in the same refining or steel making process.
- The direct smelting process and direct steel making process is outside the scope of this project.
- Sponge iron provided the main source of iron and steel for many centuries before the blast furnace was developed around 1300 A.D.
- Sponge iron was produced in relatively shallow hearths or shaft furnaces, using charcoal as both fuel and reductant.
- The product of these early smelting processes was a spongy mass of coalesced granules of nearly pure iron intermixed with considerable slag.
- Usable articles of wrought iron were produced by hammering the spongy mass, while still hot, to expel most of the slag and compact the mass.
- By repeated heating and hammering, the iron was further freed of slag and forged into the desired shape.
- All of the methods whereby low carbon wrought iron can be produced directly from the ore are referred to as direct processes.
- After the development of the blast furnace, which made large quantities of iron having a high carbon content available, low carbon wrought iron was produced by refining this high carbon material.
- Because two or more steps were involved, the processes came to be known as indirect processes.
- Direct methods are still in use and have never been wholly abandoned even by the most advanced nations.
- The ease with which iron ores are reduced makes the direct processes appear simple and logical, primarily because the reduction takes place at relatively low temperatures.
- In modern times, sponge iron has found increasing use in various industrial processes other than in the manufacture of wrought iron.
- The iron produced in sponge form has a very high surface area is used in the chemical industry as a strong reducing agent.
- It is chemically much more active than steel or iron in the form of millings, borings, turnings or wire.
- Sponge iron may be produced as a granular material or as a sintered mass, depending upon the methods of manufacture. In the purified granular form, commonly known as powdered iron, it is used in the manufacture of many useful articles by the techniques of powder metallurgy.
- The iron powders are compacted by pressure into the approximate shape of the finished article, and then sintered at 950–1095°C (1740–2000°F) in furnaces provided with a protective atmosphere to prevent oxidation and finally pressed or machined to their final shape.
- Iron powders are produced not only by direct reduction of iron ores or oxides using solid carbonaceous reducing agents and gaseous reducing agents such as carbon monoxide and hydrogen, but also by electrolytic processes and by thermal decomposition of iron carbonyl, $\text{Fe}(\text{CO})_2$

Conventional versus DRI steel Making:

- Molten pig iron is used for steel making in conventional B/F route which requires metallurgical grade coke as primary fuel and reductant. At present the conventional blast furnace route produces about 70% of the world total steel. The limitation of this route is becoming more critical in recent times due to following reasons:
 - a. Huge capital investment requirement
 - b. Non-availability of coking coal
 - c. Higher degree of environmental pollution
- Due to decreasing availability and sharp rise in the prices of steel scraps, attention has been focused on alternative raw materials like DRI.
- Therefore, direct reduction processes are gaining higher importance and wider acceptance as DRI has proved itself to be excellent substitute of scrap steel.
- On the other way, DRI has a well-defined chemical composition and is almost free from any tramp elements while the steel scraps have variable and unknown chemical composition rendering the subsequent steel making difficult.
- Consistent size distribution of DRI versus the varied sizes of steel scraps makes the latter difficult to handle and transport. Presently, DRI is the primary raw material for the electric steel making with charge mix around 70%.

Direct Reduction of Iron ore:

Oxides of iron:

1. Wustite (FeO):-

- ✓ It has a cubic lattice of the NaCl type
- ✓ It is a close packed oxygen lattice in which iron atoms are arranged in the octahedral interstices.
- ✓ It is unstable below 560°C and dissociates eutectoidally into alpha-iron and magnetite accordingly to the reaction: $4\text{FeO} \longrightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$
- ✓ Wustite is considered to be an iron deficient oxide of iron.

2. Magnetite (FeO.Fe₂O₃):-

- ✓ It is referred as ferroso-ferric oxide.
- ✓ It is strongly magnetic and contains 72.4% Fe and 27% oxygen in pure state.
- ✓ Its colour varies from grey to black with a specific gravity of 5.0
- ✓ It crystallizes into close-packed cubic lattice.
- ✓ The common impurities associated magnetites are oxides of titanium, magnesium, aluminum, nickel, chromium, vanadium and manganese.

3. Hematite (Fe₂O₃):-

- ✓ Hematite or ferric oxide is most important mineral of iron.
- ✓ It contains approximately 70% Fe and 30% oxygen in pure state.
- ✓ Its colour varies from red to steel grey to black with a variation in specific gravity from 4.9 to 5.3
- ✓ It contains silica, alumina, calcium oxide, magnesium oxide as impurity.

Table 1.1.

Oxides	Crystal Structure	Melting Point (°C)	Heat of Formation at 298°C(cal/mole)	Oxygen Content (%)
Fe ₂ O ₃	Hexagonal	1536	-197300	30.05
Fe ₃ O ₄	Cubic	1597	-267300	27.64
FeO	Cubic	1377	-63649	22.6

1.6. Minerals of Iron:

Oxides:	Hematite (Fe ₂ O ₃)
	Magnetite (Fe ₃ O ₄)
Hydroxides:	Limonite (Fe ₂ O ₃ · 3H ₂ O),
	Goethite (Fe ₂ O ₃ · H ₂ O)
Carbonates:	Siderite (FeCO ₃)
Sulphides:	Iron pyrites (FeS)
Complex:	Ilmenite (FeO · TiO ₂)

1.7. Iron Ore Reserve in India:

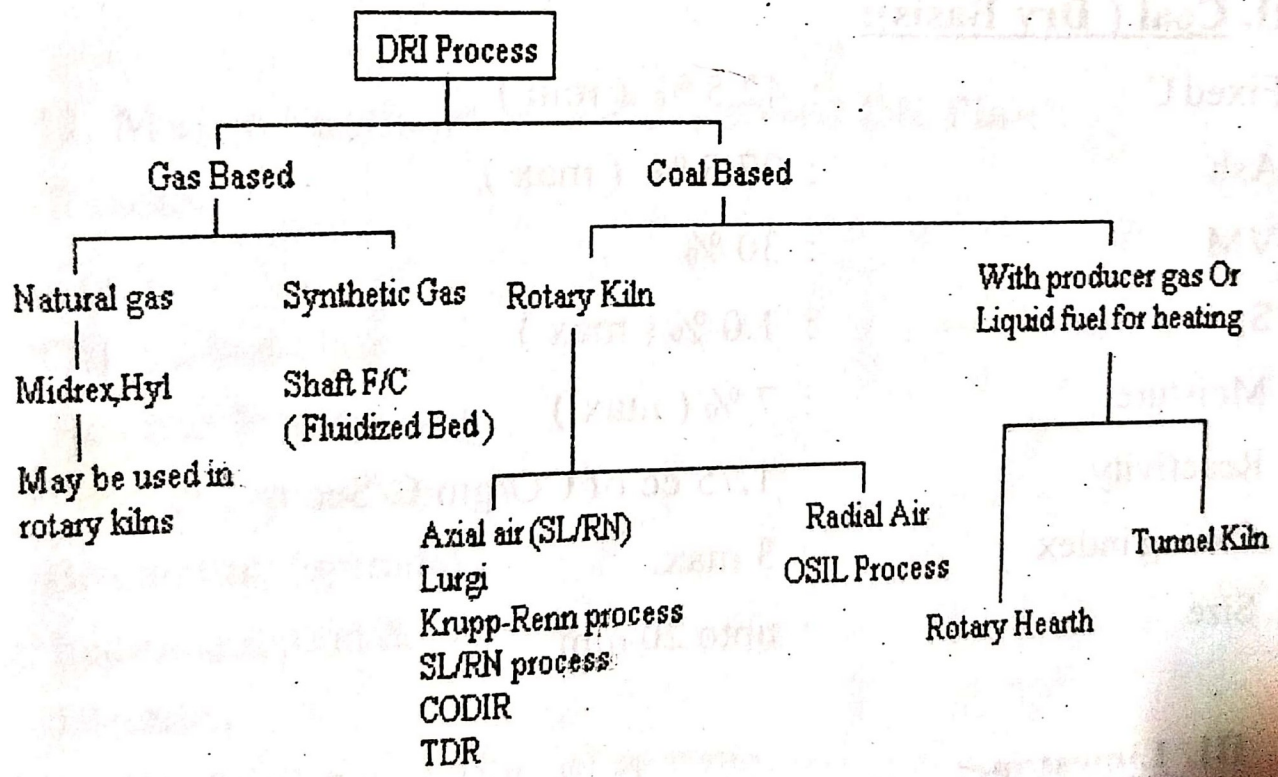
It is estimated that India has a proven iron ore deposit of around 23,000 million tons out of which 85% is hematite and 8% is magnetite. Of the total reserve, 43% is in the states of Jharkhand and Odisha while the rest 57% is distributed in the states of Chattisgarh, Karnataka, Goa, Maharashtra, Andhra Pradesh.

Direct Reduction of Iron Ore:

DRI or sponge iron refers to porous iron produced by the DR process. The DR process is a solid-state reaction process (i.e., solid-solid or solid-gas reaction) in which removable oxygen is removed from the iron oxide, using coal or reformed natural gas as reductants, below the melting and fusion point of the lump ore or agglomerates of fine ore. The external shape of the ore remains unchanged. Due to removal of oxygen (about 27–30% reduction in weight occurs), a honeycombed microstructure develops suggesting the name Sponge Iron (i.e., solid porous iron; lumps/pellets with many voids filled with air). DRI is obtained when iron oxide (generally lump iron ore or pellets) is reduced to metallic form in solid state. Since there is no melting, the external shape is retained. Color changes from red to black. The true density ranges from about $3.5 \cdot 10^3$ to $4.4 \cdot 10^3$ kg/m³. The true density of pure iron is $7.8 \cdot 10^3$ kg/m³. Thus, there is about 45–56% reduction in true volume and this is manifested in the formation of pores throughout the interior of sponge iron pieces.

Based on the types of reductant used, the DR processes can be broadly classified into two groups:

1. Using solid reductant, that is, coal-based DR process
2. Using gaseous reductant, that is, gas-based DR process



Coal-based processes:

- In coal-based DR processes, non-coking coal is used as reducing agent.
- In solid reduction processes, iron oxides together with solid reductant (non coking coal) are charged into the reactor.
- The generation of reducing gas (mainly CO) takes place in the reduction reactor, and the product has to be separated from excess reductant, ash, and/or sulfur absorbing materials (lime, dolomite) by magnetic separation after discharge at low temperature, which makes product handling more complicated. Because of the presence of these substances in DRI, hot briquetting and hot feeding are not possible for coal-based process.
- Magnetic separator also does not work at high temperatures to separate the DRI. Coal-based DR processes like SL/RN (1970), ACCAR (1973), KRUPP (1973), CODIR, and TDR (1975), using rotary kiln as a reactor and coal as a reductant, have been developed worldwide.
- India, due to its large reserve of non-coking coal, has shown keen interest in pursuing these technologies using such coal as a cheap energy source for highest DRI production in the world. These processes are highly sensitive to the types of raw materials used.
- The following are coal-based processes:

1. Rotary kiln-based processes
SL/RN, CODIR, ACCAR, DRC, TDR, SIIL, OSIL, Jindal
2. Shaft furnace-based processes
Kinglor, Metor, NML, Vertical Retort
3. Rotary hearth furnace (RHF)-based processes
INMETCO, FASTMET, Comet

▪ **The main advantages of coal-based processes are as follows:**

- (i) They do not require high-grade coal that is scarcely available.
- (ii) They use non coking coal.
- (iii) They can be installed at lower capacity.
- (iv) They can be easily installed at places where small reserves of coal and iron ore are available.
- (v) Modules of small-scale operation are available.

▪ **Disadvantages of coal-based processes are as follows:**

- (i) Lower economy of scale.
- (ii) High energy consumption (16.0–21.0 GJ/t).
- (iii) Low carbon content in the product (<1.0%).
- (iv) Lower productivity (0.5–0.9 t/m³/day).
- (v) Hot feeding to the steelmaking furnace and hot briquetting are not possible due to the presence of residual char and ash in DRI.

Gas-based processes:

- Reformed natural gas is used as a reducing agent. Iron ore lumps or pellets are reduced in the solid state and oxygen from iron oxide is removed by a gaseous reducing agent.
- The processes based on gaseous reduction are confined to the areas where natural gas is available in abundance at a reasonable price.
- The following are gas-based processes:
 1. Retort processes:-HyL I, Hoganas
 2. Shaft furnace processes:- Midrex, HyL III, Plasma red, Armco, Purofer, NSC, HyL IV
 3. Fluidized bed processes:- FIOR, Finmet, Circored

Gas-based processes have the following advantages:

- (i) High productivity
- (ii) Lower energy consumption (10.5–14.5 GJ/t)
- (iii) Higher carbon content in the product (>1.0%)

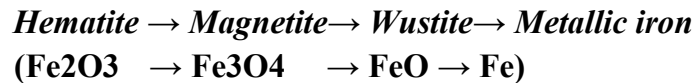
Model questions:

1. What is sponge iron?
2. Why DRI is called sponge iron?
3. What are the uses of sponge iron?
4. What is the difference between sponge iron & pig iron?
5. Which are the areas of major iron ore deposit in Odisha?
6. What are the different technologies now being adopted worldwide for production of sponge iron?

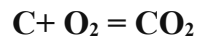
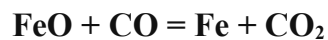
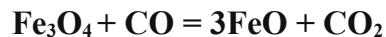
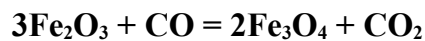
CHAPTER 2: THERMODYNAMICS OF SPONGE IRON MAKING

Principles of Direct Reduction Reactions:

- Direct reduction uses high iron content ore usually hematite as raw material and non-coking coal as reductant.
- The carbon in coal gets converted to CO which subsequently reacts with Fe_2O_3 to produce metallic iron as per the overall reaction: $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + \text{CO}_2$
- The reduction process proceeds in several steps progressively reducing Fe_2O_3 to metallic iron as represented below:



- The degree of reduction in each step of the above progressive reduction varies widely and involves a series of complex reactions.



- The resultant net reaction is an important mechanism for processes that produce DRI directly from coal without prior gasification of its fixed carbon. At approximately 1200°C (2192°F), considered to represent close to the upper limit for the direct reduction process, a pasty, porous mass forms. Above this temperature the metallic iron formed will absorb any carbon present with resultant fusing or melting of the solid even though the melting. The terms associated with measuring the effectiveness of the reduction reaction.

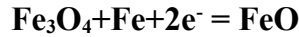
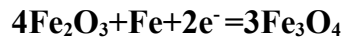
Reaction between Coal, Oxygen and Carbon Dioxide:

Carbon from the coal reacts with oxygen to form carbon dioxide with release of heat. The heat released raises and maintains the operating temperature inside the kiln. As the carbon dioxide emerges from the bed it reacts with fresh carbon to form carbon monoxide. Then CO is available for iron ore in the subsequent stages.

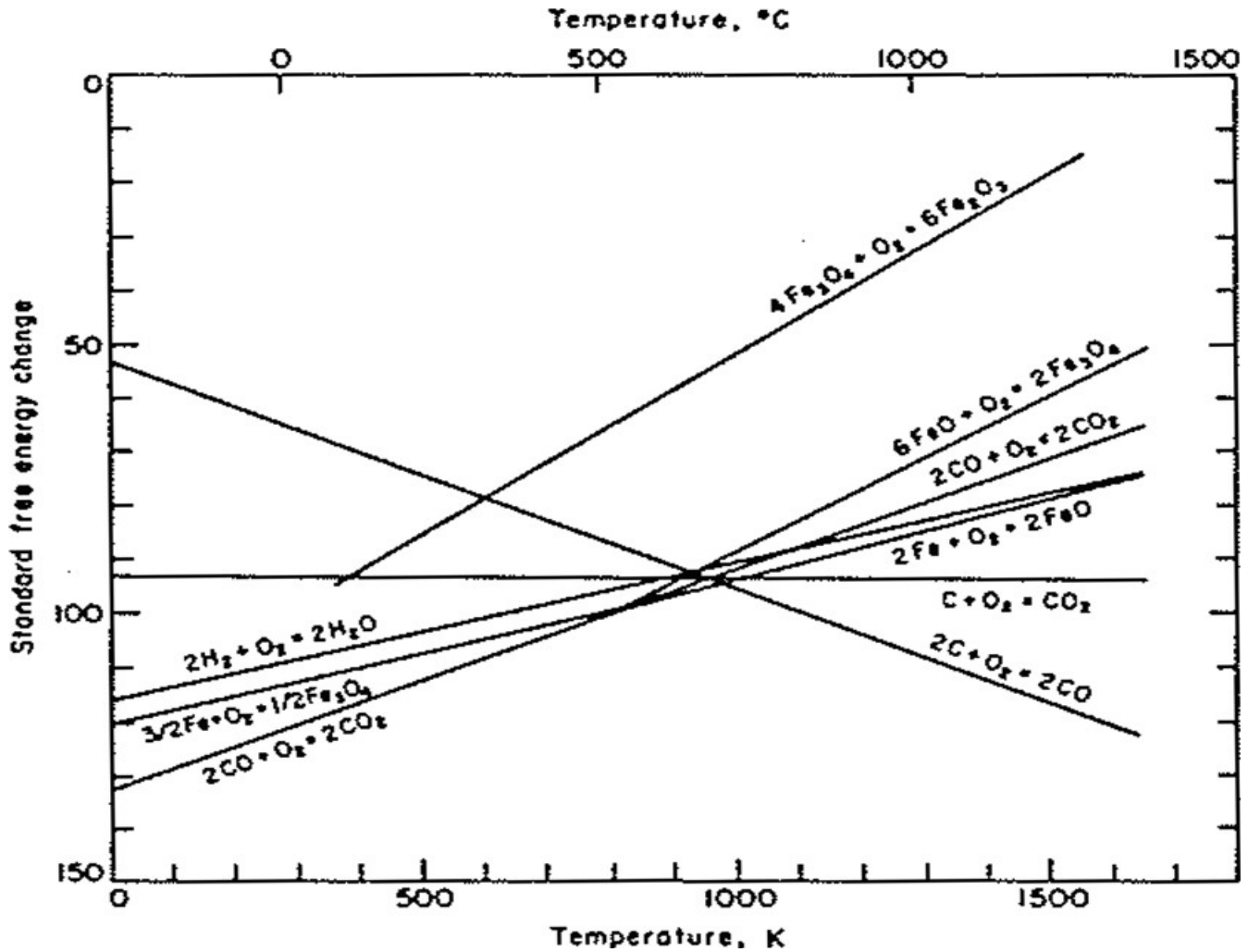
Reaction between iron ore and CO:

1. Diffusion of the hydrogen and CO gas across the
2. Boundary, macrospores and Micro pores in the ores.
3. Phase boundary reaction.
4. Diffusion of water vapour through the micro pores and macrospores
5. Diffusion of water vapour across the boundary layer migration of Fe^{++} and $2e$ to the iron nucleolus.

The diffusion of iron and electron the following pathway:



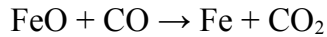
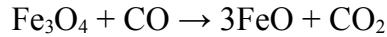
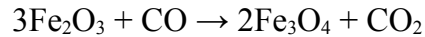
According to above mechanism O_2 is removed from the iron oxide at the iron wustite interface only. CO and Hydrogen diffuse inwards through the iron layers and the product gas CO_2 and water vapors diffuse outwards. The flow rate of gases through the bed of solid particles must be large enough so that a stagnant layer of gas cannot build up around each solid particle. For continuous effect of reaction, the reduction must get into the interface and solid may attain desired reduction. The coal gasification process in air to CO_2 entirely depends on rate of removal of carbon or coal reactivity which mainly depends on pore structure of coal, particle size.



(Free energy vs. temperature diagram for main oxides)

Reduction by CO (indirect reduction):

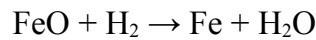
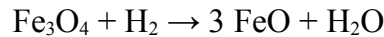
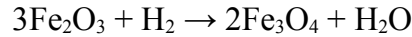
Above 570 °C, iron oxide is reduced by CO in three stages:



Below 570 °C, Fe₃O₄ is directly reduced to Fe bypassing the wustite (FeO) stage.

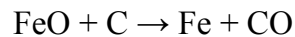
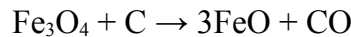
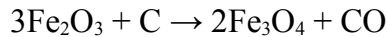
Reduction by Hydrogen (indirect reduction):

Reduction by Hydrogen occurs in three stages as follows:



Reduction by Carbon (direct reduction):

For solid carbon in a DR process, the following three reduction reactions can be written:



Only a negligible amount of reduction will occur by direct contact of carbon particles with iron oxide particles since such solid-solid reactions are very slow. The actual reduction process occurs through the intermediary of CO.

Rate laws in reduction:

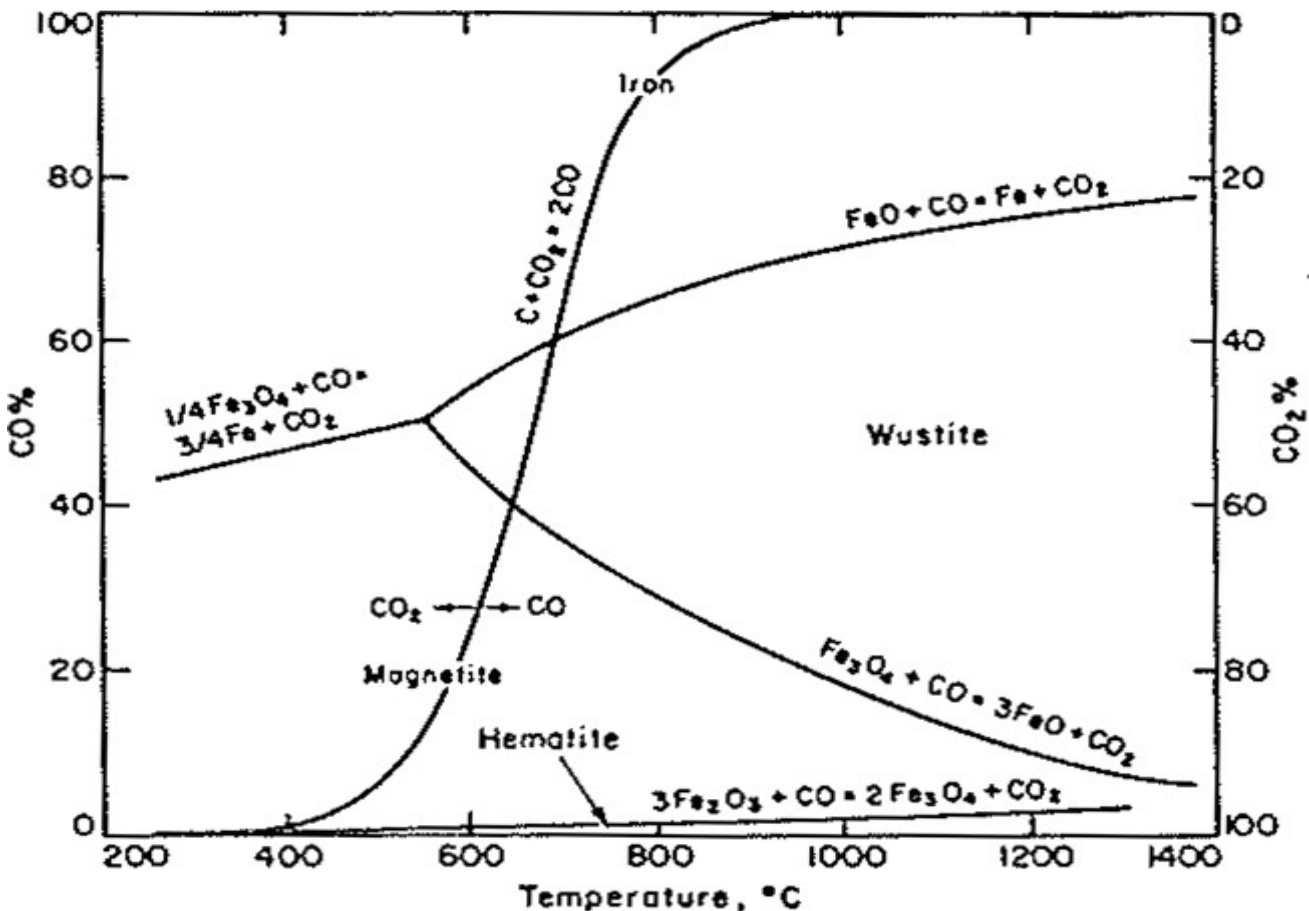
The reduction of the iron oxides takes place in a series of sequential steps. The overall rate will be determined by the slowest process in the series. The possible consecutive steps are:

- 1) Transport of gaseous reductant from the bulk gas phase to the particle surface through a boundary gas film.
- 2) Molecular diffusion of the gaseous reductant through the product layer to the reaction interface.
- 3) Adsorption of the gaseous reductant at the interface.
- 4) Reaction at the interface (reaction between adsorbed reductant and oxygen of the lattice).
- 5) Desorption of the gaseous products from the interface.

- 6) Mass transport of iron and oxygen ions and transformations in the solid phase, formation and growth of reaction products e.g. magnetite, wustite, iron.
- 7) Molecular diffusion of gaseous products through the product layer to the particle surface.
- 8) Transport of the gaseous products from the particle surface through the boundary gas film to the bulk gas phase.

KINETICS OF DIRECT REDUCTION PROCESS

Reaction kinetics of iron ore reduction deals with the rate at which iron oxide is converted to metallic iron by removal of oxygen. The rate at which the ore is reduced influences the production rate, which ultimately determines the economic feasibility and competitiveness of the process technology involved. Thus the reaction rate in DR process is of prime importance. The reduction of iron oxide to metallic iron proceeds through various kinetic steps and one of them is the slowest step, which control the overall reaction rate.



(Fe-O-C system)

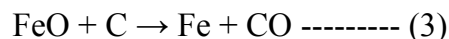
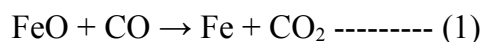
Boudourd reaction and reduction by carbon:

This is commonly known as the Boudouard reaction or gasification reaction. This reaction has very important consequences in iron oxide reduction when carbon is used as the reductant, because it regenerates the reducing gas by converting CO₂ to CO. It is strongly endothermic, and since the activation energy of an endothermic reaction must be larger than the heat of the reaction, the rate of reaction is sensitive to the crystalline structure and impurities of carbon and temperature. To the left of this curve which is at low temperature, CO is an unstable gas phase. Carbon monoxide tends to decompose into carbon dioxide and to deposit carbon in the form of soot. This carbon soot accounts for some of the carbon found in DRI. At high temperatures carbon dioxide reacts with carbon to produce carbon monoxide. Again this is an endothermic reaction and is favored by high temperature.

Note that at temperatures above 1000 °C (1273 K), the reaction is essentially completed, that is, 100% CO is formed. This means that thermodynamically, carbon dioxide cannot exit at temperatures above 1000 °C(1273 K) in the presence of carbon. Therefore, this suggests that CO cannot reduce FeO .

However, reduction does take place and this appears to be on account of reactions (1) and (2) taking place separately.

The two reactions can be combined as:



Reaction (3) is often referred to as direct reduction (DRI by carbon, whereas reaction (1) and reaction (2) are known as indirect reduction by carbon and gasification reaction, respectively. It should be noted that the Boudouard equilibrium curve crosses the wustite–iron line at 700 °C (973K) and the magnetite–wustite line at 650°C (923 K). This means that thermodynamically, wustite cannot be reduced at temperatures below 700 °C (973 K) and magnetite cannot be reduced at below 650 °C (923 K) because the carbon monoxide decomposes into carbon dioxide and carbon.

Carbon deposition

As stated earlier, carbon forms at low temperatures by the backward reaction. Although thermodynamic calculation shows that carbon deposition is highly favored by low temperatures and high carbon monoxide concentrations, it is unlikely that this reaction ever goes completely to a state of equilibrium because reaction rates are very slow at low temperatures and also because the deposition of carbon requires the nucleation of carbon on some catalytic site that may not always be available. Undoubtedly some of the carbon found in DRI is soot formed by this reaction. In addition, iron carbide (Fe₃C) can be formed by the following reaction:



Like carbon deposition, reaction (4) is also favored by low temperatures and high carbon monoxide concentrations.

1. Boundary Layer Control

In boundary layer control the overall reduction rate is controlled by the diffusion of gas and heat through the boundary layer of the gas which builds up around each particle. The rate of diffusion of the gas through the boundary layer is proportional to the gas concentration gradient across the layer. Secondly, the rate of heat flow to the particles is proportional to the temperature gradient across the boundary layer. In most direct reduction process contact between gas and solids is achieved by counter current flow of preheated gas to the movement of the bed of solids.

2. Phase Boundary Reaction Control

The chemical reaction at the wustite -iron interface is the rate controlling factor. In this case the rate of reduction per unit area of the remaining iron oxide is found to be constant with time. This mechanism is called “Phase Boundary Reaction Control”. When counter diffusion of reducing gas and product gas on the reduced outer layer is sufficiently fast, the concentration of reducing gas at the reacting surface is effectively the same as it’s concentration at the particle surface. In such case the rate of reaction at the wustite-iron interface would control the overall reduction rate. This mechanism is unlikely at the very start of the reduction, when the iron layer is very thin, or for very small porous grains of iron oxide.

3. Gaseous Diffusion Control

The rate of reducing gas inward and product gas outward through the reduced iron layer can control the rate of reduction of iron oxides. This phenomenon is generally associated with large ore particle and is known as “Gaseous Diffusion Control”. When gaseous diffusion is the rate controlling step, the rate of diffusion of reducing gas inward and product gas outward through the porous layer of metallic iron surrounding the unreduced inner core particle, is slower than the rate of reaction. During such occurrence the concentration of the reducing gas will decrease that of product gas will increase at the interface. The change in the gas composition will slow down the reduction rate until a pseudo steady state is established. This is the pre dominant rate controlling mechanism for high temperature reduction of large (greater than 7 mm) particle beyond 50% reduction, when iron layer thickness exceeds about 1mm.

4. Mixed Control

When both Gaseous Diffusion Control and Phase Boundary Reaction Control combine influence the rate of reduction, the mechanism is referred to as “Mixed Control”. Mixed control has been proposed by several experiments to reconcile the complexities and conflicting results obtained from direct reduction of iron oxides with simpler mechanism. In mixed control, the gas boundary layer, the phase boundary reaction and gaseous diffusion act together under pseudo steady state condition to determine the overall reaction rate.

Factors influencing the reducibility of iron ore:

This property of the iron ore depends on following factors:-

1. Nature of Iron Oxide

The major deposition of iron oxide in nature is mainly in the form of hematite & magnetite. The oxygen enrichment in hematite iron ore is more than the magnetite. Hematite iron ore is the saturation point of oxide ore which is more stable in nature. The purest hematite iron ore may contain maximum 1% of magnetic or magnetic in nature.

2. Ore Size

The deposition of iron ore in nature is usually in hard and massive form. But when the ore is considered for DRI process its size and shape are very much important for the of reduction reactions.

3. Porosity

The porosity of ore is one of the important factors which affect the reducibility. It is observed that the reducibility of soft hematite iron ore is greater than that of hard hematite and magnetite ore. The reducibility of natural ore show that for 90% reduction, reciprocal of time varied linearly with percentage porosity.

4. Nature & Composition of Gangue

It observed that natural ore contains gangue oxide of Si, Al, Cr, Ti etc. in different from. In some of the ores wustite is present as complex compound such as 2FeOSiO_2 , FeOAl_2O_3 , FeOCr_2O_3 where wustite exist in a state of low activity. These oxides tend to the decrease the reducibility of iron ore in kiln in reducing atmosphere.

5. Swelling

Some ores show abnormal increase in volume at temperature between 900 to 1000°C. This is referred as swelling of ore. The cause of swelling has not been understood fully. Various investigators have in opinion that it is associated with mechanism of nucleation and growth having of wustite.

6. Temperature

The rate of reduction of iron oxide increases with increase in temperature of iron oxide. In solid gas reduction it is advantageous to use a temperature above 1000° C because boundary reaction is maximum for producing CO with CO₂ and C combination. It is observed that if iron ore is reduced to metallic iron at low temperature, this forms a layer of dense metallic iron on the ore body which affects reduction at higher temperature region.

7. Gas Compositions

The coal after gasification becomes a composition of CO_2 , H_2 , some water vapors, CO_2 etc. It is observed that by increasing the partial pressure of reducing gases the rate of reduction can be increased. It has been proved that hydrogen is better reducing gas than CO but at higher degree of reduction CO reduce iron oxide at faster rate.

8. Pressure

The increase in pressure is expected to increase the rate of reduction as increase the partial pressure of the reducing gas.

Model questions

1. What are the typical oxides of iron ores? Mention them with their colors.
2. What are the purposes of using coal in DRI kilns?
3. Mention the reaction involved in sponge iron making?
4. Which are the areas of major iron ore deposit in Odisha?
5. What do you mean by reoxidation?

CHAPTER 3: MAJOR DIRECT REDUCTION PROCESSES

Coal based DR process using rotary kilns:

- Coal-based processes are broadly classified into two categories:

1. Rotary kiln process
2. Rotary hearth process

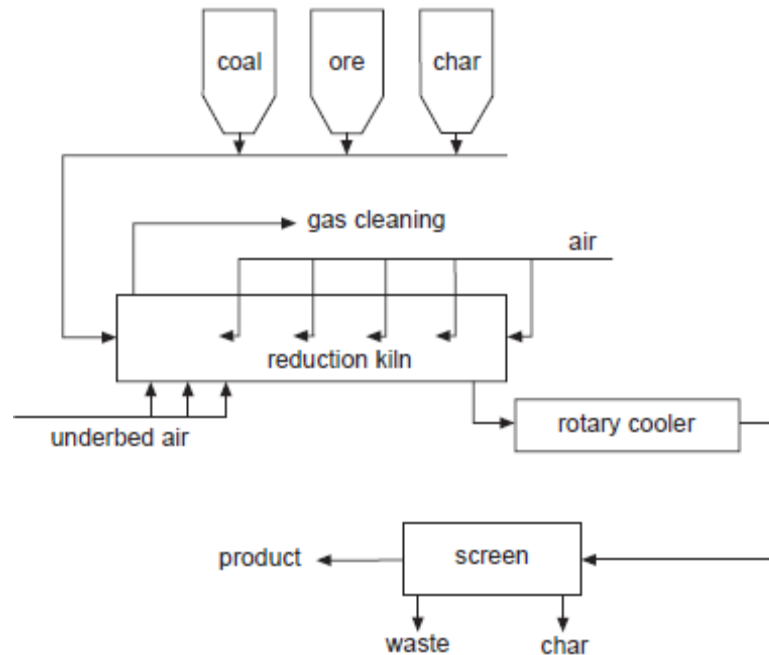
- Rotary kiln processes are SL/RN, ACCAR, KRUPP, CODIR, TDR etc.

SL/RN PROCESS:

Introduction:

- The forerunner to the SL/RN process, the R-N process (for Republic Steel Company and National Lead Corpora) was developed in Norway, primarily to recover TiO_2 from titaniferous ores for producing pig-ments.
- Further development showed that other iron bearing ores could also be treated to produce iron and a pilot plant was built in the United States.
- In 1964 Lurgi Chemie acquired the R-N patents and world rights and developed the technology further in cooperation with the Steel Company of Canada, Ltd. (Stelco) to form the SL/RN process.
- The reduction kiln is very similar to the system used in CODIR and the other coal based plants described later.
- The major differences between SL/RN and CODIR are that in SL/RN the product is cooled by indirect water sprays on the outside of the cooler, and the kiln off gas is cooled in a waste heat recovery boiler.
- Indirect product cooling requires a longer cooler than does direct cooling, however, there is no loss of metallization during indirect cooling.
- In the direct spray cooler, the loss of 0.5–1.0% metallization by reoxidation off-sets the economic advantage of a smaller cooler.
- By 1998, 15 SL/RN kilns were in operation in Brazil, India and South Africa for the production of DRI for steelmaking. Their combined annual capacity is about 1.68 million tonnes

Process description:



SL/RN direct reduction process flowsheet.

- The SL/RN process is fed with indurate pellets and/or lump iron ore. Iron sands are used at New Zealand Steel, with design modifications to provide efficient operation.
- A wide range of fuels and reluctant including lignite, char, low temperature coke, coke breeze and anthracite coal have been used satisfactorily.
- Depending on the fuel used, the proportion of the reluctant fed through the inlet of the kiln with the oxide feed and the proportion fired through the burner at the kiln exit will be adjusted.
- With very low-volatile coal, a supplementary fuel such as natural gas or fuel oil is fed through the central burner or through the air tubes to maintain the proper temperature profile in the kiln. Smooth kiln operation is achieved when operating with a relatively high volatile coal charged together with the iron burden through the kiln feed end.
- Coals with a high reactivity, low free-swelling index and high ash fusion temperature are preferred. The coal should also be non-coking.
- A low ash fusion temperature will promote formation of accretions in the kiln.
- The coal ash composition is also important because a siliceous ash might react with ferrous oxide to form the low melting compound, ferrous silicate, and interfere with the reduction to metallic iron.
- The kiln exit gases pass through a settling chamber for coarse dust removal and a two-stage after-burner. Combustible gases are burned in the first stage, followed by fine carbon particles in the second stage.

- The afterburner chamber temperature is controlled by means of water sprays. In some plants, the gas emerging from the afterburner is passed through waste heat boilers, scrubbed and then discharged through the stack.
- The DRI is discharged at about 1000°C. An enclosed chute at the discharge removes lumps and transfers the hot DRI to a rotary cooler.
- The cooler, a horizontal metal cylinder 3.6 m (12 ft.) diameter and 40–60 m (131–197 ft) long is immersed in a water trough and has water sprayed on the upper surface.
- The cooler discharges the DRI into a hopper, which serves as an air lock to prevent air ingress. Trommel screens located at the hopper outlet separate the discharge into fractions which then pass through magnetic separators.
- Screens downstream separate the nonmagnetic portions.
- Recent experiments show that air admitted through ports below the bed in the preheat zone will burn some of the gases that would otherwise leave the kiln unburned. Such a practice would also permit the use of lignite with up to 60% moisture without pre drying.
- This technique would greatly improve the efficiency of the process and arrangements are now being made to install it on several existing SL/RN kilns.

PROCESS ADVANTAGES:

- Use of any iron bearing material.
- Wide variety of reductants.
- Proven DRI technology.
- Economic production of DRI

CODIR PROCESS

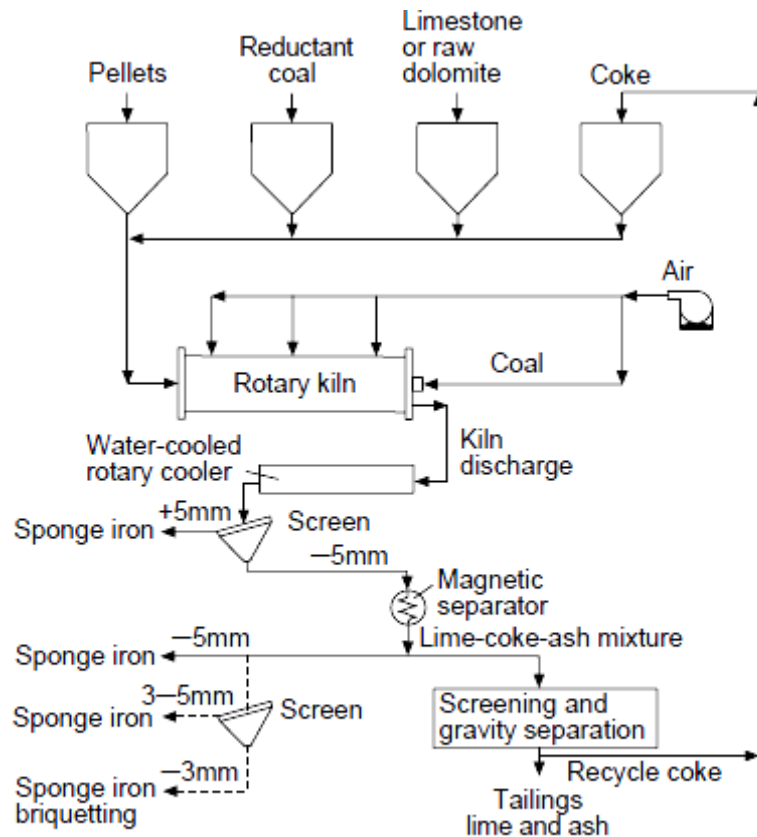
Introduction:

- The CODIR process of Krupp Industries, West Germany, stems from the original Krupp Renn process developed in the 1930s to treat high silica ore without the addition of limestone to produce an agglomerated product for subsequent conversion to steel.
- CODIR operates at a lower temperature than Krupp-Renn and produces a standard DRI product. Limestone or dolomite DRI product.
- Limestone or dolomite in the furnace charge absorbs a substantial part of the sulphur introduced with fuel.
- A CODIR plant designed to produce 150,000 tonnes per year started operation in 1973 at the Dunswart Iron and Steel Works, Ltd. at Benoni, Republic of South Africa.
- The reduction kiln in this plant is 4.0 m (14.2 ft.) inside diameter and 74 m (243 ft.) long.

- The energy consumption is approximately 15.9 GJ/tonne (13.7 MBtu/ton) of DRI when low-volatile anthracite is used for the reduction coal.
- The gross energy requirement increases when higher volatile matter coals are used.

Process description:

A schematic flow sheet of the plant is shown below.



CODIR process flowsheet.

- The reduction kiln is fed continuously at a controlled rate with sized iron ore or pellets, dolomite for sulphur absorption and coal for reduction and energy.
- As the raw material charge moves to the discharge end it is progressively heated to approximately 1000°C (1830°F) by the hot kiln gas generated by partial combustion of coal with air in a burner at the discharge end of the kiln.
- The kiln is fitted with six shell mounted fans that supply air to burner tubes that enter through the shell and discharge air along the kiln centerline.
- This added air burns CO formed during reduction as well as volatiles from the coal and helps maintain the kiln temperature between 905–1050°C over approximately 60% of its length, enabling attainment of a high degree of metallization.
- The solids leaving the kiln are cooled to 150°C by water sprays in a rotary cooler.
- The DRI is then separated from the ash, recycle char and spent dolomite by screening and magnetic separation.

- The kiln off gas passes through a dust settling chamber and an after burning chamber where the remaining combustibles are burned prior to scrubbing in a conditioning tower, final cleaning in an electrostatic precipitator and exhausting to the atmosphere through an induced-draft fan and clean gas stack.
- The recovery of energy from the kiln off gas by including a waste heat boiler in the circuit has been adopted in some CODIR plants.
- The reductant coal normally is –10 mm. Coal containing 79% fixed carbon, 10% volatile matter and 10% ash and a calorific value of 29, 330 kJ/kg is typical.
- Pulverized coal is used as the burner fuel, with a typical analysis of 57% fixed carbon, 26.5% volatile matter, and 16.5% ash and a calorific value of 25,140 kJ/kg.
- Fuel oil and natural gas have also been used as the burner fuel. The desulfurizing agent used is raw limestone or raw dolomite.
- The discharge from the cooler is screened into the following four fractions:
 - (1) The +5 mm portion is DRI, which goes directly to product storage
 - (2) The magnetic portion of the –5 mm, +3 mm fraction is DRI and goes to product storage while the nonmagnetic portion consisting of char is returned to the char bins to be recycled
 - (3) The magnetic portion of the –3 mm, +1 mm fraction is DRI and goes to product storage while the nonmagnetic portion, a mixture of char and coal ash, is treated by air jigging to separate the char from the ash
 - (4) The magnetic portion of the –1 mm fraction is also DRI and is generally briquetted while the nonmagnetic portion is mainly ash and is discarded.

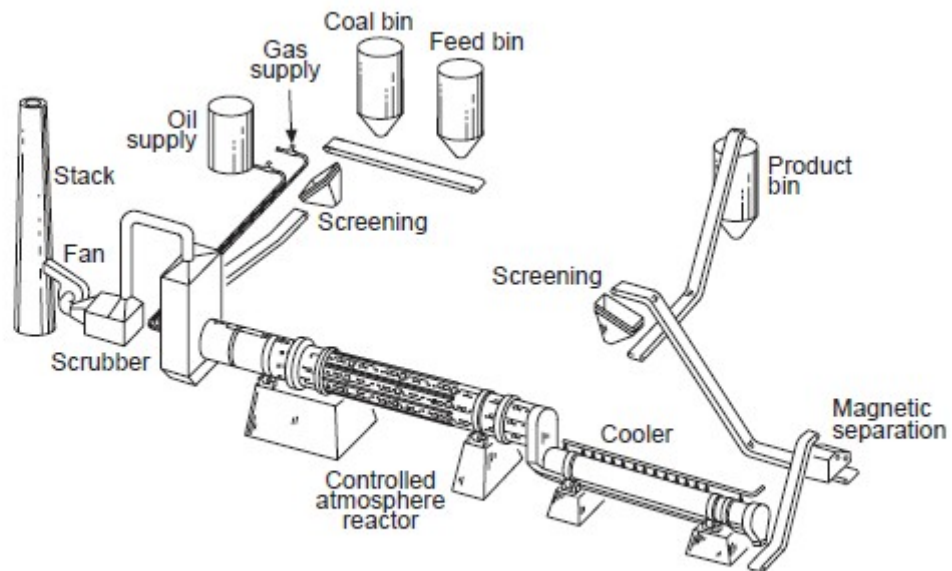
ACCAR/OSIL PROCESS

Introduction:

- The Allis-Chalmers Controlled Atmosphere Reactor (ACCAR) produces highly metalized DRI in a ported rotary kiln. Liquid, solid and gaseous fuels, singly or in combination, are used directly in the kiln without an external reformer or gasifying plant.
- The ACCAR kiln is equipped with an intricate port system and with valuing arranged radially around the circumference of the kiln and spaced uniformly along its length for liquid and/or gaseous fuel injection under the bed and for air injection above it.
- The flow rates through the ports are controlled to maintain optimum temperature profile and gas composition along the length of the kiln. Versatility in the use of fuel permits use of the most economical fuels available.
- The ACCAR process was developed by the Allis-Chalmers Corporation, Milwaukee, Wisconsin. Allis-Chalmers conducted direct reduction experiments in 1960 with an unlined metal kiln mounted concentrically inside a larger ceramic lined kiln.

- Iron oxide pellets were charged into the unlined kiln co-current to a mixture of fuel, steam and air. Pellet reduction and fuel reforming took place in the inner kiln.
- The gas leaving the inner kiln was mixed with air and burned in the annular space between the two kilns to provide the heat for reduction and reforming.
- The exhaust gases from the annular space were used to preheat the pellets.

Process description:



Schematic flowsheet of ACCAR/OSIL process.

- In 1965, Allis-Chalmers developed a laboratory kiln called the controlled atmosphere furnace. Reducing gas from an external source could be introduced through ports in the lower arc of the kiln below the surface of the bed of solids.
- As the kiln rotated, the reducing gas shut off and air was introduced when the bed reached the upper arc of the kiln.
- The air burned the excess reducing gas in the freeboard and generated the heat for the process. Experiments showed that hydrocarbons injected below the bed of iron oxide pellets would be reformed into reducing gas within the bed.
- In 1969, a pilot plant based on the ported kiln concept was constructed in Milwaukee. This kiln, which was 0.6 m (2 ft.) in diameter and 7 m (23 ft.) in length, was used to obtain operating and design information for scale-up. In 1973, a demonstration plant with an annual capacity of about 35,000 tons of DRI was constructed by modifying an existing kiln at Niagara Metals Limited.
- In 1976, the SL/RN direct reduction plant at the Falconbridge Nickel Iron Refinery at Sudbury, Ontario was revamped to convert it to the ACCAR System.

- This plant had an annual capacity of about 200,000 tonnes of DRI. These plants were subsequently dismantled.
- The only commercial plant based on the ACCAR system currently in operation is at Orissa Sponge Iron Limited (OSIL) in India. Originally rated for 120,000 tonnes per year, this plant was designed to use both coal and fuel oil.
- The plant now operates with 100% coal as the reductant and fuel. The process is now called the OSIL process and is marketed by Orissa Sponge Iron Limited.
- A 150,000 tonnes per year unit based on the OSIL process has been installed by Lloyd's Steel in India and is operational.
- A second unit of identical capacity is under construction at Lloyd's Steel.
- The OSIL process is similar to the other coal-based rotary kiln processes, except that it has a ported rotary kiln, The kiln is refractory lined and has a 2% slope from the charge to the discharge end.
- The injection ports are located beyond the preheat section of the kiln in rings around the shell. Fuel and air are alternately introduced through the ports by means of valving. A dam at the discharge end maintains the desired depth of material in the kiln.
- A central burner through the discharge hood which fires axially along the kiln is used for start-up, but can also be used to provide supplementary fuel to the port manifolds.
- The air for the manifolds is supplied by electrically driven fans mounted on the kiln shell. Hot DRI is transferred to the cooler through a refractory lined chute.
- The cooler is an unlined rotating steel cylinder with external water sprays. Following the cooler, there are screens and a magnetic separator.
- The waste gases from the kiln are cooled and scrubbed before being discharged to the atmosphere through the stack.
- The carbon content of the DRI can be controlled at any desired level up to about 2.5% by adjusting the ratio of air-to-fuel along the length of the kiln. The DRI product is cooled to 100°C in the rotary cooler.

Rotary hearth process

Some processes based on RHF are as follows:

1. INMETCO process (1970)
2. FASTMET process (1990)

- Among all these processes, the FASTMET process has been a commercial success.
- ITmk3 and FASTMET processes are noteworthy DR processes that involve simple operation, lower unit consumption, lower production cost, and superior environmental compatibility. The typical features of RHF based processes are as follows:
 - Basically, the commercial scale is 0.5 Mt per annum of product.
 - The main raw materials are iron ore concentrate or iron-bearing waste/dust of iron and steel industries and noncoking coal fines.
 - Fines are used in the form of green pellets or briquettes. Though it depends on the quality, approximately 1.5 t and 0.5 t of iron ore and noncoking coal are used, respectively.

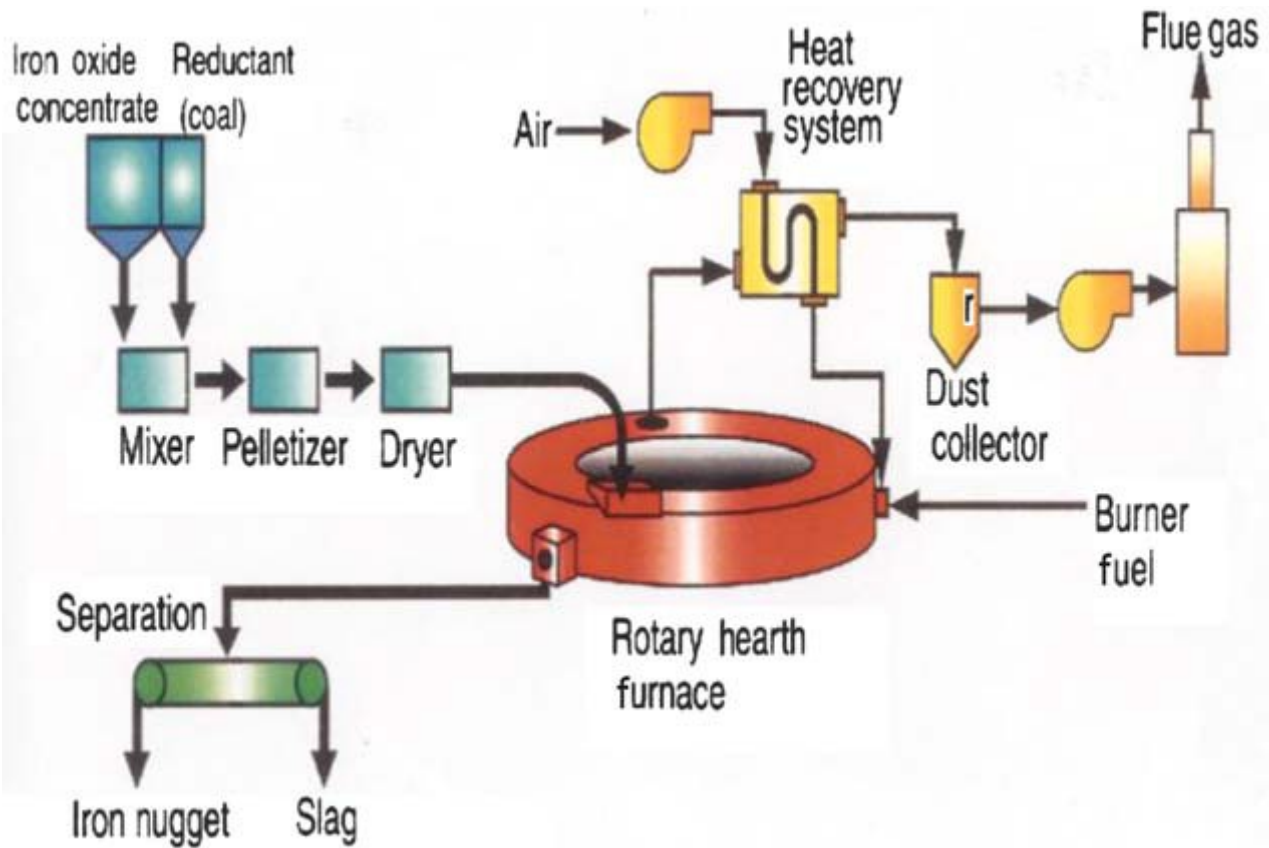
- Direct use of coal as a reducing agent in pellets. The heat requirement is met through firing gas to heat the furnace.
- These processes are developed in order to supply iron nuggets or hot metal for those countries endowed with noncoking coal.

FASTMET process:

- The success of the RHF-based DRI technology has led to the development of the FASTMET Process.
- The FASTMET process is very attractive as a proven technology for dust recycling.
- The FASTMET process is a solid reductant-based RHF process. Iron ore concentrate fines along with reductant fines (such as charcoal or other carbon-bearing solid) are pelletized to form iron oxide–carbon composite pellets, dried, and then charged directly to the RHF.
- If the mill scale or other wastes of steel plant are used as feedstock of iron oxide, then they are briquetted along with a solid reductant before charging to the RHF. As the hearth rotates, the pellets/ briquettes are heated to 1250–1400 °C (1523–1673 K) by combustion of natural gas, oil, or pulverized coal.
- The pellet layers on rotary hearth are of one to three pellets deep, and burners and post combustion of CO provide the heat to raise the pellets to reduction temperature.
- CO is generated from the carbon present in the charcoal or other carbon-bearing solid in the composite pellets as well as by the combustion of liquid or gaseous fuels in burners installed above the rotating hearth.
- The agglomerates containing the solid reductant get reduced to metallic iron. The reduction is accomplished by intimate contact between the carbon and iron oxide particles within the pellets/briquettes at relatively high temperature.
- The rate of reduction is very fast; hence the residence time of the charge in the hearth is typically as less as 6–12 minutes, during which 90–95% of the iron oxide is reduced.
- The product can be cold DRI, hot DRI, HBI, or hot metal depending on end use requirements.
- The DRI produced is continuously discharged at around 1000 °C(1273 K) from the furnace, either into refractory-lined container for hot charging to the melt shop or into briquetting machines for the production of HBI or directly cooled in inert atmosphere to get directly reduced pellets.
- The carbon content in the product can be controlled between 1.0% and as high as 6.0%, if required. Additional heat from the exit gas of the process can be recovered by Producing electrical power.
- FASTMET DRI (HBI) is melted by electric energy to produce hot metal, hence another name of the FASTMELT process.

ITmk3 process:

- The ITmk3 process is considered to be the third generation of iron making technology, the first two generations comprising BF and DR processes. Representing the next generation of modern iron making technology.
- ITmk3 processes iron ore fines into almost pure pig iron nuggets within 10 minutes. The result is a conveniently sized, slag-free material ideally suited for further processing by conventional technologies into high-quality steel products and foundry iron castings.
- The Mesabi Nugget demonstration plant, commissioned in July 2004, achieved continuous, reliable production of pig iron nuggets under commercial operation conditions. Ten thousand metric tonnes of quality pig iron nuggets were produced during the four test campaigns.
- In ITmk3, the iron ore fines and noncoking coal are formed into green iron ore–coal composite pellets. ITmk3 uses the same type of mixing and agglomeration steps and RHF as FASTMET. The composite pellets are fed to an RHF and heated to 1300–1450 °C (1573–1723 K)
- At this temperature range, the pellets are reduced to form iron nuggets.
- The temperature of RHF is raised thereby melting the reduced iron and enabling it to easily separate from the gangue. This iron making process takes only 10 minutes against 10 hours in the BF process and 8 hours in the rotary kiln process. Iron and slag get separated and the product is called nuggets.
- Iron nuggets can be fed directly into BOF or EAF as a pure iron source and a substitute of scrap. By substituting scrap, it can dilute tramp elements like Cu, Pb, Sn, and Cr.
- The process produces iron nuggets within a very short reduction time (10–12 minutes) in an RHF.
- Impurities are removed to some extent in the form of slag. The iron nuggets contain high carbon (2–3%) and low sulfur, but in solid form. Coal consumption is reported to be 500 kg/t iron nuggets, which is fairly low.
- The process is flexible as far as the types of raw materials are concerned. The iron nuggets can be fed directly to the EAF/IF to make steel along with steel scrap or DRI.
- The iron nuggets are easy to transport and handle. High in density, they do not reoxidize or generate fines

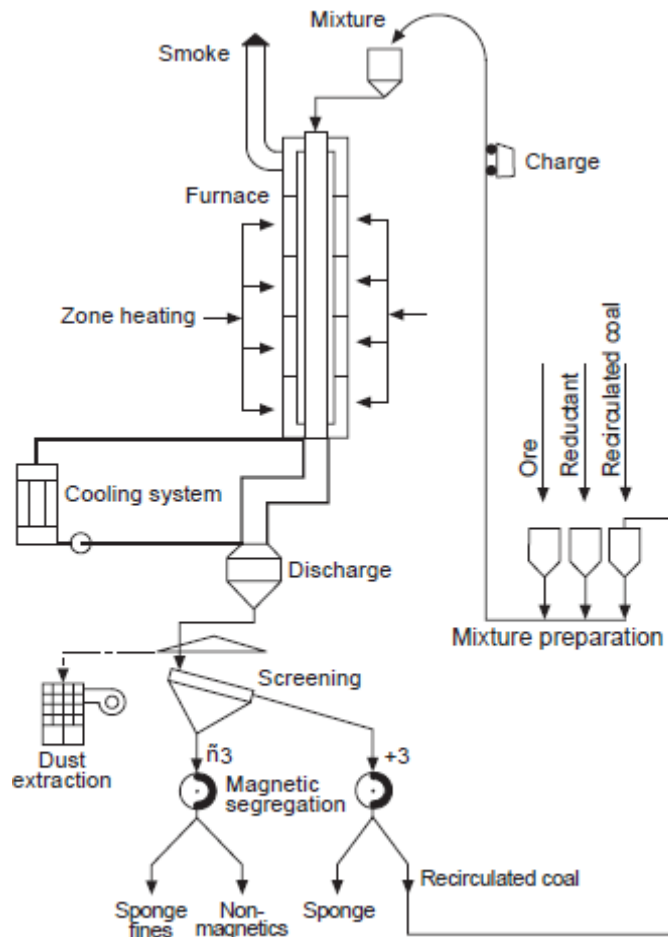


(FLOW SHEET OF ITmk3 PROCESS)

KINGLON METER PROCESS

Introduction:

- The Kinglor-Meter process produces iron continuously by heating a mixture of ore and coal in an externally-fired rectangular shaft or retort.
- Kinglor-Meter shafts are constructed with retort walls of highly conductive silicon carbide. Additional energy is provided by burning some of the carbon monoxide generated during reduction with air in a preheating zone in the upper part of the retort.



Schematic flowsheet of the Kinglor-Metor process.

Process description:

- A pilot plant comprising two reactors was installed at Buttrio, Italy by Danieli & Cie SpA and started operations in 1973.
- The reactors were vertical shafts of conical shape approximately 11 m (36 ft.) high with a top diameter of 0.4 m (1.3 ft.) and a bottom diameter of 0.7 m (2.3 ft.).
- The pilot plant operations demonstrated the process to be simple to construct, easy to operate and flexible with respect to feed and reductant requirements.
- A commercial plant capable of producing 40,000 tonnes/yr. was installed by Ferriere Arvedi & Cie., SpA in Cremona, Italy in 1978. The plant consisted of two identical 20,000 tonnes/yr modules.
- Each module contained six vertical retorts 13 m (42.7 ft.) high, 12.5 m (41 ft.) long and 3 m (9.8 ft.) wide. Solid fuel requirements of approximately 8.5 kJ/ tonne of DRI and gaseous fuel requirements of approximately 7.9 kJ/tonne were claimed.
- A plant was also installed in Burma in 1981 and is the only plant still in operation.

Gas-Based Processes

Gas-based processes are broadly classified as follows:

1. Midrex process
2. HYL process
3. Purofer process
4. Finmet process
5. High iron briquette (HIB) process

MIDREX PROCESS

Introduction:

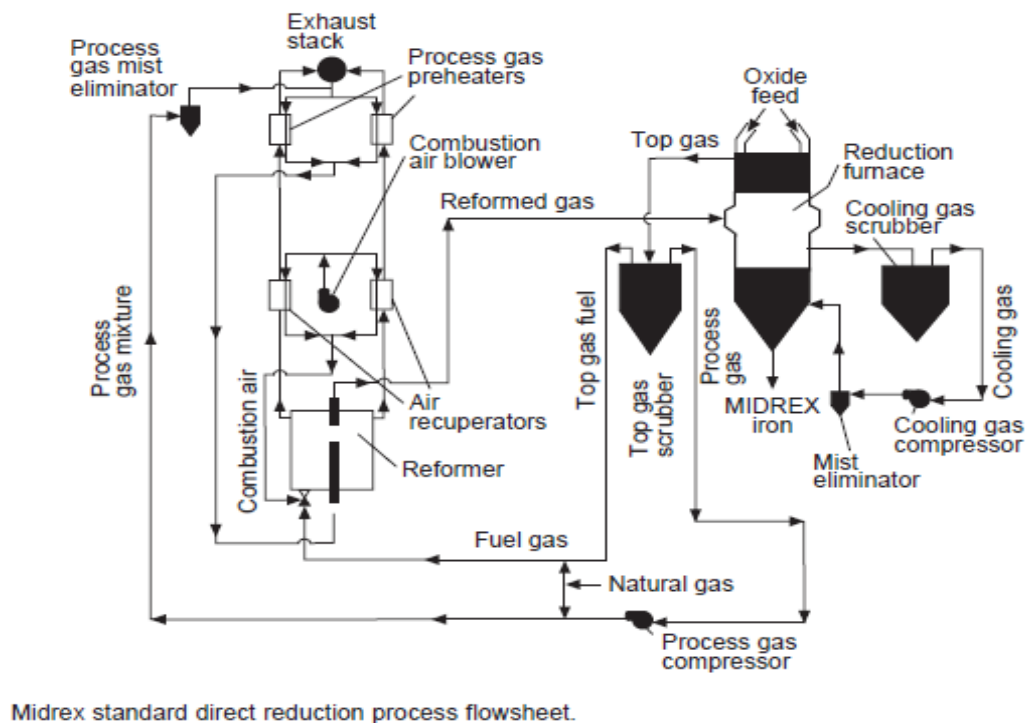
- The Midrex process was developed by the Surface Combustion Division of Midland-Ross Corporation in the mid-1960s.
- The Midrex Division became a subsidiary of Korf Industries in 1974. Midrex was subsequently acquired by Kobe Steel, Ltd. in 1983.
- The first commercial Midrex plant was installed near Portland, Oregon and started production in 1969.
- The plant included two shaft reduction furnaces of 3.4 m (11.2 ft) inside diameter and had a total capacity of 300,000 tonnes per year.
- The average energy consumption of this early plant was approximately 15 GJ/tonne (12. MBtu/ton) of DRI.
- The Midrex Direct Reduction process is based upon a low pressure, moving bed shaft furnace where the reducing gas moves counter-current to the lump iron oxide ore or iron oxide pellet solids in the bed.

Process description:

- The iron oxide feed to a Midrex shaft furnace can be in the form of pellets, lump ore or a mixture of the two (in 0 to 100% proportions).
- The solid feed is discharged into a feed hopper on top of a proportioning hopper that evenly distributes the solids into the shaft furnace.
- A dynamic seal leg keeps the reducing gas inside the furnace. The shaft furnace operates at low pressure, under 1 bar gauge, which allows dynamic seals to be used on the furnace inlet and discharge.
- The iron ore burden in the shaft furnace is first heated, then reduced by the upward flowing, counter-current reducing gas that is injected through tuyer located in a bustle distributor at the

bottom of the cylindrical section of the shaft. The ore is reduced to a metallization typically in the range of 93% to 94% by the time it reaches the bustle area.

- Below the bustle area, it goes through a transition zone (with design to reduce agglomeration or lumping) and then reaches the lower conical section of the furnace.
- Lower carbon reduced iron (<1.5% C) is cooled using a circulating stream of cooled exhaust gas that is introduced in the conical section for cold DRI discharge.
- Higher carbon DRI (up to 4.0% C) can be produced by introduction of natural gas into this cooling gas. It readily reacts (and cracks) with the highly reactive metallic DRI.
- For hot discharge of DRI to be used for hot charging of EAF's (i.e. Midrex's Hotlink Process) or for feed to hot briquetting presses (to produce HBI), the lower part of the furnace is modified to allow handling of hot burden.
- The Midrex gas generation system consists of a CO₂ reformer using their own catalyst.
- The feed to the reformer is a mixture of process gas recycled from the furnace and makeup natural gas.
- The top gas leaving the shaft furnace at a temperature of 400 to 450°C is cooled and dust is removed in a top gas scrubber. About two-thirds of the gas is recycled back to the process (process gas) and the rest is used as a fuel.
- The process gas is compressed, mixed with natural gas and is preheated in the reformer recuperates before entering the tubes of the reformer.
- The reformed gas comprising of mostly CO and H₂ exits the reformer at about 850°C and passes through collection header to the formed gas line. The ratio of H₂ to CO is controlled at about 1.5 to 1.8, and reducing quality at 11 to 12 for best operation.



PROCESS ADVANTAGES:

- World-wide commercial use proven. Performance “Relatively-forgiving” operation. Raw material flexibility.
- CO₂ reformer eliminates need for steam system, reformed gas quench, reducing gas heating and CO₂ removal system

HYL PROCESS

Introduction:

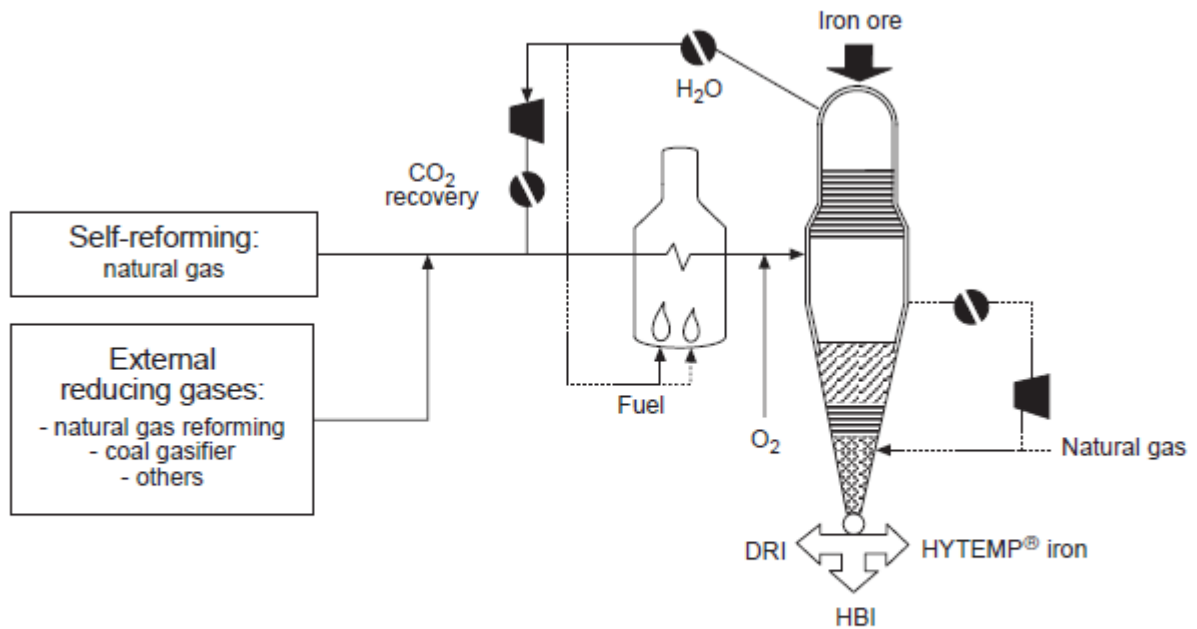
- In the HYL process developed by Hojalata y Lamina S.A. (Hylsa) of Monterrey, Mexico, lump ore and fired pellets are reduced in fixed-bed retorts by reformed natural gas.
- The first commercial HYL plant was installed at Monterrey and started production late in 1957. This plant has a capacity of 200 tonnes per day of DRI and the reactors are approximately 2.5 m (8.2 ft.) in diameter and hold approximately 15 tonnes of ore in a 1.5 m (4.9 ft.) deep bed.
- The reactors in the more recent plants are 5.4 m (17.7 ft.) in diameter and 15 m (49.2 ft.) high. Design capacity is approximately 1900 tonnes per day of DRI having an average reduction of approximately 90%.
- The energy consumption in the most recent plants is 14.9 GJ/tonne (12.8 MBtu/ton) of 90% reduced DRI.
- In the more recent plants of the HYL II design, high temperature alloy tubes in the reducing gas reheating furnaces are used, which permits heating the gas to high temperatures, and the number of heating furnaces was reduced to two units from the original four units.
- In the HYL II process, reducing gas is generated by reforming natural gas with excess steam, to prevent carbon formation and to promote long catalyst life.
- The reducing section consists of a set of four reactors, three of which are in operation, while the fourth is engaged in discharging and charging operations.
- The HYL process is a cyclical batch operation, and the three on-line reactors operate in series. Reduction is performed in two stages, an initial reduction stage and a main reduction stage. Cooling, carburization (Fe₃C) and the final adjustment of metallization are performed in the third stage.
- Each stage takes roughly three hours. An intricate system of valves permits the reactors to be connected in any desired order so that any one reactor can be connected in its correct process stage.
- In 1979, a 9,000 tonnes/yr pilot plant investigated moving-bed technology as an alternative to fixed-bed technology. The first moving bed plant was a conversion of the second plant at Monterrey.
- The four fixed-bed reactors were replaced by the new shaft furnace and the process, then called HYL-III, was started up in Monterrey.
- The compatibility of the HYL and HYL-III processes made it possible to convert and modernize HYL plants to the new technology. HYL 3M in Monterrey and 2P in Puebla, Usiba in Brazil and P.T. Krakatau Steel in Indonesia were converted to HYL-III. Commercial DRI and HBI installations based on HYL technology currently in operation or under construction in Latin America, the Middle

East. The flexibility of the process has allowed for numerous changes and upgrades, such that the generational label is no longer accurate.

- HYL has, since 1997, referred to its technology as simply the HYL process.
A general diagram of the HYL process, which has the flexibility to produce three different product forms, depending on the specific requirements of the user.
- Cold DRI is normally used in adjacent melt shops close to the direct reduction facilities. This product is also shipped and exported safely on a routine basis, following approved guidelines to avoid reoxidation.
- Hot briquetted iron can be produced from hot discharged DRI. HBI is generally exported. HBI production can also be used to process low quality, friable iron ores that cannot be used to produce cold DRI.
- Reducing gases are generated by self-reforming in the reduction reactor, feeding natural gas as make-up to the reducing gas circuit and injecting oxygen at the inlet of the reactor.
- The partial oxidation of natural gas with oxygen in a combustion chamber generates reducing gases and energy.
- Required for the reduction. Further cracking and reforming reactions are carried out in the shaft due to the catalytic effect of metallic iron. In addition to the self-reforming of reducing gases within the reduction reactor, the HYL process can use externally supplied sources of reducing gas.
- Some of the alternative gas sources include gases from natural gas steam reformers and from coal gasification units. Other reducing gas sources may be hydrogen, coke oven gas, gases from smelters gasifies, and tail gases from other direct reduction processes.

Process description:

- The components in the reducing gas circuit are the reactor reduction zone, the top gas quenching/scrubbing system, the reducing gas recycle compressor, the CO₂ removal system and the process gas heater.
- The natural gas stream or reducing gas make-up is mixed with the reducing gas recycle stream from the CO₂ removal system.
- The reducing gas stream is heated to 933°C in the gas heater. Hot reducing gas is fed to the reduction zone at 5.5 kg/cm³ and flows counter to the solids.
- Off gas from the reactor at about 400°C passes through a quenching/scrubbing system where water produced during reduction is condensed and removed along with most of the dust in the gas.
- Scrubbed gas is fed to the CO₂ removal system by means of the reducing gas recycle compressor. Decarbonated reducing gas is mixed with the natural gas stream or reducing gas make-up to close the reducing gas circuit.



HYL process diagram.

- A belt conveyor transports iron ore pellets and/or lump ores to the top of the reduction tower where an automated system of bins and pressure locks receives the ore at atmospheric pressure in an open bin, pressurizes it in intermediate bins and charges it continuously to the reactor.
- Oxygen is removed from the iron ore in the upper section of the reactor by the reducing gases and the product is then carburized.
- A rotary valve at the outlet of the reactor regulates the continuous flow of the charge through the reactor. DRI is removed by automated pressurized bins and pressure locks.
- In the production of cold DRI, the cooling gas circuit comprises the reactor cooling zone, the cooling gas quenching/scrubbing system and the cooling gas recycle compressor.
- The cooling gas is fed at the lower conical part of the reactor, at roughly 40°C, flowing counter to the descending DRI.
- The gas distribution is uniform throughout, with good contact between the gas and the solid material. The cooling gas leaves the reactor at the upper conical part at about 460°C and is then quenched/scrubbed by means of cooling water.
- Scrubbed cooling gas passes through the cooling gas recycle compressor for recycle to the reactor after being made up with natural gas injected to the cooling gas circuit for optimum efficiency and control of the cooling and carburization processes.
- In the HYTEMP® iron process, hot DRI, at 700°C, is discharged continuously from the reactor to the pneumatic transport system. The product is transported by means of a reducing carrier gas to surge bins located above the melt shops for controlled feeding to the electric arc furnace.
- For the production of HBI, hot DRI, at 700°C, is discharged continuously from the reactor to the hot briquetting machines arranged below. The HBI is cooled to about 80° in vibrating cooling conveyors using cooling water, and then discharged to the HBI transport conveyor.

- The expected specific consumption figures in the HYL process for two typical production options are presented.

PROCESS ADVANTAGES:

- Proven equipment performance (uses HYL II and HYL III reactor technology)
- Raw material flexibility
- Not sensitive to S in natural gas or ore
- No reformer – lower Capital costs
- High-energy efficiency (87% in comparison to 70% for most efficient other DRI plants).

Production of reducing gas: The reducing gas is produced in a steam reformation. The high-pressure material gas is first desulfurized with activated carbon to prevent poisoning of the catalyst in the reformer. The gas is then mixed with superheated steam. This mixture is preheated and then passed through heated Cr–Ni alloy tubes containing a Ni catalyst.

Reducing gas temperature and pressure: The reducing gases for both the primary and secondary steps are first preheated to about 800 °C (1073 K) in tubular heaters. After that the gas is elevated to a temperature of 980–1230 °C (1253–1503 K) by injecting a controlled quantity of heated air into the reducing gas steam.

CHAPTER-4: PARAMETERS OF SPONGE IRON MAKING:

- For successful operations the process of DR technology has specified the characteristics of raw materials to be used in the process

❖ IRON ORE

❖ CHARACTERISTICS OF IRON ORE

- Lumps or pellets have high iron content, low gangue content, and good mechanical strength and are readily reducible and of non-decrepitating variety. Iron ore feed to the reactors have the following characteristics:

- Chemical composition
- Reduction properties
- Physical characteristics

❖ Chemical composition.

- The only chemical change in the DRI process is the removal of oxygen from the iron ore in the solid state by reducing gases containing CO and H₂.
- Since sponge iron is in solid state, all impurities in the oxide feed remain as such in the product.
- Therefore, iron content of the ore should be as high as possible preferably 65-68%. The ore containing more than 68% iron may not be of advantage as generation of more fines would occur due to low abrasion resistance.
- High gangue content in the DRI would require additional energy.
- Fluxes and refractories during melting, adversely affect the operation of arc furnace. This also affects productivity of the furnace and the quality of steel produced. Therefore, gangue content of the ore feed should not exceed more than 5%.
- The SiO₂ content of the gangue should not be too low as it results in swelling and decrepitating.
- Alumina being acidic will require extra flux increasing the slag volume in steel making
- The total (SiO₂+Al₂O₃) should not be more than 4%.
- Alkali content of the ore gives rise to swelling which causes degradation and creates operational difficulties.
- Phosphorus has no effect on the DRI .But it is a must for good quality steel. The sulphur content of the ore should be below 0.02% as it plays an important role in DRI process.
- Addition of limestone and dolomite increases the strength of the fired pellets.

❖ PHYSICAL CHARACTERISTICS OF THE ORE SIZE DISTRIBUTION:

- Size of the iron ore pellet is very important for the production of DRI.
- The optimum size is determined by its reducibility characteristics.
- The feed materials for DRI production should have narrow size range as far as possible to get a uniform metalized product.
- In shaft furnace narrow size of feed material is essential for good permeability of the bed.
- Ore fines of the size range of 3-5mm can be processed in the rotary kiln through ore slinging mechanism.

- The mechanical properties like abrasion index of the ore/ pellet and cold compression strength of the pellet are normally specified as for blast furnace feed.
- The ore pellets must have strength greater than 200kg, and abrasion index 600 micron.
- Some ore/ pellets tends to crumble on heating at lower temperature thus, generating fines. This is called decrepitating.

❖ REDUCIBILITY:

- Reducibility of the ore has great influence on the productivity.
- Higher the reducibility lower is the retention time. Therefore the ore must have high reducibility.
- Generally hard dense lump ore and over fired pellets do not show good reducibility.
- Magnetite exhibits poor reducibility as compared to hematite.
- In shaft furnace process, the reducibility should be 90-95% within a residence time of 6 hours in the temperature range of 800-1000oC.

❖ TESTS ON NON COKING COAL:

- The consumption of coal for production of dry depends on the reaction stoichiometry, fixed carbon content and loss of fixed carbon.
- Therefore, evaluation and selection of coal for the process is very critical and should be done every carefully. In selection of coal following characteristics shall be considered:
 - a. Proximate analysis
 - b. Ash fusion temperature
 - c. Sulphur content
 - d. Caking and swelling index
 - e. Calorific value
 - f. Coal char reactivity
 - g. Char strength
 - h. Sinter fracture load
 - i. Coal size
 - j. Ash chemistry
 - k. Proximate analysis:
 - l. Fixed carbon:
 - m. The fixed carbon aspect of coal is most important aspect of
 - n. proximate analysis.
 - o. Volatile matter

❖ THE VOLATILE MATTER

- contributes to heat as well as helps in reduction of the iron oxide in the kiln.

- Low volatile matter coal shall not provide adequate heat Very high volatile coal is not preferred as it affects the composition of the DRI.

- Therefore Indian coals containing 25-35% volatile matter at amen ash value 22% are preferred.

❖ ASH CONTENT:

- The ash content affects the thermal requirement and productivity of the kiln adversely.

- The ash is an inert material occupying the space in the kiln.

- A value of 15% ash is considered to be good. However under Indian conditions the ash content in the coal should not exceed 24%.

❖ MOISTURE:

- The moisture in the coal is in two forms Free moisture Combined moisture

- The moisture content increases the thermal load in the kiln.

- The total moisture content should be less than 5%.

❖ ASH FUSION TEMPEARTURE:

- The ash fusion temperature of the coal is very important property of the non-coking coal. This is the temperature where pure coal starts to fuse.

- Ash fusion temperature should be at least 200oC higher than operating temperature of the kiln.

- The coal ash inside the rotary kiln comes in contact with other chemical compounds forming low eutectics promoting accretion formation on the kiln wall.

- This reduces the productivity of the kiln

❖ SULPHUR CONTENT:

- Sulphur maybe present in coal as organic sulphur in combination with carbon and hydrogen.

- Sulphur maybe also present as FeS and sulphate.

- The amount of sulphur as sulphate is very less.

- The organic sulphur is released gradually.

- The sponge iron in the bed absorbs sulphur as the temperature increases.

- Sulphur content in the bed increases exponentially.

❖ CAKING AND SWELLING INDEX:

- High caking index causes sintering and reduces char reactivity of coal with CO₂.

- It also causes accretion build up in the kiln therefore a coal of caking index more than 3 is not preferred for DRI.

- Coal has the property of swelling when it is heated.

- The coal forms big masse with less density. These agglomerates of low density may disintegrate to generate more fines which may be lost in the kiln.

- Swelling index of coal should be less than 3.

❖ CALORIFIC VALUE:

- The thermal requirement of the process is met by burning coal.

- The calorific value of the coal increases with increase in carbon content.

- Low calorific value means high consumption of coal.

❖ CHAR REACTIVITY:

- Reactivity of coal char is a measure of the rate of conversion of CO_2 to CO according to Boudouard reaction.
- The gasification of coal char is complex. It depends on various factors like rank of coal, volatile matter, porosity, specific surface, charring temperature, rate of heating etc., Coals with high reactivity are preferred in the rotary kilns because it is easier to operate at lower temperature.

❖ CHAR STRENGTH:

- After removal of moisture and volatile matter, the degradation of char in the kiln depends on char strength. The char strength increases with coal rank.

❖ COAL SIZE:

- The size of coal should be such that it should mix well with the charge.
- The size of the coal should not be very fine otherwise it causes carbon loss. The proportion of -1mm size should not be more than 5-10%.

4.9. Process Parameters of Sponge Iron Production:

4.9.1. Raw Materials:

To produce one ton of sponge iron following raw materials of indicated amount and specifications are required:

Iron ore: 1.7 tons (FeT: 64 - 65%)

Coal: 1.4 tonne (FC: 37-38%)

Dolomite: 30 kgs

Air: 2200-2400 m³/hr.

4.10.2. Iron Ore Feed Rate:

To produce a rated capacity of 500tons of DRI /day, the ore feed rate is maintained at 31tons/hr as one ton of iron ore yields around 0.675tons of DRI. Initially the ore feed rate is maintained at 25-26 t/hr for stabilizing the kiln operation during a fresh campaign. Once the kiln operation stabilizes the feed rate can be raised in small steps upto the rated capacity. Normally the ore feed rate is not reduced below the rated capacity unless there is some problem in the kiln. It is adopted as corrective action to rectify the prolonged low-grade situation. Kiln should be operated at a minimum level of 80% of the rated capacity for break even.

4.9. 3. Coal Feed Rate and C/Fe ratio:

Around 390kg of fixed carbon is required to produce 1ton of DRI as per the iron ore and coal specifications. Adhering to this value plants maintain a C/Fe ratio of 0.4-0.46 which indicates the quantity of carbon feed to the kiln.

The ratio of fixed carbon to iron is one of the major process control parameters in sponge iron making. This ratio indicates the amount of coal required for a given amount of iron ore to be reduced provided their chemical compositions are known. To maintain the C/Fe ratio within the specified range, the coal feed rate is varied without disturbing the ore feed rate. For a new campaign, the C/Fe ratio is maintained around 0.48 and as the iron ore feed is raised to the rated capacity this ratio is reduced to around 0.46. At least once in a shift, the quality of the iron ore is checked to adjust the coal feed rate for a specified C/Fe ratio. Mathematically,

$$C/Fe = \frac{\text{Coal feed rate} \times (100 - \text{moisture in coal}) \% \times \% \text{ of carbon in coal}}{\text{Iron Ore feed rate} \times (100 - \text{moisture in ore}) \% \times \% \text{ of iron in ore}}$$

A higher C/Fe ratio indicates excess coal consumption while a lower C/Fe indicates lower coal consumption and overall reduction in cost of DRI production. However, a low C/Fe ratio may result in carbon starvation in the kiln causing reoxidation of the product and accretion formation. So, to keep a balance between them, the C/Fe ratio is maintained in the range of 0.45-0.49. However, there are situations where specifically a higher C/Fe ratio is maintained as listed below:

- i. At the beginning or end of a kiln campaign.
- ii. To control high temperature in the kiln.
- iii. When fused mass is noticed in the kiln.
- iv. When there is a collapse accretion in the kiln.
- v. When the ash percentage in the coal is high.
- vi. When the moisture is high.

4.9. 5. Dolomite Feed Rate:

Dolomite feed rate is monitored according to the percentage of sulphur in coal and its feed rate. Generally, sulphur in Indian sponge irons varies between 0.01- 0.02%. Its percentage is little higher in fines and lower in lumps. A 40% FC coal of 0.6 % sulphur requires a C/Fe ratio of 0.42 and needs around 26 -28 kgs of dolomite per ton sponge iron produced.

4.9.6. Ratio of Coarse and Fines in Blow Coal:

Coal particles of -5mm size in the blow coal is generally treated as fines. Normally a ratio of 2:1 is maintained between coarse and fines in the blow coal. Depending upon the use of secondary air the quantity of fines may be increased upto 48%. For normal operation the quantity of fines in the blow coal is regulated within 35- 40% to achieve a stable process. Increase in blow coal fines ensures a reducing atmosphere in the kiln and also improves the temperature of the preheating zone. Low ash coal fines is always desirable. Ash fines at high operating temperature soften and act as binder in the accretion formation process at the discharge end.

4.9.7. Blow Coal Pressure:

Consistent maintainance of blowing pressure is essential to have uniform throw of the blow coal. Blow coal pressure is different for differently designed kilns. It is so adjusted that the blown coal particles should reach at least 80% of the total length of the kiln measured from the discharge end. The required blow pressure is adjusted considering the following parameters:

- i. Change in blow coal size.
- ii. Change in the moisture content of the blow coal.
- iii. Air leakage from the blowing system.
- iv. Wear out of the rotary feeder.
- v. Wear out of the blow coal pipe.

- vi. Clogging of the suction filter.
- vii. Opening of the safety valve.
- viii. Jamming of the blow coal pipeline.
- ix. Malfunction of the bleed off control valve.

The possible causes of any change in blow pressure is analysed and necessary corrective actions are taken. Maintaining the blow pressure consistently at the required level is of utmost importance. Kiln operation is found to be stable when the blow pressure is maintained within a narrow range.

4.9.8. Temperature Profile:

Temperature profile is the outcome of the air profile, fuel availability and enthalpies of various reactions taking place in the kiln. Further, the temperature inside the kiln is also influenced by the filling degree of the charge burden. Higher the degree of filling lesser is the heat loss and higher is the temperature in the kiln. Though higher temperature makes the reduction faster it leads to acute accretion formation problem in the kiln. Sometimes, even at lower temperature accretion is formed due to occurrence of low melting point eutectic compounds in the charge materials. Temperature is controlled immediately at different locations of the kiln by controlling the air input to the kiln through the eight onboard fans and the secondary air fan. Each fan has a damper with ninety notches at the discharge. These dampers are calibrated for a particular volume of air with respect to the damper opening. By adjusting the notch position a typical air profile can be set to stabilize the kiln operation. As the feed rate is increased to the rated capacity, secondary air is increased up to around $10,000\text{m}^3/\text{hr}$. Based on the QRT temperature readings, product quality & accretion build-up in the kiln can be assessed. If there seems to be any trouble, the air profile is varied as a corrective measure. Coal feed rate is also changed to control the kiln temperature.

There are thirteen onboard thermocouples which are continuously monitored to know the temperature trend in the kiln. However, QRT readings are taken to be the actual temperature. Based on their readings, corrective actions are taken. Higher gas temperature indicates the need to control the combustion by reducing the air flow in the corresponding zones. If required, blow coal quantity is also reduced to control high gas temperature. Higher bed temperature may have many possible causes as listed below:

- i. Gas temperature is high so the bed temperature has increased.
- ii. Filling degree is low or has reduced due to interruption in feeding.
- iii. Filling degree is very high and hence air from shell air fan is in contact with the bed material.
- iv. No reduction reaction is taking place to absorb the heat.
- v. Exothermic reoxidation reaction is taking place due to carbon starvation.
- vi. There is an air leakage from the tuyer.

The above possibilities are analysed and necessary actions are taken to control high bed temperature as listed below:

- a. Reduction of air flow into the kiln.
- b. By increasing the amount of reduction coal and by decreasing the amount blow coal.
- c. Increasing the iron ore feed rate.
- d. Increasing the operating speed of the kiln.

4.9.9. Kiln Speed:

The rotating speed of the kiln influences the followings:

- i. Filling Degree.
- ii. Retention time of feed material at various locations of the kiln.
- iii. Heat transferred from the kiln.

All the above parameters are interrelated and influence the reduction process. As the feed rate is increased, the kiln speed is also increased so as to keep the filling degree unchanged.

Filling Degree is measured by the formula:

$$F.D = \left(\frac{\theta}{360} - \frac{\sin \theta}{2\pi} \right) \times 100, \theta = \frac{l}{T} \times 100$$

Where, l = Time span that the QRT remains in the ore bed during one complete rotation of the DRI kiln.

T = Time taken by the DRI kiln to make one complete rotation.

As accretion in the kiln increases, the filling degree calculation becomes unreliable. In such a situation back spillage is considered for adjusting the kiln speed instead of filling degree. Kiln speed is a control tool by which the material movement inside the kiln is controlled.

4.9.10. Cooler Discharge End Pressure:

Cooler discharge end pressure is always maintained positive compared to the atmospheric pressure throughout the kiln operation to avoid any false air getting into the kiln. The false air is the unwanted excess air which can increase kiln temperature and cause accretion. It may also re-oxidize the product affecting its quality. The firing hood pressure is controlled within 0.5-0.6 milli bar. When kiln is required to be inspected or when accretion pieces are required to be removed from the kiln, a negative pressure is maintained temporarily at the kiln firing hood.

4.9.11. Nonmagnetic Percentage in the Kiln Discharge:

The percentage of non-magnetics separated from the sponge iron with its carbon content indicates the manner in which the kiln has been operated. It is directly not a process parameter but can help indirectly to adjust the process parameters. The carbon percentage of the nonmagnetics depends on the C/Fe ratio, reduction coal to blow coal ratio, temperature profile and the nature of coal used in the kiln. Normal range of nonmagnetics in the sponge iron is around 18-22% with a carbon content of around 32-38%.

An increase in these suggested values indicates some error in the kiln operation as listed below:

- i. Coal input to the kiln is more.
- ii. Feed coal size has shifted towards upper size range.
- iii. Kiln temperature is low. Hence, carbon consumption is less.
- iv. Blow coal throw is not proper.
- v. Coal reactivity may be less.

Similarly a lower percentage of nonmagnetics indicates:

- i. Carbon starvation or less coal input to the kiln..
- ii. High temperature in the kiln.
- iii. Accretion formation.
- iv. Air tuyer damage.
- v. Accretion collapse.
- vi. Increase in percentage of fines in the reduction/blow coal.

After analysing the causes suitable corrective actions are taken. When there is a substantial drop in the percentage of nonmagnetic in the sponge iron, the coal feed rate is immediately increased to check severe accretion growth in the kiln prior to any detailed analysis regarding the problem.

A detailed analysis may include the following parameters:

- i. Quantity and quality of the feed raw materials .
- ii. Percentage fines in the coal and ore.
- iii. Moisture content of coal.
- iv. Cleaning of necessary equipments.
- v. Low thermal expansion or stability of volume.
- vi. The feed rate of iron ore required as per kiln condition.
- vii. As per ore feed rate, the amount of feed & blow coal used.
- viii. The feed rate of dolomite.
- ix. Size distribution of the feed coal.
- x. Injection pressure for proper distribution of coal throughout the kiln.
- xi. Kiln speed for required retention time.
- xii. Air flow adjustment for required temperature at required place.

CHAPTER 5: DRI PLANT OPERATION AND ABNORMALITIES

- DRI, whether in the form of particles, pellets, or molded briquettes, tends to revert to the oxide state when exposed to natural environments. The large pore surface area of DRI makes it susceptible to spontaneous reoxidation.
- Spontaneous reoxidation is undesirable because of the possible temperature rise during storing or shipment. Even if ignition can be prevented, DRI will gradually lose metallization because of reoxidation due to weathering.
- When the oxygen in the gas in contact with the DRI becomes depleted, the DRI also reacts with moisture to produce hydrogen gas. This could produce a flammability or explosion hazard in confined spaces.
- Because of the potential hazards, the loss in value, and the possible harmful effects during subsequent melting, producers and users usually protect DRI from contact with water.
- The stability and behavior characteristics of DRI depend on a number of variables affecting the pore surface area.
- These include the mineralogy of the oxide ore or agglomerate, reduction temperature, time at the reduction temperature, gas composition, age and previous history of exposure and handling. As one example, the DRI stability increases with reduction temperature because the pore surface area decreases as the temperature is raised.
- Other methods of improving the stability involve making the iron in the pore surfaces unavailable for reoxidation or decreasing the pore surface area mechanically.
- To prevent the deterioration of DRI, the industry has studied the techniques used for the protection of structural metals from corrosion. Impervious coatings have been developed utilizing oxide passivation, chemical solutions, oily organic rust inhibitors, paints, etc. Midrex has patented the Chemaire process, a sodium silicate air passivation treatment. While some coatings potentially contaminate steel, passivation produces an iron oxide coating consistent with the steelmaking process.
- Passivation involves treatment with a mildly oxidizing gas at temperatures below 540°C (1000°F) for the formation of a tightly bonded magnetite layer that is essential for the protective process to work.
- Passivation to increase stability from spontaneous combustion in a dry atmosphere can be achieved by oxidation without measurable loss of metallization. Given sufficient time, the internal surface area of porous DRI pellets or lumps also acquires the oxide coating which tends to increase the stability of fines generated in subsequent handling.
- Some autogenous passivation occurs during aging of DRI in a protected ambient atmosphere. Passivation is usually performed between 90–200°C (200–400°F) with various gases, including combustion gases and reducing gas containing less than approximately 2% oxygen.

- At the current state of the art, passivation or economical coatings acceptable in the subsequent melting process are not completely reliable. Incidents of heating of DRI in the holds of ships have been reported.
- The problem may be intensified by contamination with seawater or by lack of uniformity in the DRI as produced or treated. To avert possible catastrophes, an emergency supply of inert gas should be available for ship holds or enclosed storage bins.
- Such storage areas could be flooded with the inert gas should the temperature rise above a safe minimum or should an explosion hazard arise.
- The inert medium should probably be nitrogen rather than flue or exhaust gas, which contains carbon dioxide. It is possible that carbon dioxide can be a source of oxygen for the oxidation of DRI, however, the generation of poisonous carbon monoxide is the more important concern. While coating procedures attempt to protect the iron in the pores from reoxidation, hot briquetting decreases the pore surface area of DRI.
- In the FIOR process, the –2 mm product is briquetted while the material is hot and malleable. The individual briquettes attain densities greater than 5.0 g/cm³.
- This DRI product, now referred to as hot briquetted iron (HBI), can be stored in the open prior to loading, can tolerate a fine spray of fresh water to control dust accumulation and can be unloaded under less restricted weather conditions. Still, HBI requires adequate surface ventilation and should not be loaded if the briquette temperature exceeds safety standards.
- Ship holds or bilges that are used to store the briquettes should be dry and weatherproof. Also, because the briquettes may deplete oxygen in the storage compartments, caution should be exercised when entering.
- The hot molded DRI concept has also been extended to processes producing DRI in the form of larger coarse particles or pellets.

Chapter-7: Environmental Management in DRI Plants

- Sponge iron units are highly air polluting industries. They also generate huge amount of solid waste as char from the process and fine dust retained in the air pollution control devices.
- The hot flue gas which flows in counter current direction of the materials inside the rotary kiln finally passes through ABC (After Burning Chamber) where residual carbon or CO is burnt by the excess air available at high temperature at about 1000 °C.
- The heavier dust particles settle in dust settling chamber and the flue gas containing high quantity of fine dust particles (P.M. – 30gm/Nm³) is released to the atmosphere at a temperature of 900OC in the form of dense fume through a chimney. If no pollution control device is installed, it becomes a major source of air pollution, which is responsible for dust pollution in the surrounding area.
- Most of the fugitive dust and source emission from sponge iron process are invisible micro fine respirable particulate matter which causes varieties of human ailments like respiratory ailments leading to loss in work efficiency.
- Air Pollution is one of the biggest hazards from Sponge Iron plants where fine coal dust and fugitive emissions will play a vital role in damaging plants and health of the inhabitants if properly not controlled

❖ AIR POLLUTION POINT SOURCES

1. Kiln Flue Gases after ABC (Control equipment ESPs / Bag Filters/ Wet
2. Scrubbers)
3. Emergency Stack / Safety Cap above the ABC to maintain positive
4. Pressure inside kiln and avoid CO related explosions
5. Cooler Discharge
6. Product House
7. Iron Ore and Coal Crushing

❖ FUGITIVE EMISSIONS SOURCES

1. Raw material handling yard (Unloading, stacking, reclaiming operations)
2. Product discharge system (Cooler discharge conveyers transfer points,
3. Junction house, screens, magnetic separators, storage silo, truck loading and parking operations- Control equipment of water sprinklers, bag filters, covered product house, covered conveyor belt).
6. The source of fugitive emissions and their control measures are given below

Sl.No	Sources of fugitive dust emission	Control measures prescribed
1.	Raw material handling & preparation area	Automised water spraying System. Work zone should be concreted
2.	Crushing and screening of coal (Coal circuit)	Pulse jet Bag Filter & automised water spraying nozzles
3.	Crushing and screening of iron ore (Iron ore circuit)	Pulse jet Bag Filter & automised water spraying nozzles
4.	All material transfer points and Conveyor belt	Enclosures and Pulse jet Bag Filter
5.	Discharge points of Raw material Storage bins	Pulse jet Bag Filter
6.	Raw material feeding point into kiln	Pulse jet Bag Filter
7.	Coal injection point into kiln	Pulse jet Bag Filter with recycling of coal fines back into the coal injection system
8.	Leakage from slip rings of the rotary kiln	Realignment of the kiln and changing of seal/ packing materials during shutdown period
9.	Cooler discharge circuit	Pulse jet Bag Filter
10.	Intermediate bins in between cooler discharge area and product separation unit	Pulse jet Bag Filter
11.	Product separation unit	Pulse jet Bag Filter
12.	Wind-blown dust from solid waste Dump yard	Provision of boundary wall around the dump yard, covering by earth and automised water spraying on the dump area by rotating nozzles

• Even after installation all pollution control devices in the plant, the ambient air quality with regard to SPM and RSPM, do not meet the standard many times due to the following reasons:

1. Bad housekeeping,
2. Internal and approach roads not black topped/ concreted, work zone not concreted. Loose dust periodically not removed from roads, which become airborne.
3. Unloading of raw materials, loading of chars and fines carelessly.
4. Trucks not covered and there is spillage of materials on the road during transportation.
5. Fine loose dust from the work zone and raw material and solid waste dump yards become wind borne during stormy weather.
6. Leakage of flue gas through kiln cap in between power failure and startup of D.G.
7. Bad maintenance and malfunctioning of ESP/ Bag Filters/ dust handling systems.
8. Inadequate water sprinkling.

9. ESP/ BF dust handling system not mechanized. Dust collection points under the hoppers properly not enclosed.
10. Most of the sponge iron industries do not have dedicated team for proper housekeeping and attending to pollution problems

❖ **SOLID WASTE GENERATION**

- Char & Dolo Char
- Flue Dust,
- GCT /GCP Plant sludge
- Fly Ash and
- Kiln accretions

❖ **CHAR & DOLA CHAR STORAGE SHED:**

- The Production of Char & Dola Char will be 40% of the total production of Sponge Iron and this is easily salable to Brick Kilns, and power generation units.
- Maintain less stones and not to allow the material exposed to water.
- Cost of the shed is Rs.30 lakhs.
- Payback period one to two years
- Quantity of dust collected per day is 40 tons and sold at Rs.200/- per ton.

❖ **CLEANER PRODUCTION OPTIONS FOR SPONGE IRON INDUSTRY**

Selection of Quality Raw Materials:

- The quality of raw materials selected will effect quality of the product at the same time will determine the amount of pollution load generated and wastes generation. Hence the higher grade of raw materials (Iron ore, Coal and Dolomite) may be selected for better yields of Sponge Iron production.

Waste Heat Recovery:

- Pre-heating system can be provided for raw material feed for units having production capacity of 50 TPD and 100 TPD to recover the waste heat from kiln flue gases. One such unit has already been in operation at Bellary, Karnataka.

- The following are the benefits of preheating system:

1. The cost of production as compared without pre-heater is low.
2. As the preheating system is provided which will ensure reduction of coal consumption in the preheating zone of the kiln and for the material may consume less time to reach in the reduction zone, this may enhance production.
3. The unburnt carbon particles, volatiles, dust and left over carbon monoxide will be burnt in presence of excess air in the pre-heater, their by reducing the emission levels substantially.
4. The consumption of water will be substantially reduced in the GCT due to low flue gas temperature

CO-GENERATION:

- Sponge Iron plants of 2X100 TPD / 3X100 TPD and more capacities with FBC boiler will give consistency in power generation which can be used for production of steel as a downstream facility to make the project economically viable. This will not only help in gaining carbon credits for more financial gains but also ensures continuous power supply for plant operation.

AUTOMISATION / OPTIMISATION OF PROCESS:

- Entire process may be automated through Programmed Logic Control (PLC) to eliminate human errors causing pollution and affecting the quality of the product. The opening and closing of the cap of bypass stack shall be electronically recorded with time and duration. Interlocking facility should be provided between ESP operation and raw material feeding.

SOLID WASTE MANAGEMENT:

- The various types of solid waste generated in the process can be used as a raw material for making use as detailed below
 1. Coal fines collected in the coal crushing dedusting system can be mixed with char fines and made into briquettes which can be used as a fuel in any system.
 2. Maximum utilization of solid waste like Char and Dolchar, for brick making, cement making should be taken up.
 3. Fly ash collected from the waste gas cleaning system (ABC, GCT & ESP) can be used for making fly ash bricks.
 4. Bag filter dust collected in the product circuit can also be used as activated carbon in edible oil refineries.
 5. Kiln accretions and slag may be used in filling the low lying areas, abandoned mines and for road making.

❖ ENVIRONMENTAL STANDARDS AND CODE OF PRACTICE FOR POLLUTION PREVENTION FOR SPONGE IRON PLANTS AS PROPOSED BY CPCB.

- CPCB has proposed environmental standard and Code of Practice for Pollution Prevention for Sponge Iron Plants comprising of Stack Emission Standards, Stack Emission Standards from dedusting units and Fugitive Emission Standards Code of Practice for Pollution Prevention for
 - Raw Material handling and Preparation
 - Cooler Discharge and Product Separation Unit, Effluent Discharge Standards,
 - Noise Levels Standards and Solid Waste Management.

CHAPTER-8: PRODUCTION OF FERRO ALLOY

• Ferroalloy refers to various alloys of iron with a high proportion of one or more other elements such as manganese (Mn), aluminum (Al), or silicon (Si). They are used in the production of steels and alloys. The alloys impart distinctive qualities to steel and cast iron or serve important functions during production and are, therefore, closely associated with the iron and steel industry,

DIFFERENT FERROALLOYS: the main ferroalloys are

- FeAl – Ferro aluminum
- FeB – Ferro boron
- FeCe – Ferro cerium
- FeCr – ferrochromium
- FeMg – Ferro magnesium
- FeMn – ferromanganese
- FeMo – ferromolybdenum
- FeNb – Ferro niobium
- FeNi – ferronickel
- FeP – ferrophosphorus
- FeSi – ferrosilicon
- FeSiMg – ferrosilicon magnesium
- FeTi – ferrotitanium
- FeU – ferrouanium
- FeV – ferrovanadium
- FeW – ferrotungsten

• Ferro alloys production can be divided into 3 groups depending on the reduction process namely

1. Carbothermic
2. Silicothermic
3. Aluminothermic

1 .CARBOTHERMIC REDUCTION.

- More commonly, ferroalloys are produced by carbothermic reactions, involving reduction of oxides with carbon (as coke) in the presence of iron. Some ferroalloys are produced by the addition of elements into molten iron.
- Carbothermic processes are mainly used for the large scale production of ferrosilicon, ferromanganese, ferrochromium, ferronickel and ferrotungsten.
- Carbothermic processes for the production of Ferro boron, ferrotitanium, ferrovanadium, and ferromolybdenum have been largely replaced by metallothermic processes, mainly aluminothermic and silicothermic.

- Ore are smelted along with the reductant like coke in a submerged electric furnace where reduction of oxide with carbon takes place resulting the formation of alloy and slag.

2. SILICOTHERMIC REDUCTION PROCESS:

- This process is chosen for the production of low carbon alloys.
- Here silicon is used as reductant in the form of silicon chrome for chrome alloys and silicomanganese for manganese alloys
- The reaction is highly exothermic with generation of a lot of heat. Hence refractory control is more important
- There are two different method.in one method calcined lime and preheated ore are melted together in an open arc furnace and the ore lime melt is allowed to react with silico chrome in the ladle outside.
- In the second method ore, lime and the reductant fed in an open arc furnace and after the reaction complete metal and slag are tapped.
- Extra low carbon alloy can be produced by this method

3. ALUMINOTHERMIC REDUCTION PROCESS:

- This method is used for small scale production of low and medium carbon alloys.
- Pure metallic aluminum is used as a reductant for reducing the oxide of chrome or manganese ore.
- The reactions are carried out in a thermit vessel and the ground raw material are fed after through mixing and preheated in the vessel.
- An ignition mixture is given for initiating the reactions.
- Low carbon ferrochrome, ferromanganese and all noble alloys are produced by this method.

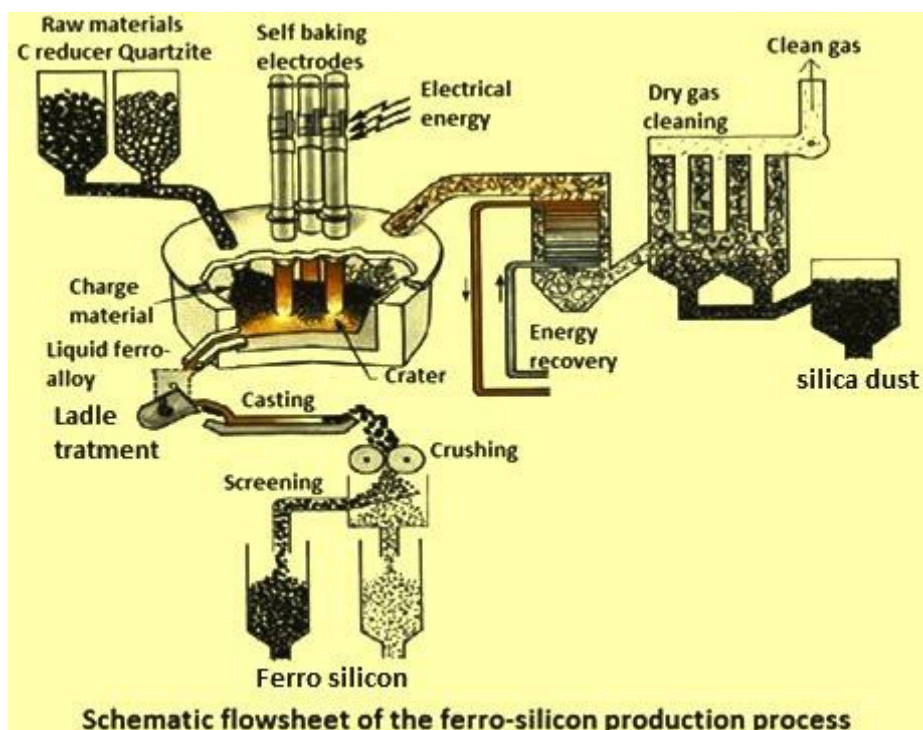
FERROSILLICON (FeSi);

- Ferrosilicon is an alloy of iron and silicon with average silicon content between 15 and 90 weight percent.
- The Ferro-alloy normally contains Si in the range of 15 % to 90 %. The remainder is Fe, with around 2 % of other elements like aluminum (Al) and calcium (Ca).
- Fe-Si is produced industrially by carbo-thermic reduction of silicon dioxide (SiO_2) with carbon (C) in the presence of iron ore, scrap iron, mill scale, or other source of iron.
- The smelting of Fe-Si is a continuous process carried out in the electric submerged arc furnace (SAF) with the self-baking electrodes.

RAW MATERIAL:

- Quartz
- Coke or charcoal
- Iron ore or steel scrap.

PRODUCTION OF FERROSILICON:

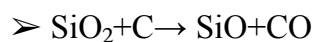


- Iron ore (Fe_2O_3), quartz (SiO_2) and carbon (C), in the form of coal, coke and bio carbon, is added at the top of the furnace.
- Three electrodes in the furnace is heating the material. At approximately 2000°C the carbon reacts with the oxygen in the quartz and we are left with liquid silicon.
- The iron oxide in the iron ore pellets reacts with the carbon through a similar reaction and forms pure iron. Melted iron and silicon mix and is then tapped in ladles.

- Reactions in the furnace occur according to the simplified scheme:



- Side reactions also occur that result in a lower yield of the desired product, especially when insufficient carbon is used:



- Gaseous SiO is oxidized by atmospheric oxygen at the burden surface to give SiO_2 dust, which is carried out of the furnace with off-gas.

- Ferrosilicon production is a slag-free process, which means that all the impurities present in the raw materials are transferred to the product. To obtain high purities the alloy must be purified by further treatment outside the furnace.

FERROMANGANESE

• Ferro-manganese (Fe-Mn) is an important additive used as a deoxidizer in the production of steel. • It is a master alloy of iron (Fe) and manganese (Mn) with a minimum Mn content of 65 %, and maximum Mn content of 95 %. • It is produced by heating a mixture of the oxides of Mn (MnO_2) and iron (Fe_2O_3) with carbon (C) normally as coke or coal. • There are several grades of Fe-Mn which are divided into many groups. The three main groups are ➤ high C Fe-Mn, ➤ medium C Fe-Mn, ➤ low C Fe-Mn. • High Carbon Fe-Mn can be made in BF and in SAF.

RAW MATERIAL:

- The raw materials required for the production of high –carbon ferromanganese are
 - manganese ores
 - Fluxes such as limestone, dolomite, or silica
 - Coke
 - Iron ore

PRODUCTION OF FERROMANGANESE IN BLAST FURNACES

- Ferromanganese can be produced in blast furnaces in a manner similar to pig iron; however in the western world only four producers employ this method.
- These are Thyssen Stahl (Germany), BSC Cleveland (United Kingdom), SFPO (France) and Mizushima (Japan). The choice of the use of blast furnaces over electric furnaces is based on the relative price of coke and electricity. The product produced from blast furnaces generally contains 76%Mn and 16%Fe.

RAW MATERIAL SELECTION AND PRETREATMENT:

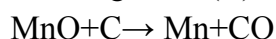
- The raw materials required for the production of high –carbon ferromanganese are manganese ores, Fluxes such as limestone, dolomite, or silica, and solid fuels and reductants such as coke.
- In order to produce ferromanganese of the required grade a single ore is seldom suitable because the desired Mn/Fe ratio of the charge determines the Mn content of the final product. Ores from various sources are therefore blended to achieve the ideal ratio and to limit the contents of the deleterious components silica, alumina, and phosphorus in the raw material mix.
- The raw material is crushed and screened to 5-30mm. alternatively, sintered or pelletized fine ore can be used. Some deleterious components can be partially removed from the ore prior to melting by dense – medium separation or flotation. Slagging components can be added to the sintered or pelletized ore, which results in cost savings in the blast furnaces.

BLAST FURNACE OPERATION

- In comparison to iron making, high gas temperatures are required in ferromanganese production because of manganese (II) oxide takes place at a higher temperature than is required for the reduction of wustite.
- This is achieved by oxygen enrichment of the hot blast or, in the case of SFPO, by heating the blast with non-transferred arc plasma torches. The plasma arc increases the flame temperature from 2200°to2800°C and considerably reduces the coke consumption, which usually ranges from 1270 to 2000kg/t.
- The recovery of manganese in the alloy is usually 75-85%.This is influenced by the MnO content of the slag, the slag to metal ratio, and losses in the flue gases.
- The MnO content of the slag is highly dependent on the basicity ratio (CaO+MgO)/SiO₂

THE REDUCTION PROCESS IN THE BLAST FURNACE

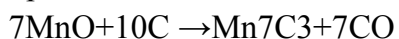
- The reduction of the higher manganese oxides to manganese (II) oxide takes place in the upper zone of the shaft .These generally occur below 900°Cand are indirect. The reactions are exothermic and the heat generated causes high top temperatures and necessitates water cooling of the furnace top.
- The reduction of manganese (II) oxide;



is highly endothermic, in contrast to the weakly endothermic reduction of wustite. This requires higher temperatures and, consequently, higher coke rates are required for the smelting of ferromanganese in blast furnaces.

PRODUCTION OF HIGH CARBON FERROMANGANESE IN ELECTRIC ARC FURNACES:

- The material descends rapidly down the side of the electrode into the semi-active zone where preproduction of higher manganese oxides to MnO takes place. Thereafter, the material moves into the active zones of the furnace where reactions take place between the manganese oxide in the melt and the coke particles in the coke bed:



- Equilibrium between the slag and metal was thought to exist under each electrode, and further from the electrode, layers of unreacted ore and coke were found to be present.
- This suggests that heat is concentrated under each electrode. The path of electrical transfer was deduced to be from the electrode tip through the coke bed and into the alloy layer
- The efficient production of high-carbon ferromanganese therefore depends on the degree of the reduction of MnO by carbon as well as the preproduction that occurs in the upper region of the furnace
- The ratio of CO and CO₂ in the off-gas is important and can be used to monitor the condition of the furnace. The higher the CO₂ content of the off-gas, the higher is the energy efficiency of the process, because the reducing potential of the gas is being more fully utilized.

- Good operation of the furnace is indicated by a $\text{CO}_2/(\text{CO}_2+\text{CO})$ ratio of 0.55. This ratio, as well as the MnO content of the slag, can be used to control the coke rate of the furnace. Undercooking of the furnace is indicated by high MnO content of the slag and a low CO_2 content in the off-gas.

FERROCHROMIUM

- Ferrochromium is a master alloy of iron and chromium, containing 45-95% Cr and various amounts of iron, carbon, and other elements. The ferrochromium alloys are classified by their carbon content;
 1. High-carbon ferrochromium with 4-10 % C
 2. Medium-carbon ferrochromium with 0.5-4% C
 3. Low-carbon ferrochromium with 0.01-0.5% C
- The mechanical and chemical properties of steel can be improved by alloying it with ferrochromium. Chromium combined with nickel gives stainless steel excellent chemical resistance.

RAW MATERIALS

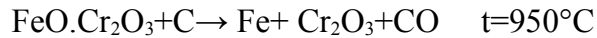
- The only raw materials for the production of ferrochromium are chromite ores. The mineral chromite has spinel structure and its formula may be written as $(\text{Fe}^{2+}, \text{Mg})\text{O} \cdot (\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_3$.
- A high Cr:Fe ratio is advantageous to produce an alloy with high chromium content. In the production of high-carbon ferrochromium, which is by far the alloy in greatest demand, generally a lumpy type of chromite ore is necessary. The submerged arc smelting of high-carbon ferrochromium by the direct reduction of carbon in large Low-shaft electric furnaces generally require lumpy chromite ores to allow the reaction zone to the top of the furnaces where the burden is continuously charged.
- The reducing agent for chromite is usually carbon in the form of coke; its contents of S and P should be low. Silicon as a reducing agent is used in the form of ferrosilicochromium or ferrosilicon to produce low-carbon ferrochromium. Fluxing agents, e.g. Quartzite or alumina and lime, are charged with the burden for slag formation. In the carbothermic production of ferrosilicochromium, chromite and quartzite are used as the raw materials

PRODUCTION

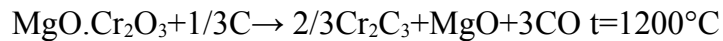
- The oxides of iron and chromium present in the chromite can be readily reduced at high temperature with carbon. Because of the tendency of chromium to form carbides, a carbon containing alloy is obtained.
- The oxides can also be reduced with silicon, aluminum, or magnesium. However, only carbothermic and silicothermic reductions are used commercially. The reducibility of chromite depends on its composition.
- A chromite rich in iron ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) can be reduced by carbon at lower temperature than ore rich in magnesium ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$). Carbides with higher carbon content formed initially at lower

temperature react at higher temperature with Cr_2O_3 and form carbides with lower carbon content; finally, reduction of SiO_2 starts at higher temperature

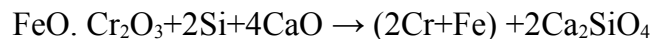
- Therefore, production of ferrosilicon-chromium alloys requires high temperature.
- In practice the reactions are somewhat more complicated because iron-containing chromium carbides are formed. In high-carbon ferrochromium, the double carbide $(\text{Cr,Fe})_7\text{C}_3$ is present. IN this compound, two to four Cr atoms can be substituted by iron atoms.



- For the Cr_2O_3 reduction:



- Because the difference in temperature between these two reactions is slight and because iron also facilitates reduction of chromium oxide, selective reduction of iron is difficult.
- In carbothermic reduction process, unreduced oxides from the chromite ($\text{MgO}, \text{Al}_2\text{O}_3$) and from the gangue are collected in a slag, which generally contains 30 % SiO_2 , 30 % MgO and 30% Al_2O_3 . The remaining 10% is composed of $\text{Cr}_2\text{O}_3, \text{CaO}, \text{MnO}$ And FeO . Control of lag composition is important with respect to melting temperature and fluidity.
- Low-carbon ferrochromium is produced by the silicothermic reduction of chromite ore. Silicon is used in the form of ferrosilicochromium, which is produced in submerged arc furnaces by carbon reduction of chromite ore and quartzite. The solubility of carbon in the FeSiCr alloy depends on the silicon content; if the silicon content is higher, the carbon content is lower.
- The reduction of Cr_2O_3 by Si is enhanced by addition of lime (CaO), which reduces the activity of SiO_2 in the slag. The reduction may be written as follows:



FERRONICKEL

- The rotary kiln electric furnace smelting process is now used almost universally for the production of ferronickel from oxide ores.

ROTARY KILN-ELECTRIC FURNACE PROCESS

- In the electric furnace the calcined ore was smelted with reductant to form immiscible layers of slag and ferr nickel.
- The New Caledonian ores, with their high magnesia and silica contents (2.5%Ni, 10-15%Fe), require no additional flux for slag formation.
- Virtually all the nickel and 60-70% of the iron in the ore are reduced to metal to yield a ferronickel grading about 20%Ni; the slag contains only 0.1%Ni.
- The degree of reduction achieved in the kiln depends on the composition of the ore and on the reactivity of the reductant. Iron and nickel silicate minerals are generally less reactive than nickel oxide minerals.

- Usually lignite's and charcoal are the most reactive reductants, and high volatile coals are more reactive than low-volatile coals, anthracite, or coke.
- Typically, under optimum conditions, up to 40% of the nickel is reduced to metal in the kiln, while the iron oxides are reduced to iron (II) oxide (FeO)
- In the electric furnace the charge must be heated to 1400-1650°C to permit the separation of distinct slag and metal phases.
- Operation of the electric furnace is simplest when the slag melting temperature is higher than the metal melting temperature (1300-1400°C). For such a system the furnace is operated with a covered bath.
- The hot ore charge is allowed to build up on top of the molten slag, and the electrodes are not immersed in the slag layer. Under these conditions much of the reduction reaction occurs in the hot charge layer before it melts.
- The high-iron limonite ores, which produce slags with melting points well below the melting point of the metal phase, can be smelted if the distance between the electrode tips and the slag metal interface is reduced significantly. The electrodes must therefore penetrate deeply into the molten slag layer

FERRONICKEL PROCESS

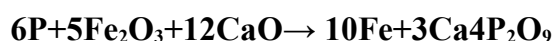
- In the rotary kiln-electric furnace process excess carbon is normally added to the furnace charge to ensure quantitative reduction of nickel oxide. As a result more iron oxide is reduced to metal than is desirable, decreasing the ferronickel grade and leaving a high residual carbon level, typically 1-3% in the product.
 - In the Uginde Process the ore is dried and calcined in a rotary kiln and melted in an electric furnace without addition of reductant to produce a melt of iron and nickel oxides.
 - No slag separation occurs in the electric furnace. The molten ore is transferred to a ladle furnace where it is reduced by reaction with ferrosilicon at 1650°C. The two phases are mixed by repeated pouring of the mixture from one ladle furnace to another
 - The nickel oxide and some of the iron oxide are reduced to metal. The balance of the iron is removed as slag.
- $2\text{Fe}_2\text{O}_3 + \text{FeSi} \rightarrow 4\text{FeO} + \text{SiO}_2 + \text{Fe}$
- $2\text{NiO} + \text{FeSi} \rightarrow 2\text{Ni} + \text{SiO}_2 + \text{Fe}$
- $2\text{FeO} + \text{FeSi} \rightarrow 3\text{Fe} + \text{SiO}_2$
- The reduced ferronickel contains 30-50% Ni and very low levels of carbon and sulfur.
 - The majority impurity is phosphorus.

FALCONDO FERRONICKEL PROCESS

- The Ore is carefully blended to maintain a constant chemical composition, particle size, and moisture content, so that it can be briquetted without a binder.
- The briquettes are calcined and reduced in twelve open-top shaft furnaces.
- The hot reducing gas at 1250°C is first cooled to 1150°C before being supplied to the shaft furnace through the primary tuyeres.
- The gas flows upwards, countercurrent to the ore briquettes which are fed to the open top of the furnace
- The gas reduces the nickel oxides to metal and the iron oxides to FeO.
- The hot reduced briquettes are discharged from the bottom of the shaft furnace at 880°C and are transferred to one of three electric furnaces. The crude ferronickel, which is tapped at 1475-1500°C, contains 32-40% Ni.
- The slag, containing about 0.15%Ni, is tapped at 1500-1600°C. The crude ferronickel, which typically contains only 0.15%S, 0.03%P, 0.04%Si, and 0.02%C, is refined to remove sulfur and phosphorus.

REFINING OF FERRONICKEL

- Crude ferronickel produced by the conventional rotary kiln-electric furnace process usually contains high levels of carbon and sulfur.
- Sulfur is generally removed under reducing conditions by adding soda ash, lime, or calcium carbide to the molten ferronickel. Sulfur reacts with the fluxes to form sodium or calcium sulfides, which are slagged off with the silicates formed by reaction of flux with silicon;
 - $3\text{Na}_2\text{O} + 2\text{S} + \text{Si} \rightarrow 2\text{Na}_2\text{S} + \text{Na}_2\text{SiO}_3$
 - $\text{CaC}_2 + \text{S} \rightarrow \text{CaS} + 2\text{C}$
- Removal of silicon, carbon, and phosphorus is normally conducted in an oxygen-blown converter or an oxygen lanced ladle. Phosphorus is oxidized either by blowing the melt with oxygen or by adding iron ore and fluxing the phosphorus (V) oxide with lime:



- The slags are removed by skimming after each refining step.

FERROTUNGSTEN

❖ COMPOSITON

- Commercial ferrotungsten is a tungsten-iron alloy containing at least 75%W, and having a very fine grained structure and a steel-gray appearance.

❖ PRODUCTION

- The raw materials used for ferrotungsten production are rich ores or concentrates containing the minerals wolframite, hubnerit, ferberite, and scheelite.
- Ferrotungsten can be produced by carbothermic reduction in an electric arc furnace or by metallothermic reduction aluminum.
- The carbothermic or silicocarbothermic method is preferred for cost reasons.

❖ CARBOTHERMIC PRODUCTION

- Because of the high melting point of ferrotungsten, the so-called solid block melting process is normally used, as tapping off is not possible at the furnace temperatures that are required.
- In this process, the ferrotungsten accumulates in the hearth of the furnace vessel, which is constructed in sections. After the desired weight has been produced, the furnace lining is removed and the metal ingot can be removed after cooling.
- The solid block is cleaned, crushed, and sorted

CARBOTHERMIC AND SILICOTHERMIC PRODUCTION

- This process is carried out in three successive stages in a three-phase electric arc furnace lined with magnetite. Of the oxygen in the WO_3 , 60% reacts with carbon and 40% with silicon.
- In the first stage, ferrotungsten is produced by sub stoichiometric carbon reduction. This ferrotungsten is formed in a pasty consistency under a WO_3 -rich slag, and can be scooped out with ladles. Details of the individual processes are as follows:
- Stage1: reduction of tungsten ore concentrates by carbon under a WO_3 -rich slag and scooping out the ferrotungsten
- Stage2: Reduction of the WO_3 -rich slag with FeSi75 and addition of scrap iron. Tapping off the low- WO_3 slag. The metal, with reduced tungsten content remains in the furnace.
- Stage3: refining of the low-tungsten metal by adding tungsten concentrates. A WO_3 -rich refining slag is formed, and the tungsten content of the metal increases.
- The advantages of the process is the continuous method of operation; thus the furnace can be operated for considerably longer periods without interruption for relining than in the solid block process.

METALLOTHERMIC PRODUCTION

- Tungsten oxide can be reduced by silicon and/or aluminum. Compared with carbothermic reduction, metallothermic production of ferrotungsten requires purer raw materials, as the reactions proceed very rapidly, and the impurities are chemically reduced as well as the raw materials.
- The tungsten concentrates in finely divided form are mixed with coarsely powdered aluminum and silicon. Pure silicon or ferrosilicon cannot be used, as these would not give a self-sustaining reaction, the heat evolved being insufficient to melt the ferrotungsten and slag formed. Aluminum and silicon in the ratio 70:30 are therefore used.
- The reaction mixture is charged into a refractory-lined furnace vessel and preheated to 400-500°C.
- The reaction is started at the top by igniting initiators, which are mixtures of BaO_2 and aluminum powder. A purely aluminothermy mixture burns completely in a few minutes, but silicothermic –

aluminothermic mixtures react more slowly. After cooling, the furnace vessel is removed, and the blocks of metal and slag separated. This method produces ferrotungsten ingots of 700-2000 kg

- The metal ingot is cleaned, crushed, and sorted. Pieces with adhering slag are sent back for remelting.
- The metallothermic production process has lost much of its importance in recent years, owing to the high costs of the aluminum and silicon reducing agents, and the necessity for using pure and therefore expensive raw materials.
- Advantages of the process include the simple, low-cost plant, and the minimal tying-up of materials resulting from the short processing time.
- The tungsten yield is 96%

❖ FERROBORON

- Ferroboron is basically an iron-boron alloy containing 10-20%B. It is used mainly in the steel industry.
- Ferroboron was first produced in 1893, by HENRI MOISSAN, from boric acid, iron, and carbon in a single phase electric-arc furnace lined with carbon.
- The introduction of the thermite reaction by GOLDSCHMIDT in 1898 led to the aluminothermic reduction of boric oxide to ferrobaboron, for years the main commercial method for producing ferrobaboron. Recently though the carbothermic process has again found use for the production of ferrobaboron.

RAW MATERIALS

- The following boron minerals can be used for the manufacture of ferrobaboron:
- Colemanite (51%B₂O₃),
- pander mite (48% B₂O₃),
- Priceite (51% B₂O₃), and
- Boracite (62% B₂O₃).

However, the raw materials most commonly used are boric oxide (=99% B₂O₃) and boric acid(=57% B₂O₃)

PRODUCTION

- Boric oxide can be reduced by carbon, aluminum, or magnesium.
- Reduction by silicon is incomplete. For commercial production, either reduction by carbon (carbothermic or endothermic) or reduction by aluminum, sometimes with some magnesium (aluminothermic or exothermic) is usual.

CARBOTHERMIC PRODUCTION

- In order to produce a carbothermic ferroboration with a low content the boron content must be high, the higher the boron content the lower the carbon solubility and thus carbon pick up.
- The reduction of boric oxide by carbon requires high temperature; the process is carried out in an electric arc furnace.
- In a Japanese patent their carbothermic production of ferroboration from boric acid, iron powder, and charcoal in a Heroult-type electric-arc furnace with carbon lining is claimed. One example describes the production of an alloy with 10.3% B, 2% Si and 0.98% C in a three phase electric –arc furnace. The mix is 100 parts boric acid, 135.8 parts iron powder (92.9%Fe), and 57 parts charcoal powder. The boron recovery is 81.7%.
- The production of ferroboration from pig iron and boric acid in an electric arc furnace with a final oxygen blow leads to an alloy with 16.3%B, 0.03-0.06%Al, and 0.03-0.06%C.the boron recovery in small scale runs is said to be 60-65%.

ALUMINOTHERMIC PRODUCTION

- Ferroboration can be made batch wise in convenient way by the reduction of boric oxide and iron oxide with aluminum powder. Some magnesium in the aluminothermic mix is beneficial; magnesium is the stronger reducing agent at the temperatures below its boiling point, whereas aluminum is more effective above the boiling point of magnesium, where such metallothermic reactions generally take place
- The aluminothermic coreduction of boric oxide and iron oxide (Fe_2O_3) is highly exothermic, and only a little additional energy is necessary for a self-propagating reaction.
- The thoroughly mixed compounds are charged into refractory-lined pot and ignited, either the whole mix or by igniting a starting mix, the rest then charged as the reaction proceeds over a few minutes.

The liquid metal slag separate on account of differing densities, and after cooling the metal button, up to 1500 kg, is removed. After mechanical cleaning, the mineral button is broken and crushed to the desired size.

❖ FERRONIUM

- Approximately 85-90% of the total niobium production is used in the steel industry in the form of iron niobium alloy containing 40-70% niobium.

❖ PRODUCTION

- Ferro niobium is usually produced by aluminothermic reduction of niobium oxide ores with the addition of iron oxides ores, with the addition of iron oxides if the niobium ore used contains insufficient iron.
- The starting materials are mainly columbites and pyrochlore concentrates.
- The enthalpy of the reaction between Nb_2O_5 and Al is -276.1kJ/mol Al , which is lower than the threshold value for self-sustaining aluminothermic reactions

- The mixture must therefore either be preheated or mixed with oxygen releasing compounds such as BaO₂, CaO₂, etc. Concentrates with lower percentages of niobium can also be treated by the aluminothermic process in an electric arc furnace.
- Also, a two stage electroaluminothermic process for the production of Ferro niobium from columbite has been developed. The method of operation is to charge the mixture of niobium concentrate with the additives to refractory lined reaction vessels.
- Either the whole mixture is reacted, or a small amount is set aside, ignited with a special exothermic mixture, and added to the bulk mixture.
- The molten reaction product is allowed to solidify in the furnace, and the block of metal separates from the slag.
- After cooling, it is broken into pieces of the required size.

❖ FERROTITANIUM

- Ferrotitanium is described in DIN 17566 as a master alloy containing at least 28%Ti, obtained by reduction of the corresponding raw materials or their concentrates. The International Standard for ferrotitanium is ISO 5454-1980, which specifies a Ti content of at least 20% and allows greater variation in the Al content.

❖ PRODUCTION

- The starting materials for the production of ferrotitanium are limonite, leucoxene, perovskite, and slag concentrates produced from limonite.
- Because of the increasing availability of titanium scrap, this is also used to an increasing extent for the production of ferrotitanium.

❖ REDUCTION WITH CARBON.

- Carbothermic production in electric arc furnaces leads to high carbon contents in the ferrotitanium. However, as the main use of ferrotitanium is to combine with the carbon in steel, the presence of carbon in the ferrotitanium is undesirable, and this production method is therefore now hardly used.

❖ METALLOTHERMIC PRODUCTION.

- Ferrotitanium containing 28-50% Ti and 4.5-7%Al. These are mainly produced by the aluminothermic process. The reduction of TiO₂ by Al proceeds via TiO.
 - $3\text{TiO}_2 + 2\text{Al} \rightarrow 3\text{TiO} + \text{Al}_2\text{O}_3$
 - $3\text{TiO} + 2\text{Al} \rightarrow 3\text{Ti} + \text{Al}_2\text{O}_3$
- If there is too much TiO₂ in the reaction mixture, TiO can be formed as a third phase besides the metal and slag. In the aluminothermic production of ferrotitanium there is a high consumption of aluminum, as it reacts both with the iron oxide in the ilmenite and with the oxygen –producing substances added to increase the exothermicity.
- An aluminothermic mixture, consisting, for example of 4320 kg Australian ilmenite(58.55%TiO₂), 480 kg rutile (96.7% TiO₂), 190 kg calcined limestone, 107 kg potassium

perchlorate, and 1693 kg Al powder, is placed in a refractory-lined combustion vessel and ignited to start the reaction. After cooling, a 2250 kg block of ferrotitanium is obtained containing 39.8%Ti, 6.7%Al, 3.4%Si, and 0.02%C, which separates well from the slag. The titanium yield is 50%, and the specific consumption of aluminum is 1.89kg Al/kg Ti.

❖ **PRODUCTION FROM TITANIUM SCRAP AND SPONGE.**

- As the availability of titanium scrap is increasing with the growth in the consumption of titanium, it is being increasingly used for the production of ferrotitanium and ferrotitaniumsilicon.
- Because of its low melting point (1100°C) the alloy containing 70% titanium melts comparatively readily when alloyed with iron in an induction furnace, in an arc furnace with consumable electrodes under vacuum or argon, or in an electro slag melting furnace.