

LECTURE NOTES
ON
Manufacturer of Sponge Iron & Ferro alloys

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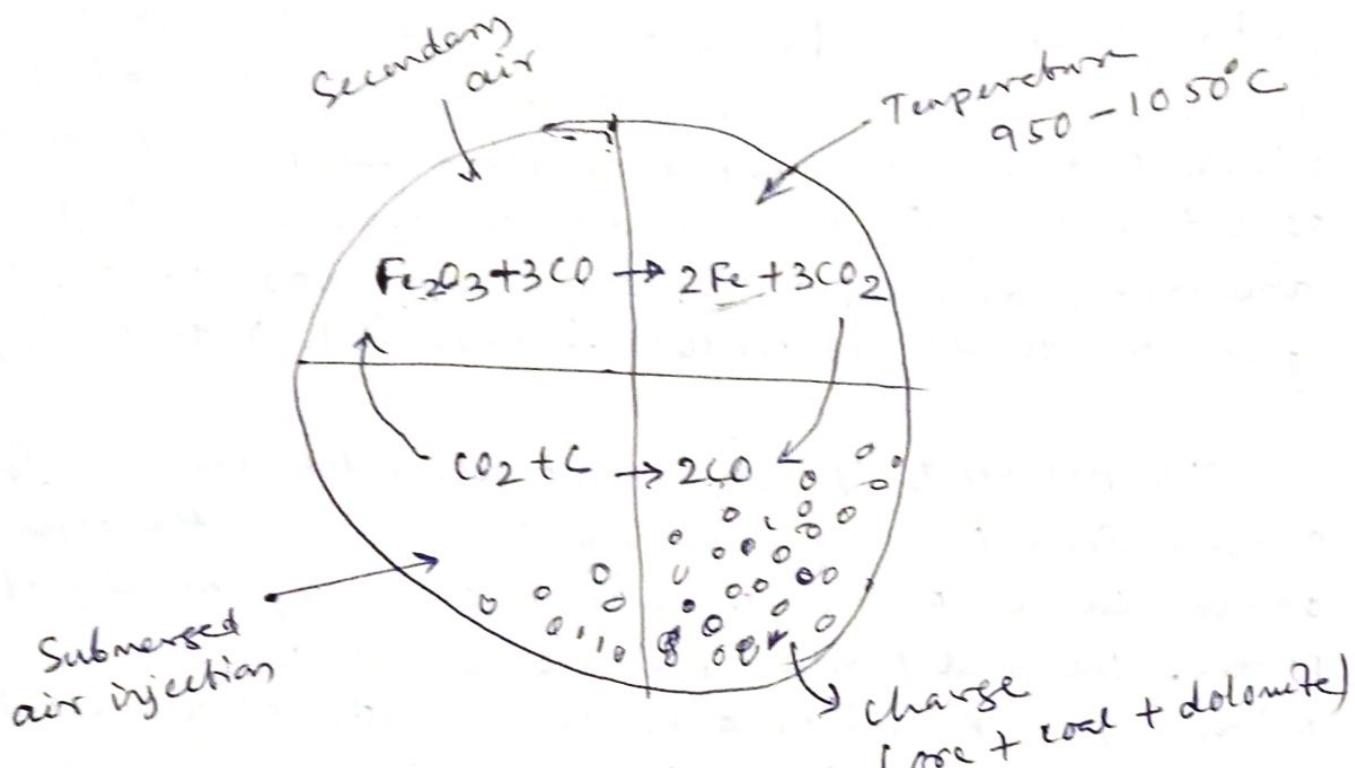
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Physical Chemistry of the Process

Introduction → Production of steel through the conventional blast furnace requires coking coal of which India has limited source. Therefore, evolution of a technology for the reduction of iron ore using abundantly available non-coking coal was contemplated giving rise to direct reduction iron (DRI) technology.

The process of sponge iron involves the removal of oxygen from iron ore. During this process, the deoxygenation causes micro-pores in the ore body making it porous. The final product, when observed under a microscope, resembles a honeycomb structure, looking spongy in texture, hence the name sponge iron. Iron ore (haematite) and non-coking coal are the prime raw materials for the production of sponge iron. These are charged into a rotary kiln in requisite proportion along with some dolomite. Coal plays a dual role in the process by acting as a reductant as well as a fuel for providing heat to maintain the requisite temperature inside the kiln at $950^{\circ} - 1050^{\circ}\text{C}$. The reduction process occurs in solid state. The crucial factor in this reduction process is the controlled combustion of coal and its conversion into carbon monoxide to remove oxygen from the iron ore. The overall process requires a duration of approximately ten to twelve hours inside the kiln, during which iron ore is optimally reduced and discharged to a ~~rotary~~ cooler for cooling.

below 120°C , before coming out into the finished product circuit



(Fig- Rotary kiln Cross Section)

DRI is a high quality metallic product produced from iron ore, used as a feed stock in electric arc furnaces, blast furnaces, and other iron & steel making processes.

Hot briquetted iron (HBI) is a denser and compacted ~~form~~ form of DRI designed for the ease of shipping, handling and storage.

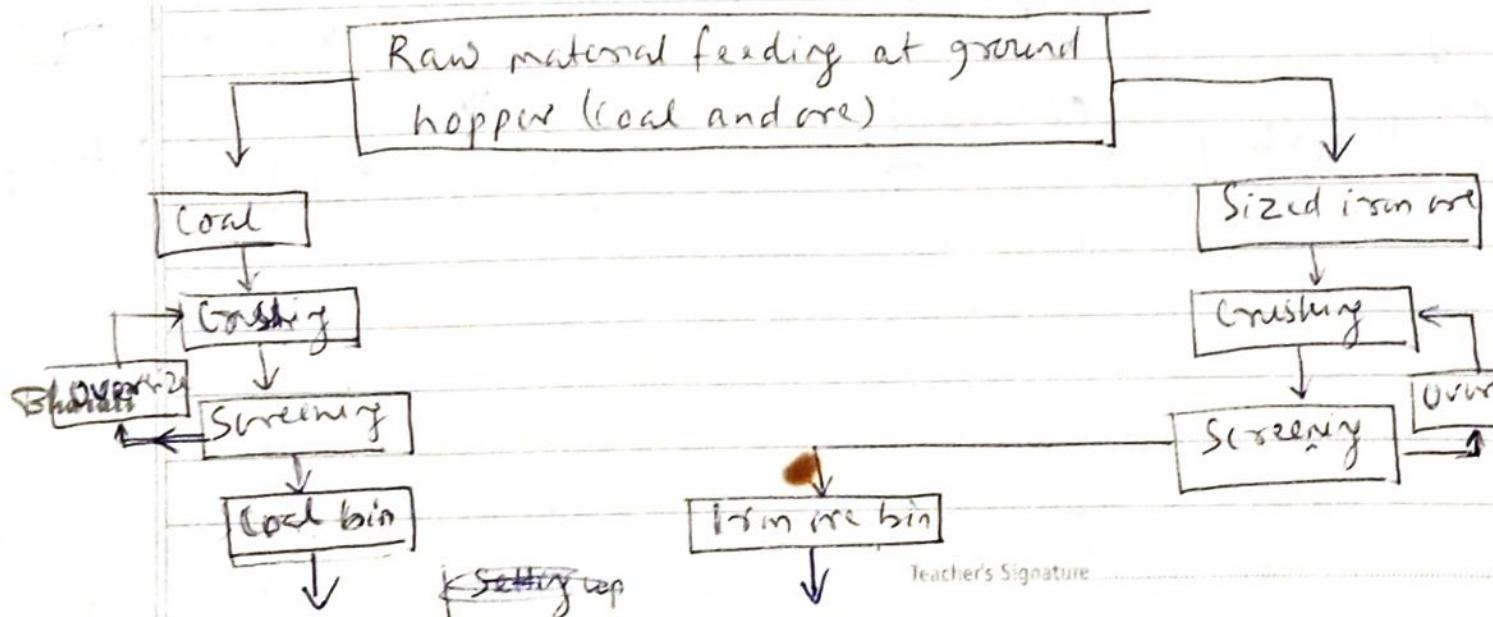
Composition of DRI →

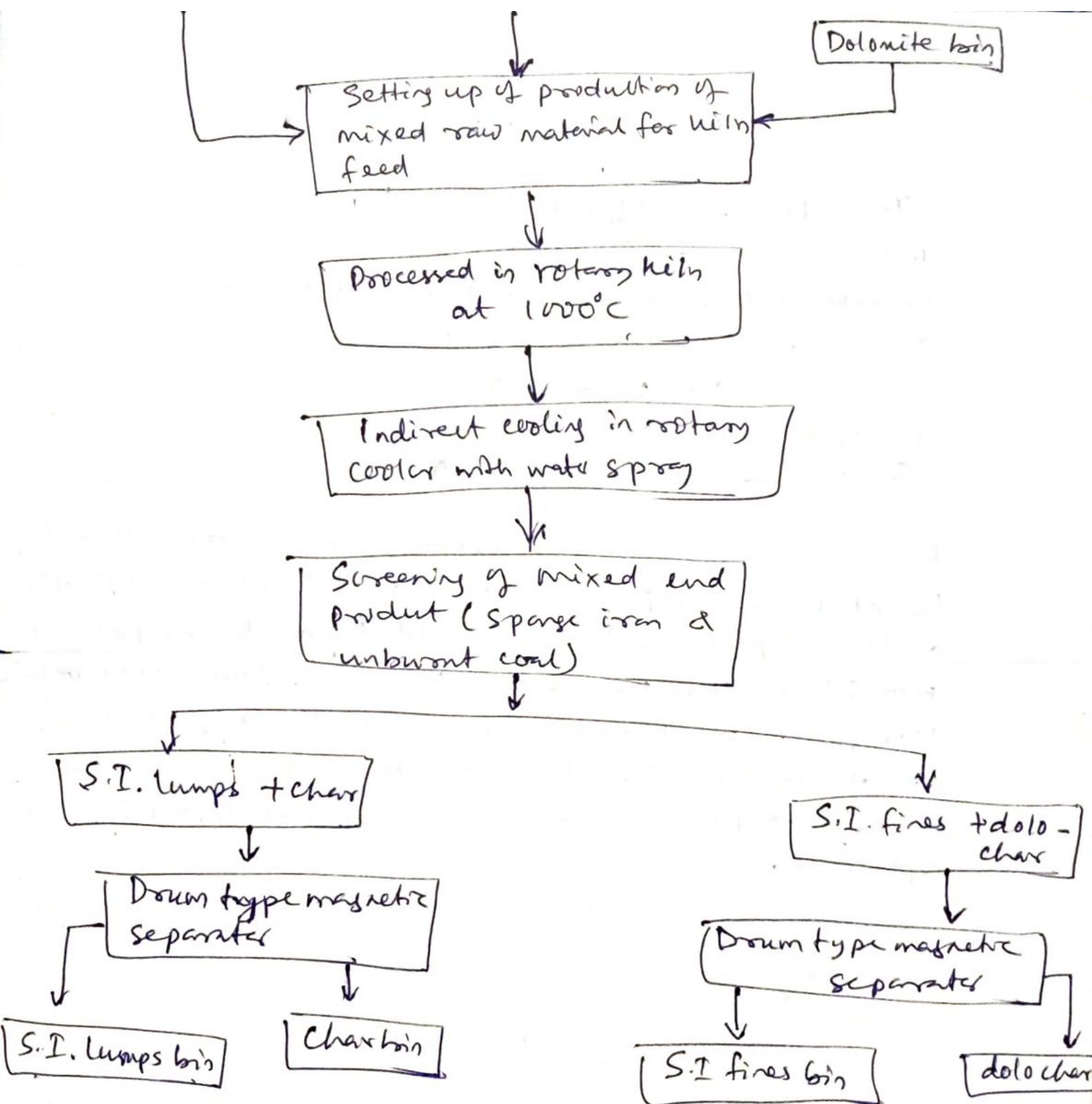
The usual chemical composition of DRI / HBI traded in international market is as follows:

Total Fe — 94-95%
 Metallic iron — 88-90%
 Degree of metallisation — $93-95 \pm 1.2\%$.
 Carbon — $1.0 - 1.5 \pm 0.3\%$.
 Sulphur — $0.0005 - 0.015\%$.
 Phosphorus — $0.02 - 0.09\%$.
 Silica — $1.0 - 2.0\%$.

For maximum yield, the metallic iron content should be at the higher possible level with sulphur and phosphorus as low as possible. Carbon should be as low as possible with silicon less than 2.5% to ensure lower slag volume, less power consumption for achieving higher productivity. Size of the DRI should be less than 3 mm fraction to prevent losses during charging and handling operations.

Process flow chart for sponge iron unit





(2)

| | |
|------|------------|
| Date | 10/12/2022 |
|------|------------|

Evolution & growth of sponge iron plant in Odisha

Orissa Sponge Iron Limited (OSIL) was established in the year 1979, with a 100,000 TPA, at Polaspanga area of Keonjhar district. At present (30.4.2009), there exists around 107 number of sponge iron plants in the state. The trend of growth of sponge iron plants in Orissa is given below:

| <u>Year</u> | <u>Plants</u> |
|---------------|---------------|
| Before - 2000 | 07 |
| 2000-2001 | 4 (11) |
| 2001-2002 | 5 (16) |
| 2002-2003 | 4 (20) |
| 2003-2004 | 16 (36) |
| 2004-2005 | 26 (62) |
| 2005-2006 | 18 (80) |
| 2006-2007 | 13 (93) |
| 2007-2008 | 14 (107) |

Sponge iron plants operating in different districts of Odisha

| <u>Sl. No.</u> | <u>District</u> | <u>No. of units</u> | <u>Total no. of units</u> |
|----------------|-----------------|---------------------|---------------------------|
| 1. | Sundargarh | 47 | 111 |
| 2. | Keonjhar | 20 | 54 |
| 3. | Angul | 3 | 04 |
| 4. | Dhenkanal | 04 | 10 |
| 5. | Jajpur | 05 | 11 |
| 6. | Mayurbhanj | 01 | 02 |

| | | | | |
|--------------|------------|------------|--|-----------------|
| 7. | Sambalpur | 10 |  | 20 |
| 8. | Iharsuguda | 13 | | 28 |
| 9. | Cuttack | 04 | | 07 |
| Total | | 107 | | 247 nos. |

List of sponge iron plants in odisha As on (14.12.2005)

| Sl. No | Name of Industry | Location | District |
|--------|---|------------------------------|------------|
| 1. | M/s Shisti Ispat Ltd (Sponge iron div.) | Budha Kata | Sundergarh |
| 2. | M/s Sri Mahavir ferro- alloys pvt. limited | Kalunga Industrial Estate | " |
| 3. | M/s Suraj products Ltd. | Rajgangpur | " |
| 4. | M/s Mangalam Ispat (P) Ltd | Kreamunda | " |
| 5. | M/s Neepaz Metalliks pvt. Ltd. | Kreamunda | " |
| 6. | M/s OCL India Ltd. | Lomlozi (Rajgangpur) | " |
| 7. | M/s Maa Tarini etc. India (P) Ltd | Kalunga | " |
| 8. | M/s T.R. Chemicals (P) Ltd | Barpali (Rajgangpur) | " |
| 9. | M/s Prabha sponge (P) Ltd. | Ihagar pur (Rajgangpur) | " |
| 10. | M/s Shree metalliks Ltd. | Mulkund pur | Anugul |

| <u>Name of the Industry</u> | <u>Location</u> | <u>District</u> |
|--|------------------------------|-----------------|
| 11. M/s Shiva Metalliks Ltd. | Mancheswar | Cuttack |
| 12. M/s Shree Jagannath Metalliks Industries | Polaspanga | Keonjhar |
| 13. M/s Orion Ispat Ltd | Ranchandrapur | Keonjhar |
| 14. M/s N.K. Bhajani (P) Ltd | Barbil | Keonjhar |
| 15. M/s Surya Sponge Iron Ltd | Kalkala | Tajpur |
| 16. M/s Pawan Jay sponge Iron Ltd | Kunjharia | Sundargarh |
| 17. M/s Orissa s sponge Ltd | Polaspanga | Keonjhar |
| 18. M/s Utkal Metalliks Ltd. | Kalunga Industrial Estate | Sundargarh |
| 19. M/s Shiva Shakti sponge iron Ltd | Sukruli | Mayurbhanj |
| 20. M/s Ganeshha Sponge Metalliks Ltd | Chandrahariharpur | Sundargarh |
| 21. M/s Hima Ispat Pvt Ltd | Barpada | Keonjhar |
| 22. M/s Grewal Associates (P) Ltd | Barbil | Keonjhar |
| 23. M/s Pawansut sponge (P) Ltd | Badmale | Sambalpur |
| 24. M/s L+N. Metalliks (P) Ltd | Siripura | Jharsuguda |
| 25. M/s BeeKay steels and power Ltd | Nalda | Keonjhar |
| 26. M/s Khedaria Ispat Ltd | Kuarmunda | Sundargarh |
| 27. M/s Cracker India Alloys (P) Ltd. | Deojhar | Keonjhar |
| 28. M/s Sponge Udyog (P) Ltd | Kalunga | Sundargarh |

| | | | |
|--|---------------------------|---------------------------|------------|
| 29. M/s Sunrit Metalliks (P) Ltd | Bardil | Korjhar | |
| 30. M/s Arati Steels (P) Ltd | Athagarh | Cuttack | |
| 31. M/s Rungta Mines Ltd (Sponge iron division) | Bardil | Korjhar | |
| 32. M/s Agrasen sponge (P) Ltd | Mandla Khadar | Sundergarh | |
| 33. M/s Bajrang Ispat (P) Ltd | Kuarmunda | Sundergarh | |
| 34. M/s Vedvyas Ispat (P) Ltd | Kuarmunda | Sundergarh | |
| 35. M/s Sri Ganesh sponge Iron (P) Ltd | chipinda | Korjhar | |
| 36. M/s Tata sponge Iron Ltd | Joda | Korjhar | |
| 37. M/s Kusum power Met (P) Ltd. | chipinda | Kalunga Industrial Estate | Sundergarh |
| 38. M/s Meta sponge (P) Ltd | Kuarmunda | Sundergarh | |
| 39. M/s Govindam project (P) Ltd | Thakurani | Korjhar | |
| 40. M/s OMDC Ltd | kalunga Industrial Estate | Sundergarh | |
| 41. M/s Puja sponge (P) Ltd | Hirwa | Thasuguda | |
| 42. M/s SMC power generation (P) Ltd | Kalunga Industrial Estate | Sundergarh | |
| 43. M/s Kalinga sponge Iron Ltd | Karmundo | Sundergarh | |
| 44. M/s Rungta Mines Ltd | | | |

↓ ↓ ↓ ↓

Status of S.I. Plants in odisha

Since 2002, India has been the largest producer of sponge iron in the world. (about 20% from India)

most of it is produced primarily through the coal based method of production..

In odisha - 10~~7~~ sponge iron plants 2014

coal based industries are extremely polluting

Red categories industries - Sponge iron plants.

(highest pollution, ~~so~~ cause serious health hazards.)

During operation, it emits SO_2 , CO , CO_2 unburnt carbon, silica particles. \rightarrow causing air pollution.

DR plants

Sundargarh - 47 DR plant

Koraput - 20

Jharsuguda - 13

Sambalpur - 10

Tajpur - 5

Dhenkanal - 4

Angul - 3

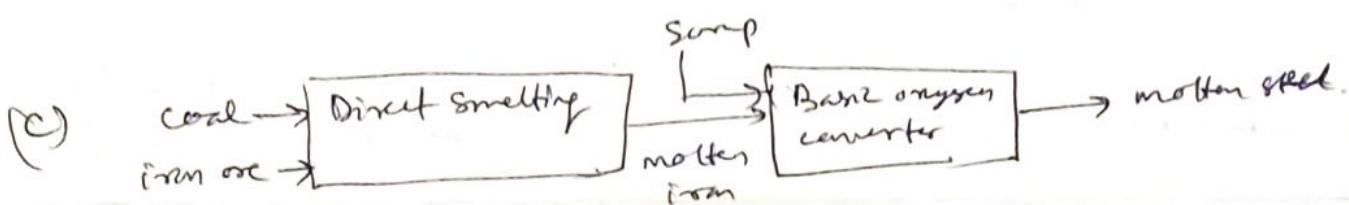
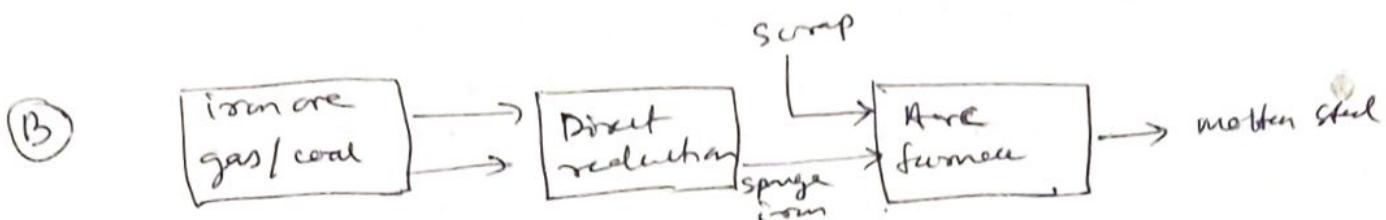
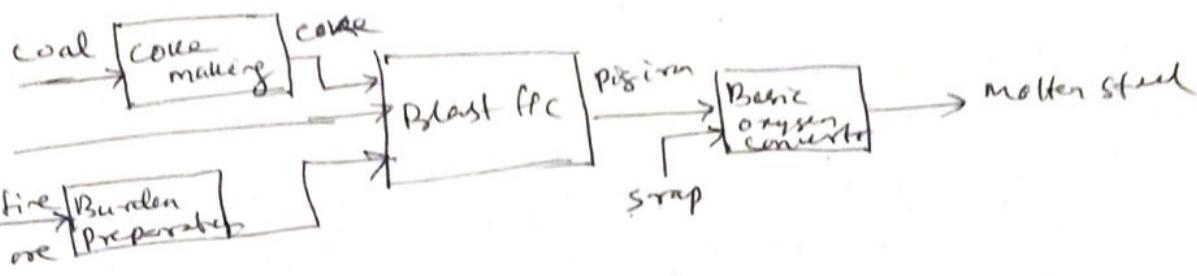
Mayurbhanj - 1

31-12-2008 - 33140 TPD (Tonne per Day) Total

Alternative methods of ironmaking

(1)

At present there are three basic methods of making liquid steel beginning with iron ore or scrap, as shown in the figure.



Direct Reduction process

✓ Sponge iron
The processes that produce iron by reduction of iron ore below the melting point of iron are generally called direct reduction processes and the products are known as Direct reduced iron (DRI). That means, iron produced as a solid by the reduction of iron oxide is known as direct reduced iron or sponge iron. It is often compacted to reduce porosity to convert into hot briquetted iron (HBI) for storage or sale.

In direct reduction process, the iron ore in the form of lumps or pellets, is reduced to the solid state either by solid or gaseous reducing agents. Reformed natural gas or non-coking coal is generally employed as a reductant as well as primary source of energy. The final product from all DR processes is a solid, which has to be melted during steel making. In India, coal based direct reduction processes are more popular because of restricted and localized availability of natural gas.

History 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 use charcoal as reductant fuel. The product of these early smelting process was a sponge mass of coalesced ~~grains~~ granules of nearly pure iron intermixed with considerable slag. ~~Heated~~ Usable articles of wrought iron were produced by hammering the sponge ~~iron~~ mass, while still hot, to expel most of the slag and compact the ~~iron~~ mass. By repeated heating and hammering, the iron was further freed of slag and forged into the desired shape.

In modern times, sponge iron has found increasing use in the manufacture of wrought iron and as a substitute of scrap during steel making.

Chronological evolution of sponge iron making processes

The basic concept of DR process was mooted more than 3000 years ago. This was the chronology of development of iron making because the lower temperatures required for solid state reduction of iron ore ($850-1050^{\circ}\text{C}$) were more easily attainable in early times than required for melting.

DR was first successfully commercialized ^{when}. The Hagnas process was developed in Sweden in 1909, followed by the grant of Patent for the Wiberg process in 1918, again in Sweden in 1952.

Another DR process (Norsk Stahl) was patented in 1925 in Bochum, Germany, but DR really got off the ground with installation of a HYL plant in Mexico in 1957. Since then around 80 DR units have been installed or are under construction in various countries of the world.

In India, DR was widely ~~practised~~ practised on ancient times and steel made in small quantities through this route.

Indians were the first to master the technique of producing steel applying the DR technique using wood charcoal as reducing-cum-heating agent.

Reasons for Rapid growth of DR processes See also *

Reasons for the tremendous growth of the DR process could be attributed to the advantages of using sponge iron or DRI in electric arc furnaces., partly substituting scrap, the canal charge to the furnaces.. Further the ~~use~~ use of sponge in other steel manufacturing processes has also been well proved. The advantages of DRI use in EAF are

- (1) Uniform known compositions
- (2) Low levels of residual elements
- (3) Capability to maintain phosphorus in steel within 0.002%
- (4) Maintenance of Sulphur in steel by its removal in sponge iron manufacture.
- (5) Low content of dissolved gases
- (6) uniform size and higher bulk density as compared to scrap
- (7) Capability of forming protective cover of foamy slag in the bath
- (8) Lower refining requirements of steel produced,
- (9) Potential of sensible heat recovery from waste gases
- (10) Possibility of producing variety of steels.

conventional steel making Vs DR Steel making

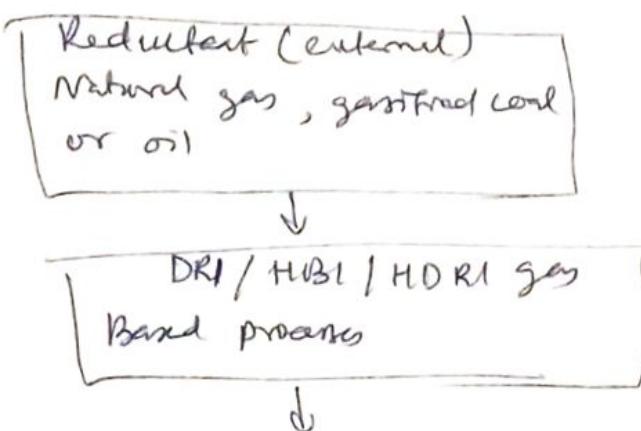
✓ The conventional route for making steel consists of sintering or pelletising plants, coke ovens, blast furnaces and basic oxygen furnaces. Such plants require high capital expenses and raw materials of stringent specifications. Coking coal is needed to make a coke strong enough to support the burden in the blast furnace. Integrated steel plants of less than 1 Mt annual capacity are generally not economically viable. The coke ovens and sintering plants are polluting and expensive units.

Direct reduction, as an alternative route of iron making, has been developed to overcome some of these difficulties of conventional blast furnaces.

DRI is successfully manufactured in various parts of the world through either natural gas or coke based technology.

Iron ore is reduced in solid state at 800-1050°C either by reducing gas $H_2 + CO$ or coal. The specific investment and operating costs of direct reduction plants are low compared to conventional blast furnace process, and more suitable for many developing countries where supplies of coking coals are limited. DR route is energy efficient.

Direct reduction processes may be classified according to the type of reactor used and kind of reducing agent used. The classification of processes is shown below.



(1) Batch processes

- (i) HYL - HYL-I, ~~II~~, II

(ii) midrex process (developed by Midland Ross corporation of Cleveland, USA)

(2) Fluidised bed processes

- (i) FIOR (Fluidised Iron Ore Reduction)

(developed by Esso Research and engg. company, USA)

- (ii) Fimmet (developed by Australia)

(iii) MIDB (High Iron Biscuitte), earlier called Nef iron process

- (iv) Cicored process

(3) shaft furnace processes

- (i) HYL-II (~~III~~ III - means third generation)

(ii) Armco (Developed by Armco steel corporation, USA)

- (iii) Purofer (Developed by Germany)

(iv) NSC-DR (Nippon Steel Corporation)

TDR - (TISCO Direct Reduction) - developed in India by Tisco Steel

DRC - (Direct Reduction Corporation) - developed in Australia

ACCAR - (Allis Chalmers Controlled Atmospheric Reduction), developed by Canada

SL/RN - originally developed by the Steel Company of Canada, Lurgi Chemie, Republic Steel Company and National Steel Corporation.

This is now owned by Lurgi. ~~It is called Oto Kumpu process~~

HYL - Hojalata Y. Laminas,

SAIL — sponge Iron (India) Limited, first cold band DR plant set up in India, 1980.

Jindal — was developed by Jindal strips Ltd, Hissar, 1991, in India

Imetco — developed by International metal company (IMCO), Canada

Fastmet — developed by USA

IT MK₃ — (Iron-milling technology - 3rd Generation)
developed by both Arcelor and Kobe steel

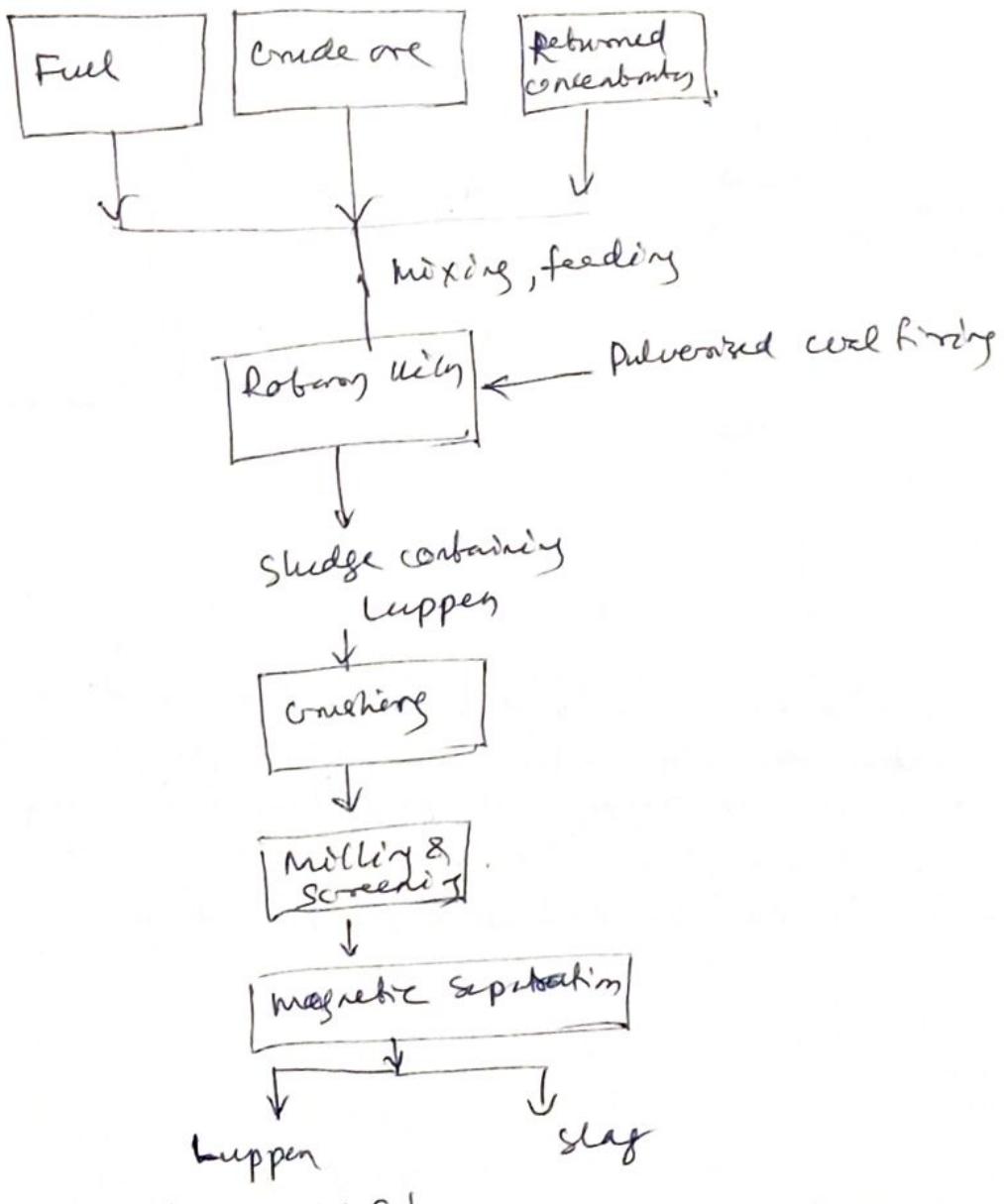
Kingtor-motor — ~~developed~~ by Monteforno (Switzerland)
and Daniel (Italy)

Hoganas — developed by Hoganas AB, in Sweden, 1908

① Knupp-Renn Process

- It was developed in 1930's to treat high-silica ore with a basicity ratio as low as 0.2-0.3 with the addition of limestone. In this process, a mixture of -64 mm ore and ~~the~~ fine ground carbonaceous reducing agent (coke breeze, or bituminous coal fines) is fed continuously in rotary kiln.

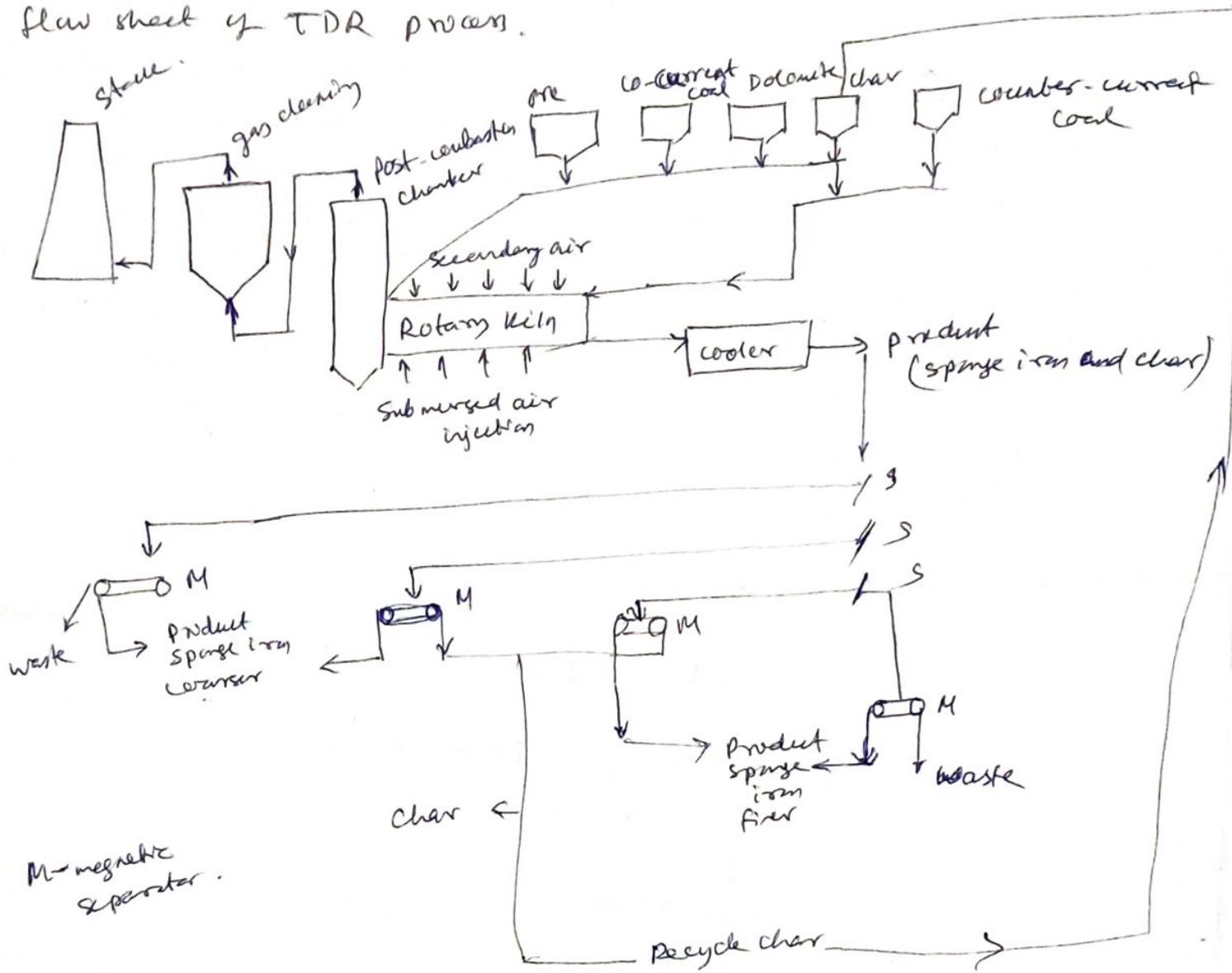
The max. temp. of the kiln is kept at 1230°C to 1260°C , which is sufficient to convert the gangue in the ore to a very ~~to a very viscous~~ high silica sludge and also to effect coalescence of the sponge iron obtained from the reduction of the iron ore. The reduced iron welds into nodules called "Luppen" (which embeds in the pasty sludge). This product is discharged from the kiln. After cooling, it is crushed and luppen is magnetically separated from the sludge. The recovery of iron in the luppen is 94 to 98%. The flow sheet of Knupp-Renn process is given below.



(94-98)%

② TDR Process

In 1983, Tata Steel established a sponge iron plant at Beliipada, near Joda of Keonjhar district of ~~Orissa~~ Odisha, and named it Tata Sponge Iron Ltd. The process adopted is called TISCO Direct Reduction (TDR). The following figure shows the flow sheet of TDR process.



In this process, non-coking coal is used as reductant and fuel oil is used for preheating the kiln at the beginning of the process. Coal is introduced in specified size ranges and proportion from both ends of the kiln along with a flux. Dolomite is used as the flux to remove sulphur. The normal carbon content of the product is 0.2%.

(3)

OSIL process

(5)

Orissa Sponge Iron Limited (OSIL) was set up using ACCAR technology. *

In OSIL process, iron ore (size 6-18 mm), limestone or dolomite, and about 45% of the total coal are charged into the reactor from the feed end while the remaining 55% of the coal and some iron ore fines (size 3-6 mm) are introduced from the discharge end. For one ton of sponge iron produced, the raw materials size and consumption are

| Raw material | Size (mm) | Consumption (kg) |
|--------------|-----------|------------------|
| coal | -20, +18 | 890 |
| iron ore | -20, +18 | 1430 |
| HSD oil | - | 90 litre. |
| limestone | +1, -6 | 60 |

Air is admitted into the reactor radially through the ports for ~~close~~ close temperature control. Sponge iron, unburnt char, spent lime, is discharged into the cooler where these are cooled by indirect cooling. Metallized product is separated through a magnetic separator. The product has degree of metallization of $+\text{90}\%$. The gases exit from the inlet and contains some combustibles, which are burnt in air in an after burner. Hot gases from the after burner are quenched and passed through a wet venturi scrubber. The clean gas is discharged into the atmosphere.

* It was set up in 1983 in Palaspara of District Keonjhar in Orissa. The diameter of the reactor is 4 meters and the length is 84 meters. The kiln output is 300 tons/day.

(4) Popurri Popuri process (Popuri Engg)

Mr. Popurri Ankineedu was one of the engineers associated with the SAIL project, who later left SAIL and started marketing this process, known under the brand name of Popurri Engineering.

(5) Inmetco process

The Inmetco process is currently operated by the International Mettle Reclamation Co Inc. in Ellwood city, Pennsylvania for the recovery of waste iron ore dust. The Inmetco process is based on ~~a~~ a rotary hearth furnace which reduces briquettes made out of iron ore fines, waste from iron bearing materials and pulverised coal to produce hot, metallized DRI that can be directly charged to an electric melter. This process operates at high temperatures and under slightly negative pressures. (flow sheet (figure)-~~book~~)

In this process, iron ore in the form of disc oxide pellets made of iron ore under 250 micron size and fine coal or coke char with less than 25% volatiles, are ~~fed~~ fed into a rotary hearth furnace. The hearth rotates continuously and the pellets are heated by burners located on the inner and outer circumference of the rotary hearth to 1250°C to 1300°C , during a period of 10 to 15 minutes. The hot DRI produced are either collected or fed into the electric furnace for melting.

Gas based processes

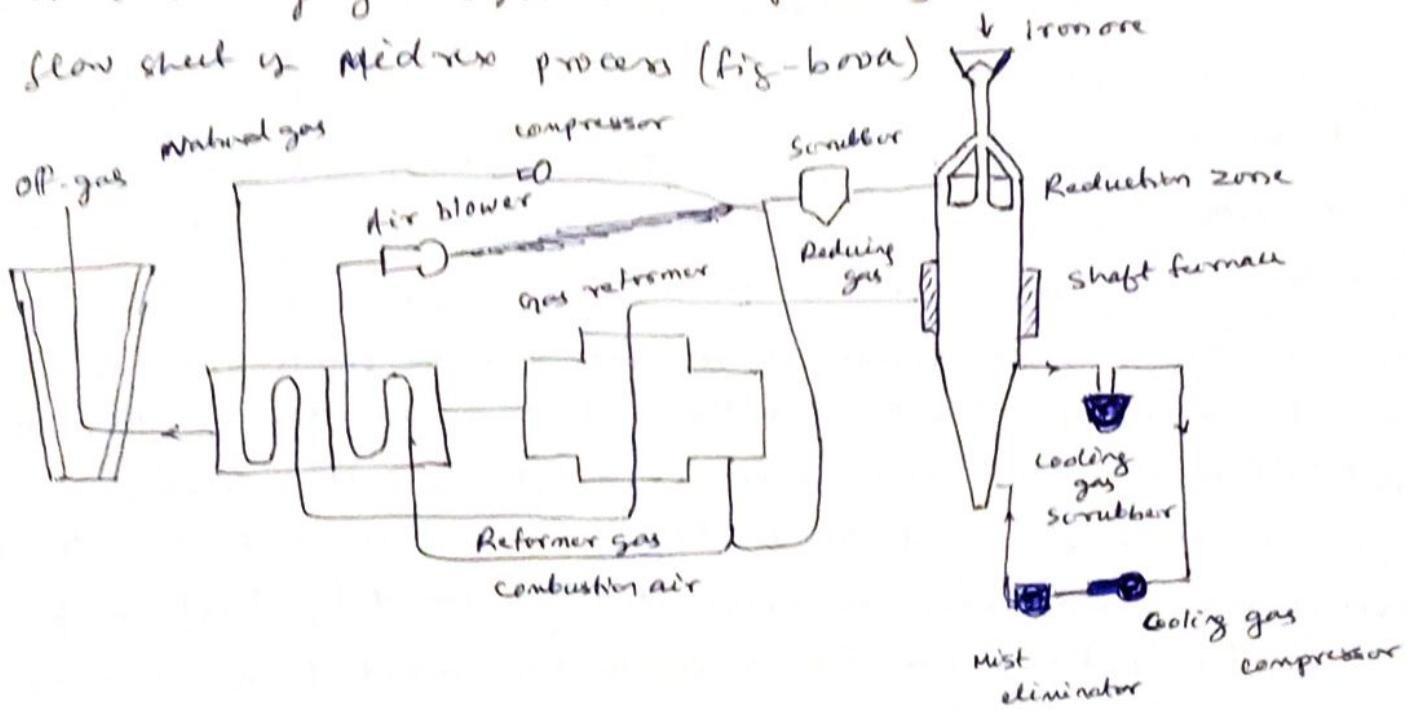
(b)

(A) shaft furnace (moving bed) process

(1) Midrex process

Midrex process, In 1974
surface combustion division of Midland developed the
Midrex process.

The Midrex process is based on a low pressure, moving bed shaft furnace where the reducing gas moves counter-current to the lump iron oxide pellet in the bed. The reducing gas is composed as 10-20% CO, 80-90% H₂ is produced from natural gas. The Midrex process converts iron oxide pellets with or lump ore to form high purity direct reduced iron (DRI) in the shaft furnace as reduction unit. It is basically a counter-current shaft reactor where reformed natural gas is used as reductant and source of heat. The main components of the process are the shaft furnace, the reformer, heat recuperator and cooling gas system. The following figure shows the flow sheet of Midrex process (fig-bova).



(Fig- MIDREX process)

Fluidised bed process

(1) FIOR (Fluid Iron Ore Reduction) process

The FIOR process is a continuous direct reduction process developed by Esso Research and Engineering company, in 1973.

The FIOR process reduces iron ore fines in a series of four fluid bed reactors. In addition the process uses a reformer to produce fresh reducing gas and a briquetting section in which reduced iron fines are compacted. The fluid bed reactors are built in tower structure, thus enabling gravity to enhance the flow of solids between stages. Ore is fed continuously to the preheating reactor, where residual water is driven off and the ore is heated to about 800°C . The combustion product is used to fluidise and heat the ore. As the ore level builds up in the preheated zone, it starts overflowing to the first of three reduction reactors. Compressed reducing gas enters the bottom of the lowest reactor and flows counter ~~current~~ current to the descending ores.

(2) HIB (High Iron Briquette) process

In the HIB process, iron oxide fines are reduced in a fluidized bed reactor by reformer natural gas. In this process, ore fine feed stock is first preheated to 810°C in two stage fluidised bed reactors during which it is reduced to FeO utilising the partially spent gases from the reduction reactors. Then the solids from the second reactor ~~operates~~ flows to the reduction reactor where FeO is reduced to iron by fresh reformer gas. This reduction reactor operates at 750°C and the product at this stage is 75% reduced iron fines. These fines are briquetted and cooled by inert gases. Alternatively, the reduced fines can be transferred to a second reduction reactor where they are further reduced to produce 92% metallized & direct reduced iron fines. These fines can also ~~be~~ be briquetted and cooled by inert gases to produce HIB.

Retort / tunnel processes

(7)

(i) Kinglor - Metor process

It is based on the concept of producing DRI continuously by heating of ore and coal in an externally fired rectangular shaft or retort.

In this process, iron ore lump or pellet of size 6-25 mm, non-coking coal of 5-20 mm size and recycled char as reductant and limestone as desulphuriser are used as feed materials. From the top of the retort furnace, mixture of calculated amount of feed materials are charged, which is heated from outside by solid or gaseous fuel. In the pre-reduction zone, charge is heated by radiation and convection upto a temperature of 900°C and in the reduction zone, the temperature is maintained at 1050°C . The total residence time of the charge is maintained at 16 to 17 ~~to~~ hours and sponge iron is discharged at a temperature of 70°C approximately.

(2) ~~Hoga~~ Hoganas process

This process was developed at Hoganas, in Sweden in 1910.

It involves carbothermic reduction in horizontal tunnel kilns. In this process, alternative layers of fine-grained high grade ~~iron~~ iron ore, dry coke breeze and limestone are charged into cylindrical ceramic containers. These containers are heated to a temperature of 1260°C in a tunnel kiln type furnace. The furnace is heated by burning producer gas and carbon monoxide evolved by the reduction of ore. The containers are cooled in the furnace, removed and reduced iron is separated and cleaned.

✓ Rotary hearth furnace processes

(i) Fastmet process - It consists in mixing and pelletising iron ore concentrate along with pulverised coal, drying the pellets on a grate, pre-reducing the pellets on a rotary hearth and cooling the pellets in a shaft cooler.

As the hearth rotates, the pellets / briquettes get heated by radiation to 1200-1400°C before iron oxide is reduced to metallic iron. Reduction of iron ~~oxide~~ oxide is accomplished primarily by the carbon. The residence time of the charge on the hearth is 6-12 minutes. In one complete rotation of the hearth, 90-95% of the iron oxide is converted into metallic iron. DRI is continuously discharged from the furnace at around 1000°C and cooled.

② IT MK3 (Iron making Technology 3rd generation)

Developed in 1996 by Kobe Steel

1st generation - B.R.

2nd Generation - DR process

3rd Generation - IT MK3

This process is similar to Fastmet in the sense that in both processes, fine iron ore is reduced by pulverised non-coking coal and making composite pellets from these two feed materials. The composite pellets are the feed to the rotary hearth furnace. Binders are added to give sufficient mechanical strength to the pellets. The pellets are dried and screened to yield 17-19 mm green balls. After drying the pellets are distributed onto the rotary hearth furnace and heated upto 1300-1400°C and there reduction, melting and separation of iron and slag take place. Molten iron is solidified into nuggets in the furnace, discharged after cooling and separated from the slag.

Since ~~it~~ the process operates at relatively high temperature, the amount of gangue in the iron ore gets removed.

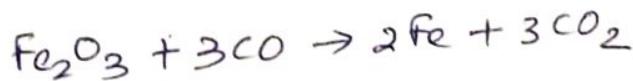
Thermodynamics of sponge iron making

Ch-2

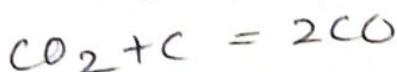
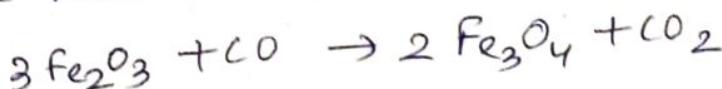
- 2.1. Principles of Direct Reduction Reactions -
- 2.2. Reaction between coal, oxygen and Carbon dioxide (Set-I)
- 2.3. Reaction between Iron ore and CO (Set II)
- 2.4. Reaction mechanism in coal based DRI
- 2.5. Reaction mechanism in gas based DRI
- 2.6. Reduction by carbon monoxide.
- 2.7. Reduction by hydrogen
- 2.8. Boundary Reaction and Reduction by carbon.
- 2.9. Carbon Deposition
- 2.10. Kinetics in DRI
- 2.11. Factors affecting the reducibility of iron ore
- 2.12. Rate controlling factors

2.1 Principles of direct reduction.

In direct reduction, iron ore is converted into metallic iron in the solid state (below the m.p. of the iron). Iron ore is reduced by a reducing agent, usually non-coking coal. The carbon in coal gets converted to CO which subsequently reacts with Fe_2O_3 to produce metallic iron. The overall reaction is being



But the reduction proceeds in several stages as given below.



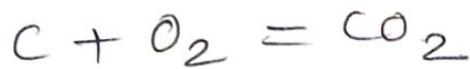
Haematite \rightarrow Magnetite \rightarrow Wustite \rightarrow Metallic iron.
Usually, two sets of heterogeneous reactions take place in

the reactor;
Set-I. Reaction between coal, O_2 and CO_2 , particularly in coal based DRI process

Set-II. Reaction between iron ore and CO, particularly in gas based DRI processes.

Set-I. Reaction between coal, O₂ and CO₂

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



Set-II. Reaction between iron ore and CO.

Each ore particle may be considered to be porous as it contains large number of micro pores. Further the reaction between the ore particles and gaseous reactants is thought to occur in five successive ~~steps~~ steps as below.

Step-1. Diffusion of gaseous reactant through the film surrounding the solid ore particle.

Step-2. Penetration and diffusion of ~~other~~ reactants through the layer of already reacted outer zone to the interface of the unreacted core of the ore.

Step-3. Reaction at the reduced ~~area~~ - unreacted interface by gaseous reactant in the solid.

Step-4. Diffusion of gaseous products through the reacted layer to the exterior surface of the solid.

Step-5. Diffusion of gaseous products through the gaseous film surrounding the ore particle to the outer atmosphere.

(2)

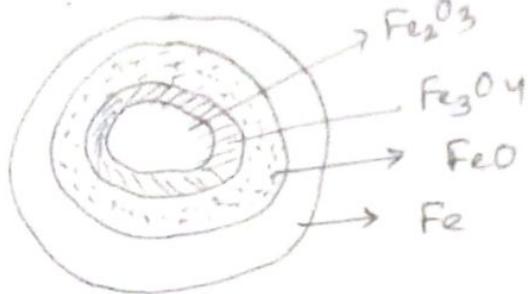
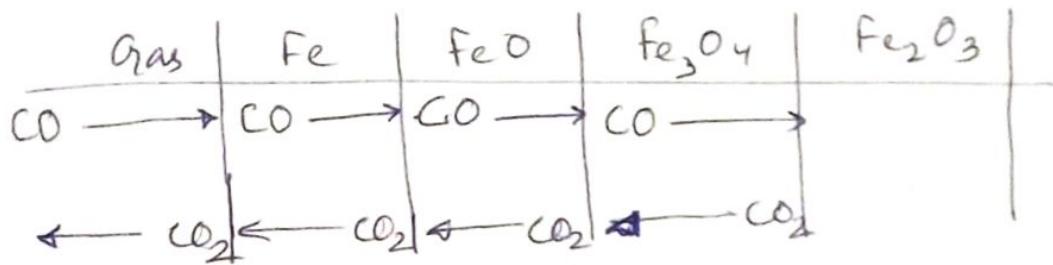


Fig. Partially reduced dense ore particle



Reduction Mechanisms in ~~the~~ sponge iron making

Reduction mechanism in coal based DRI processes

Iron ore reduction by coal begins only at the point of contact between them and stops once metallic iron is formed in the outer most layer of the ore particle. There after, the reduction can proceed only by diffusion of carbon atoms through the metallic iron layer to the residual oxide at the core. For sustained reduction, solid coal must get converted to carbon monoxide. Carbon monoxide is produced by the reaction between the carbon in the coal feed and carbon dioxide produced by the reduction of ore (according to Boudouard / Larson loss reaction $\text{CO}_2 + \text{C} = 2\text{CO}$). As this reaction is endothermic, it is favored only at temperature above 1000°C . carbon dioxide does not exist above 1000°C and reduction of iron oxide is not feasible below 600°C . Therefore, in a coal based DRI making, reduction of iron oxide and Boudouard reaction takes place simultaneously. A characteristic feature of this type of DR process is that the reducing gases react with the iron oxide from all sides and reduction drops drastically beyond 80% metallization as removal of oxygen becomes increasingly difficult.

Reduction Mechanism in gas based DRI processes

The gas based processes are more popular because of the following reasons:

- (i) Natural gas is available in plenty worldwide. It is economical and ~~pollution~~ pollution free to use as compared to coal.
- (ii) ~~Natural~~ Reformed natural gas is a superior reductant as compared to coal. It performs reduction utilizing both H_2 and CO .

At $700^\circ C$, the extent of reduction for dense hematite with pure CO stops around 40%, while at $800^\circ C$, the reduction is extended upto 85%. Carbon deposition on the surface of the ore particle seals the surface pores and prevents any further diffusion of reductants leading to incomplete reduction.

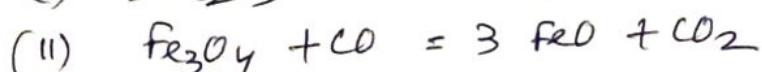
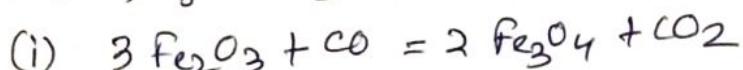
Addition of hydrogen improves the reduction.



When the reduction is carried out with CO and H_2 mixture, the metallic iron phase of the reduced ore particle consists of two layers. Of the layers, the outer layer is relative porous and primarily iron carbide (Fe_3C) while the inner layer is metallic iron. This carbide layer is absent when reduction is performed by hydrogen only. With increasing CO/H_2 ratio, more and more iron carbide is formed.

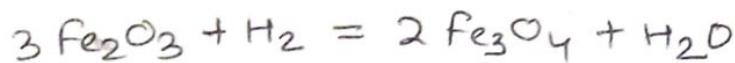
Reduction by carbon monoxide

Above $570^\circ C$, iron oxide is reduced by CO in three stages, yielding metallic iron as

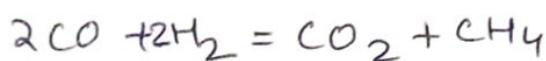


Reduction by Hydrogen →

Reduction reactions of iron oxides by hydrogen can be represented as



Use of both CO and H₂, in the DR processes may lead to the formation of methane according to the reaction



Boudouard Reaction and Reduction by Carbon →

the reaction

$\text{CO}_2 + \text{C} = 2\text{CO}$ is called as Boudouard reaction or carbon loss reaction. This gas-solid heterogeneous reaction is faster than the reaction $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$, which causes reduction of iron ore. Hence only a negligible amount of reduction occurs by direct contact between the solid carbon and iron ore particles. Primarily iron ore is reduced by CO gas which is produced according to Boudouard reaction as stated above, the reactions $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$ and $\text{C} + \text{CO}_2 = 2\text{CO}$ are faster compared to the reaction $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$. So indirect reduction of iron ore is more predominant.

The reduction of FeO by ~~the~~ carbon is referred to as direct reduction while reduction of any iron oxide by CO is called indirect reduction.

Carbon Deposition reaction → The reverse of the Boudouard reaction ($\text{CO}_2 + \text{C} = 2\text{CO}$) is known as carbon deposition reaction i.e. $2\text{CO} = \text{CO}_2 + \text{C}$. At 600°C, the Boudouard reaction will continue from right to left with deposition of solid carbon.

Reaction Kinetics in DRI

(3'')

Reduction kinetics of iron ore deals with the rate at which iron oxides are converted to metallic iron with the removal of oxygen. The rate at which the ore is reduced influences the rate of production and ultimately determines the economic feasibility and competitiveness of the DRI process. The reduction can be performed by CO, H₂ and Carbon as per the following reactions.

I. Reaction with carbon monoxide



II. Reaction with hydrogen.



III. Reaction with carbon



The evaluation of reduction kinetics for iron ore is very complex as the oxides undergo a series of stepwise changes till the conversion is complete. However, the slowest of the steps in the process determines the overall reduction rate and is called as the rate controlling step.

Factors influencing the reducibility of iron ore

The ease with which oxygen can be removed from the ore by the reductant is defined as the reducibility. The reducibility of iron ore in a DR process is influenced by the following factors:

- (i) Size, shape and size distribution of the ore particle
- (ii) Average density, porosity and crystal structure of the ore particles
- (iii) Percentage gangue and its distribution ⁱⁿ the ore

(i) particle size, shape and particle size distribution →

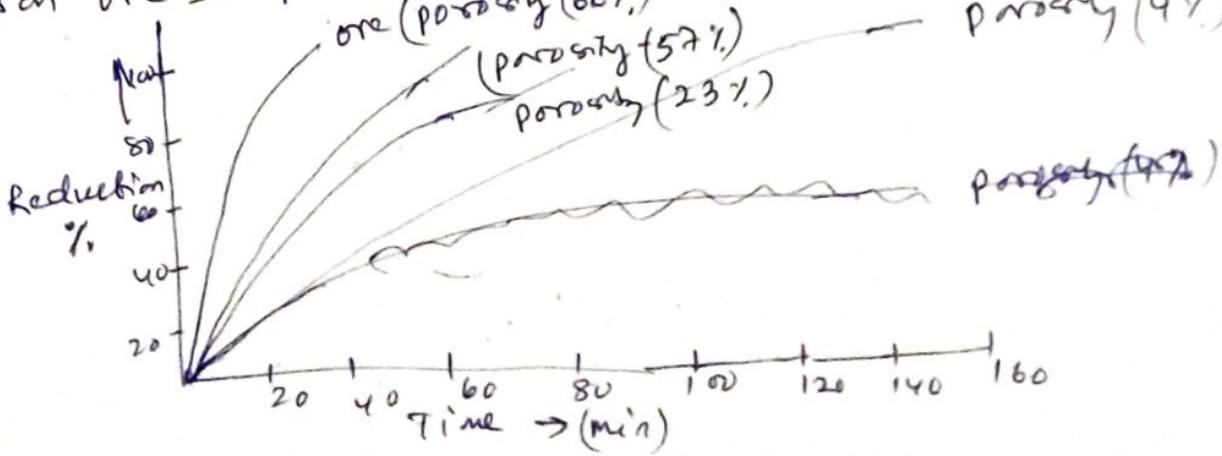
While selecting iron ore for sponge iron making, special attention should be paid to the reducibility of ore. Hence ore preparation should be carried out in such a manner to provide maximum possible surface area as far as practicable. Hence crushing, sizing and removal of fines are desired for better reducibility. It is found that particles in the size range of 5-18 mm is ideal for DRI production. Larger particles provide lesser surface area while fines tend to choke the ore bed creating hindrance to the passage of reducing gases. Agglomerated pellets from high grade ore concentrate, exhibit excellent reducibility. Further particle size distribution is also an important parameter which controls the reducibility of the ore.

(ii) porosity → The porosity of the ore is one of the most

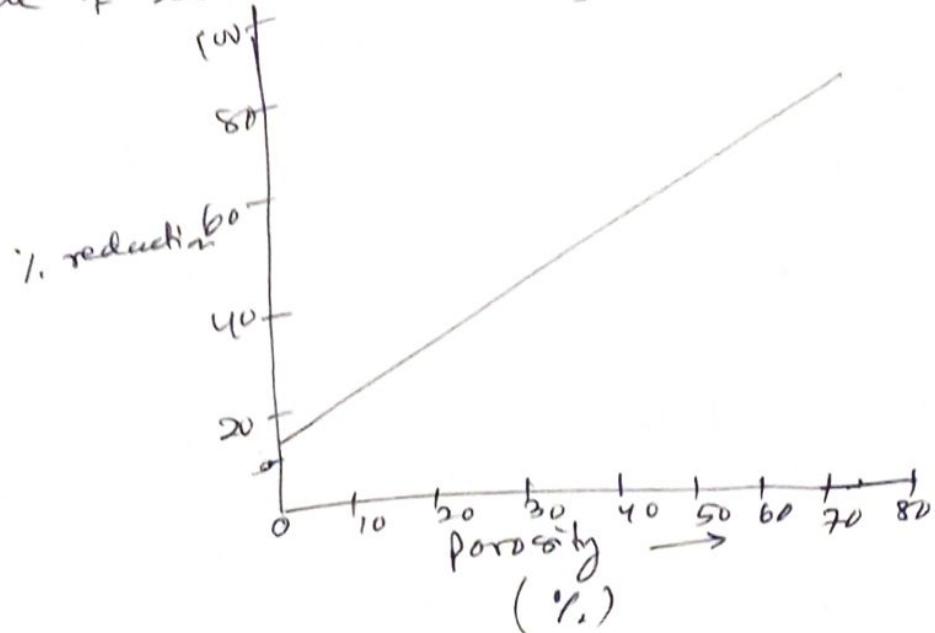
important parameter affecting the reducibility. The reducibility of soft haematite is greater than that of hard and dense hematite and hard dense magnetic ore. It has been seen that the reciprocal of time required for 90% reduction, varied linearly with percentage of porosity.

The following figure shows the percentage reduction Vs time for iron ore samples of various porosity.

for iron ore samples of various porosity.



The following figure shows the degree of reduction as a function of time of several ores having different porosity.



Rate controlling theories

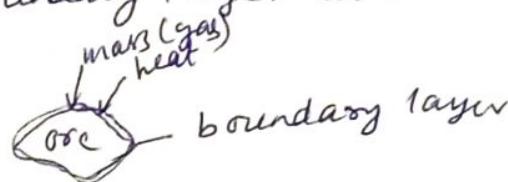
Rate controlling theories

(5)

Various rate controlling theories are

1. Boundary layer ~~theories~~ control
2. Phase boundary reaction control.
3. Crassous diffusion control
4. Mixed control.

1) Boundary layer control → The major considerations under this theory are the rates of heat and mass transfer across the boundary layer at the outer surface of the ore particle.



Under this theory, the overall reduction rate is controlled by the rate of diffusion of gas and heat through the boundary layer of gas that builds up around each ore particle. The rate of diffusion is proportional to the concentration gradient of the reducing gas across the boundary layer. The rate of heat flow into the particle is proportional to the temperature gradient across the boundary layer.

2) phase boundary reaction control → According to this theory,

reaction at the wustite-iron interface is the rate controlling factor and the rate of reduction per unit area of remaining iron oxide surface is found to be constant with time. When counter diffusion of reducing and product gas across the reduced outer ~~layer~~ iron layer is sufficiently fast, the concentration of reducing gas at the reacting surface is effectively the same as its concentration at the particle surface. In such a case, the rate of reduction at the wustite-iron interface would control the overall reduction rate.

3) Crassous Diffusion Control → According to this theory, the

rate of inward diffusion of reducing gas and outward diffusion of product gas through the reduced iron layer, control the rate of reduction.

(5)

Such a phenomenon is known as Gaseous Diffusion Control or Iron pose control. This mechanism is applicable only to the reduction of large sized ore particles. Under this mechanism, the rate of gaseous diffusion is less than the rate of ore reduction. Hence, the concentration of reducing gas decreases and that of the product gas increases at the interface. This change in the gas composition will slow down the reduction rate till a steady state is established where the rate of reducing gas supply exactly balances the rate of reduction.

4. mixed control →

When both gaseous diffusion and phase boundary reactions act together to influence the rate of ore reduction, the mechanism is known as mixed control.

Kinetics of iron oxide reduction (Rate of iron oxide reduction)

The reaction kinetics of iron ore reduction determines the rate at which iron oxides are converted to metallic iron by the removal of oxygen. It is well known that the rate of any chemical reaction increases as the temperature increases. In direct reduction processes, where iron is reduced in solid state and no melting occurs, the maximum rates are slower and production rate of DR processes is generally lower than the blast furnace.

The mechanisms involved in iron oxide reduction are very complex because the oxide ~~to~~ charged has to go through a series of changes, step-by-step before the conversion to the final product is complete. The slowest step in the entire process chain determines the ~~the~~ overall reaction rate and is referred to as the rate controlling step.

Factors affecting the reducibility of iron ore

The reducibility is the ease with which oxygen can be removed from the iron oxides by the reducing gases.

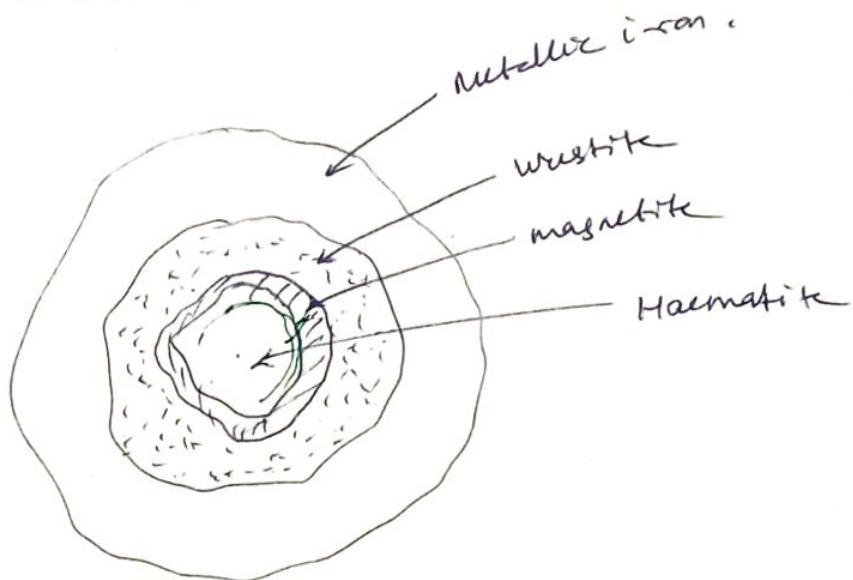
It is influenced by its particle size, particle shape, particle size distribution, density, porosity, crystal structure and composition. All of these have an influence on the relative surface area of the iron oxide exposed to the reducing gases and hence affect reducibility. Porosity of iron ore particles is one of the most important variables controlling reducibility. Soft hydrated ores have best reducibility followed by the soft ~~to~~ haematites, then come the hard haematites and finally the hard dense magnetites. The importance of porosity can also be gauged from microscopic examination of the cross-section of iron ore lumps or pellets. (as shown in the figure). The figure shows the cross section of a partially reduced dense iron ore particle, which shows a core of haematite surrounded by three concentric

Chapter 8

Thermodynamics of Sponge iron Making

① Principle of Direct reduction reactions →

Layers - an inner layer of magnetite, a layer of wustite and an outer layer of metallic iron.



(fig- Cross section of a partially reduced dense iron ore particle)

For the reduction reaction to take place, the reducing gas must come in contact with the surface of iron oxide phases. It must diffuse inwards and the product gas outwards, at least through the outer layer to reach the wustite layer.

Rate controlling steps

In addition to the extent and properties of the reacting surface exposed to the reducing gases, there are other factors that affect the rate of reduction of iron oxides. The first factor is the rate of heat and mass transfer across the gas-flow boundary layer at the outer surface of the solid phase particles. These rates are a function of the design and operation of the reactor in which the reduction takes place. When the reaction rate is controlled by the boundary layer resistance, it is known as boundary layer control. In another case, the rate of diffusion of the reducing gas inwards and product gas outwards through the reduced iron ore layer can control the rate of reduction of iron oxide.

Raw materials for sponge iron making

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The basic raw materials required for production of DRI are

1. Iron ore (lump or pellets)
2. Coal, Natural gas or oil (fuel and reductant)
3. Limestone or dolomite (desulphuriser)

The desirable characteristics of these raw materials depend on the type of the process used (vertical shaft, rotary kiln or fluidised bed) and the product quality.

Selection of iron ore for DRI production →

The following parameters are considered for the selection of iron ore for the production of DRI

- (1) Chemical composition
- (2) Physical properties
- (3) Strength properties
- (4) Reducibility

(1) Chemical composition →

Since sponge iron is the solid state reduction of iron ore, the impurities present like SiO_2 , Al_2O_3 , CaO , MgO , 'P' etc available in ore, remains as such in sponge iron. By reduction, the oxygen present in oxide ore is removed and iron present as oxide is converted to metallic iron.

Therefore, the iron content of the ore should be as high as possible, preferably 65-68%. The ore containing more than 68% iron ~~may~~ not be great advantages because very small amount of gangue may cause generation of more fines due to abrasion. High gangue content in 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 the gangue content of the ore should not exceed more than 5%. The following are the effects of gangue on sponge iron.

SiO_2 — The SiO_2 content of the gangue should not be too low as it results in swelling and decarporation. Too low silica also develops sticky tendency during sedimentation, which creates difficulties in operation. Low silica ore produces DRI of low strength causing degradation during handling. High silica content in the gangue increases the volume of the slag and energy consumption during steel making.

Al_2O_3 — Alumina being acidic in nature, will require extra flux increasing the slag volume in steel making. The total $\text{SiO}_2 + \text{Al}_2\text{O}_3$ should not be more than 4% in the gangue.

Alkali — Alkali content of the ore gives rise to swelling which causes degradation and operational difficulties.

Phosphorus — Phosphorus content has no effect in DR process.

However, it should be as low as possible to produce a good quality steel having phosphorus below 0.05%. Therefore, feed materials containing very low phosphorus content (< 0.03-0.5%) should be selected for quality steel making. (Indian ore contains 0.04-0.08% P)

Sulphur — The sulphur content is very important in a DR process where the off gas is recycled to a reformer because of catalyst poisoning. The sulphur content of the ore should be below 0.02%. Fortunately, the sulphur content of the Indian ore lies between 0.01-0.02%.

CaO and MgO — CaO and MgO are desirable material in the

direct reduction and steel making processes. Addition of dolomite and limestone increase the strength of the fired pellets & decreases the requirement of flux in steel making process.

Therefore, while selecting iron ore for effective sponge iron production considering all parameters, it is found that 65% Fe ore is not suitable due to high percentage of gangue in it. Ore having more 65% Fe with less than 5% gangue are best suited for sponge iron making. So the desirable composition of iron ore for DR process is

| <u>constituent</u> | <u>Desirable</u> |
|--------------------------------|--------------------|
| Fe Total | 66.69 %. |
| SiO ₂ | 1.5 - 2.5 % |
| Al ₂ O ₃ | 0.3 - 0.5 % |
| CaO | 0.4 - 1.0 % |
| MgO | 0.01 - 1.0 % |
| P - | 0.03 - 0.5 % (max) |
| S - | 0.02 % (max) |

Definitions

Swelling — Some ore shows abnormal increase in volume at temperature around 100°C, which is known as swelling of the ore.

Degradation — The fragmentation or breakage with the production of fines, which the materials experienced by abrasion, handling, transportation etc.

Degradation Index — The total degradation percentage in terms of weight;

Decrepitation — Some ore/pellets tend to crumble on heating at lower temperatures (500°C), thus generating fines. This called decrepitation.

Thermal degradation Index (TDI)

It is a measure of the tendency of the iron ore to undergo size degradation as a result of either thermal shock or reduction or both. The term decrepitable is also used in place of degradation.

Bulk density — The bulk density of coal plays an important role in the productivity performance of the kiln. Generally the coal with higher volatile matter have smaller bulk density, and occupy larger space in the kiln, by reducing the available kiln volume for production.

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Since ores, sinters, pellets possess inherent mechanical instability or they develop it during heating and reduction, a few methods are used to determine their cold strength as well as their physical behavior during hot reduction. To ascertain these properties, some testing methods are developed.

- (1) cold strength
- (2) porosity
- (3) decrepitation
- (4) swelling & volume change

① cold strength

cold strength measurement comprises of tumbling or drum test for abrasibility, shatter test for impact and compression test for load during storage.

(a) Tumbler test or drum test - It measures the susceptibility of ore or coke due to breakage due to abrasion during handling, transportation, charging or inside the furnace itself. In this test, a certain weight of the material within a selected size range is rotated in a drum of given size for a given time with certain no. of revolutions. The abrasion strength is given by the percentage weight of +6.3 mm surviving the test and the dust released by the percentage of -0.6 mm for good pellets the respective percentages are 85-95 and 3-7, for sinters 60-80 and 5-10 and for ores 60-95 and 2-25

(b) Shatter test — It measures the susceptibility to break down due to impact during loading, unloading and charging into furnace. In this test, a certain weight of material is allowed to fall on a steel plate from a certain height for a given time and the amount of undersize measured. For sinters, the percentage +10 mm surviving is above 80%.

(c) Decrepitation — Dust formation can occur during transportation or while charging in the shafts, and in the furnace in case of materials having a low tumbler or shatter index or due to decrepitation in the furnace when temperature is as high as 400°C.

Decrepitation can occur due to internal pressure developed from evaporation of moisture and chemically combined water or crack formation arising from sudden heating and expansion.

The following table shows strength properties of iron ore for DRI

| <u>Strength Properties</u> | <u>Size (mm)</u> | <u>Limit %</u> |
|----------------------------|------------------|----------------|
| Abrasion Index | -0.5 mm | 5% (max) |
| Tumbler Index | -6 mm | 15% (max) |
| Shatter Index | -5 mm | 5% (max) |
| Thermal degradation index | -6.3 mm | 5% (max) |

Reducibility — The reducibility of ore has great influence on the productivity. Higher the reducibility of the ore, lower is the retention time and hence, increased productivity. Therefore, the ore must have high reducibility. Generally, hard, dense lump ore and overfired pellets do not show good reducibility because of low porosity. Magnetite exhibits poor reducibility compared to hematite. Therefore iron ore with 100% Fe₂O₃ is preferable. The maximum size of the ore or pellet is determined from its reducibility. In Shaft furnace, the reducibility should be 90-95% within a residence time of 6 hrs in temperature range 800-1000°C. For rotary kiln, it should be $\left(\frac{dR}{dT}\right)_{40\%} = 0.5\%$ per minute.

Porosity of iron ore — It is one of the important parameters which affects the reducibility of ore. A ~~high porosity ore has~~ ~~high~~ ~~reducibility~~, The high porosity ore may show better ~~reducibility~~. The high porosity ore may show better reduction behaviour but due to high porosity the strength deteriorates and causes more generation of fines. Hence a hard dense hematite ore having 3 to 5% porosity is better for productivity.

Thermal degradation — The thermal degradation index is the fragmentation and breaking up points showing generation of fines when the material is subjected to heating in an oxidizing or reducing atmosphere.

The decrepitation effect of oxide feed is the combined effect of thermal degradation and reduction degradation which causes fines. The permissible limit of decrepitation of iron ore is as follows:-

Oxidizing atmosphere

$$TDI \quad \cancel{6.3 \text{ mm}} = 10\%$$

$$TDI \quad 3.15 \text{ mm} = 5\% \text{ (max)}$$

$$TDI \quad 0.5 \text{ mm} = 1\% \text{ (max)}$$

reducing atmosphere

$$TDI \quad 3.15 \text{ mm} = 25\% \text{ (max)}$$

$$TDI \quad 0.5 \text{ mm} = 10\% \text{ (max)}$$

Size of ore for DRI

The rate of reduction of iron ore depends on size of the particle. The optimum size is determined by its reducibility characteristics. The feed materials for DRI production should have a narrow size range as far as possible to get a uniform metallized product. In shaft furnace, narrow size range of feed of material is essential for good permeability of the bed. In case of pellet a size range of 5-15 mm is desirable while in case of lumpy ore 5-20 mm is considered to be desirable. However, ore fines of 3-5 mm can be processed in rotary kiln, only fluidized bed can process -3 mm to 5 micron size feed material.

Magnetite - Some hematite ores contain few percentage of magnetites (Fe_3O_4). Since the reducibility of magnetite is less than hematite, the presence of magnetite in the ore should not more than 1%.

~~COAL (Fuel & Reductant)~~

Coal (Fuel & Reductant)

Many processes like rotary hearth and rotary kiln have been developed for the production of DRI using coal as reductant. Rotary

In direct reduction process, the iron oxide of the ore is reduced to metallic iron by using carbon, hydrogen or carbon monoxide in a reactor. The reducing agent in the reactor acts as a fuel for meeting the heat requirement of the process and reduces the iron oxide to metallic iron. The fuel used may be solid, liquid or gaseous depending on the availability, which in turn determines the process. In rotary kiln process, solid fuels like non-coking coal and lignite are used and in Midrex, HYL Processes gaseous fuel is used.

2.

Coal (Fuel and Reductant)

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Many processes like rotary kiln and rotary hearth have been developed for production of DRI using coal as reductant. Rotary kiln processes have proved to be commercially successful.

The consumption of a particular coal for production of DRI depends on reaction stoichiometry, fixed carbon content and loss of fixed carbon. Under Indian conditions, it has been observed that specific consumption of coal is 1.1 ton per ton of sponge iron produced. An approximate estimate indicate that cost of coal is about ~~at~~ alone 75% of the cost of DRI making in rotary kiln. The quality of coal will affect the overall cost of production of the sponge iron. Therefore evaluation and selection of coal for the process is very critical and should be done very carefully. In the rotary kiln, iron ore and coal come in contact with each other in the solid state. Therefore it is essential that coal shall be completely non-coking.

Any caking tendency in coal may lead to agglomeration inside the kiln, caking tendency also affects material flow characteristics and helps in agglomeration formation in the kiln, Hence non-caking coals are used for production of sponge iron

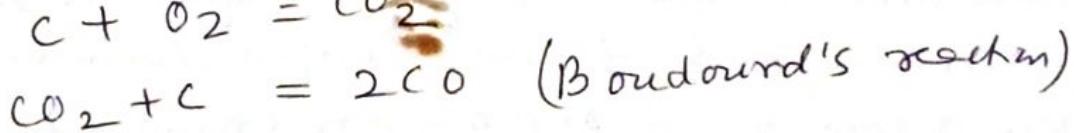
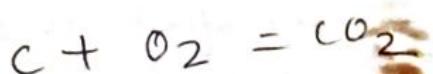
In selecting non-caking coal as fuel for heating and reductant, the following characteristics should be considered.

- 1) Proximate analysis
- 2) Ultimate analysis of ~~coal~~ coal
- 3) Ash fusion temperature
- 4) Sulphur content
- 5) Caking & swelling index
- 6) Calorific value
- 7) Coal char reactivity
- 8) Coal strength, Sinter fracture load
- 9) Coal size
- 10) Ash chemistry.

① proximate analysis →

The proximate analysis of coal gives ash, volatile matter, fixed carbon and moisture content in percentage.

(a) fixed carbon → The fixed carbon content of coal is most important aspect of proximate analysis. In general coal with higher fixed carbon content have higher calorific value



coals with 30% fixed carbon can be used. A value of about 50% carbon is preferred.

(b) volatile matter → The volatile matters contribute heat as well as helps in reduction in PR process. The volatile matters are combinations of methane, ethene, tar etc. Some of gas reacts with CO_2 and generate CO atmosphere.



This also helps in reduction.

The low volatile matter coal will not produce adequate heat and reducing conditions. The high V.M. coal attributes rises to waste heat. The optimum volatile matter is found to be between 28 - 34%.

(c) Ash content → This is an impurity in coal. It affects the thermal requirements and productivity of the kiln adversely. The ash is inert material occupying space in the kiln. A high ash content coal reduces the available space for the iron ore reducing the productivity of the kiln. It has been reported that productivity goes down by 2% for every 1% increase in ash content of coal. A value of 15% ash is considered to be good. However, under Indian conditions, the ash content in the coal should not exceed 24%.

(d) moisture → The moisture content increases the thermal load in the kiln. The total moisture content should be less than 5%.

(2) Ash fusion temperature →

The ash softening temperature of the coal is very important property for DRI process. This is the temperature at which pure coal ash starts to fuse. The ash fusion temperature should be at least 200°C higher than the kiln operating temperature.

The coal ash inside the rotary kiln comes in contact with many other chemical compounds forming low melting eutectics promoting accretion formation on the kiln wall. This reduces the productivity of the kiln and creates operational problems until the kiln is shut down for cleaning the accretion.

(3) Sulfur content →

Sulphur may be present in coal as organic sulphur in combination with carbon and hydrogen. Sulphur may also be present as FeS and Sulphates. The amount of sulphur as sulphate is usually very low. However, this should be checked because this may be the reason for lowering the ash fusion temperature. Sponge iron absorbs sulphur as the temperature increases. Sulphur can be controlled by the addition of limestone or dolomite to the kiln feed. For the above reasons, the sulphur content of the coal should be low, preferably below 1.0%.

(4) Caking and Swelling index →

A high caking index causes sintering and ~~causes~~ reduces char reactivity of the coal with CO_2 . It also causes accretion build up inside the kiln. Therefore, a coal with more than 3 caking index should not be used.

Coal has the property of swelling when it is heated to elevated temperature. Due to this the coal forms big masses with less density. It occupies higher volume in the kiln. These agglomerates segregate inside the kiln, higher volume in the kiln, these agglomerates of low density may ~~not~~ disintegrate to generate

(2)

more fines, which may be lost from the kiln. This leads to carbon depletion and low metallization. Therefore, the swelling index of the coal should be less than 3, however less than 3, preferable.

(5) Calorific Value →

The thermal requirement of the process is met by burning coal. Therefore, the calorific value of the coal is important from design point of view. The calorific value of coal increases with increasing in fixed carbon content. Low calorific value means more coal consumption per ton of DRI and more heat loss due to high gas volume. Therefore, calorific value of coal should be higher, preferable above 5000 Kcal/kg.

(6) 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 reaction 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 rotary kiln because it is possible to operate the kiln at lower temperatures. This gives potential to increase productivity. The reactivity of coal shall be more than 2 c.c. of CO /gr of C per second.

(7) Char strength → After the removal of moisture and volatile matter, the degradation of the char in the kiln depends on char strength. The carbon value of the exhaust gas dust will be high if the char strength is low. Therefore, to prevent carbon loss, the char strength should be high.

The char strength increases with rank of coal.

⑧ Coal Size → The size of the coal should be such that it mixes well with the charge and the volatile matter is evolved smoothly as the charge moves along the kiln from feed end. The size of the coal should not be very fine otherwise it causes carbon loss. The proportion of 1-1 mm size from the feed end should not be more than 5-10%.

⑨ Ash Chemistry →

⑩ Limestone / Dolomite,

As charge materials to remove sulphur from sponge iron.

* Ultimate analysis of coal

Determination of total carbon, hydrogen, oxygen, nitrogen, and sulphur percentages in coal comprises its ultimate analysis.

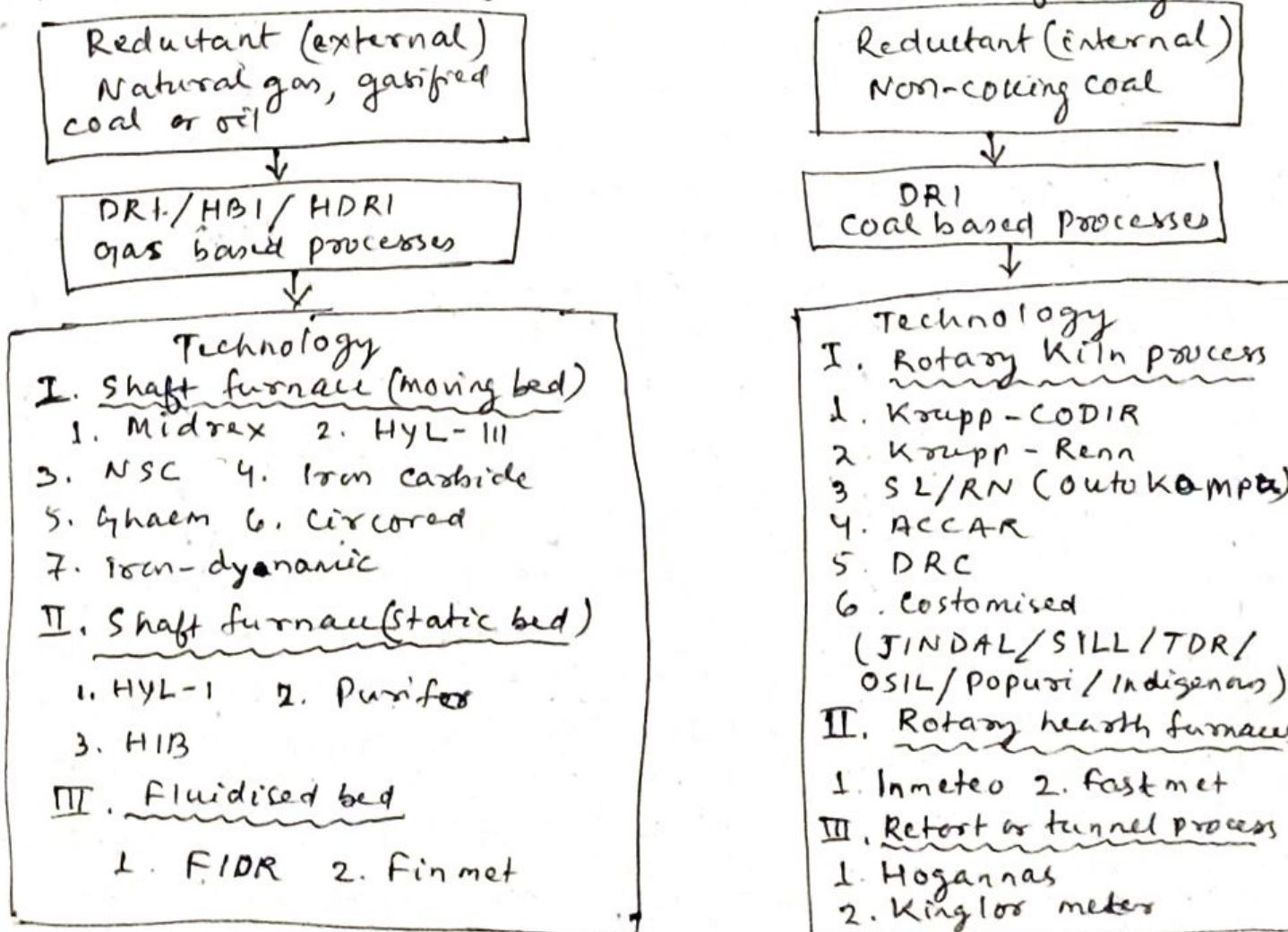
2.4 Effect of iron ore size on reduction

Size of the ore is very important for DRI production. The particle size, shape and its distribution affect the reducibility of the ore. The rate of reduction of iron oxide increases with decrease of the size of the iron ore. The size is determined by its reductivity. It has been observed that, the best results are obtained with size ranging from +6 to +18 mm, with particle diameter of 10.5 mm to 11.5 mm.

Major Direct Reduction processesWRITING SPACE

The direct reduction is the process in which metallic iron is produced by the reduction of iron ore, below the melting temperature of any of the materials involved. About 100 DR processes have been developed since 1920 for large scale production. These processes use different types of apparatus including rotary and stationary kiln, rotary hearth furnaces, pot furnaces and fluidised bed furnaces, and static and moving bed furnaces. Different kinds of fuels such as coal, char, lignite, anthracite, fuel oil, natural gas and gasified coal are used in these processes.

Direct reduction processes may be classified according to the type of reactor used and kind of reducing agent used. The classification of processes is shown in the following table



World DRI Production by process

| | |
|--------------------|------------|
| Midrex | - 64.5 %, |
| Hyl-III | - 18.4 % |
| Hyl | - 1.3 %, |
| Coal based | - 10.20 %, |
| Others (gas based) | - 5.6 %, |

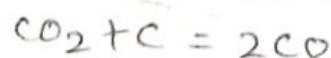
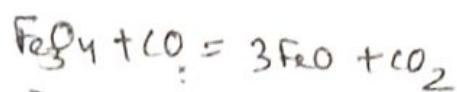
Commercial coal based processes

1. ROTARY KILN PROCESSES

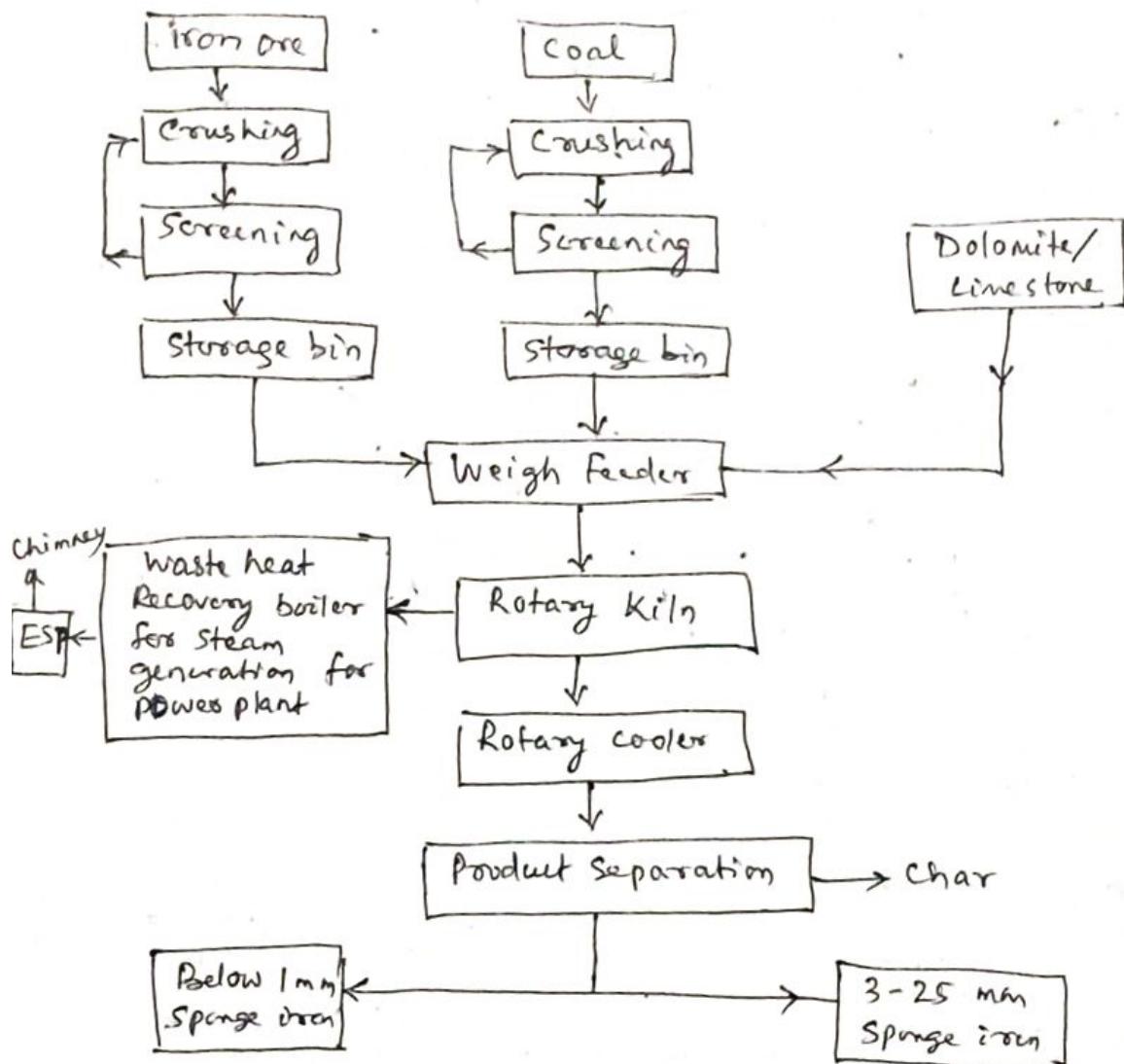
Coal based rotary kiln processes are widely used for the production of DRI. These processes are similar with respect to the main component consisting of a solid feed system, the rotary kiln, product cooler, magnetic separator and off-gas cleaning system.

The rotary kiln reactor is a cylindrical shell lined inside with refractory material. The shell is 70-80 meters in length and a few meters in diameter and is kept inclined from the horizontal at an angle of 3% to 4% from the feed end to the discharge end. It is rotated slowly around its own axis. In coal based DR Process, 4-15 / 4-18 / 4-20 mm lump ore or 9-20 mm pellets (both 1550-1600 kg/t of DRI), a relatively coarse fraction of non coking coal (6-20mm), limestone and dolomite are fed into the rotary kiln at the inlet end. These burden travels through the kiln by the rotary action and gravity. A burner located at the discharge end of the rotary kiln initially heats the kiln. Pulverised coal or fuel oil is supplied to the burner, which operates with deficiency of air to maintain a reducing atmosphere. The additional heat is supplied by combustion of volatile matter of the coal and carbon monoxide coming out from the kiln bed. Combustion air is supplied from the ports spaced along the length of the kiln. Controlled quantity of air is supplied to maintain proper temperature in the kiln and to maintain a neutral or slightly reducing atmosphere above the bed. The kiln gas flows counter currently ~~to~~ to the flow of solid. The temperature of the charge bed inside the kiln is limited to a maximum of around 950-1050 °C in order to ensure that the ash in coal does not fuse. As a result, the entire reduction occurs in the solid state. The burden passes through the preheating zone where coal is devolatilised, flux is calcined and the burden is heated to the operating temperature for reduction. In the reduction zone, iron oxide is reduced by the following reactions



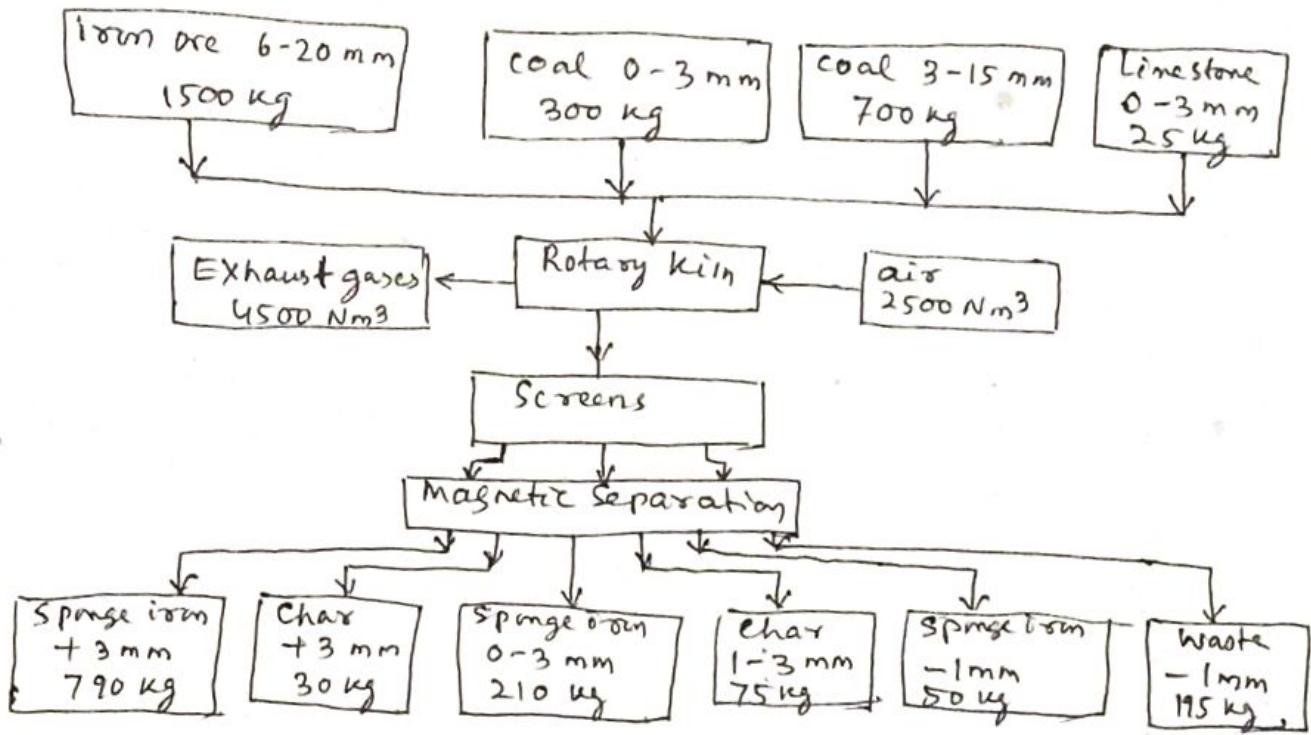


The product discharged from the kiln at a temperature of 950-1050°C is cooled to below 120°C in a water cooled rotary cooler. The solids are then screened and magnetically separated. The following figure shows a flow diagram of direct reduction in a rotary kiln.

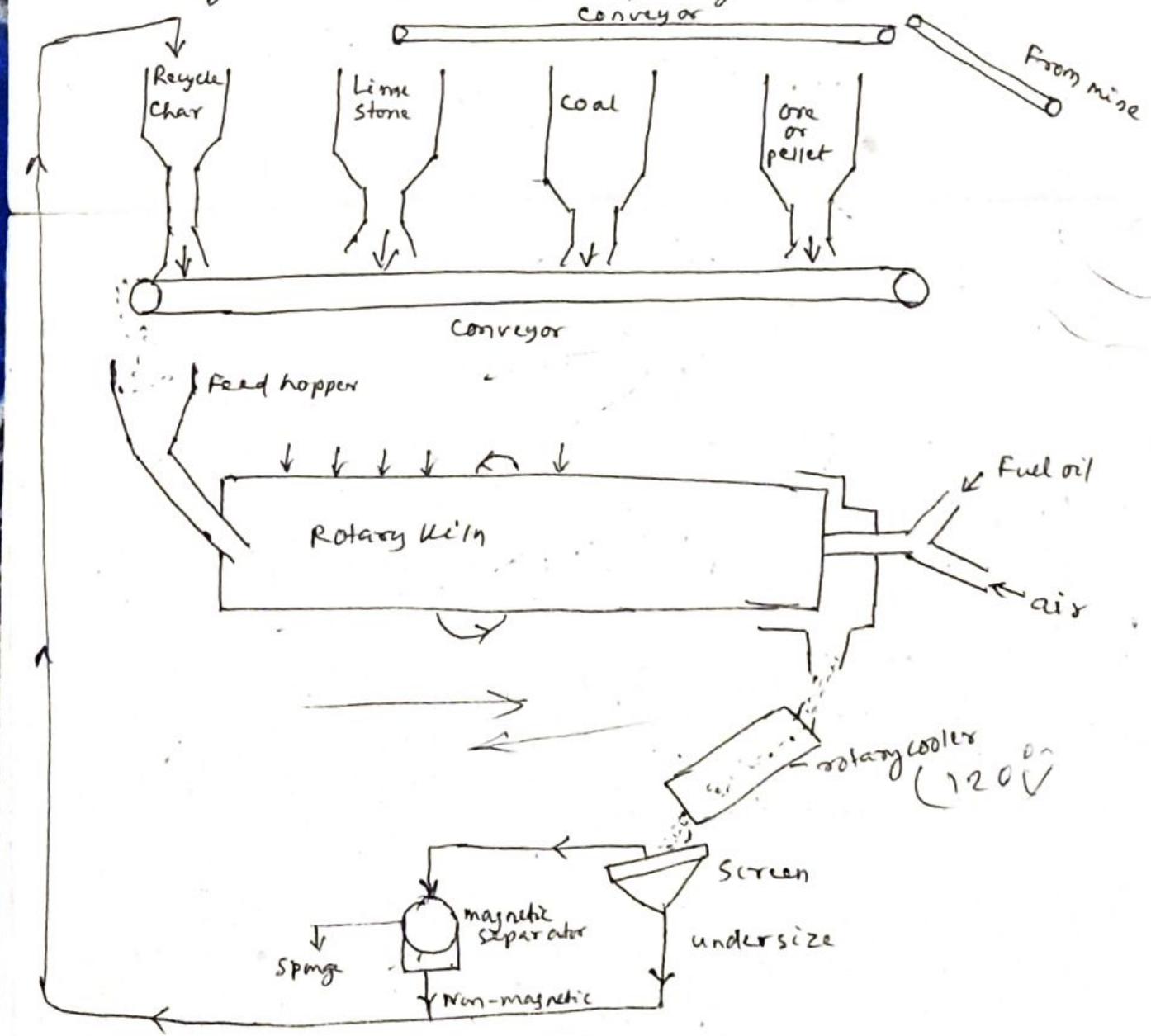


(Fig - Process Flow diagram for Rotary Kiln)

The following figure shows a typical material balance in Rotary Kiln direct reduction per tonne of DRI.



The following figure shows a scheme of rotary kiln plant

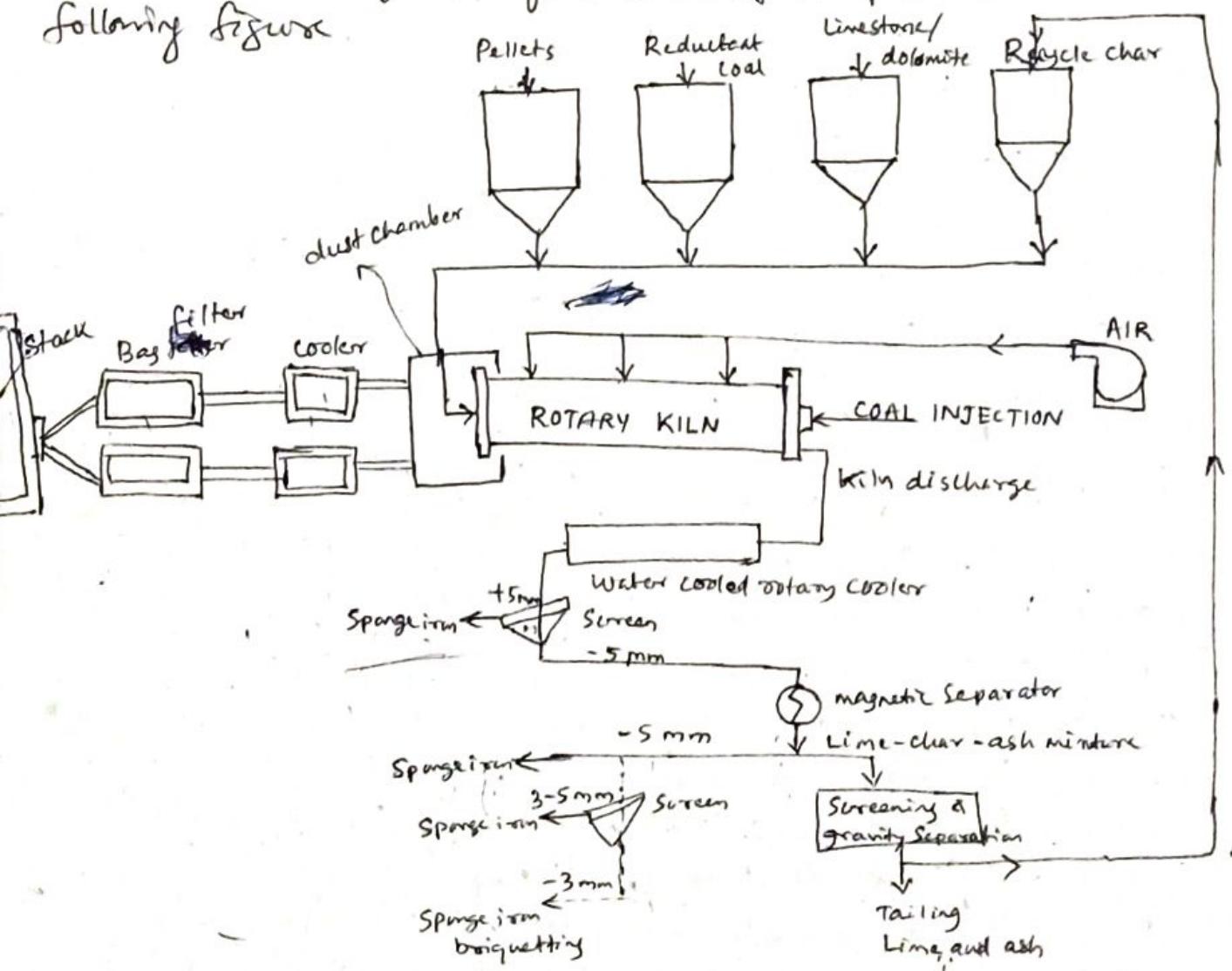


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Different DR processes using rotary kilns are described briefly below:

(a) Krupp - CODIR (Coal ore Direct Reduction process)

The Krupp - CODIR process was developed on the Krupp's experience with rotary kiln process (Waelz process) for recovery of Zn from low grade ore in 1920 and Krupp - Renn process to recover iron from ores low in high silica, in 1930, carried out in Germany. The flow sheet of the process is shown in the following figure.



In this process iron ore or pellet is fed into the inclined rotary kiln together with solid reductant, dolomite or limestone as flux and the recycled char from the bins. Feed size is closely controlled for better separation at the latter later stage in the process.

Primary heat is supplied by the combustion of pulverised coal injection at the discharge end of the kiln. In CODIR process, the majority of coal is injected from the discharge end of the kiln and distributed in such a way that the bed temperature does not fall below 950°C to 1000°C . The coarse coal particles that settle in the high temperature zone of the kiln are mixed with the burden, while releasing the volatile matter so that these can also participate in iron ore reduction process, thus substituting fixed carbon. Secondary heat is supplied by blowing air into the kiln gas space through tubes placed along the entire length of the kiln. ~~Secondary~~ Secondary air is introduced axially (along the kiln centre line) in the direction of the gas flow. The air supplied to the length of the kiln is metered for close control of temperature and gas atmosphere in the kiln. In this process, heating zone extends from 25% to 40% along the length of the kiln and in the reduction zone, a uniform charge temp. profile is maintained between 950°C to 1050°C .

The DRI, char, coal ash and spent flux leave the kiln and is subjected to cooling in a shield rotary cooler. The cooled solids are subjected to screening, magnetic separation. Char is separated by gravity for return to the kiln feed, and spent flux and ash are disposed.

Salient features of CODIR process

- (i) In CODIR process, highly reactive coal injection over a large range of size from 5-25 mm upto 35 mm is possible.
- (ii) In this process, a uniform charge temperature profile between 950 and 1050°C is easily maintained by injecting majority of coal from the discharge end.
- (iii) The ~~coarse~~ coarse coal particles which settle in the starting region of isothermal zone of the kiln, get mixed with the burden while releasing the volatiles so that these can also participate in the reduction of iron oxide, thus, substituting fixed carbon.
- (iv) In case the coal quality allows effective char recovery, even the entire amount of fresh coal can be injected and only

The recycled char is added together with the feed.

(8)

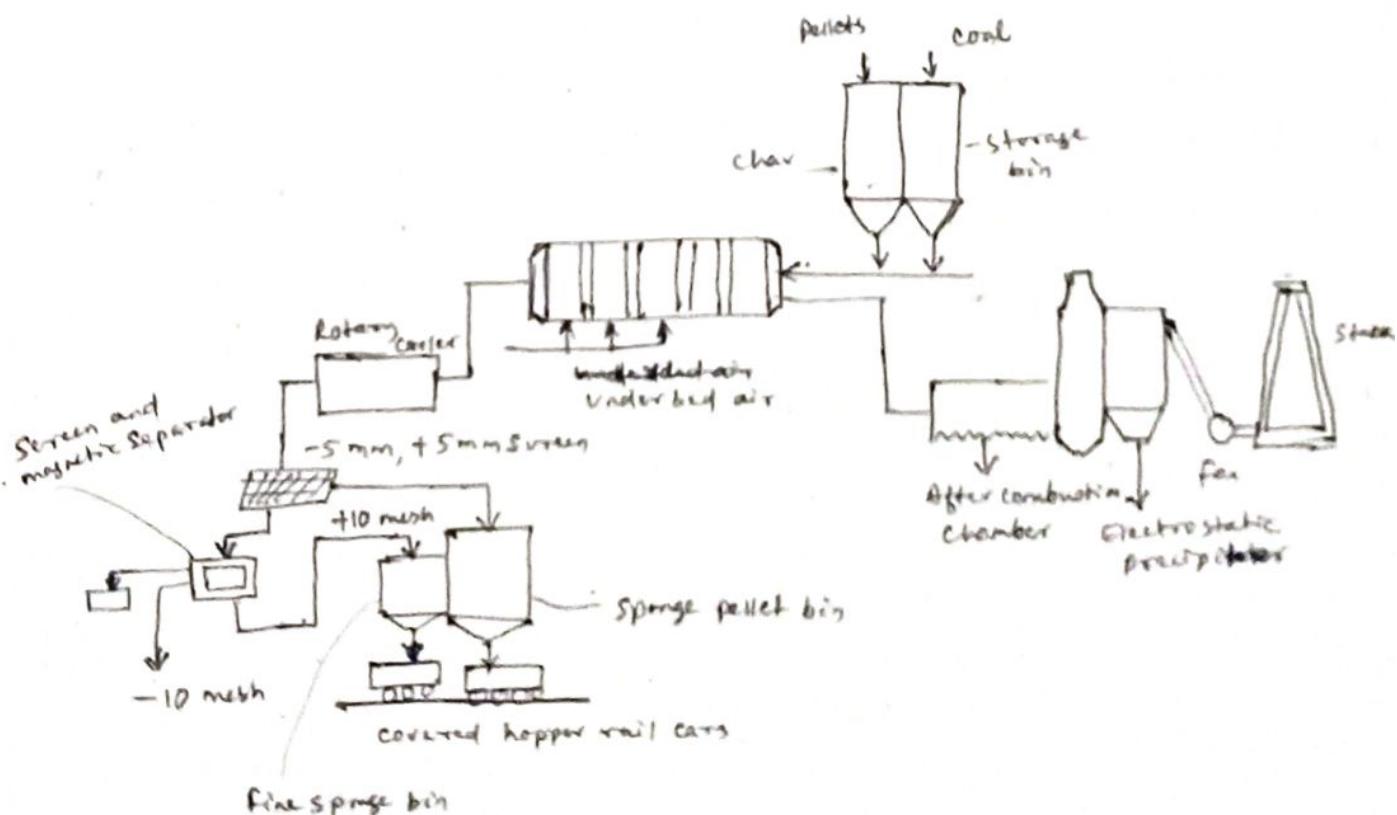
(v) The coal injection system makes use of coal volatiles for reduction, thereby reducing the coal requirement to a minimum.

(vi) With finer coal injection, energy consumption decreases from 20 GJ/t DRI to 15 GJ/t DRI .

A commercial Krupp-CODIR plant designed for a capacity of 1,50,000 metric tons, started operations in 1973, at the Dunsward Iron and Steel Works Ltd at Benoni, South Africa. The reduction kiln in this plant is about 4.6 meters ^{inside} diameter and 74 meters long. In India, Sunflag Iron and Steel Company Ltd. at Bhandra, western India, has installed a CODIR plant of capacity 150,000 tpa in 1989 with inner diameter 5.0 meters and length 80 meter.

(2) SL/RN process

Originally developed jointly by Stelco (steel company of Canada), Luwigi Chemie, ~~Republiek~~ Republic Steel Company and National Lead Corporation in 1964. This is the most widely used coal based DR process. This process is now owned by Luwigi and is known as Okukanga process. Flow sheet of SL/RN process is shown in the figure.



(Flow sheet of SL/RN process)

In this process, material consists lump ore or pellets, coal, recycle char and flux are charged into the kiln. The burden materials move towards the discharge end and thereby progressively heated to the reduction temperature of about $1020-1100^{\circ}\text{C}$. In the kiln preheated zone, the charge is heated to about 980°C by counter flowing hot freeboard gases. To increase the efficiency of the kiln, the preheat zone is made as short as possible, usually about 40 to 50% of the kiln length. When the charge reaches temperature in excess of 900°C , reduction begins. To maintain a uniform reduction zone temperature by burning combustibles released from the bed, air is blown by shell mounted fans into the freeboard gas stream and through burner tube spaced uniformly along the length of the kiln. Air is introduced axially into the kiln and additional combustion air is blown into the kiln through a central airport of the discharge end. The off gases from the kiln come out through the feed end of the kiln at about 900°C . These gases pass through a dust settling chamber, after burner where the combustibles are burned. The gas is then cooled and released to the atmosphere.

The solid products are discharged from the rotary kiln into a sealed rotary cooler via transfer chute. Where temperature of products comes down to 95°C in a non-oxidising atmosphere, Discharge materials are continuously separated into DRI, DRI fines, non-magnetics by a system of screen and magnetic separation. Char is separated from the waste by gravity separation. Nowadays, kilns are equipped with nozzles for under bed injection of about 25% air in the preheating zone of the kiln.

Salient features —

- (1) Use of a wide variety of solid fuels ranging from anthracite to lignite including charcoal,
- (2) flexibility with regard to the type of iron bearing materials which can be used such as Lump ore, pellets, ilmenite, iron sands and steel plant wastes
- (3) Improved heating of the charge by Submerged air injection in the preheating zone of the kiln plants installed recently.
- (4) optimized coal injection facilities.
- (5) waste gas conditioning by controlled post combustion.
- (6) In some cases, waste gas heat is recovered for power generation through steam generation.

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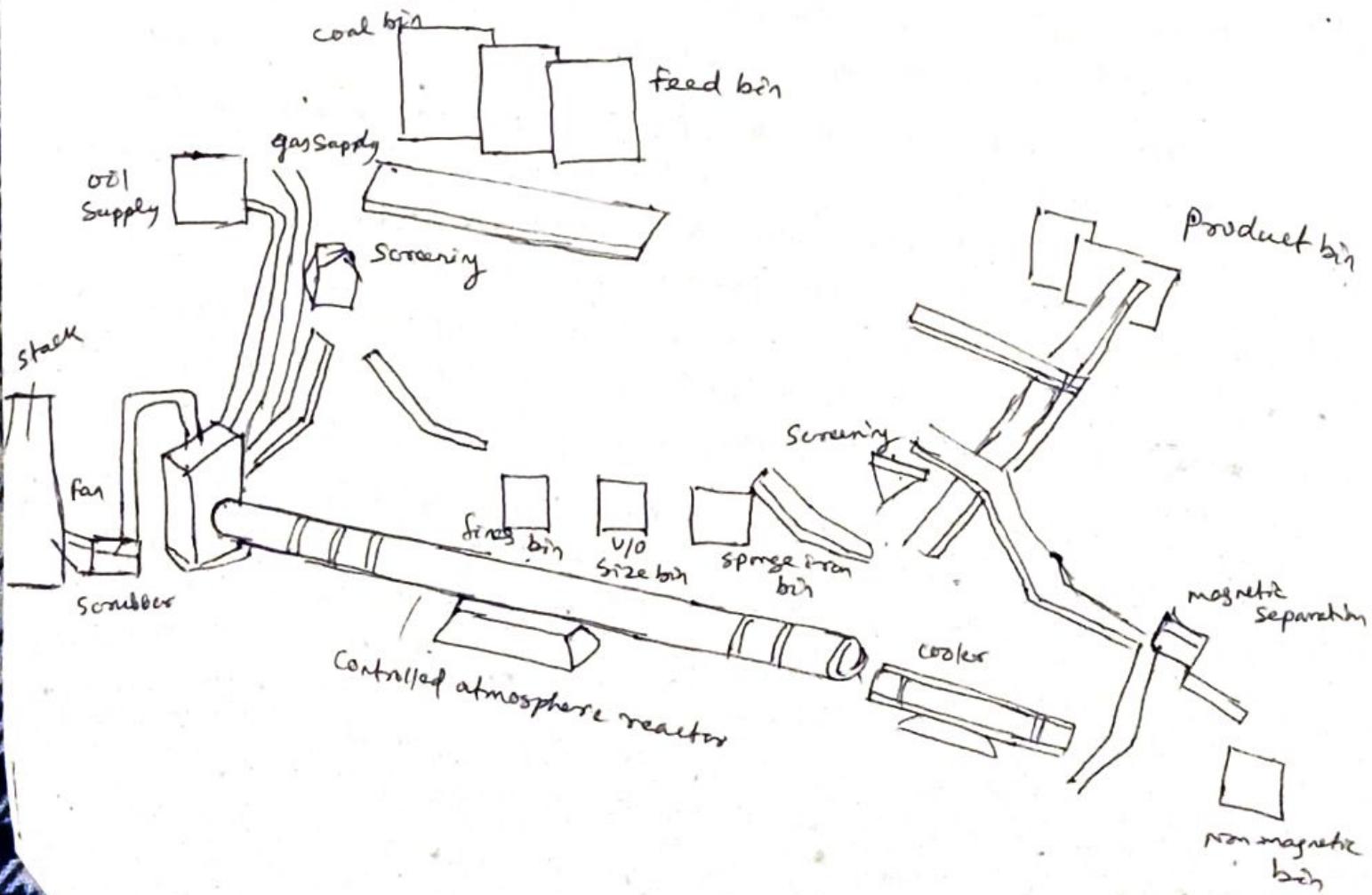
3. ACCAR Process

(OSIL, Keonjhar)

The Allis Chalmers Controlled Atmosphere Reactor
OR

The Allis Chalmers Controlled Atmospheric Reduction

It produces highly metallized DRI in rotary kiln. In this process, liquid, solid and gaseous fuels singly or in combination are used directly in the kiln with an external reformer or gasifying plant. Except for this fundamental difference i.e. use of gas + coal or oil + coal, keeping the coal percentage at a maximum of 80%, in both cases, the process is similar to SL/RN or CODIR process.



In the ACCAR process, coal is charged along with the oxide feed, whereas oil or gas is injected directly into the ore bed, along the length of the reactor through radial ports, arranged in equally spaced rows and located upto 80% of the length of the kiln from the discharge end. The arrangement of the ports and valves is such that oil or gas and air are alternately injected through the same port. When a particular port is under the charge bed, oil is injected, and when the same port approaches above the bed position, air is injected through it. This radial-cum-air distribution system permits closer control of the temperature profile along the entire length of the reactor. As the coal and the iron oxide travel through the kiln, reduction is accomplished by CO generated in the kiln bed.

The final degree of reduction is achieved by introducing liquid ~~and~~ or gaseous fuel through the kiln ~~shell~~ shell port near the product end of the kiln as they pass under the solid bed. Solid products are discharged from the rotary

Kiln into a rotary cooler where cooling is done by continuous external water ~~supply~~ spray. The DRI is separated from the coal ash by magnetic separation and is then screened for different size products.

Salient features →

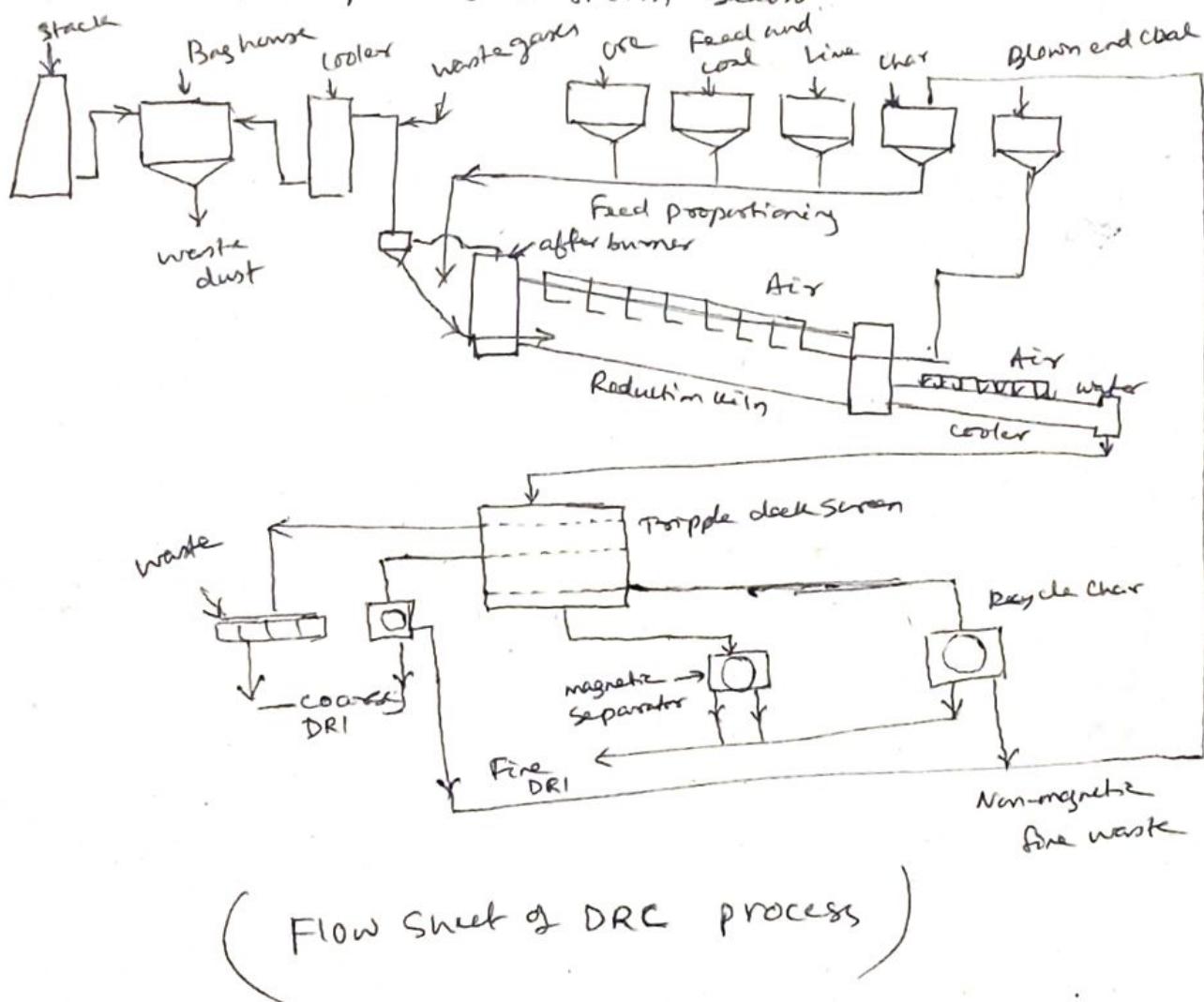
- (i) In ACCAR process, when coal plus oil is used as a fuel-cum-reductant, product containing high carbon with high degree of metallization is obtained at a lower operating temperature with lower energy consumption over other rotary kiln DR processes, where coal is exclusively used as a reductant.
- (ii) In ACCAR process, operating temperature is low as compared to the other rotary kiln processes, which is a significant advantage particularly when coal of low ash fusion temperature are used.
- (iii) Sponge iron from ACCAR process, contains extra carbon (due to the deposition of carbon in the sponge iron following the cracking of oil, especially at the exit end of the kiln) which is advantageous for electric furnace steel making.
- (iv) In ACCAR process, presence of radial port holes along the length of the kiln helps in controlling the temperature profile along the entire length of the kiln.

The ACCAR process was developed in 1972 at Niagara Falls (Canada). The process was commercialized in 1983 in a 500 tpd plant of Orissa Sponge Iron Limited (OSIL) at Keonjhar (Orissa). ACCAR process was no longer used in OSIL. Subsequently claimed that they had developed a new technique of their own which is now being marketed for 100,000 - 150,000 tpa modules. A 150,000 tpa plant has been set up by Lloyds metals at Bughur in Maharashtra based on inputs from OSIL.

(9) DRC - (Direct reduction Corporation) Process —
 (Davy reduction corporation).
 ✓

The DRC Process of the Davy Reduction Corporation has developed from the Hockin process of Western Titanium Ltd, Australia, formerly Azion.

The first commercial plant was commissioned for Scaw metals, in Germiston, South Africa. The flow sheet of DRC process is shown below.



The kiln shell diameter is 4.5 meters and length is 60 meters having rated capacity of 75,000 t/annum. In this process, raw materials consisting of lumps ore / pellets & coal and limestone are continuously fed fed to a refractory lined kiln rotating at a very low rpm (less than 1 rpm). Passage of the burden through the preheat zone and reducing zone in the kiln flows typically in the ^{upward}_{kiln} operation. Shell-mounted fans via internal air tubes supply combustion air. Process heat is supplied by burning combustible in the kiln for which required air is supplied by shell-mounted fans via internal air tubes spaced along the length of the kiln.

Coal is blown from the discharge end to supplement the heat generated by combustion of carbon monoxide escaping from the bed. The bed and gas temperature profile are accurately measured by the thermo couples installed along the length of the kiln, and allows close control by adjustment of the air input throughout the tube.

In the reduction zone, iron oxide is reduced to metallic iron. The max. kiln bed temperature is 1060°C . with a maximum kilngas temperature of about 1160°C . To achieve higher degree of reduction higher value of CO/CO_2 ratio is maintained.

The product is discharged via scaled transfer chute to an indirectly cooled rotary cooler and then sent for screening and magnetic separation.

Salient features

- ① In this process, air injection inside the kiln ensures optimum heat evolution and heat transfer in various zones.

DATE SIGNATURE OF INSTRUCTOR

Screening of Raw materials and products

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To maintain size fractions both in raw material as well as product, effective screening systems are very much important. Screening is a process by which a separation is made between the larger and smaller particles by passing through the aperture opening to pass through or reject out. This gives an idea in a given feed. The higher the ratio of undersize to the oversize, ~~the~~ the better is the separation.

Efficiency of Screening — The ratio of the amount of undersize passing through the screen to the amount present in the feed is called the efficiency of screening. It depends upon the type of screening medium. The screen surface is usually made of woven net of wire or rods.

Screening is carried out for the following purposes:

- ① Elimination of rejects to reduce the cost of handling.
- ② Minimises the fines.
- ③ Elimination of oversize before feeding.

Sampling — The word "Sample" is a small portion of a mass, which accurately represents the mean composition of the whole of the mass. Sampling is a process of taking small portion of an article so that the ~~consistency~~ consistency of that portion should be representative of the whole.

The important conditions affecting and governing the selection of true average sample from a large block of material are —

- (1) Thorough mixing of the bulk
- (2) The fineness of the division or the size of the constituents forming the bulk
- (3) The mode of occurrence of the metallic constituents.
- (4) the weight of the sample taken is directly depend upon the size or degree of fineness of the ore particles.
- (5) The ratio of the weight of the first sample to the total weight of the bulk. It is usual to cut out for 1st Sample from one fifth to one-twentith of the bulk.
- (6) the method of cutting out the Sample.

Methods of Sampling -

The various methods of manual Sampling are

- ✓ (1) Coning and quartering (practised in mineral fields)
- (2) Trench & pit Sampling
- (3) Grab Sampling
- (4) Shovel Sampling
- ✓ (5) Split Shovels Sampling.
- ✓ (6) Groove ~~or~~ charnel Sampling
- ✓ (7) Bulk Sampling

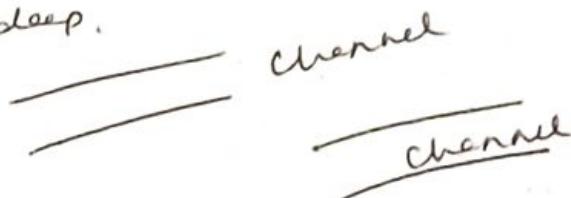
① Coning & quartering - It is a well-known process of Sampling. This method may be made to yield fairly accurate results when properly carried out, but it is a slow and tedious process, requiring most conscientious work on the part of a labourer to ensure correct results. It can be made systematically in the hands of a skilled operator. Coning and quartering method is a hand cutting method. Ores and similar materials, unless already fine enough, are broken or crushed to a proper size. The crushed material is shovelled into a conical pile, each shovelful being thrown upon the apex of the cone so that it will run down evenly all around. When the cone is completed, it is worked down into the form of a flat truncated cone by men who walk around, drawing their shovels from centre to periphery. After flattening, the cone is divided into four quarters by means of a sharp-edged board or steel bladed quarters. Two opposite quarters are removed

and rejected and the remaining two are taken for sampling.

The Sample may again be mixed by coning and quartering or it may be crushed if necessary and then coned and quartered. These operations are repeated until a sample is obtained which may be conveniently be reduced to a degree of fineness required for analysis.

② Groove or Channel Sampling -

In groove Sampling, the sample is cut either by chisel a chisel and applied either to a bedded deposit or a dipping lode. Before cutting the sample, the exposure's mineral vein or lode would have ~~been~~ to be cleaned to remove dust, lime and soluble salts. This may be done by washing the exposure with a jet of water or by scraping the outer surface of exposure. When the surface is clean, the next ~~the~~ step is to mark out the location of the channel by inscribing two parallel lines on the exposure about 0.0762 to 0.152 metres apart using the point or chalk for drawing the lines and the channels are being 0.05 to 0.76 meters deep.



After this, the job of cutting begins. The operator cuts an even groove straight across the exposure and ~~at~~ at right angles to the direction of dip. As the material is broken, it is ~~not~~ caught by an assistant. Every necessary precaution is taken to ensure that there is no contamination and the correct amount of rock is removed from each channel.

This a tiring job.

③ Bulk Sampling - Bulk Sampling is done in case of irregular mineral deposits. The bulk samples should be ~~not~~ ~~too~~ ~~representative~~ representative of the whole.

Coal Sampling - For a DRI plant, coal samples are done from the following

- (1) Sampling from the wagons
- (2) Sampling from the truck.
- (3) Sampling from the stack.

① Wagon Sampling - Coals are brought on the rakes basis from the colliery to the destination where average analysis of the coal for entire rake (ranging from 1800-2000 Mts) is required to assess the grade. While drawing samples from the wagons, the sampler must see the entire quantity of coal from each wagon ~~dealing~~ and collect samples from a wagon if the coals are from the same mine. The samples are collected during loading the time of loading or unloading. The coal sample shall be collected in the following manner:

(i) The total sampling shall be aimed on 0.25% minimum for ~~to~~ a rake load of coal.

(ii) Coal upto 200 mm can be collected by scoop

(iii) Coal, which can not be held in scoop, shall be picked by hand.

(iv) The inclusions of foreign materials shall be considered.

Similarly samplings from truck and stack shall be done as per ISI method.

Methods of Sponge iron Sampling

(i) When loaded from bins to trucks \rightarrow the loading of sponge iron direct from the bin to truck takes hardly 5 minutes and sampling of sponge iron from the truck at the time of loading is not possible. In such a case random sampling as per ISI Specification is done.

(ii) Manual Sampling \rightarrow If trucks are loaded manually from stacks of sponge iron, the following procedures are to be adopted for sampling

(a) if loading is from one stack \rightarrow the sampling shall be made at the time of loading.

WRITING SPACE

The Sampler must ~~not~~ mix up the stacks before being loaded.
Whether possibilities of mixing foreign materials
(b) If loading is from different stacks & when loading is made at a time from different stacks having different grades of materials, the sampler should collect samples proportionally from each grade of sponge iron and combined together shall represent the lot.

Chemical Analysis

In the laboratory, the following analyses are done in every shift a day.

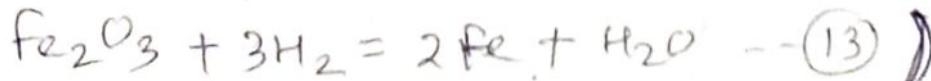
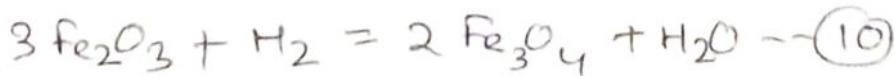
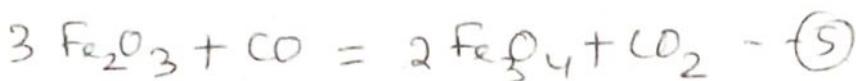
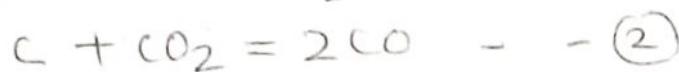
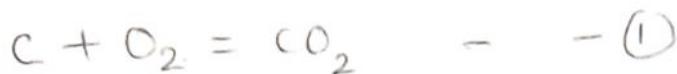
1. FeT - Total iron in sponge iron
2. FeM - metallic iron in " "
3. Fe - Iron in ore
4. SiO₂ - in sponge iron and ore
5. Sulphur - " " " " "
6. Phosphorus - " " " "
7. Al₂O₃ - " " " "
8. CaO - in limestone & dolomitic
9. MgO - in " " "
10. water - \oplus pH, hardness, Alum dozey's test, chloride, iron, calcium, magnesium, Turbidity sulphate
11. coal - moisture, Ash, VM, FC, chemical analysis of ash
12. chemical analysis of Alum
13. chemical analysis of caustic

14. Chemical analysis of steel & alloys
15. Sp.gr. of solids and liquids
16. Apparent density of solid
17. Gas analysis
18. Useful heat value of coal.

Effect of Temperature

Principle of reaction in Rotatory Kim

The chemical reactions involved in iron ore reduction are:



Reactions (1) and (2) take place at high temperatures in the reactor where carbon is oxidised by oxygen of the air. Reaction (3) is the sum of the reactions (1) and (2). Reaction (2) is known as Boudouard reaction which takes place between carbon and CO_2 produced by the reactions (5), (6) and (7). Reaction (4) takes place between carbon and water vapour from the combustion air or moisture from the raw material in the reactor. The reduction of iron oxide takes place in steps which refers to reactions (5), (6) and (7) known as indirect reduction reactions.

reaction (8) is a combination of reactions " (5), (6) and (7) Reaction (9) is the direct reduction by carbon. This reaction however, does not take place to any extent. Reactions (10), (11) and (12) are those which happens due to hydrogen like reactions (5) (6) and (7). In a reactor, where carbon is used as reducing agent it has been established that most reduction reactions takes place mostly through CO intermediate. In the direct reduction process, the iron oxide ore is used in the lumpy form or as pellet.

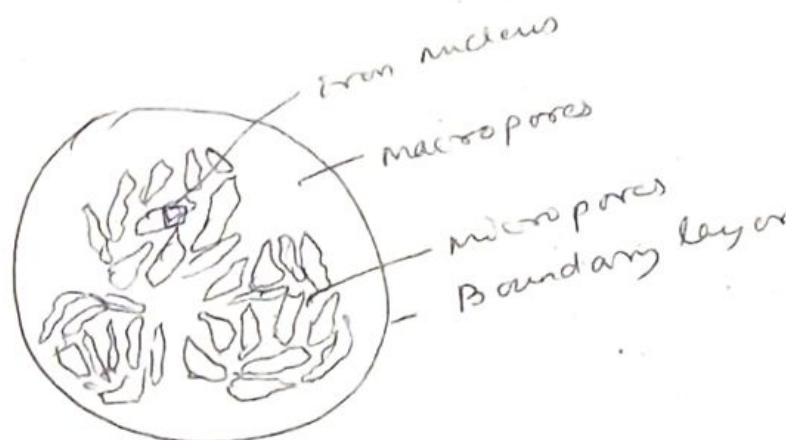


fig-1 (Reduction mechanism for porous iron ore)

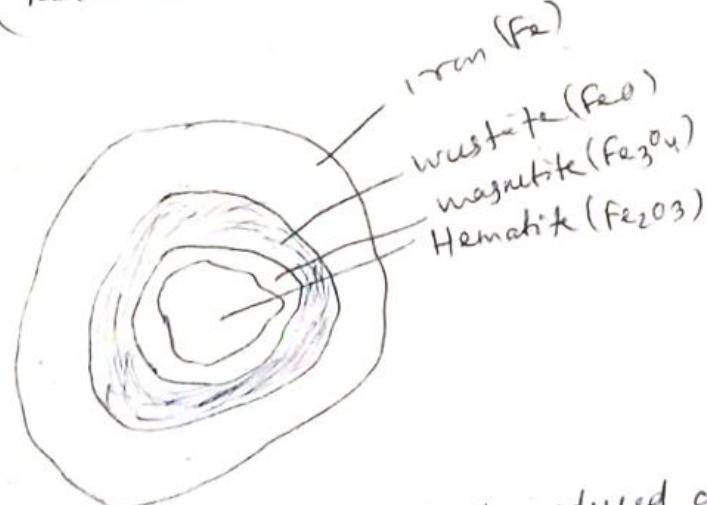
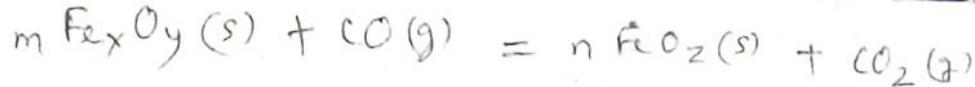


fig-2 (cross section of a partially reduced dense iron ore)

The ore may be considered to be composed of several granules. The large gap between the granules are known as macro pores, and the smaller pores within the groups are known as micropores. The reducing gas flows through the space between the lumps of ore or pellets. A boundary layer is formed around the individual lumps. The micro, macro pores and boundary layer are shown in fig 1.

The reduction reaction of iron oxide in the ore, which takes place in steps, may be written in general equation as

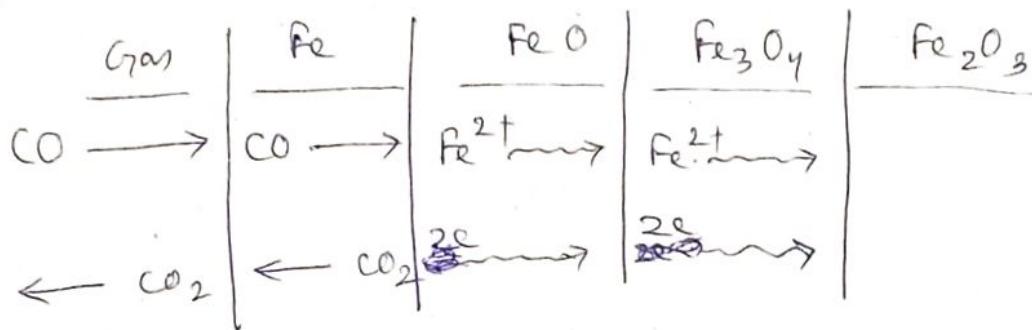


where m, n, x, y, z are integers $0, 1, 2, 3, 4$ depending on specific iron oxide or metallic iron.

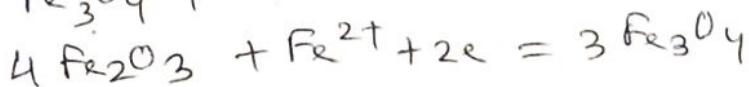
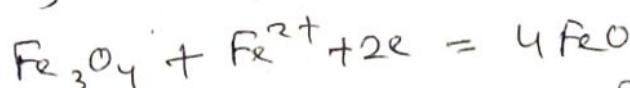
Mechanisms of iron oxide reduction - Several mechanisms for step wise reduction have been proposed, so the important mechanisms are

- Edstrom mechanism. (applied to hardened ore)
- McKeown mechanism. (applied to very porous ores)
- Lien mechanism.

(a) Edstrom mechanism

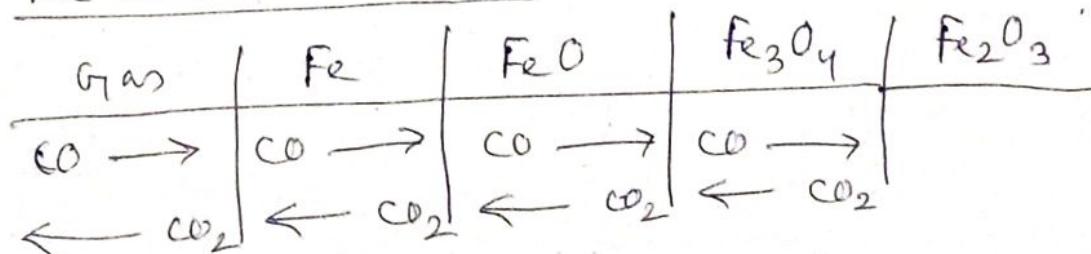


According to this mechanism oxygen is removed from the iron-wustite interface according to reaction (7) or (12). The other oxides are reduced to the next lower oxides by diffusion of iron cations and electrons according to the following reactions.



According to this mechanism, oxygen is removed from the iron oxide at the iron-wustite interface only by the reaction with reducing gas CO or H₂ which diffuses inwards through the iron layer and the product gas CO₂ or water vapour diffuses outwards.

(b) Mc Keown mechanism

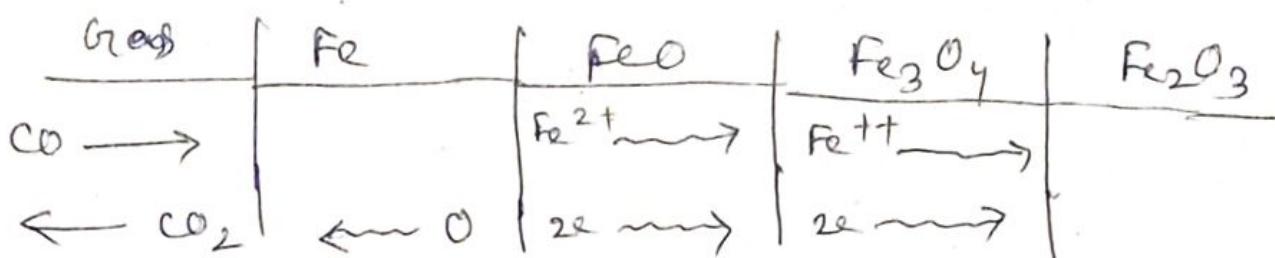


In this mechanism, oxygen is removed by reducing gas simultaneously at all interfaces. In this case reaction

WRITING SPACE

takes place according to reactions (5), (6) and (7)

(c) Lien mechanism.



[→ gaseous diffusion through pores]
 [← Solid diffusion through solids]

According to this mechanism, C or H₂ reduces magnetite to iron which is absorbed on the outer surface of a dense layer of impurities to reducing gas.

In all three mechanisms, several steps are involved any one of which could be the rate controlling. The steps that could be rate controlling are

- (i) mass transport between bulk gas flow and the solid specimen surface. i.e boundary layer diffusion.
- (ii) mass transfer between sample surface and reaction interface.
 - (a) Solid diffusion through a lower oxide.
 - (b) Solid diffusion through a dense metallic iron phase.
- (iii) interparticle diffusion of gas species.
- (iv) chemical reaction at the solid interface.
- (v) Nucleation and growth of iron phase.
- (vi) heat transfer to the reaction interface.

For reduction to occur, the reductant must get into the interface and the product must come out.

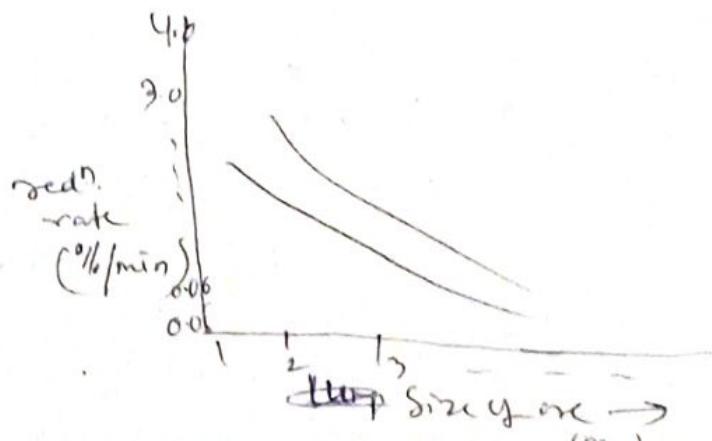
These are affected by several factors, any one of which could be rate controlling.

Some of the rate determining steps in iron ore reduction are associated with the nature of the reaction system and the contact between the reacting phases others are associated with the nature of the ore. The latter determines the ease with which oxygen can be removed from the oxides in the ore by the reducing gases. This property of the ore is called reducibility of ore. The factors that affect the reducibility of the ore briefly described below:

1. Nature iron oxide in the ore →

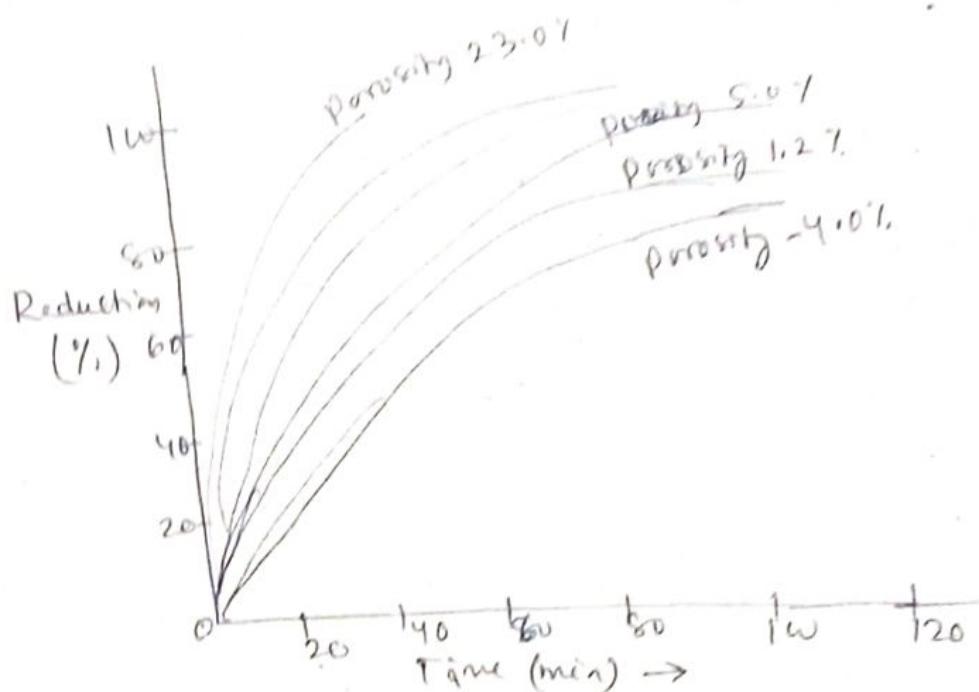
It has been found that, the reducibility of hematite is greater than that of magnetite although the amount of oxygen to be removed is 12% more in case of hematite than magnetite. The higher reducibility hematite may be due to change in crystal structure during reduction of hexagonal to cubic magnetite and wustite. In the 1st stage of reduction, transformation from hexagonal lattice to cubic lattice is accompanied by about 25% increase in volume resulting in exposure of higher surface area for the reduction. Whereas during transformation from magnetite to wustite, there is only a small increase in the volume.

2) Ore Size & Shape → The rate of reduction of ore also depends on the size and shape of the particle. The shape of the particle, however, is not important for the size range used in commercial practice. The shape of the particle is important when the size is below 0.25 mm. It has been observed that the rate of reduction increases with decrease in size of the ore.



3. Porosity and crystal structure →

The porosity of the ore is one of the most important parameter affecting the reducibility. The reducibility of soft hematite ore is greater than that of hard dense hematite and hard dense magnetite ore. The following figure shows the Percentage of reduction Vs. time for iron ore samples of various Porosity.



It is observed that the reducibility of iron ore increases with an increase of porosity or an decrease of ore size.

④. Nature and composition of gangue →

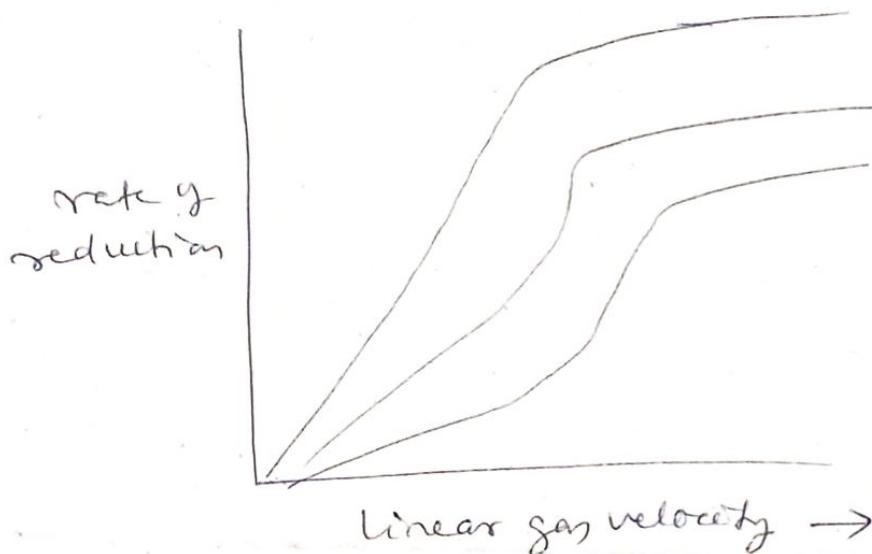
High gangue content in DRI would require additional energy, fluxes and refractories during melting, adversely affecting the operation of arc furnace. Therefore the gangue content of the ore should not be more than 5%. Natural ore contains gangue as oxides of Si, Al, Cr, Ti etc. in different forms. In some of the ore, wustite is present as complex compound such as $2\text{FeO} \cdot \text{SiO}_2$, $\text{Fe}_2\text{Al}_2\text{O}_5$, $\text{FeO}(\text{Cr}_2\text{O}_3)$, $\text{FeO} \cdot \text{TiO}_2$ etc., where the activity of wustite is low. These oxides tend to decrease the reducibility of the ore in the kiln in reducing atmosphere.

5. Swelling → Some ores show abnormal increase in volume at temperature between 900 and 1000°C, which is known as swelling of the ore. Such swelling increases the rate of reduction of the ore because of highly porous reduction product. However, if the swelling is too large,

It gives rise to a product porous product without sufficient strength.

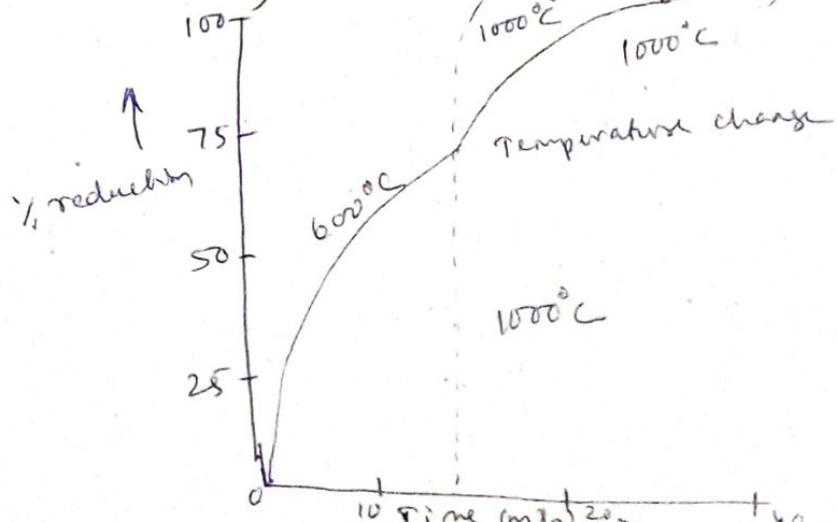
b. Linear gas velocity →

The increase in linear velocity of the reducing gas increases the rate of reduction of iron oxide ore. However the rate of reduction remains constant after a certain critical velocity of the reducing gas.



7. Temperature → In general, the rate of reduction of iron oxide ore increases with increase in temperature. In solid-gas reduction, it is advantageous to use a temperature above 1000°C because Boudouard reaction attains a maximum value for producing CO.

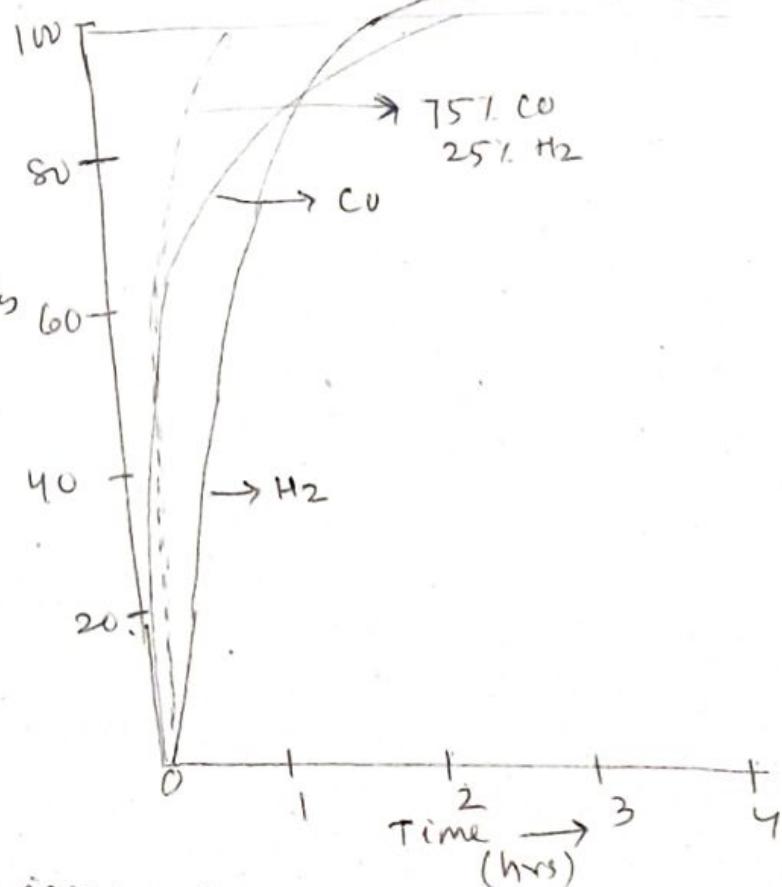
The following figure shows the difference between reduction rate of a spherical hematite pellet reduced at first 60% at 600°C and the remainder at 1000°C (solid lines) and that of the pellet reduced fully at 1000°C (dotted lines).



WRITING SPACE

8. Gas composition → The coal after gasification becomes a composition of CO , H_2 , water vapour, CO_2 , ^{and} ~~and~~ Nitrogen. The gas composition affects the reduction kinetics, it is observed that by increasing the partial pressure of reducing gases, the rate of reduction can be increased. It is proved that H_2 is the better reducing agent than CO in the beginning of the reduction but at high degree of reduction, CO reduces iron oxides at faster rate. The mixture of 75% CO and 25% H_2 gives better result. The following figure shows the difference in the reduction rates of iron oxides with ~~pure~~ CO , pure H_2 and their mixture.

From the graph, it is observed that, for complete reduction with gas mixture is 90 minutes whereas with pure CO and pure H_2 , the time for the same reduction is 2 hrs and 4 hrs respectively.



9. Gas pressure → The increase in pressure is expected to increase the rate of reduction as it increases the partial pressure of the reducing gas. The rate of reduction increases with increase in H_2 pressure from 1 atm to 10 atm beyond which it remains constant.

Ferro-alloys are produced by reducing metals from their oxides. The starting materials are ores or ore concentrates. Ferro-silicon, Ferro-manganese and Ferro-chrome are manufactured from ores as these have a high content of an element to be reduced. The ores for making Ferro-tungsten, Ferro-molybdenum, Ferro-vanadium and Ferro-titanium are poor in the useful element and should be concentrated.

When making an alloy, a suitable reductant should be selected and conditions should be formed so as to ensure a high recovery of the valuable elements from the starting material. The most common reductants in the manufacture of ferro-alloys are carbon, silicon and aluminum. Carbon is the cheapest among them and is used in the manufacture of silicon alloys, high carbon ferro-manganese and high carbon ferro-chrome.

Ferro-alloy furnaces → Ferro-alloy furnaces may be of either reducing or refining type. The former operates, as a rule by a continuous process. The reductant is usually carbon. The electrodes in these furnaces are immersed into the solid charge, the furnace is recharged as the solid charge is being melted and the alloy and the slag are periodically removed. Continuous process is employed for smelting Ferro-silicon, high-carbon ferro-chrome, high carbon ferro-manganese, Silico-calcium, Silico-chrome, and Silico-manganese. Some reducing processes are periodic. Furnaces for this type are provided with powerful transformers (7000-60000 kVA).

In refining furnaces, the process is carried out with full meltdown of the charge. The processes occurring in them are also of reducing nature, but the usual reductants are silicon or aluminium-containing alloys. At the beginning of the melting, the electrodes are immersed into the charge and subsequently they are lifted as a pool of molten metal accumulates and the arcs burn openly. At the end of melting, the alloy and slag are tapped from the furnace. Furnaces of this type are equipped with less powerful transformers (3000-6000 kVA).

Ferro-alloy furnaces may be open or closed at the top fixed, tilttable on a horizontal axis or ~~rotatable~~ rotatable on a vertical axis.

Manufacture of Ferro-Silicon (Fe-Si)

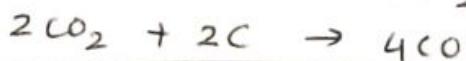
Ferro-silicon is used for deoxidation and alloying of steel.

Raw materials → The ore components of the charge for making Fe-Si are minerals having a high content in silicon such as quartz, quartzite and chalcedony. Good grades of quartzite contain 96-97% SiO_2 and around 1% Al_2O_3 , roughly 1% CaO and MgO and not more than 0.02% P_2O_5 . The best reducers are charcoal and pitch and petroleum coke. The material that is used most commonly for the manufacture of ferro-silicon is coke breeze i.e. fines remained from screening of blast furnace coke. A large ~~disadvantage~~ disadvantage of coke breeze is a high moisture content.

Furnaces → Fe-Si is made in the three-phase furnaces of a power of 29,000 - 60000 KVA operating at a voltage of 145-175V. Closed type stationary & tilting furnaces are mainly used. The hearth and lower portion of walls of a furnace are lined with carbon bricks and upper portion of walls with fire-clay bricks.

Process → Upon heating of a newly made furnace lining, the furnace is charged with a charge for making 45% ferro-silicon, with the charge level and the power and voltage supplied being raised gradually. Normal operating conditions are established in 2-2.5 days from beginning of charging.

The reduction reaction of Silicon from silica occurs with solid carbon.



In a melt of ferro-silicon, the iron dissolves the reduced silicon and removes it from the reaction zone. With high temperature reduction which is typical of the process of smelting ferro-silicon, the process of reduction of SiO_2 into silicon is most likely to occur in two stages.



Carbon causes final reduction of silica. The latter reacts with carbon both at the surface of the lumps of coke breeze and in their depth.

Procedure → The charge materials should be stored separately in furnace bay bins. Before supplying to the furnace, they should carefully be weighed and mixed. A dosing carriage is loaded first with coke breeze, then with turnings and quartzite and finally with graphitization wastes.

The composition of charge may be

quartzite - 300 kg

coke breeze - 141 kg

Iron turnings - 170 kg.

Smaller capacity of the charging carriage will result in a more uniform charge being fed to the furnace. The charge is fed into an open-type furnace by means of a charging machine, care being taken that the charge being distributed around all three electrodes in the form of cones placing the charge in the form of cones is needed to diminish the losses of heat and silicon and to increase the heat concentration under the electrodes. It is assumed that a well forms under an electrode, its walls are formed by the ~~semi-baked~~ semi-baked charge that is heated to a high temperature, the bottom is formed by the melt and the roof, by the electrode. The walls of the well are being continuously melted, the silica is reduced and the silicon is dissolved in molten iron, the melt passes along the channels and new proportions of the charge are supplied to the reaction zone. Smelting of ferro-silicon is a continuous process. Tapping is done periodically 12-15 times a day.

Page 3

With a small number of tappings, the melt may become overheated and remove much heat from the furnace. With too frequent tappings, the loss of metal with ladle may increase. Under normal conditions, the tap hole is opened with a crow bar. The melt first runs out in a thin jet, but quickly erodes the hole and begins to pass out more powerfully. The tapping time for a normally run furnace is around 15 minutes.

Manufacture of Ferro-chrome (Fe-Cr)

Grades of ferro-chrome → Fe-Cr can be produced by various processes depending on the specified content of carbon in it. The various types of Ferro-chrome grades are

1. High carbon Fe-Cr.
2. Foundry Fe-Cr
3. Medium carbon Fe-Cr
4. Low carbon Fe-Cr.
5. Extra low carbon Fe-Cr.

High carbon Ferro-chrome and foundry Ferro-chrome are made from chrome ore by reduction smelting with coke breeze being as a reducer. Medium carbon, low carbon and extra low carbon ferro-chrome is made by a more intricate processes using three smelting plants. One furnace serves to produce foundry ferro-chrome which has an increased content of silicon (around 3%) as compared to high carbon ferro-chrome. The second furnace operates on a charge composed of quartzite, coke breeze and foundry ferro-chrome to make an alloy with ~~0.3-0.7%~~ 30-50% Cr, 30-40% Si, 20% Fe and 0.3-0.7% C. (ferro-silico chrome). Finally in the third furnace, chrome ore is reduced with silicon in the ferro-silico-chrome and the product is ferro-chrome with ~~extra coke breeze~~ the carbon content directly depending on that in the ferro-silico-chrome used for final melt.

Manufacture of High Carbon Ferro-chrome →

The charge for making high carbon ferro-chrome may be composed of

- (i) Chrome ore - ~~Mg~~ chromospinelides: $(Mg, Fe) Cr_2O_4$ (Magnesio chromite)
 $Fe(Al, Cr)_2O_4$ (Alumino chromite)

Chromospinelides may contain upto 62% Cr_2O_3 , the balance usually being iron, aluminium and magnesium oxides. A typical composition of a chrome ore is

| | |
|-----------------|----------|
| Cr_2O_3 - | 45-62% |
| FeO - | 12-16% |
| SiO_2 - | 3-6% |
| MgO - | 12-20% |
| Al_2O_3 - | 7-11% |
| Cr_2O_3/FeO - | 3.4: 4.1 |

(ii) coke breeze

(iii) quartzite as flux

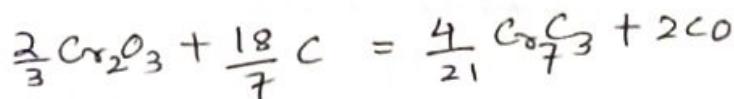
High carbon ferro-chrome is made in three-phase open top or closed top furnaces of a power of 10000-16500 KVA with electrodes 950-1150 mm in diameter, operating at a voltage of 140-190V. The hearth and walls of the furnace are lined with magnesite bricks and the upper portion of walls with fire clay brick.

Chrome ore is blended to equalise its particle size and composition. The size of the lumps is usually not more than 80mm. The amount of lumpy ore in the mixture should be not less than 50%. The reducer may be graded coke breeze in lumps 10-25 mm in size.

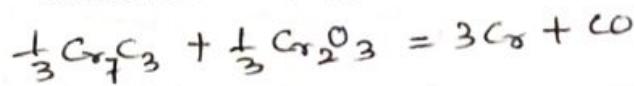
Process → The following processes take place when making high carbon ferro-chrome.

- removal of volatiles and moisture from the charge and heating of the charge by the heat of burning gases
- reduction of iron and chromium with simultaneous formation of Chromium and iron carbides.
- melting of the elements reduced with the formation of molten Fe-Cr.
- formation and melting of the slag.
- reduction of chromium and silicon from the slag.

The principal reactions for the reduction of chromic and iron oxides with the carbon of the coke breeze are



Reduction of chromium from ore begins at 1100-1150°C, continues at an increasing rate in hotter zones of the furnace and ends in the hearth, where chromium is reduced from the chromic oxide of the slag. At a sufficiently high temperature, the melt being formed can be decarbonised by the reaction.



Decomposition of carbides requires much heat and therefore, high temperature is essential for smelting high carbon ferro-chrome. The temperature in the hearth is determined by the slag composition. The melting temp. of an alloy with 4% C and 70% Cr is near 1550°C.

Procedure → A melt for high carbon Fe-Cr is carried out with the furnace top being closed. The mixed charge consisting chrome ore, coke breeze and quartzite, is delivered to the furnace from furnace bays. Charging is done periodically as the previous charge has settled at the top. The following measures are essential to maintain the top in normal conditions:

- (a) The charge should always have the specified composition.
- (b) The charge should be given evenly to each phase electrode.
- (c) Charge cones should be pierced periodically.

The electrodes are slipped every shift or sometimes twice a day.

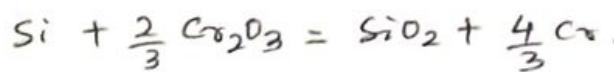
The metal and slag are tapped simultaneously three times a day shift.

The ladle for tapping is mounted on a carriage under the tap hole, the slag flows over the ladle nose into the slag pot. High carbon Fe-Cr is teemed into shallow moulds.

Manufacture of Low-carbon and Extralow carbon Ferro-chrome

In the manufacture of ferro-chrome with a low content of carbon, chrome ore is reduced with the silicon of ferro-silico-chrome.

Process → The reduction of oxides in chrome ore with the silicon of ferro-silico-chrome follows the reactions



The reactions are exothermic, can proceed more fully at lower temperatures. The reduction of iron from oxides of the ore facilitates the course of the reaction, since iron lowers the melting point of the alloy and lowers the concentration of chromium in it.

Smelting procedure → Low carbon and extralow carbon Fe-Cr is produced in three phase open-top furnaces of a power of 3000-5500 KVA operating at a voltage of 280-350V. Both tilting and stationary furnaces are used. The process may be divided into two stages (1) the period of smelting and (2) the period of refining. During the first period, the operation is done at a high voltage tap and full power while in the refining period both the voltage and power are lowered. When smelting extralow carbon ferro-chrome, use is made of graphitized electrodes and for smelting other grades of Fe-Cr, self-baking electrodes are used.

Charging of the furnace is mechanised. Ore, lime and ferro-silico-chrome are delivered into the furnace. The furnace is equipped with an automatic control system to maintain current and voltage constant during operation. The smelting process includes the following stages.

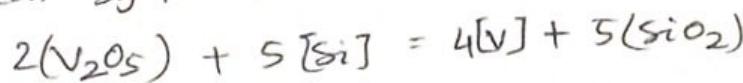
- (a) Fettling of the bath (b) charging of the reducer, charging of the main charge, melting of the 1st batch of charge
- (c) melting of the second batch (d) charging of ferro-silico-chrome
- (e) slagging off (f) melting of the third batch and tapping of metal and slag.

Manufacture of Ferro-vanadium (Fe-V)

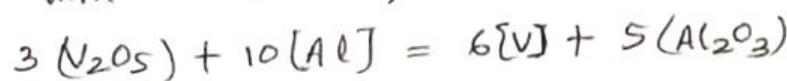
Raw materials for manufacture of ferro-vanadium →
The chief raw materials include:

- (a) fused vanadium pentoxide (V_2O_5)
- (b) Ferro-silicon
- (c) Aluminium
- (d) Iron trimmings
- (e) Lime.

Process → Vanadium pentoxide may be reduced to vanadium with silicon by the reaction



or with aluminium by the reaction



or else with both silicon and aluminum (Silico-aluminothermic process)
The reduction with silicon can proceed more fully if the silica that is formed is combined by calcium oxide into $2CaO \cdot SiO_2$ silicate.

~~Without~~ Without using calcium oxide, vanadium pentoxide can be reduced partially to V_2O_3 trioxide by the reaction



Smelting procedure → Smelting is done in a magnesite-lined arc furnace, the furnace power may be 1500 - 3000 KVA at a voltage of 110 - 220V. A specified mass of lime and iron trimmings is placed onto the furnace hearth, then refining slag (high in vanadium oxide) from the previous heat is ~~skipped~~ poured in. During smelting, the furnace is charged with a mixture of vanadium pentoxide, ground ferro-silicon and lime. Upon melt down, the bath is covered with a layer of free running slag, with all vanadium and great portion of silicon having passed to metal. With an excess of reductants, the slag contains not more than 0.5% V_2O_5 , 26-30% SiO_2 , 50-52% CaO , 9-12% MgO , and 6-7% Al_2O_3 . The molten metal contains 25-30% V, 16-18% Si, and 0.3-0.5% C. The time of melt down of the charge and reduction of the first portion of mixture is roughly an hour. The slag is skimmed off and a new portion of a mixture of ~~the~~ vanadium pentoxide, lime, ferro-silicon and aluminium is given on to the metal. Upon melt down of this mixture, the bath is stirred thoroughly. The end of reduction is determined by the slag breaking up into a white powder. The melt after the second ~~period~~ period contains at least 35% V, 9-12% Si and 0.6% C. Since the ~~reduction~~ reactions with silicon and aluminium are exothermic, the second period of heat is carried out at a reduced power or even with the current switched off. The period takes about an hour.



A third period is then carried out to oxidise the excess of silicon i.e. to refine the metal. The reducing slag is poured off and skimmed, and a mixture of vanadium pentoxide and lime is given onto the exposed surface of metal. Upon melt-down of this mixture, the bath is stirred. The excess silicon is oxidised by vanadium pentoxide. The temperature of the bath should be moderate. The vanadium and iron reduced in this process pass to the metal.

Manufacture of Ferro-Titanium (Fe-Ti)

Ferro-titanium is employed for final deoxidation and degassing of critical grades of structural steel, since titanium has a high affinity for oxygen and forms a stable nitride which is insoluble in steel. Titanium metal has found wide applications in the manufacture of refractory alloys.

Smelting of Ferro-Titanium: →

The charge materials → The principal titanium minerals are ilmenite ($\text{FeO} \cdot \text{TiO}_2$), rutile (TiO_2), Titanite ($\text{CaO} \cdot \text{SiO}_2 \cdot \text{TiO}_2$) and Perovskite ($\text{CaO} \cdot \text{TiO}_2$).

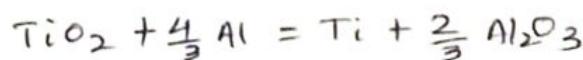
The charge materials for ferro-titanium are

- (i) Ilmenite concentrate ($\text{FeO} \cdot \text{TiO}_2$)
- (ii) Aluminium powder
- (iii) Iron ore
- (iv) Ferro-Silicon
- (v) Return scrap

The content of silica in the concentrate should not exceed 2.5 %, since the content of silicon in ferro-titanium is limited. Titanium concentrate is subjected to oxidising roasting at 800-1100°C during which upto 0.4% is removed. Roasting is done in hearth or rotary tubular furnace. In view of the necessity to preheat the charge before smelting, roasted concentrate is delivered to mixing at 400-500°C. A typical composition of roasted ~~ilmenite~~ ilmenite concentrate is 40% TiO_2 , 1% MnO , 0.3% CaO , 2% MgO , 2.5% Al_2O_3 , 17% FeO , 35% Fe_2O_3 , 0.05% S and 3% SiO_2 . Apart from titanium concentrate, the charge for smelting ferro-titanium contains iron ore, lime, aluminium powder and ferrosilicon. Scrap of titanium metal and titanium alloys is also utilised in the manufacture of ferro-titanium.

Ferro-silicon

Process- The reduction of titanium dioxide with carbon requires a large supply of external heat. Titanium can be reduced with carbon in a powerful electric furnace. The reduction reactions are



The temperature of the process in off-furnace smelting of ferro-titanium may reach 1600°C . The slag from the off-furnace has the composition 68.72% Al_2O_3 , 8-12% TiO_2 and Ti_2O_3 , 1.5% FeO , 8-12% CaO and MgO and roughly 1% SiO_2 . The recovery of titanium is 75-80%.

Ferro-titanium is smelted in a non-heated shaft whose height is chosen so that the solid block of metal and slag can occupy $\frac{3}{4}$ of its height. The diameter of the metal block is roughly 5-6 times its height. The built-up cast iron shaft is placed onto bottom plate carried by a carriage. A layer of high alumina slag is made on the bottom of the shaft, then a cylindrical templet made of roof iron, is placed inside. The space between the templet and shaft ~~walls~~ walls is filled with ground slag or magnesite powder. The assembled shaft on the carriage is run into an ignition chamber and the charge is poured from the bin onto the shaft bottom and ignited by ignition mixture. The ignition mixture may be magnesium chips or salt petre. The mixture is placed into a recess made in the centre of the charge layer and ignited by ~~a~~ means of electric spark, torch etc. The burning mixture first ignites the adjacent portions of the charge and then whole mass of the charge. At the end of smelting, the thermite mixture is given on to the slag surface. The melt is left in the shaft for 10 hours to solidify into a block and cool, then the shaft is disassembled, its upper half is removed and the solid block of metal and slag on the carriage is left to cool, for another 10 hours. The ferro-titanium thus produced is crushed into pieces of a mass not over 10 kg.

— The End —