1. General Process Scheme.

Direct Reduction (DR) consists in the removal of oxygen from iron ores at temperatures below the melting point of the solid material, for the production of a product with a high content of metallic iron and a certain level of carbon mainly as iron carbide (Fe₃C). This product is named Direct Reduced Iron (DRI).

In gas based DR processes, the separation of oxygen is carried out by the action of the reducing agents hydrogen and carbon monoxide. In solid based reduction processes, coal is used as the reducing agent.

Table BC-I lists the direct reduction technologies currently in operation or under construction, indicating installed DRI capacity and the source of reducing agents for each process. Gas based processes account for 91% of the total world DRI/HBI capacity.

Process	Energy	Units	Product	Capacity	Start Up		
				(Thousand ton/year)			
HYL	Natural Gas	28	DRI/HBI	16,325	1957		
Midrex	Natural Gas	50	DRI/HBI	29,665	1969		
Purofer	Natural Gas	1	DRI/HBI	330	1970		
SL/RN	Coal	16	DRI	1,780	1970		
K-M	Coal	2	DRI	40	1973		
CODIR	Coal	4	DRI	600	1973		
Fior	Natural Gas	1	HBI	400	1976		
DRC	Coal	5	DRI	630	1983		
OSIL	Coal	2	DRI	250	1983		
SIIL	Coal	13	DRI	590	1984		
DAV	Coal	1	DRI	40	1985		
TDR	Coal	2	DRI	240	1986		
Jindal	Coal	8	DRI	800	1993		
Iron Carbide	Natural Gas	1	IC	320	1994		
GHAEM	Natural Gas	1	DRI	600	1996		
Circored	Natural Gas	1	HBI	500	1999		
Finmet	Natural Gas	8	HBI	4,300	1999		
Total		144		57,410			
Leading DR Technologies, with 80% of the world DRI/HBI capacity.							

Table BC-IDirect Reduction Processes

Figure BC-1 shows a general scheme of the direct reduction process, indicating the main inputs and outputs related to this system.



Figure BC-1 Direct Reduction Process

1.1. Inputs.

• Iron ore.

This is the source of iron units for the process. Usually, it contains some non-reducible oxides such as alumina, silica, lime and magnesia. It can be used in its natural form as lump ore or fines, or concentrated in the form of pellets.

• Thermal energy.

In direct reduction, thermal energy is used for two main purposes: As a source of reducing agents for the process, and as fuel for thermal equipment. Natural gas is the energy source commonly used in gas based DR processes to produce the reducing agents, hydrogen and carbon monoxide.

• Electricity.

Energy required to operate mechanical equipment. The process can be adapted to minimize the electric power consumption using steam driven equipment, consuming thermal energy for steam generation inside the plant battery limits.

• Water.

Water is used for equipment cooling and for condensing excess water from the top reducing gas, reformed gas and cooling gas streams. It is also used for steam generation in processes that use steam as oxidant in the reforming process.

• Miscellaneous.

In this category are classified other materials required for the plant operation, such as inert gas, air, catalyst, chemicals for water treatment, spare parts and maintenance materials.

1.2. Products.

• Direct Reduced Iron (DRI).

Main product of a direct reduction processes. It is a porous solid with high metallic iron content and a certain level of carbon mainly as iron carbide (Fe₃C), which is incorporated during the process. The main use of this product is as raw material for steelmaking in the electric arc furnace, but it can be used also in blast furnaces and converters.

The main DRI quality parameters are the product metallization and the total carbon content. DRI metallization is defined as the ratio of metallic iron to total iron in the product, which is:

For economical reasons, DRI is produced with metallization levels up to 95%.

One process parameter which correlates directly with DRI metallization is the reduction degree, defined as the ratio of oxygen removed from the ore to the amount of oxygen originally present in the ore:

% Reduction = <u>Oxygen removed</u> x 100 Reducible oxygen in the ore

DRI carbon content is reported as total carbon, including combined carbon as iron carbide (Fe₃C), which represents the highest percentage (> 90%), and also free carbon in the form of graphite.

For maximum benefits using DRI in the electric arc furnace, the carbon content of the DRI can be controlled between 1.2% and 5.5%.

1.3. Byproducts.

Byproducts are basically water and carbon dioxide, which are formed during the reduction process. Water is separated in direct contact condensers and the method used for carbon dioxide removal varies with the DR process. In the HYL process, CO_2 is removed selectively from the reducing gas stream, whereas in other technologies, CO_2 is purged from the system as a fraction of the top reducing gas.

1.4. Losses.

Fines, dust and purges from the cooling water systems which are lost during the process. This term is also applied to heat losses from the thermal equipment and flue gases.

2. Process Sections.

The main direct reduction processes are divided into two operating sections:

- Reducing gas supply.
- Iron ore reduction.

2.1. Reducing gas supply.

In the HYL process, reducing gases are generated by self-reforming in the reduction reactor, feeding natural gas as make-up to the reducing gas circuit and injecting oxygen at the inlet of the reactor. The partial oxidation of natural gas with oxygen generates reducing gases (H₂ and CO) and increases the operating temperature, which are required for the iron ore reduction. Once in contact with the solid material inside the reactor, further cracking and reforming reactions are carried out due to the catalytic effect of metallic iron. These partial oxidation and reforming reactions are the following:

 $\Delta H^{\circ}rxn$ (cal/gmol)

CH_4	+	1/2O ₂	>	CO	+	2H ₂	-8527
$2H_2$	+	O ₂	>	$2H_2O$			-115,596
CO_2	+	H_2	>	CO	+	H_2O	+9838
CH_4	+	H_2O	>	CO	+	$3H_2$	+49271

An alternative source of reducing gases for the HYL technology is based on natural gas-steam reforming. This type of process is also the most utilized technique for the production of hydrogen in the chemical process industry. The natural gas-steam reforming reactions are the following:

ΔH°rxn (cal/gmol)

CH_4	+	H_2O	>	CO +	$3H_2$	+ 49271
CO	+	H_2O	>	CO ₂ +	H_2	- 9838

In order to assure that some carburization reactions will not take place in the reformer, it is necessary to promote the reforming reactions using an excess of steam in the presence of a nickel based catalyst. The mixture of natural gas and steam is fed to the reformer with a steam to carbon ratio of 2.2/1 to 2.6/1 by volume.

Sensible energy from the reformed gas stream is recovered for the generation of steam and for the heating of boiler feed water, before being passed through a quench tower where excess water is eliminated from the gas stream.

2.2. Iron ore reduction.

Several heterogeneous reactions may occur in the process for iron ore reduction, between a solid phase and a gas phase. Main phenomena in each of these phases are the following:

• Solid Phase.

The solid phase passes through different stages of reduction, cooling and carburization.

Reduction

Iron ore is initially preheated up to the temperature level required for the reduction process by means of heat transferred from the hot reducing gases. After this preheating stage, the oxygen removal from the ore is initiated by the action of the reducing gases, hydrogen and carbon monoxide.

The mechanism of the reduction process can be represented as follows:

Reduction by Hydrogen

 $\Delta H^{\circ}rxn$ (cal/gmol)

$3Fe_2O_3$	+	H_2	>	$2Fe_3O_4$	+	H_2O	- 2798
Fe ₃ O ₄	+	H_2	>	3FeO	+	H ₂ O	+ 18502
FeO	+	H_2	>	Fe	+	H_2O	+ 5702

Reduction by Carbon Monoxide

∆H°rxn (cal/gmol)

3Fe ₂ O ₃	+	CO	>	$2Fe_3O_4$	+	CO ₂	- 12636
Fe ₃ O ₄	+	CO	>	3FeO	+	CO ₂	+ 8664
FeO	+	CO	>	Fe	+	CO ₂	- 4136

As it can be observed from the reported heats of reaction, the reduction by hydrogen is an endothermic process and the reduction process with carbon monoxide is exothermic.

For the gas composition used in the HYL technology, with high hydrogen content in the reducing gas, the overall reduction process is endothermic.

• Cooling and carburization.

In direct reduction processes, besides the oxygen removal from the iron ore, it is also important to have a controlled carburization process.

During this stage, the gas composition and temperature of operation must be favorable for the carburization process, incorporating most of the carbon into the product in the form of iron carbide (Fe₃C).

The main reactions, which may occur during the carburization stage, are the following:

Carburization

 ΔH°_{rxn} (cal/gmol)

3Fe	+	CH ₄	-> Fe ₃ C	+	$2H_2$	+23579
3Fe	+	2CO	> Fe ₃ C	+	CO ₂	- 70473
3Fe	+	CO + H ₂ ;	> Fe₃C	+	H ₂ O	- 25692
		CH4	> C	+	$2H_2$	₊ 17889

Gas Phase

Regarding the gas phase, it is important to use reducing gases with the highest possible reducing potential, which means a high ratio of reductants to oxidants (H_2+CO/H_2O+CO_2) . Because of this, it is convenient to regenerate the gas reducing potential through the reduction stages of either sequential or recycle processes, eliminating the oxidation products, water and carbon dioxide.

Another important aspect of the reduction process is the operating temperature. Reducing gases must be fed at the highest possible operating temperature to assure that the reduction reactions are thermodynamically feasible and to achieve satisfactory reaction kinetics in the process.

In the gas phase, depending on the operating conditions such as temperature and pressure, gas-gas reactions may occur in the different process stages. The main gas-gas reactions, which normally occur in the reduction and cooling stages, are the reforming reaction and the gas shift reaction. These reactions are the following:

Gas-Gas Reactions

 ΔH°_{rxn} (cal/gmol)

CH_4	+	H ₂ O	>	CO +	$3H_2$	+49271
CO	+	H_2O	>	CO ₂ +	H_2	-983