

# IRON

## 1. Introduction

Iron [7439-89-6], Fe, from the Latin *ferrum*, atomic number 26, is the fourth most abundant element in the earth's crust, outranked only by aluminum, silicon, and oxygen. It is the world's least expensive and most useful metal. Although gold, silver, copper, brass, and bronze were in common use before iron, it was not until humans discovered how to extract iron from its ores that civilization developed rapidly (see MINERALS RECOVERY AND PROCESSING).

Pure iron is a silvery white, relatively soft metal and is rarely used commercially (1). Electrolytic (99.9% pure) iron is used for magnetic cores (2) (see MAGNETIC MATERIALS, BULK). Native metallic iron is rarely found in nature because iron which commonly exhibits valences of +2 and +3 combines readily with oxygen and sulfur. Iron oxides are the most prevalent form of iron (see IRON COMPOUNDS). Generally, these iron oxides (iron ores) are reduced to iron and melted in a blast furnace. The hot metal (pig iron) from the blast furnace is refined in steelmaking furnaces to make steel (qv).

Iron is alloyed with other elements for commercial applications. The most important alloying element is carbon. Small amounts of carbon alloyed with iron lower the melting point, as illustrated in Figure 1. The distinction between steels and other irons is based on properties and defined by the iron-carbon phase diagram. Steel is generally classified as those iron-carbon alloys (0–2% C) which have a high melting point and can be hot rolled. Iron with carbon up to about 2% can be heated to a temperature at which only one phase (gamma iron) exists. Gamma iron is face-centered cubic (fcc) in structure, and therefore is plastic, or malleable, which allows hot rolling. Cast irons are those which contain sufficient quantities of the eutectic (about 2–5% C) to make the metal too brittle to hot roll; thus the requirement that it be cast. Pig iron from the blast furnace is liquid iron saturated with carbon (>4.3% C) depending on the temperature corresponding to the liquidus line.

Iron is indispensable in the human body (see MINERAL NUTRIENTS). The average adult body contains 3 grams of iron. About 65% is found in hemoglobin, which carries oxygen from the lungs to the various parts of the body. Iron is also needed for the proper functioning of cells, muscles, and other tissues (4).

The earliest record of human usage of iron dates to ca 2000 BC (5) in Egypt, Asia Minor, Assyria, China, and India. It is almost certain, however, that the first iron to be used was not processed but was obtained from meteorites (1). One of the few places where native iron is found is in Greenland, where it occurs as very small grains or nodules in basalt (an iron-bearing igneous rock) that erupted through beds of coal.

Processed iron was first produced around 1300 BC. It is presumed that the first iron was made accidentally as a result of very hot fires built on top of some iron-bearing rocks or soil. The iron-bearing rocks could have been reduced to iron by being heated in the presence of hot charcoal and in the absence of air. Upon raking out the ashes, the first ironmaker probably found a sponge-like chunk of hard but malleable metal having considerable slag in its pores. Reduced iron sponge had to be hammered and squeezed while still hot to expel most of the

slag in order to make effective use of the metal. This hammering and working process produced wrought iron.

The first furnaces specifically made for smelting iron ore were low shaft furnaces: low box-like hearths made of stone, open at the top, and having an opening near the bottom for air intake. The Catalan hearth furnace for making wrought iron is described in writings from Central Europe in the twelfth and thirteenth centuries AD. These Catalan furnaces were low stone shaft furnaces having hearth dimensions of ca  $60 \times 60 \times 75$  cm. As better blowing devices were invented and the height of the furnaces was increased, it is probable that, when the fires became hot, liquid high carbon iron, which was not malleable, was produced and could be used to make cast-iron articles.

The Stuckofen or old high bloomery appeared in Germany in ca 1300 AD. This type of furnace was 3–5 m high and enclosed a tapered vertical shaft that was 1–1.2 m in diameter. Small openings near the bottom were provided for nozzles (tuyeres, pronounced *tweers*) that permitted air, supplied by bellows, to be blown into the furnace. Modern blast furnaces have essentially the same fundamental design.

Eventually, processes were developed for converting the high carbon product of the blast furnace to wrought iron. In the puddling process, solidified pig iron first was melted and then silicon, manganese, and carbon were oxidized by the hot gases and the iron oxides that were added. During this operation the puddler continually stirred the bath. As the decarburization approached completion, the metal began to solidify. A series of hammering and squeezing operations separated the slag from the iron to produce wrought iron.

In the United States, the first ironworks was built at Jamestown, Virginia, in 1619. The Hammersmith furnace in Saugus, Massachusetts, built in 1645, operated until 1675. This early American ironworks has been restored and is called the Saugus Iron Works. Iron blast furnaces appeared in many localities where there were deposits of iron ore. Small bodies of iron ore in New Jersey, Connecticut, Massachusetts, Pennsylvania, and New York formed the basis of many small colonial furnaces.

Ironmaking in the United States did not expand rapidly until after the Revolutionary War. Then, as the colonists moved westward, the need for iron prompted the establishment of ironworks near the new settlements. A blast furnace built by Jacob Anschutz in 1796 was the beginning of the iron and steel center in Pittsburgh, Pennsylvania.

The early U.S. blast furnaces of the nineteenth century were in the form of a truncated cone or pyramid, 6–9 m in height, enclosing a shaft 1.2–2.4 m in maximum diameter, and constructed of stone. The output of these furnaces was from 1–6 metric tons per day. Many changes were made in furnace design and operation: the shaft was enclosed in a metal shell, the top was closed to prevent the escape of top gases, the blast air was preheated, and the furnaces were enlarged. By 1900, a single blast furnace made as much iron as 200t/d. Improvements continued to be made, but generally modern blast furnaces are only larger than their nineteenth century ancestors. The modern blast furnace may have a hearth as much as 14 m in diameter, be over 60 m in height, and produce up to 10,000 t/d.

In 1979, there were 168 blast furnaces in the United States, most located in Pittsburgh and Chicago, and these produced  $8 \times 10^7$  t of pig iron. By 1992, most of the blast furnaces in the Pittsburgh area had disappeared. Only 44 blast furnaces were operating in the United States, producing  $4.7 \times 10^7$  t of pig iron. The drop in pig iron production was attributed to decreased and more efficient use of steel products, competition from steel imports, and rapid growth of scrap-based steelmaking.

## 2. Properties

Typical properties of iron are given in Table 1.

Direct reduction is the process of converting iron ore into metallic iron without melting. Direct reduced iron (DRI) can be produced in pellet, lump, or briquette form. When produced in pellets or lumps, DRI retains the shape and form of the iron oxide material fed to the DR process. The removal of oxygen from the iron oxide during direct reduction leaves voids, giving the DRI a spongy appearance when viewed through a microscope. Thus, DRI in these forms tends to have lower apparent density, greater porosity, and more specific surface area than iron ore. In the hot briquetted form it is known as hot briquetted iron (HBI). Typical physical properties of DRI forms are shown in Table 2.

HBI is produced by molding hot (ca 700°C) DRI into pillow-shaped briquettes using a pocketed roll press. HBI is almost twice as dense as nonbriquetted DRI and it has substantially less surface area, which makes it 100 times more resistant to reoxidation. It is stronger and more massive, making it more resistant to fines generation, and it takes up less volume for storage and shipping owing to its high bulk density. It has minimum water absorption when saturated, thus it is ideally suited for merchant applications where shipping, handling, and storage characteristics are important.

## 3. Iron Ores

**3.1. Minerals.** Iron-bearing minerals are numerous and are present in most soils and rocks. However only a few minerals are important sources of iron and thus called ores. Table 3 shows the principal iron-bearing minerals. Hematite is the most plentiful iron mineral mined, followed by magnetite, goethite, siderite, ilmenite, and pyrite. Siderite is unimportant in the United States, but is an important source of iron in Europe. Ilmenite is normally mined for titania with iron as a by-product. Pyrite is roasted to recover sulfur in the form of sulfur dioxide, leaving iron oxide as a by-product.

**3.2. Sources.** Iron ore deposits were formed by many different processes, eg, weathering, sedimentation, hydrothermal, and chemical. Iron ores occur in igneous, metamorphic, and sedimentary deposits. Normally, as-mined iron ore contains 25 to 68% iron.

The main iron ore deposits in the United States lie near Lake Superior in Minnesota (Mesabi range) and Michigan (Marquette range). These deposits were formed by sedimentation during the Precambrian era. The original formation

consisted of layers of iron oxides, iron carbonates, and iron silicates that were interbedded with layers of chert (a dense sedimentary rock). Leaching by ground-water and oxidation of the iron minerals produced local bodies of enriched oxides, usually soft hematites and limonites (goethites), that can be mined commercially without needing significant beneficiation. The unaltered iron formation, when containing 20% or more of iron in the form of magnetite, is called taconite; if in the form of hematite, it is referred to as jaspilite. Taconite and jaspilite are of importance because these are readily amenable to beneficiation. All of the mining in this area is done by open pit. The iron ore is beneficiated by magnetic separation and/or flotation (qv) and pelletized (see SEPARATION, MAGNETIC SEPARATION).

Other iron ore deposits of lesser importance in the United States are located in Missouri, Utah, Alabama, Wyoming, Texas, California, Nevada, Pennsylvania, New York, New Jersey, and Wisconsin. Of these deposits, only Missouri and Utah have mines operating. The Missouri deposit is located southwest of St. Louis near Sullivan and is a steeply dipping igneous intrusion in surrounding rock. The ore is composed principally of magnetite with some hematite, and minor amounts of quartz, apatite, and pyrite. The crude ore is mined by underground methods and is upgraded from 56 to 70% iron by magnetic separation. The upgraded ore is used for specialty iron oxide applications such as pigments, ceramics (qv), and powdered metals.

The Utah deposit is located in southwestern Utah near Cedar City. The iron ore deposits are of contact metamorphic origin. The crude ore contains 35 to 65%, primarily in the form of magnetite and goethite. Mining is done by the open pit method. The crude ore is crushed, screened at -75 mm (-200 mesh size) and shipped as lump ore containing 54% iron. The ore is rescreened at the steel mill to produce lump ore (10-64 mm) for the blast furnace and sinter feed (0-10 mm) for the sinter plant.

Canada's chief deposits occur along the borders between Quebec and Newfoundland in an area called the Labrador Trough, and in an area north of Lake Superior. Most of the deposits are similar to those found in Minnesota and Michigan. The Labrador Trough deposits are the main ones being mined. However, some direct shipping ore, containing mostly siderite, is produced in the Michipicoten range north of Lake Superior for use in sinter plants.

Other countries that have large iron ore deposits include Brazil (Carajas and Quadrilatero Ferrifero deposits), Australia (Pilbara deposits), Ukraine (Krivi Rog deposit), Russia (Kursk deposit), Venezuela (Cerro Bolivar deposit), India (Bihar-Orissa, Hospet, Kudremukh, and Goa deposits), South Africa (Sishen and Thabazimbi deposits), and Sweden (Kiruna, Svappavaara, and Malmberget deposits). A list of world iron ore production and reserves for 2002-2003 by country is shown in Table 4.

**3.3. Beneficiation.** Iron ore coming from the mine must be properly sized. A gyratory crusher is normally used for primary crushing down to approximately 300 mm (see SIZE REDUCTION). Secondary crushing down to 25 mm can be done in a cone crusher. Fine grinding can be done by rod mills followed by either ball or pebble mills. In some cases, autogenous grinding can be used to replace the cone crusher and rod mills.

High grade ore, containing over 60% total iron, can be used as direct shipping ore and normally is sized at 6–40 mm. High grade ore fines, in a size range of less than 6 mm, can be sold as sinter feed or further ground and agglomerated into pellets. Low grade iron ore must be ground to an acceptable size (to liberate gangue components) followed by concentration. The unit operations used for concentrating (or upgrading) low grade iron ores include washing, screening, heavy media separation, magnetic separation, froth flotation, and electrostatic separation (7).

Iron ores of different characteristics and compositions can be blended to a more uniform composition. This can be accomplished during handling operations involved in transporting ore to its point of use, or through special blending facilities, such as stacking and reclaiming.

Sand and clay can be removed from iron ore by washing in a log-washer or classifier followed by screening. If the sized ore consists of loose particles of mostly iron oxide mixed with loose particles of mostly gangue such as quartz and calcite, it is possible to upgrade the ore through gravity concentration based on differences in specific gravity. Heavy media separators using ferrosilicon suspension in a rotary drum are normally used for coarse-sized ore (10–25 mm). Heavy media separators using a magnetite suspension in hydraulic cyclones are used for medium-sized ore (0.8–6.7 mm). Humphrey's spirals are used for upgrading fine ores (–2.3 mm) (see SEPARATION, SIZE SEPARATION).

Low intensity magnetic separators are used to upgrade iron ores containing magnetite. Dry separators are used for coarse (up to 100 mm in size) ore and wet separators are used for fine (–9.5 mm) ores.

High intensity magnetic separators are used to upgrade iron ores containing hematite or ilmenite. Dry separators require ore that is finely sized and bone dry. They are dusty, expensive, and have a low capacity. Wet separators have larger capacity, are less dusty and can handle ore sizes up to 1 mm.

Hematite or goethite can be converted to magnetite by reduction roasting at 500–550°C. Siderite can be converted to magnetite by roasting in a neutral atmosphere at 700–775°C. In both cases the roasted ore must be cooled in an air-free atmosphere to 100°C. The roasted ore is easier to crush and grind than unroasted ore and can be upgraded by low intensity magnetic separation. However, the cost of roasting usually is too expensive to justify.

Froth flotation can be used effectively to upgrade iron ore sized at less than 0.2 mm. Anionic flotation is used to float hematite or siderite away from quartz or chert. The reagent used is normally a fatty acid or petroleum sulfonate. Cationic flotation, employing amines as reagent, is used to float quartz and locked quartz–magnetite particles from clean magnetite particles. Electrostatic separation can be used to upgrade dry iron ores sized at 0.04–1.68 mm and free from slimes or dust coatings (see FLOTATION).

The flow sheet can be tailored to the specific characteristics of the ore. The unit operations can be combined or modified in many ways to upgrade the total iron content in the ore from levels as low as 20–38% up to levels of 65–70%.

**3.4. Agglomeration.** Iron ore concentrates are often too fine to be used directly in ironmaking processes; therefore they must be agglomerated. The agglomerating methods typically used in the iron ore industry are

pelletizing, sintering and, to a limited extent, briquetting and nodulizing (see SIZE ENLARGEMENT).

In the pelletizing process, the iron ore must be ground to a very fine size ( $<75\text{ }\mu\text{m}$  ( $-200$  mesh)). The ground ore is mixed with the proper amount of water and binder, normally bentonite, hydrated lime, or organic material, and then is rolled into small balls 9–15 mm in diameter in a balling drum or disk. These green (wet) pellets are dried, then are heated to 1200–1375°C to bond the small particles, and finally are cooled. The heating can be done on a traveling grate, in a shaft furnace, or by a combination of a traveling grate and a rotary kiln (grate–kiln). The traveling grate and grate–kiln are the most commonly used pelletizing processes.

Sintering consists of igniting a mixture of iron-bearing limestone and coke fines on a traveling grate to produce a clinker-like aggregate (sinter) suitable for use in the blast furnace. The iron-bearing fines can include iron ore fines (sinter feed), iron ore concentrates, flue dust, or other steel mill wastes. The traveling grate is shaped like an endless loop of conveyor belt forming a shallow trough with small holes in the bottom. The bed of material on the grate is first ignited by passing under an ignition burner that is fired with natural gas and air; then, as the grate moves slowly toward the discharge end, air is pulled down through the bed. As the coke fines burn in the bed, the heat generated sinters the particles. At the discharge end of the machine, the sinter is crushed to remove extra large lumps, then cooled, and finally screened.

In the briquetting process, ore fines usually are mixed with a binder and are formed into compact masses between two rotating rolls. The rolls exert pressures of 1.5–4.2 t/cm<sup>2</sup> in forming the briquettes. In the nodulizing process, which is relatively uncommon commercially, ore fines are heated in a rotary kiln to a temperature, usually 1250–1370°C, at which the ore begins to melt and bind. The ore balls in the kiln to form nodules that are discharged and cooled.

## 4. Ironmaking Processes

Ironmaking refers to those processes which reduce iron oxides to iron. By the nature of the processes, the iron produced usually contains carbon and/or other impurities which are removed in downstream processing. There are three principal categories of ironmaking processes, in order of commercial importance: blast furnace, direct reduction, and direct smelting.

**4.1. Blast Furnace.** The blast furnace is the predominant method for making iron. Established for centuries as the premier ironmaking process, blast furnace ironmaking both enabled and profited from the Industrial Revolution. Although the fundamental principles of operation are unchanged, the blast furnace has evolved into a highly efficient and productive process.

In essence, the blast furnace is a large, countercurrent, chemical reactor in the form of a vertical shaft which is circular in cross section. Iron ore, coke, and fluxes constitute the burden which is charged continually into the top. Pressures in the shaft are controlled to 100–300 kPa (1–3 atms) gauge. Preheated air (hot blast) is blown in through water-cooled nozzles (tuyeres) around the circumference of the furnace near the bottom. The oxygen in the air reacts with the coke

to form hot reducing gases (mostly carbon monoxide) which ascend through the burden and (1) provide heat for melting; (2) react with the iron ore to reduce it to iron; and (3) heat the ore, coke, and fluxes to reaction temperatures. Nitrogen in the hot blast is heated by the coke combustion, and aids in heat transfer to the burden. The gases leaving the top of the furnace (top gas) are cleaned, cooled, and used as fuel to preheat the air for the hot blast.

Molten iron (hot metal or pig iron) and slag (molten oxides) are produced and accumulate in the bottom of the furnace. The hot metal and slag are drained semicontinuously through a taphole (tapping, or casting) into a trough. The hot metal is separated from the slag by a weir/dam arrangement at the end of the trough, then flows through runners to a refractory-lined rail car. The hot metal is then transported to a nearby site for further processing. Most of all pig iron produced in the United States is used for steelmaking. The remainder is cast into pigs for remelting or used directly for iron castings.

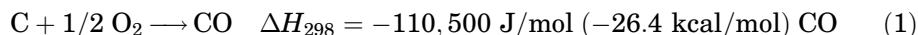
**Raw Materials.** Most of the iron enters the blast furnace as iron oxides, either hematite,  $\text{Fe}_2\text{O}_3$ , or magnetite,  $\text{Fe}_3\text{O}_4$ , in the form of pellets, sinter, or lump ore. Total iron content in the iron oxides normally ranges from 60 to 66%, but may be as low as 50% in low quality ores or in sinter using high quantities of recycled materials. Oxygen associated with the iron as iron oxide comprises about 23 to 28%. The remainder is gangue oxides, mostly silica and alumina. Silica should be less than 5%. Size control is important in order to promote permeability, so fines ( $-6$  mm) should be kept less than 2%. Pellets should be sized to at least 80% between 9 and 13 mm, with no more than 10% larger than 13 mm. Pellets are tested for handling characteristics by measuring tumble strength and compression strength. In the ASTM tumble test, 11.3 kg of pellets (screened to  $+6$  mm) are placed in a drum 0.5 m wide by 1.0 m diameter. The drum is rotated at 25 rpm for 8 min, and the pellets are rescreened to measure degradation. Compression strength is a measure of the compressive force required to break the pellets between two parallel flat plates. For blast furnace usage, pellets should have a tumble strength of at least 95%  $+6$  mm and a compression strength of greater than 200 kg. Other important properties include low swelling, little breakdown at low temperatures during reduction, and good reducibility (8). In some locations, steelmaking slag and yard scrap are crushed and magnetically upgraded to recycle iron units through the blast furnace. Metallic iron, usually in the form of direct reduced iron (DRI) or hot briquetted iron (HBI), is also sometimes added to increase productivity and lower fuel rate. Historically the overall feed mix of iron units consumed in the U.S. blast furnaces consisted of 79% pellets, 15% sinter, 2.9% lump ore, 3% ferrous scrap, and 0.1% HBI (9).

Carbon is provided by the coke, which typically consists of 85–90% fixed carbon, less than 2% volatile matter, 5–13% ash, 0.6–1.3% sulfur, and 2–10% moisture. The carbon is required as the reductant, and in addition provides heat through combustion with air. Coke is the preferred form of carbon because it provides structural support within the furnace by creating stable areas of permeability for the ascending gases, especially in the softening/melting zone. High mechanical strength of coke is important for smooth operations. Coke is most often sized to between 15 and 75 mm, with many operators specifying a more narrow range. In some cases, coke is screened to two or more different size fractions for separate charging (see COAL CONVERSION PROCESSES, CARBONIZATION).

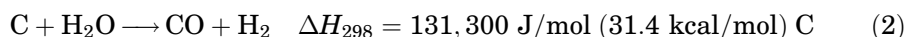
Fluxes are usually added in the form of either limestone or dolomite. The fluxes provide the basic constituents (CaO and MgO) needed to balance the acid constituents (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) from the coke and ore. These are the four primary oxides which form the slag, although minor amounts of other oxides such as MnO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and TiO<sub>2</sub>, and sulfur are also present. Proper adjustment of the slag chemistry is necessary to obtain the desired balance of chemical properties, eg, desulfurization and alkali removal, and physical properties, such as low melting point and low viscosity. There has been a growing practice of adding CaO and MgO at the pelletizing process to make fluxed pellets. The advantages of fluxed pellets go beyond simply avoiding the thermal requirement of calcining limestone and dolomite (heating to drive off volatile matter) (10,11). Pellet properties are improved, which results in improved blast furnace performance.

Air for the hot blast may also be considered a raw material. The air is preheated in stoves to between 900 and 1300°C. Over 1.5 t of air is required to produce 1 t of hot metal (pig iron). Solid, liquid, or gaseous fuels, eg, coal, fuel oil, or natural gas, may be added to the hot blast at the tuyeres to replace some of the coke. Oxygen may also be added to the hot blast to increase flame temperature.

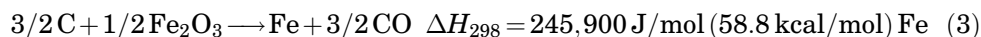
**Thermochemistry.** From an overall heat and mass balance point of view, the main chemical reactions of the blast furnace include oxidation of carbon in the zone in front of the tuyeres (raceway) to give CO plus heat,



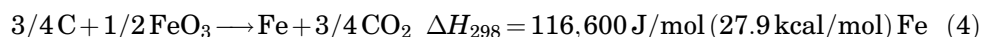
reduction of the moisture in the hot blast by carbon to form CO plus hydrogen,



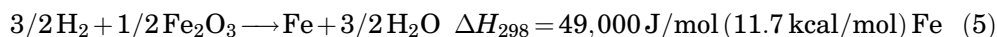
reduction of iron oxide by carbon to form iron and CO,



reduction of iron oxide by carbon to form iron and CO<sub>2</sub>,



and reduction of iron oxide by hydrogen to form iron and H<sub>2</sub>O.

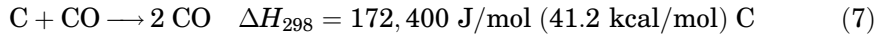
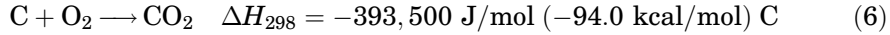


All the reduction reactions are endothermic, regardless of the reductant used. The heat for these reactions, along with the requirements for the sensible heats of the hot metal and slag, and heat losses through the furnace shell, is provided by the heat generated from equation 1 plus the sensible heat of the hot blast.

The furnace (Fig. 2) may be divided into four zones (from bottom to top). (1) Hearth and raceway: as the coke descends through the furnace, it is heated

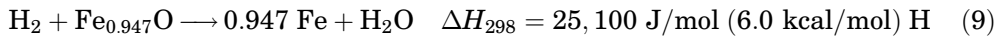
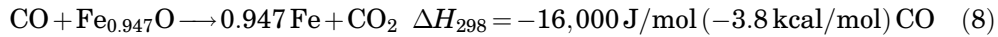


by the ascending gases to about 1370°C. When it reaches the raceway in front of the tuyeres, it reacts immediately with the oxygen in the hot blast air. Equation 1, however, is actually the combination of coke combustion (eq. 6) and coke gasification (eq. 7, also referred to as solution loss).



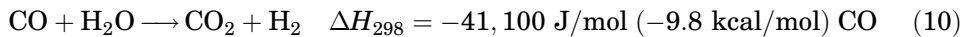
Coke gasification occurs just outside the raceway area where gaseous oxygen is no longer available to completely combust the CO to CO<sub>2</sub>. This reaction goes essentially to completion at temperatures between 1500 to 2100°C. The net heat effect is exothermic, as shown in equation 1. The endothermic equation (eq. 2) allows control of the temperature in front of the tuyeres by controlling the moisture in the hot blast.

(2) Melting (fusion) zone and final reduction of wustite: the H<sub>2</sub> and CO rise through the burden, contact wustite [17125-56-3] formed from previous reduction reactions in the upper part of the furnace, and reduce it to iron.



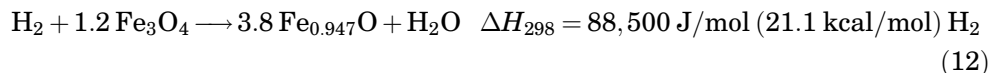
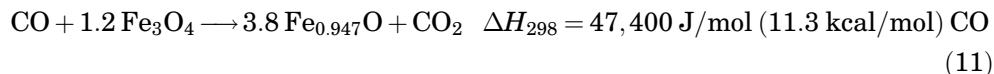
The iron absorbs carbon through contact with the coke, which melts owing to its decreased melting point. Equation 7 combines with equations 8 and 9 in a cycle which effectively regenerates CO. Owing to the highly endothermic nature of equation 7, the gases cool as they rise in the furnace. Equation (8), reduction by CO, is referred to as indirect reduction. The combination of equations 7 and 8, solution loss and indirect reduction, is referred to as direct reduction, because it amounts to reduction of the wustite directly by carbon to form iron and CO. This direct reduction is not the same terminology used in direct reduction processes, which in fact often rely on indirect reduction reactions (see IRON).

(3) Thermal reserve zone: once the gases (CO, H<sub>2</sub>, and N<sub>2</sub>) have cooled to about 925°C, the thermodynamics for equation 7 are no longer favorable. Because the predominant reaction is now equation 8 which is slightly exothermic, and because the mildly endothermic equation 9 occurs to a much lesser extent, the gases do not cool appreciably, resulting in a thermal reserve zone. The net relative amounts of CO<sub>2</sub> and H<sub>2</sub>O produced by reduction are determined by equilibrium for the water gas shift reaction,

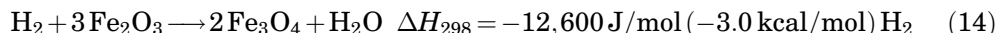
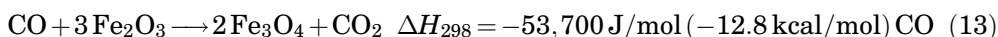


(4) Reduction of magnetite and hematite (upper shaft): as more and more CO and H<sub>2</sub> are converted to CO<sub>2</sub> and H<sub>2</sub>O, the ascending gases eventually become too weak in concentration to reduce wustite to iron. Figure 3a and b shows the regions of stability for the Fe–C–O and the Fe–H–O systems, respectively. The boundary lines represent the equilibrium conditions for the various

reduction reactions as shown. The gases, too weak to reduce wustite, are strong enough to reduce magnetite to wustite:

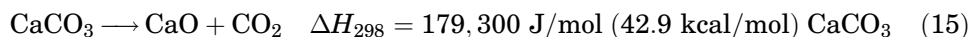


For steady-state operation, the amount of wustite produced by these reactions must exactly match the amount of wustite reduced to iron in the lower part of the furnace. Owing to equilibrium and stoichiometric considerations, there is more than enough CO generated from the wustite–iron reactions. This results in driving the region of reduction of magnetite toward the top of the furnace, and creates a chemical reserve zone of little reaction between the descending wustite and the weakly reducing (with respect to wustite) ascending gases. Because there is little heat required for this zone, the chemical reserve zone coincides with the upper part of the thermal reserve zone. The ascending gases rapidly reduce the hematite which is charged into the top of the furnace.

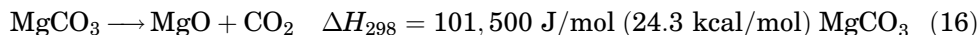


Only the slightest amounts of CO or H<sub>2</sub> are required to reduce hematite to magnetite, which is why in Figure 3 the regions of magnetite stability are shown extending all the way down to the bottoms of the graphs. Owing to the excess CO generated by the wustite reduction reactions, hematite reduction is also driven to the top of the furnace. The reduction of hematite to magnetite and magnetite to wustite is so fast that hematite, magnetite, and wustite may all be found in the same pellet, owing to the topochemical (occurring at boundaries which progress from surface to center) nature of the reactions. In this zone the gas temperature falls off rapidly because of cooling by the incoming materials, evaporation of moisture, and the net endothermic nature of the reduction reactions.

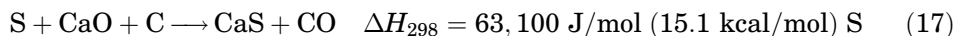
In addition to the principal equations discussed, several others occur which may be of importance, including calcination of calcium carbonate (limestone), which takes place in the upper shaft at 800–870°C,



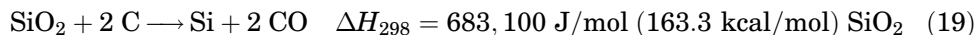
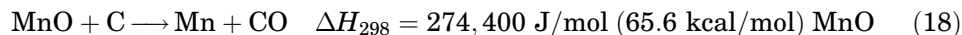
calcination of magnesium carbonate in dolomite which takes place in the top of the shaft at about 50–100°C,



fluxing of the sulfur into the slag,



and reduction of other metallic oxides,



Equations 17–20 result from contact between hot metal and slag, and the sulfur and carbon come dissolved in the hot metal. Likewise, the manganese, silicon, and phosphorus which are produced are dissolved into the hot metal. The heats of solution for these elements in some cases depend on concentration, and are not included in the heats of reaction listed above. The ratio of the concentration of the oxide (or element for sulfur) in the slag to the concentration of the element in the hot metal is the partition ratio, and is primarily a function of slag chemistry and temperature.

Mass and energy balances are used to evaluate blast furnace performance. Many companies now use sophisticated computerized data acquisition and analysis systems to automatically gather the required data for daily calculation of the mass and heat balances. Typical mass and heat balances are shown in Figure 4 and Table 5, respectively.

**Plant Layout.** Figure 5 shows the material flow diagram for a blast furnace plant. The ore and fluxes are stockpiled in a large open yard, from which these are reclaimed by crane (ore bridge) and transferred by conveyor to the stockhouse. Coke is delivered by rail or conveyor from the coke plant. The stockhouse consists of a row of bins from which the raw materials are weighed out in the desired order and amount, and conveyed by either skip car or conveyor to the top of the furnace. Special additives to the charge, such as upgraded yard scrap, manganese ore, or calcium chloride, for flushing out alkalies, are added at this location.

At the top of the furnace, the raw materials are charged into the furnace through a pressurized gas seal system, typically a double bell (see Fig. 6a). For very high pressure furnaces, three bells may be used. More recently, the Paul Wurth bell-less top has become popular, as its rotating chute design permits greater control over distribution of the burden (Fig. 6b).

The taphole is built into the refractory lining of the blast furnace. The taphole drill is used to drill a hole through the taphole material. At the end of the cast, a mud gun is used to plug the hole with a quick-hardening clay. An alternative technique (hot bar) relies on hardening the refractory around a metal bar, which is pulled out for tapping. Hot metal is tapped (cast) every three to five hours into refractory-lined railcars for transportation to nearby steelmaking facilities or to a pigging machine. The largest blast furnaces have up to four tapholes which are used alternately as the trough and runners are repaired. Slag is either transferred as a liquid in inverted bell-shaped rail cars, or poured directly into a slag pit adjacent to the blast furnace. After solidification, the slag

is crushed and sized and sold for road ballast. In addition, the slag may be granulated using a water spray to make a by-product suitable for sale to the cement (qv) industry, or used for the production of rock wool insulation.

Off-gases (top gas) leave the top of the furnace through uptake pipes, reverse direction in the downcomer, and enter the dust catcher, in which condensed water and dust are separated from the gases. The wet dust is emptied into a rail car for transport to a sinter plant for recycle or to a landfill. After leaving the dust catcher, the off-gas is washed in a venturi scrubber. The cleaned gas is then used within the plant for steam (qv) generation, to fire annealing or other furnaces, for underfiring of coke ovens, and for firing the blast furnace stoves. There are usually three or four stoves filled with refractory checkers. The checkerwork contains a multiplicity of passages through which gases may pass. The stoves alternate between absorbing heat generated by combustion of the blast furnace off-gas and releasing heat to the cold blast air as it passes down through the heated checkers.

After it leaves the stoves, the hot blast enters a large refractory-lined bustle pipe to distribute the gas evenly around the furnace. Multiple connecting pipes (tuyere stock) direct the hot blast to the blowpipes. At the ends of the blowpipes are the tuyeres, water-cooled copper nozzles set into the refractory lining of the blast furnace.

**Operation.** Because of the long residence time of the materials (8–10 h), the blast furnace process can exhibit considerable inertia, and control is usually applied where the goal is maintaining smooth, stable input conditions. One of the most important aspects of blast furnace control is supply of consistent quality raw materials, which is why there is a strong emphasis on quality control at coke plants, pelletizing plants, and sinter plants (see **QUALITY CONTROL**).

Careful attention is paid to the properties of the raw materials. Short-term adjustments to the slag basicity may be made by increasing or decreasing the amount of fluxes. In general, increasing the basicity of the slag promotes sulfur removal but decreases alkali removal. A balance is sought between the two, in addition to ensuring that the slag has a low melting point and low viscosity for good fluidity. Longer term adjustments may be made by adjusting the chemistry of the pellets and/or the sinter.

Modern furnaces rely on computerized controls for weighing and charging of the raw materials. The ore and coke are charged in alternating batches, so as to create distinct layers within the furnace which promote permeability for the rising gases. For a two-bell top, the manner in which the layers are formed is a function of the trajectory of the burden materials as these fall off the bell and rebound from the throat. Control of the layering is exercised by carefully selecting the amounts and order of materials. Sophisticated physical and computer models are used to guide the operator in deciding exactly how much and in what order the raw materials should be charged.

Moveable throat armor is used for additional control. Hanging plates or horizontally adjustable guides are used to adjust the throat diameter for each charge, thus modifying how the layers are formed in the furnace. Bell-less tops (Fig. 6b) provide even greater flexibility, as both the angle and the rotation speed of the rotating chute may be adjusted. Many furnaces use probes, radar, or laser devices to provide feedback on burden distribution.

Computer controls are likewise used for stove operation, to control delivery of the hot blast. High hot blast temperatures are generally desirable, as these reduce the coke rate. Control of the flame temperature in the raceway is effected by controlled additions to the hot blast, primarily of moisture. Injectants into the tuyeres such as coal, oil, and natural gas are often used to replace some of the coke. The effect of these injectants on flame temperature must be accounted for, and compensation is performed by lowering moisture or adding oxygen.

Tapping or casting is controlled to avoid rapid drops in the burden. Normally, the hot metal accumulates in the hearth for some period of time, then is drained during tapping. Proper selection of taphole, trough, and runner materials, improved trough and dam designs, and multiple tapholes have all allowed the proportion of time spent tapping to increase to the point where it is nearly continuous. Improved taphole clays have reduced erosion of the taphole, stabilizing the casting rate and promoting smooth descent of the burden. Careful raw materials selection, burden distribution (charging control), hot blast temperature and moisture control, tuyere injectants, and casting practices are the primary means by which the blast furnace operator keeps the ironmaking process under control.

**4.2. Direct Reduction.** Direct reduction processes are distinguished from other ironmaking processes in that iron oxide is converted to metallic iron without melting. Because this product, called direct reduced iron (DRI), is solid, it is most suitable for melting in an electric arc furnace (EAF) as a substitute for scrap (see FURNACES, ELECTRIC). The briquetted form of DRI, hot briquetted iron (HBI) is used when the product is to be transported. Briquetting increases density and chemical stability. The predominant direct reduction processes (MIDREX and HyL III) are based on natural gas as a fuel and reductant source. They are economically attractive in regions where natural gas is cheap and abundant, especially if iron ore is available nearby (see IRON BY DIRECT REDUCTION).

**Chemistry.** DRI retains the chemical purity of the iron ore from which it is produced, therefore it tends to be very low in residual elements such as copper, chrome, tin, nickel, and molybdenum. Typical ranges of DRI chemical compositions are shown in Table 6.

Metallization is defined as the percent of total iron in the DRI which has been converted to metallic iron. For example, DRI having a total iron content of 92% and a metallic iron content of 85%, has 92.4% metallization.

$$\text{metallization (\%)} = \frac{\text{metallic Fe}}{\text{total Fe}} \times 100\%$$

Reduction is the percentage of oxygen present in the ore as iron oxide which has been removed.

$$\text{reduction (\%)} = \frac{\text{oxygen removed}}{\text{initial oxygen}} \times 100\%$$

Assuming that the initial iron oxide is hematite,  $\text{Fe}_2\text{O}_3$ , and this ore is completely converted to  $\text{FeO}$ , ie, no metallic iron is formed, the reduction would be 33.33%. Thus the relationship between metallization and reduction is

$$\text{metallization (\%)} = [\text{reduction (\%)} - 33.33\%] \times 1.5$$

From this relationship it can be seen that a reduction level of 95% compares with a metallization level of 92.5%. A reduction level of 33.33% or less has a metallization level of 0%. DRI normally has at least 90% reduction or 85% metallization. Processes producing solid, partially reduced iron, ie, <90% reduced or <85% metallized, are classified as prereduction processes. The partially reduced product, called prereduced iron, is not acceptable for steelmaking but can be used as a feed for iron smelting.

Although it is theoretically possible to convert all of the iron oxide in iron ore to metallic iron, it is not economically feasible. The reduction reaction slows significantly in the last stages and to complete the reduction process would result in low production rates. In practice, it is advantageous to retain a small amount of iron oxide in the DRI. During melting in an electric arc furnace, the iron oxide in DRI reacts with carbon in the DRI to form metallic iron and carbon monoxide. The carbon monoxide foams the slag during steelmaking, and this improves the operation of the electric furnace.

The carbon content of DRI depends primarily on the direct reduction process used and the way the process is operated. Carbon content can be adjusted within limits by operating changes within the DR process. Most steelmakers prefer slightly more carbon than is required to balance the remaining FeO in the DRI. DRI from gas-based processes typically contains 1 to 2.5% carbon, mostly in the form of cementite [12169-32-3],  $\text{Fe}_3\text{C}$ . DRI containing approximately 6 to 7% carbon in the form of cementite is called iron carbide. DRI from coal-based, rotary-kiln processes contains very low (ca 0.5%) levels of carbon.

The gangue content of DRI is typically comprised of oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MnO}$ , etc, and is dictated by the chemistry of the iron ore used. The phosphorus in DRI is normally in the form of  $\text{P}_2\text{O}_5$ . Sulfur content in the DRI depends on the sulfur level in the ore and reductant, and the amount of sulfur released or absorbed by the DRI during the reduction process.

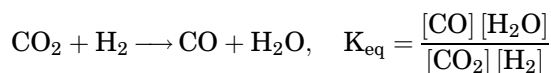
**Production.** The reduction of iron ore is accomplished by a series of reactions that are the same as those occurring in the blast furnace stack. These include reduction by CO,  $\text{H}_2$ , and, in some cases solid carbon, through successive oxidation states to metallic iron, ie, hematite [1309-37-1],  $\text{Fe}_2\text{O}_3$ , is reduced to magnetite [1309-38-2],  $\text{Fe}_3\text{O}_4$ , which is in turn reduced to wustite [17125-56-3],  $\text{FeO}$ , and then to metallic iron, Fe.

At reduction temperatures below about 1000°C, the reducing agents usually are restricted to CO and  $\text{H}_2$ . Above about 1000°C, solid carbon can react with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to renew the reducing potential of the gas. Above 1200°C, the metallic iron that has formed absorbs any carbon that is present, which results in melting point depression (from 1530°C) and subsequent fusing or melting of the solid.

Processes operating in the range of 1300–1530°C produce molten iron, called hot metal or pig iron. These processes are classified as direct smelting processes. Processes operating above 1530°C produce molten steel (qv) and are called direct steelmaking processes.

The equilibrium for the reactions of CO and  $\text{H}_2$  with the oxides of iron are well established. There is nearly complete conversion of CO to  $\text{CO}_2$  and  $\text{H}_2$  to

H<sub>2</sub>O for the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>. Below 570°C, Fe<sub>3</sub>O<sub>4</sub> is reduced directly to Fe by CO and H<sub>2</sub>; above 570°C, Fe<sub>3</sub>O<sub>4</sub> first is reduced to FeO which then is reduced to Fe. In the reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO, the conversions of CO and H<sub>2</sub> increase with increasing reaction temperature. However, in the reduction of FeO to Fe, the conversion for H<sub>2</sub> increases with increasing reaction temperature, whereas that for CO decreases. This decrease of equilibrium CO conversion with increasing temperature for the reduction of FeO to Fe is not a limitation on the overall conversion because most DR processes are operated using counter-current flow of solids and reducing gases. Thus the spent reducing gas leaves in contact with the entering solids which are in their highest oxidation state, and the equilibrium for the reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO governs the final gas composition. For DR processes that are based on reduction using mixtures of CO and H<sub>2</sub>, the final gas composition usually satisfies the equilibrium for the water gas reaction at the exit temperature, ie,



The description given applies to DR processes that are based on the use of gaseous reductants in shaft furnaces, batch retorts, and fluidized beds. In the processes that use solid reductants, eg, coal (qv), the reduction is accomplished to a minor extent first by volatiles and reducing gases that are released as the coal is heated and then by CO that is formed by gasification of fixed carbon contained in the coal char with CO<sub>2</sub>. Reduction by solid carbon and coal volatiles in kilns is insignificant.

The energy requirements for DR processes are related directly to the heats of reaction for the reduction reactions over the temperature range of practical interest for DR processes. A summary is presented in Table 7.

The reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> using H<sub>2</sub> and CO is mildly exothermic and the reduction of FeO to Fe using CO is moderately exothermic. The other reactions are moderately endothermic, with the exception of the reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO and of FeO to Fe by carbon; both are highly endothermic. The heat of reduction is not a principal factor in establishing the energy requirements for the gas-based DR processes. Instead, the energy requirements for these processes come mainly from the energy that is needed to generate the reducing gas, which in most cases is catalytic steam (qv) or CO<sub>2</sub> reforming of natural gas, and the chemical energy in the reductants that are consumed in the process (see GAS, NATURAL). For the DR processes that are conducted in shaft furnaces, total energy requirements can be minimized by recovering most of the sensible heat in the DRI and in the spent reducing gases. Such recovery is not practical in the fluidized-bed processes. For the DR processes based on the direct use of solid reductants, the highly endothermic reaction of CO<sub>2</sub> and solid carbon is compensated for by the highly exothermic combustion reactions in the free space above the reaction bed.

The productivity of DR processes depends on chemical kinetics, as well as mass and heat transport factors that combine to establish the overall rate and extent of reduction of the charged ore. The rates of the reduction reactions are

a function of the temperature and pressure in the reduction beds, the porosity and size distribution of the ore, the composition of the reducing gases, and the effectiveness of gas–solid contact in the reduction beds. The reduction rate generally increases with increasing temperature and pressure up to about 507 kPa (5 atm).

Reduction of iron ore containing magnetite in gas-based DR processes is difficult owing to the massive structure of magnetite which hinders gaseous diffusion. If the magnetite is first oxidized to hematite, the reduction proceeds much more rapidly, because of a physical change in the crystal structure which opens up the structure and enhances gaseous diffusion.

**Direct Reduction Processes. MIDREX Process.** The primary components of a MIDREX process plant include the shaft furnace, reformer, and heat recuperator. These components are supported by ancillary systems for handling iron ore, gas, water, and direct reduced iron. A flow sheet is shown in Figure 7.

Reduction is carried out continuously in the shaft furnace. Iron oxide in pellet (6–16 mm) or lump (10–35 mm) form is fed to the top of the furnace, flows downward by gravity, and is discharged from the bottom in the form of DRI. The shaft furnace has two separate processing zones, both of which use recycled gas. In the upper reduction zone, iron oxide is preheated and reduced by counterflowing reducing gas containing hydrogen and carbon monoxide. In the lower cooling zone, the reduced product is carburized and cooled by counterflowing cooling gas.

When incorporating hot briquetting in the MIDREX process, the cooling gas circuit is eliminated, and the hot DRI is continuously discharged from the shaft furnace into a hopper and directly fed into a hot briquetting machine. The resulting HBI is continuously discharged from the hot briquetting machine, separated into individual briquettes, and cooled.

Reducing gas is generated at low pressure in the reformer by catalytically reforming a preheated mixture of fresh natural gas and recycled top gas from the shaft furnace. The reformer is a gastight, refractory-lined furnace containing alloy tubes filled with catalyst. The preheated gas mixture flows through the catalyst bed where it is heated and reformed. The hot (1000°C) reducing gas leaves the reformer at near equilibrium condition, containing 90 to 92% H<sub>2</sub> plus CO. Therefore, the reducing gas can be fed directly to the shaft furnace.

**HYL I Process.** In the HYL I process (Fig. 8), four batch retorts are operated sequentially through four steps to achieve a semicontinuous operation. While one retort is discharging DRI and being filled with pellets, two other retorts are reducing pellets and a fourth retort is carburizing and cooling DRI. Reducing gas is generated in a steam reformer and must be quenched to remove excess water vapor. Heat is transferred to the cold reducing gas by using it to carburize and cool the DRI in one of the retorts. The gas is quenched after passing through each retort and is reheated by a combination of indirect firing and partial oxidation of residual hydrocarbons to about 1050°C prior to the next stage of reduction. Reducing gas flows downward through the static bed inside the retorts and leaves a reduction gradient through the bed. The product is typically 85 to 90% metallized with 2.0 to 2.5% carbon. An auger is available if necessary to help remove DRI from the retorts.



**HYL III Process.** The HYL III process is similar to the MIDREX process, however, it uses a conventional steam reformer and pressurized shaft furnace. As shown in Figure 9, sized iron ore (pellet or lump) is charged via lock hoppers into a pressurized shaft furnace wherein the ore is heated, reduced, carburized, and cooled as it descends by gravity. The upper reduction zone of the shaft furnace is separated from the lower cooling zone by an isobaric zone. The cooled product is discharged via a rotary valve and lock hoppers onto a conveyor belt. In the case of hot briquetting, the cooling gas circuit is eliminated and the hot DRI is discharged through lock hoppers into the hot briquetting units.

Fresh reducing gas is generated by reforming natural gas with steam. The natural gas is heated in a recuperator, desulfurized to less than 1 ppm sulfur, mixed with superheated steam, further preheated to 620°C in another recuperator, then reformed in alloy tubes filled with nickel-based catalyst at a temperature of 830°C. The reformed gas is quenched to remove water vapor, mixed with clean recycled top gas from the shaft furnace, reheated to 925°C in an indirect fired heater, and injected into the shaft furnace. For high (above 92%) metallization a CO<sub>2</sub> removal unit is added in the top gas recycle line in order to upgrade the quality of the recycled top gas and reducing gas.

**SL/RN Process.** In the SL/RN process (Fig. 10), sized iron ore, coal, and dolomite are fed to the rotary kiln wherein the coal is gasified and the iron ore is reduced. The endothermic heat of reduction and the sensible energy that is required to heat the reactants is provided by combustion of volatiles and carbon monoxide leaving the bed with air introduced into the free space above the bed. The temperature profile in the kiln is controlled by radial air ports in the preheat zone and axial air ports in the reduction zone. Part of the coal is injected through the centerline of the kiln at the discharge end. The hot reduced iron and char is discharged into an indirect rotary drum cooler. The cooled product is screened and magnetically separated to remove char and ash.

The latest installations incorporate a waste heat boiler in the off-gas cleaning system to recover sensible heat from the rotary kiln off-gas. There is sufficient sensible heat in the off-gas from the SL/RN process to generate 500 to 700 kWh/t of DRI, depending on the type of reductant used.

**FIOR Process.** In the FIOR process, shown in Figure 11, sized iron ore fines (0.04–12 mm) are dried in a gas-fired rotary dryer. A skip hoist delivers the dry fines to lock hoppers for pressurizing. The fines pass through four fluidized-bed reactors in series. Reactor 1 preheats the ore to 760°C in a nonreducing atmosphere. Reactors 2, 3, and 4 reduce the ore at 690–780°C. At higher (ca 810°C) temperatures there is a tendency for the beds to defluidize as a result of sticking or bogging of the reduced material.

The hot reduced fines are pneumatically transported to an atmospheric pressure holding drum from which they are fed to the briquetting machines. The hot briquettes are separated, cooled on a circular grate, and delivered to an outdoor storage pile.

Reducing gas is generated from natural gas in a conventional steam reformer. The natural gas is preheated, desulfurized, mixed with steam, further heated, and reformed in catalyst-filled reformer tubes at 760°C. The reformed gas is cooled to 350°C in a waste heat boiler, passed through a shift converter

to increase the  $H_2$  content, mixed with clean recycled top gas, heated to  $830^\circ C$  in an indirect-fired heater, then injected into reactor 4.

The reducing gas is distributed in reactor 4 by an alloy grid, passes through the fluid bed, then exits the reactor via cyclones. The gas passes through reactors 3 and 2 so that a counter flow between gas and solids is established. The spent reducing gas is scrubbed to remove dust and water vapor. Part of the cleaned top gas is recycled and the remainder is used as fuel.

**Other DR Processes.** The other DR processes, eg, the CODIR, DRC, ACCAR, and Dav Steel processes, make up 4.4% of worldwide production and mostly consist of coal-based, rotary-kiln processes. All of these are similar to the SL/RN process. In addition, one small coal-based, shaft-furnace plant based on the Kinglor-Metor process is operating. Newer processes developed recently include FASTMET and CIRCOFER, and an improved version of the FIOR process.

In the FASTMET process iron oxide fines (minus 0.1 mm), pulverized coal, and binder are mixed together and pelletized. The green pellets are heated in a dryer to remove moisture and fed to a rotary hearth furnace, where the pellets are placed on a flat rotating surface (hearth) in an even layer one to two pellets deep. As the hearth rotates the pellets are heated to  $1250\text{--}1350^\circ C$ , and the iron oxide is reduced to metallic iron in 6 to 10 minutes.

The iron carbide process is a low temperature, gas-based, fluidized-bed process. Sized iron oxide fines (0.1–1.0 mm) are preheated in cyclones or a rotary kiln to  $500^\circ C$  and reduced to iron carbide in a single-stage, fluidized-bed reactor system at about  $590^\circ C$  in a process gas consisting primarily of methane, hydrogen, and some carbon monoxide. Reduction time is up to 18 hours owing to the low reduction temperature and slow rate of carburization. The product has the consistency of sand, is very brittle, and contains approximately 6% carbon, mostly in the form of  $Fe_3C$ .

The CIRCOFER process uses a two-stage fluidized-bed reactor system to gasify coal and reduce iron oxide fines. The coal gasification and initial reduction is performed in a circulating fluidized bed and final reduction occurs in a conventional fluidized bed. The spent reducing gases are recycled after removing water vapor and carbon dioxide. The metallized product is magnetically separated at  $700^\circ C$  prior to hot briquetting.

**4.3. Direct Smelting.** Direct smelting processes use coal directly instead of coke. Several processes are under development which effectively divide the functions of the blast furnace into two separate but connected unit operations. First, the iron ore is prereduced in a shaft furnace or a fluidized bed, depending on the process and the type of ore used. Second, the prereduced ore is charged into a molten bath into which coal and oxygen or air are also introduced. The gases leaving the smelter are used to perform the reduction in the prereduction vessel.

The Corex process is the only one of the newer ironmaking processes operating on a commercial scale. In the Corex process, over 90% of the reduction is performed in the prereduction shaft; the remainder is accomplished in what is primarily a melter–gasifier. Oxygen and coal are injected into the melter–gasifier to provide heat for melting and to generate the reducing gases for the prereduction furnace. Because of the high proportion of reduction performed in the

prereducer, the off-gases leaving the melter–gasifier are necessarily highly reducing. As a consequence, the fuel rate for the melter–gasifier is higher than for processes in which the gases are more completely oxidized. This is compensated for to some extent by the low heat load required for reduction. However, the net effect is that relatively high volumes of off-gas having significant chemical heat value are generated which require large off-gas handling systems. This may be an advantage in locations where the energy value of the off-gas can be utilized fully to replace other energy sources such as natural gas or electricity.

The processes being developed by the American Iron and Steel Institute and the Department of Energy (AISI-DOE) in the United States and the Japan Iron and Steel Federation (JISF) in Japan share similar features in the smelter, but differ in prereduction approaches. In the AISI-DOE process, pellets are prereduced to wustite, about 30% prereduction, in a shaft furnace. In the JISF process, called direct iron oxygen smelting (DIOS), iron ore fines are prereduced to between 30 and 60% in one or more fluidized beds in series. For both, the prereduced ore and coal are charged into a vertical vessel containing a molten bath, and oxygen is injected to generate CO and heat. Additional oxygen is provided to post-combust the CO to CO<sub>2</sub>, thereby improving the energy efficiency of the process.

The ore melts to a liquid oxide almost immediately upon introduction into the smelter. The primary reduction reactions, then, are between the liquid oxide and carbon-saturated liquid iron or solid particles of char contained in the slag. The generation of CO within the bath results in a foamy slag. Control of slag foaming, high post-combustion levels, and high post-combustion heat-transfer efficiency are critical operating factors for these processes.

The HiSmelt process being developed jointly by CRA of Australia and Midrex Direct Reduction Corp. uses a horizontal vessel, relying on turbulence in the bath to spray particles of slag and iron into the atmosphere above the bath, where heat is transferred from the post-combustion flame to the particles. Here, air is used instead of oxygen, thus removing the requirement of an oxygen plant. This technology emphasizes bottom injection of coal and dust into the iron bath.

## 5. Cast-Iron Production

Most ferrous scrap is recycled in steelmaking processes by melting the scrap in either a basic oxygen or an electric arc furnace. However, a significant market exists for cast-iron products, which are also made by melting ferrous scrap.

Cast irons are normally produced by melting iron or steel scrap along with pig iron. The carbon and silicon levels are adjusted to obtain the desired properties. Melting is done in cupolas, electric furnaces, or air furnaces. The cupola resembles a small blast furnace, but differs in that pig iron and scrap replace the ore. Coke combustion using air provides the heat for melting of the charge. Electric arc furnaces are used to a limited extent, but induction furnaces are more popular. The air furnace is a type of reverberatory furnace which has a fireplace at one end, a stack at the other end, and a hearth in between. The cupola is the most common source of iron for casting. Cast irons may be classified as either

gray, white, malleable, or ductile iron. Silicon and carbon are the two most important elements used to adjust the compositions of cast irons, but other elements such as Mn, S, P, Cr, Ni, Mo, and Cu may also be important. The primary effect of these elements is on the form the carbon takes as it precipitates during solidification. As shown in Figure , cast irons when solidified are mixtures of alpha iron plus graphite or iron carbide,  $\text{Fe}_3\text{C}$ , or cementite.

Gray iron contains most of its carbon in graphite form as flakes. White iron has lower levels of carbon and silicon, resulting in nearly all the carbon in the form of iron carbide. Malleable irons are produced by heat treating white iron such that the carbon diffuses from the iron carbide to form graphite in a roughly spheroidal shape. It is the shape of the graphite that permits the increased malleability of the product. Ductile (or nodular) iron is produced by adding cerium or magnesium to iron having slightly higher carbon and silicon but lower sulfur than gray iron. The addition of these special agents also promotes the formation of spheroidal graphite. The success of the foundry industry results in part from its versatility. Castings can often be more intricate than would be obtainable by machining. A wide range of properties, from brittle to ductile, may be obtained. Castings may weigh as little as a few grams or several tons.

## 6. Handling, Shipping, and Storing

In handling, shipping, and storing DRI, care should be taken to avoid oxidation. Millions of tons of DRI in pellet and lump form have been shipped by barge, ocean vessel, truck, and rail. The key to avoiding oxidation is simply to keep the material cool and dry. The chemical reactions involved have been well documented. In general, oxidation of DRI takes place in two forms: reoxidation and corrosion (12).

Reoxidation occurs when the metallic iron in hot DRI reacts with oxygen in the air to form either  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$ . The reaction continues as long as the DRI remains hot and sufficient oxygen is available. Because reoxidation reactions are exothermic and DRI is a good insulator, it is possible that once reoxidation begins inside a pile, the DRI temperature increases and accelerates the reoxidation rate. Although the inner core of the pile may reach temperatures up to the fusion point of iron, the maximum temperature of the outer parts of the pile will be much lower because of heat dissipation.

Corrosion occurs when the metallic iron in DRI is wetted with fresh or salt water and reacts with oxygen from air to form rust,  $\text{Fe}(\text{OH})_3$ . The corrosion reactions continue as long as water is present. Because water evaporates at approximately  $100^\circ\text{C}$ , corrosion reactions have a low temperature limit even though the reactions are exothermic. Small amounts of hydrogen may be generated when DRI reacts with water. However, this poses no safety problem as long as proper ventilation is provided.

Allowing DRI to become wet does not necessarily cause it to overheat. When large piles of DRI are wetted with rain, the corrosion reactions are limited to the outer surface area of the pile and the resultant heat from the corrosion reactions is dissipated into the atmosphere. However, if water penetrates into the pile from the bottom, or if wet DRI is covered with dry DRI, the heat from corrosion

reactions can build up inside the pile to the point where rapid reoxidation begins. Corrosion occurs significantly faster with salt water than with fresh water. DRI saturated with water can cause steam explosions if it is batch charged into an electric arc furnace.

In comparison, HBI is almost twice as dense as DRI, and thus does not absorb as much water and is much more resistant to reoxidation and corrosion. Several methods of passivating DRI to make it more resistant to reoxidation and corrosion have been developed, but none has been as effective as hot briquetting. Guidelines for offshore shipping of pellet/lump DRI and HBI have been prepared by the International Maritime Organization.

## 7. Economic Aspects

**7.1. Iron ore.** Table 8 gives salient U.S. economic data. Table 9 gives U.S. and world salient statistics for iron and steel. The value of usable ores shipped from mines in Michigan, Minnesota, and two other states in 2003 was estimated at \$1.2 billion. The United States produced 5% of the world's iron ore output and consumed about 7%.

China has become the dominant source of growth in demand for iron ore.

**7.2. Pig Iron.** About 98% of iron ore is used to produce pig iron and the best indicator of iron ore consumption worldwide. In 1992, China became and remains the leading producing country. Japan is second. In 2002, China produced 170 million tons of pig iron; Japan produced 81 million. China's share of world pig iron production rose to 31% in the first three quarters of 2003. Japan's share was 13%.

During the first eight months of 2003, monthly pig iron production fluctuated near 7.6 million tons. Pig iron and raw steel production were trending downward during the first half of 2003. Table 10 gives world production data for pig iron and raw steel.

## 8. Environmental Concerns

The Western world iron and steel industry has made major strides in facing up to environmental problems involving air and water pollution. The most difficult problem has been the pollution from recovery coke oven batteries, which emit particulates and hydrocarbon compounds from doors during coking and when the coke is pushed from the oven on the way to the quench tower. Although most of the current batteries in operation are operating under agreements with the various pollution control agencies, there have been no new batteries built for a long time and it would be difficult to get permission to build a new one, although rebuilding existing ones is possible. One new non-recovery coke battery has been built in the United States, but it loses the economic advantage of recovering the coal chemicals and coke oven gas fuel, which is used elsewhere in the steelmaking complex. However, it does meet the air standards for a New Source, which are quite stringent.

As mentioned above, blast furnace gas is scrubbed and used as fuel. The waste stream from the scrubbing process contains iron oxide and carbon particulates, which must be collected and filtered out of the water before it is recirculated. This waste can be sent to a sinter plant for recycling, or disposed of in a landfill. The water must be treated to neutralize or remove the ammonia and cyanide absorbed from the gases.

The BOF process generates significant quantities of fine dust particles, containing principally iron and iron oxide, with small amounts of manganese and silicon oxides. This dust is collected and either recycled via a sinter plant or landfilled, as it is not hazardous.

The EAF process for steelmaking, on the other hand, also generates dust, but because it is scrapbased, the dust can contain significant quantities of zinc, cadmium and lead. These elements come from the coated steel scrap in the scrap mix, and since they are considered hazardous, EAF dust must be handled and disposed of as a hazardous waste, with all the attendant costs associated with that category. Baghouses are used to capture the dust, and no dust can be spilled in the subsequent handling until it reaches a licensed hazardous waste landfill or processor. Many processes have been proposed and attempted to recover the zinc, lead and cadmium and convert the remainder to a non-hazardous status. The Flame-reactor process and the rotary kiln process are the most successful of these. Many others have failed.

Several European countries have imposed severe limits on dioxin emissions from EAF waste gas stacks. Dioxins can be formed from waste plastics in the scrap charge. Dioxin removal to the levels required in Germany is very difficult and would cause severe economic problems if the same standards were to be implemented in the United States.

The water systems of all steel plants continuously lose water due to evaporation in cooling towers, since a major function of the water is equipment cooling. However, since much of the water comes in contact with the rolling and casting equipment, which use lubricants, and is also treated with corrosion inhibiting chemicals, the build-up of these oils and chemicals requires an amount of water be continuously removed from the system. This "blow down" has to be treated before being discarded to the sewer. This is an expensive process. Also, since the hardness of the water has to be kept low in order to avoid scaling the inside of cooling channels (thus decreasing the effectiveness of cooling) the incoming make-up water to replace the evaporation and blow down losses has to be softened, leading to a waste stream of concentrated salt, which has to be disposed of. In general, water system management is a complex and expensive subsystem operation that has a very direct effect on the cost and quality of steel made.

Unfortunately, many of the older plants in the former Communist bloc and in China have little to no environmental control systems and continue to pollute. They, of course, therefore do not have the costs associated with these controls, which gives them an unfair cost advantage in the global economy.

The largest *future* environmental problem facing the world's steel industry is that of greenhouse gas emission, specifically carbon dioxide. The preparation of sinter fines or pellets uses a large amount of electricity, in addition to hydrocarbon fuel. The production of electricity is primarily based on coal and oil, which

ends up as CO<sub>2</sub> and water. The reduction of iron ore is largely based on the use of carbon, which ultimately ends up as CO<sub>2</sub>. The oxygen used in steelmaking is produced from air using electricity, and the limestone used ultimately dissociates into CaO and CO<sub>2</sub>. Thus, the industry produces a tremendous amount of carbon dioxide. Table 11 gives the total emissions of carbon dioxide per liquid ton of steel from different process routes. The most common route, ore-pelletcoke-blast furnace-BOF, results in emission of about one tone of CO<sub>2</sub> per ton of steel.

The result is that the industry is one of the largest contributors to greenhouse gas emissions. Unfortunately, there is no economic substitute for the reductant and energy requirements of the industry at this point in history, and so the only choice to reduce these emissions is to incrementally improve the energy efficiency of the existing plants and processes. Should this become mandated, this will require increased capital investment with little or no return on the investment, which, in light of the economic situation of the industry described above, will only further decrease the overall return on capital and the incentive to modernize.

## 9. Health and Safety Factors

Iron presents minimal health risks. Skin contact should not result in any adverse health effect. Excessive inhalation of dust may be irritating to the respiratory tract. Dust may also cause mechanical irritation on eye contact. Extremely large oral doses would be required to cause gastrointestinal disturbance. The LD<sub>50</sub> toxicity rating (RTECS, 1992) for oral ingestion is 30 g/kg. Iron is not categorized as hazardous or limited under any of the following regulations: SARA Sec. 302 EHS (RQ or TPQ), SARA Sec. 313 Chemicals, CERCLA Sec. 103 RQ, or RCRA Sec. 261.33 (16).

Iron dust does present a moderate fire and explosion hazard when exposed to heat and flame. Although normally not very reactive, under certain circumstances iron can react with water to liberate flammable hydrogen gas.

## 10. Uses

United States consumption of iron ore by end use is listed in Table 12.

Over 95% of the world's DRI production is consumed in electric arc furnace steelmaking. The remaining 5% is split among blast furnaces, oxygen steelmaking, foundries, and ladle metallurgy (qv) facilities.

The primary use of DRI is as a clean supplement or replacement for the ferrous scrap charge in high quality-oriented electric arc furnace (EAF) steelmaking. By controlling the level of residual elements in the charge, steelmakers can upgrade their product mix and reduce off-grade heats. Also, a low level of residual elements in carbon steel changes its physical properties for the better.

The desired portion of DRI used in the charge depends on economics, the type of steel being produced, and the available scrap quality. When DRI represents over 35% of the charge, it is preferable to feed it continuously through the roof of the EAF. Continuous charging can eliminate the need for back charging,

thus improving productivity and energy efficiency. Most EAF steelmakers purchasing DRI on the open market use 10 to 30% DRI in the charge and do not have continuous charging systems installed in the melt shops. In this case, the DRI is batch charged along with scrap using existing scrap handling equipment and practices.

DRI, in pellet/lump or HBI form, can be added to the blast furnace burden to increase furnace productivity and reduce coke requirements. It can be used for short-term increases in blast furnace output when a facility is short of hot metal during times of high steel demand, or when one of several blast furnaces is down for a reline. It also can be justified if the increased output is sufficient to allow operation of fewer blast furnaces long-term.

HBI is used as a trim coolant or scrap replacement in oxygen steelmaking. In the oxygen steelmaking process, the molten steel often is overheated. Trim coolant is fed to the furnace to cool the molten steel to the desired temperature. HBI is preferred for this application because its high density ensures an effective slag penetration and complete melting in the molten steel bath. Steel yield is increased when HBI is used as a trim coolant instead of iron ore. Also, the violent reactions that can occur when using iron ore are eliminated. The relative cooling effect of various materials are as follows: scrap 1.0, HBI 1.2, and iron ore 2.0–3.0.

HBI is an effective trim coolant for molten steel in ladle metallurgy facilities, ladle refiners, ladle furnaces, and vacuum degassers. It provides cold iron units in an ideal size and density for penetrating the ladle slag and cooling the metal.

HBI has been successfully melted in cupolas (hot or cold blast), induction furnaces (coreless or channel), and electric arc furnaces. It can be a valuable charge material for ductile and malleable irons as well as steel. It is of particular value in making ductile iron castings because of its very low residual element content.

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Table 1. Properties of Iron<sup>a</sup>

Property	Value
atomic mass	55.847
isotopic abundance	
mass	54 56 57 58
abundance, %	6.04 91.57 2.11 0.28
melting point, °C	1537
boiling point, °C	3000
crystal structure <sup>b</sup>	bcc
density, <sup>c</sup> g/cm <sup>3</sup>	7.87
thermal conductivity at 0°C, W/(m · K)	79
electrical resistivity at 20°C, μΩ · cm	9.71
tensile strength, MPa <sup>d</sup>	240–280
yield strength, MPa <sup>d</sup>	70–140
Young's modulus of elasticity, GPa <sup>d</sup>	195
Poisson's ratio	0.3
elongation in 5 cm at 20°C, %	40–60
reduction of area, %	65–78
Brinell hardness	82–100
impact strength (izod notched bar)	
longitudinal, J/m <sup>e</sup>	4859
transverse, J/m <sup>e</sup>	2990
thermal expansion, K <sup>-1</sup>	
from 0–300°C	12.6 × 10 <sup>-6</sup>
0–600°C	14.6 × 10 <sup>-6</sup>
specific heat, J/(g · K) <sup>e</sup>	
at 100°C	0.50
500°C	0.67
800°C	1.26
transition from magnetic to paramagnetic, °C	ca 770

<sup>a</sup> Ref. 1.<sup>b</sup> Room temperature.<sup>c</sup> Hot rolled.<sup>d</sup> To convert MPa to psi, multiply by 145.<sup>e</sup> To convert J to cal, divide by 4.184.

Table 2. Physical Characteristics of DRI<sup>a</sup>

Parameter	Pellets/lump	HBI
density, t/m <sup>3</sup>		
bulk	1.6–1.9	2.4–2.8
apparent	3.5	5.0–5.5
porosity, %	50	15
saturated water absorption, wt %	12–15	2–3
nominal size, mm	4–20	30 × 50 × 110

<sup>a</sup> Produced in the MIDREX Direct Reduction Process.Table 3. Principal Iron-Bearing Minerals<sup>a</sup>

Parameter	Mineral					
	Hematite	Magnetite	Goethite	Siderite	Ilmenite	Pyrite
CAS Registry Number	[1309-37-1]	[1309-38-2]	[1310-14-1]	[14476-16-5]	[12168-52-4]	[1309-36-0]
chemical name	ferric oxide	ferrous–ferric oxide	hydrous iron oxide	iron carbonate	iron–titanium oxide	iron sulfide
chemical formula	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>	HFeO <sub>2</sub>	FeCO <sub>3</sub>	FeTiO <sub>3</sub>	FeS <sub>2</sub>
iron, wt %	69.94	72.36	62.85	48.20	36.80	46.55
color	steel gray to red	dark gray to black	yellow or brown to nearly black	white to greenish gray to black	iron-black	pale brass-yellow
crystal	hexagonal	cubic	orthorhombic	hexagonal	hexagonal	cubic
specific gravity	5.24	5.18	3.3–4.3	3.83–3.88	4.72	4.95–5.10
Mohs' hardness	6.5	6	5–5.5	3.5–4	5–6	6–6.5
melting point, °C	1565	1600			1370	
magnetism		strong			slight	

<sup>a</sup> Ref. 1.

Table 4. **World Mine Production, Reserves, and Reserve Base**  $\times 10^6 \text{ t}^a$ 

	Mine production		Crude ore		Iron content	
	2002	2003 <sup>a</sup>	Reserves	Reserve base	Reserves	Reserve base
United States	52	50	6,900	15,000	2,100	4,600
Australia	183	190	18,000	40,000	11,000	25,000
Brazil	212	215	7,600	19,000	4,800	12,000
Canada	31	32	1,700	3,900	1,100	2,500
China	231	240	21,000	46,000	7,000	15,000
India	80	80	6,600	9,800	4,200	6,200
Iran	11	11	1,800	2,500	1,000	1,500
Kazakhstan	15	18	8,300	19,000	3,300	7,400
Mauritania	10	10	700	1,500	400	1,000
Russia	84	92	25,000	56,000	14,000	31,000
South Africa	36	38	1,000	2,300	650	1,500
Sweden	20	21	3,500	7,800	2,200	5,000
Ukraine	59	63	30,000	68,000	9,000	20,000
Venezuela	18	17	4,000	6,000	2,400	3,600
Other countries	38	40	11,000	30,000	6,600	18,000
<i>World total (rounded)</i>	<i>1,080</i>	<i>1,120</i>	<i>150,000</i>	<i>330,000</i>	<i>70,000</i>	<i>150,000</i>

<sup>a</sup> Ref. 6.<sup>b</sup> Estimated.

Table 5. **Blast Furnace Energy Balance**<sup>a</sup>

Balance	Hot metal, GJ/t <sup>b</sup>	%
<i>Energy input</i>		
sensible heat of hot blast	1.64	41
combustion		
of coke	2.10	52
of injected fuel	0.27	7
<i>Total</i>	<i>4.01</i>	<i>100</i>
<i>Energy output</i>		
reduction		
of iron oxides	1.17	29
of other metalloids	0.15	4
sensible heat		
of slag	0.48	12
of hot metal	1.36	34
of top gas	0.20	5
decomposition of H <sub>2</sub> O at raceway	0.26	6
vaporization of H <sub>2</sub> O from burden	0.13	3
heat losses	0.26	6
<i>Total</i>	<i>4.01</i>	<i>100</i>

<sup>a</sup> Ref. 1.<sup>b</sup> To convert GJ to Btu, multiply by  $0.9488 \times 10^{-12}$ .

Table 6. **Composition of DRI Produced in the MIDREX Process**

Parameter	Pellet/lump	HBI
iron, wt%		
total	90–94	90–94
metallic	83–89	83–89
metallization, %	92–95	92–95
FeO, wt%	6.5–9.1	6.5–9.1
C, wt%	1.0–2.5	0.8–1.2
gangue, wt%	2.8–6.0	2.8–6.0
P, wt%	0.005–0.09	0.005–0.09
S, wt%	0.001–0.03	0.001–0.03
other	trace	trace

Table 7. **Heats of Reaction for Reductions in DR Processes, kJ/kg Fe<sup>ab</sup> –<sup>c</sup>**

Temperature, °C	Fe <sub>2</sub> O <sub>3</sub> →Fe <sub>3</sub> O <sub>4</sub>			Fe <sub>3</sub> O <sub>4</sub> →Fe <sub>0.95</sub> O			Fe <sub>0.95</sub> →Fe		
	H <sub>2</sub>	CO	C	H <sub>2</sub>	CO	C	H <sub>2</sub>	CO	C
600	–800	–6,873	21,771	17,380	7,271	54,945	16,154	–22,328	159,164
700	–1,829	–7,744	20,779	16,258	6,417	53,886	15,471	–22,006	158,716
800	–2,373	–8,129	20,256	15,882	6,300	53,539	16,459	–20,026	159,830
900	–2,541	–8,142	20,093	15,614	6,292	53,284	16,166	–19,331	159,574
1,000	–2,733	–8,183	19,892	15,463	6,392	53,112	15,672	–18,858	159,018
1,100	–2,951	–8,251	19,649	15,417	6,597	53,032	14,216	–19,364	157,410
1,200	–3,194	–8,347	19,369	15,484	6,911	53,037	12,822	–19,821	155,782
1,300	–3,462	–8,468	19,050	15,664	7,330	53,129	11,499	–20,231	154,133

<sup>a</sup> All heats of reaction are based on stoichiometric equation for 1 mol Fe in reactant oxide.

<sup>b</sup> Conventional signs are employed: negative values are exothermic; positive values are endothermic.

<sup>c</sup> To convert kJ/kg Fe to Btu/lb Fe, multiply by 0.43.

Table 8. **Salient Statistics for Iron in the U.S.**<sup>a</sup>

Statistics	1999	2000	2001	2002	2003 <sup>b</sup>
production, usable	57.7	63.1	46.2	51.6	50.0
shipments	60.7	61.0	50.6	51.5	50.0
imports for consumption	14.3	15.7	10.7	12.5	13.0
exports consumption:	6.1	6.1	5.6	6.8	6.4
reported (ore and total agglomerate)	75.1	76.5	67.3	59.0	56.0
apparent	70.1	70.2	62.0	57.9	56.1
price, <sup>c</sup> U.S. dollars per metric ton	25.52	25.57	23.87	26.04	25.00
stocks, mine, dock, and consuming plant, yearend, excluding byproduct ore	26.4	28.8	18.0	17.5	18.0
employment, mine, concentrating and pelletizing plant, quarterly average, number	6,820	6,814	5,017	4,742	4,500
net import reliance <sup>d</sup> as a percentage of apparent consumption (iron in ore)	18	10	26	11	11

<sup>a</sup> Ref. 6.<sup>b</sup> Estimated.<sup>c</sup> Calculated from value of ore at mines.<sup>d</sup> Defined as imports–exports + adjustments for U.S. Government Industry stock changes.



Table 9. Salient Iron and Steel Statistics  $\times 10^3t^a$ 

Statistics	1998	1999	2000	2001	2002
United States					
pig iron					
production <sup>b</sup>	48,200	46,300	47,900	42,100	40,200
exports <sup>c</sup>	87	82	72	44	34
imports for consumption <sup>c</sup>	5,140	4,990	4,970	4,370	4,620
Direct-reduced iron					
production <sup>d</sup>	1,600	1,670	1,560	1,200	470
exports <sup>c</sup>	5	3	2	1	1
imports for consumption <sup>c</sup>	939	950	1,090	1,650	2,010
Raw steel production <sup>e</sup>					
carbon steel	88,000	87,600	92,500	82,400	83,700
stainless steel	2,010	2,190	2,190	1,820	2,180
all other alloy steel	8,600	7,650	7,510	5,920	5,680
<i>Total</i>	<i>98,600</i>	<i>97,400</i>	<i>102,000</i>	<i>90,100</i>	<i>91,600</i>
capability utilization, percent	86.8	83.8	86.1	79.2	88.8
Steel mill products					
net shipments <sup>b</sup>	92,900	96,300	98,900	89,700	90,700
exports <sup>c</sup>	5,010	4,920	5,920	5,570	5,450
imports <sup>c</sup>	37,700	32,400	34,400	27,300	29,600
producer price index for steel mill products (1982=100.0) <sup>f</sup>	113.8	105.3	108.4	101.3	104.8
World production <sup>g</sup>					
pig iron	535,000	539,000	573,000	577,000	604,000
direct-reduced iron <sup>d</sup>	37,200	38,200	42,500	39,300	38,800
raw steel	770,000	784,000	845,000	847,000	898,000

<sup>a</sup> Data are rounded to three significant digits, except prices; may not add to totals shown.

<sup>b</sup> Data are from the American Iron and Steel Institute (AISI).

<sup>c</sup> Data are from the U.S. Census Bureau.

<sup>d</sup> Data are from the Midrex Direct Reduction Corp., Government, and companies.

<sup>e</sup> Raw steel is defined by AISI as steel in the first solid state after melting, suitable for rolling.

<sup>f</sup> Data are from the U.S. Department of Commerce Bureau of Labor Statistics.

<sup>g</sup> Data are from the U.S. Geological Survey and the International Iron and Steel Institute.

Table 10. **World Production of Pig Iron and Raw Steel,  $\times 10^6$  t<sup>a</sup>**

Country/Area	Pig Iron		Raw steel	
	2002	2003 <sup>b</sup>	2002	2003 <sup>b</sup>
United States	40.2	39.4	91.6	91.5
Brazil	27.8	31.0	29.6	27.5
China	171	190	182	200
European Union	89.4	90.4	157	159
Japan	81.0	81.7	108	110
Korea, Republic of	26.5	26.6	45.4	46.0
Russia	46.1	48.0	59.8	61.2
Ukraine	27.6	29.0	34.5	38.0
other countries	94.4	97.9	196	191
<i>World total (rounded)</i>	<i>604</i>	<i>634</i>	<i>904</i>	<i>924</i>

<sup>a</sup> Ref. 14.<sup>b</sup> Estimated.Table 11. **Carbon Dioxide Emissions by Process Route<sup>a</sup>**

Process Route	kg CO <sub>2</sub> /t liquid steel
Ore–Pellet–Coke–Blast furnace–BOF	2010
Ore–Pellet–Corex furnace–BOF	3089
Ore–Pellet–Midrex–EAF	1874
Scrap–EAF	641

<sup>a</sup> Ref. 15.

Table 12. U.S. Consumption of Iron Ore, by End use<sup>a,b,c</sup>

Year	Blast furnaces	Steel furnaces	Sintering plants <sup>d</sup>	Miscella- neous <sup>e</sup>	Subtotal integrated iron and steel plants <sup>f</sup>	Direct- reduced iron for steel- making <sup>g</sup>	Non- steel end uses <sup>h</sup>	Total
2001	57,300	35	4,560		61,900	1,800	756	64,400
2002	52,900	301	5,620	1	58,800	470	675	60,000

<sup>a</sup> Ref. 13. 10<sup>3</sup> t and exclusive of ore containing 5% or more manganese.

<sup>b</sup> Data are rounded to no more than three significant digits; may not add to totals shown.

<sup>c</sup> Includes agglomerates.

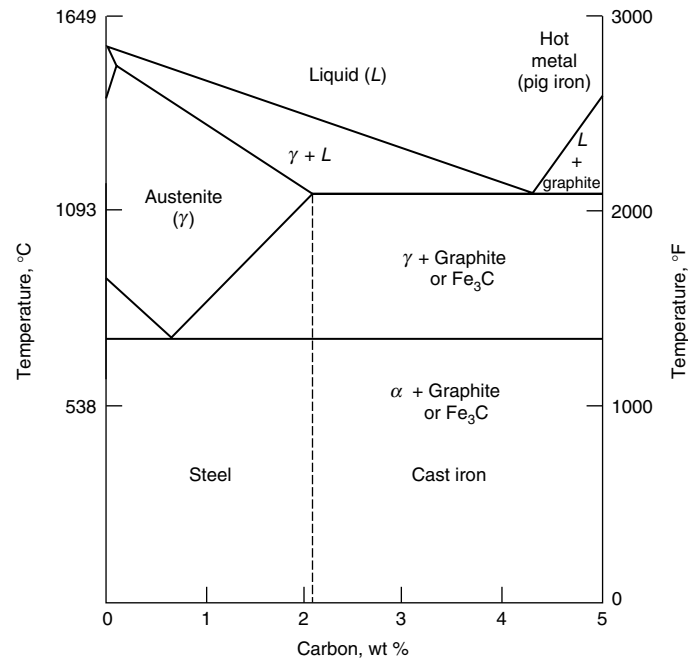
<sup>d</sup> Excludes dust, mill scale, and other revert iron-bearing materials.

<sup>e</sup> Sold to nonreporting companies or used for purposes not listed.

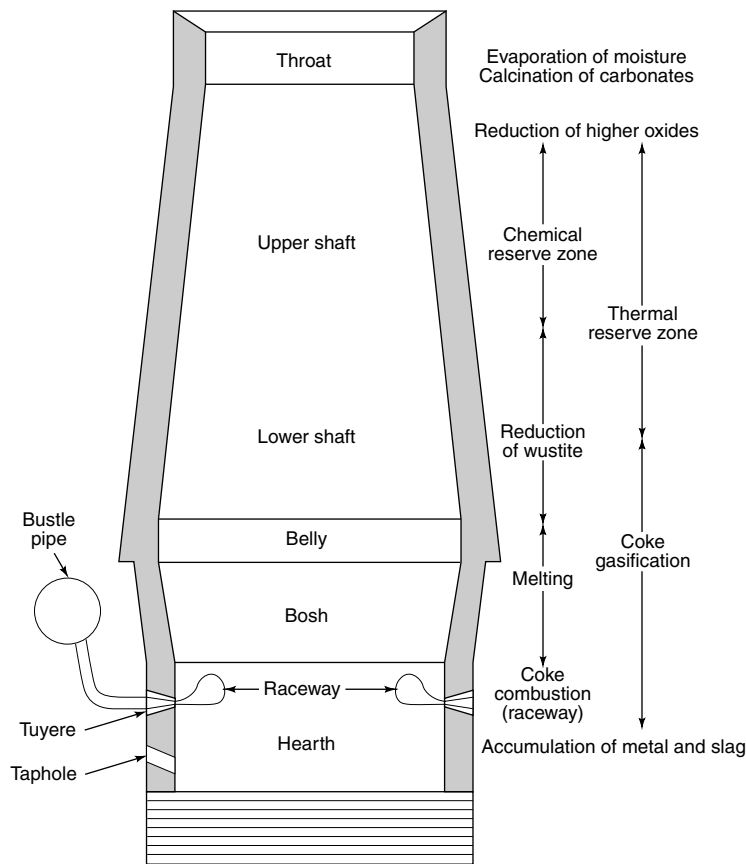
<sup>f</sup> Data from American Iron Ore Association.

<sup>g</sup> U.S. Geological Survey estimates based on production reports compiled by Midrex Corp.

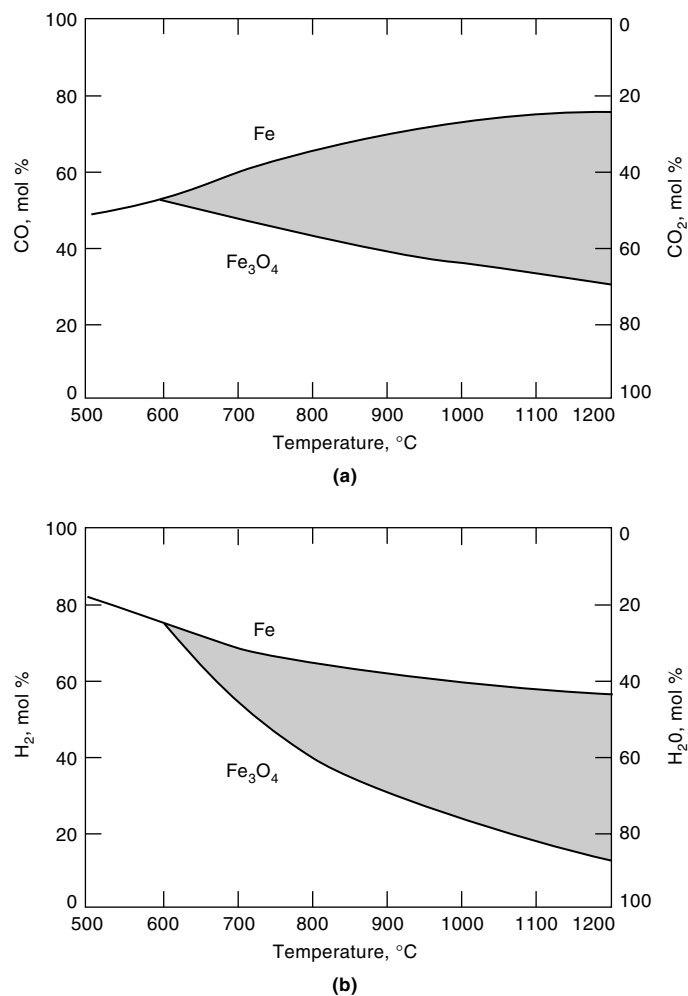
<sup>h</sup> Includes iron ore consumed in production of cement and iron ore shipped for use in manufacturing paint, ferrites, heavy media, cattle feed, refractory and weighing materials, and for use in lead smelting.



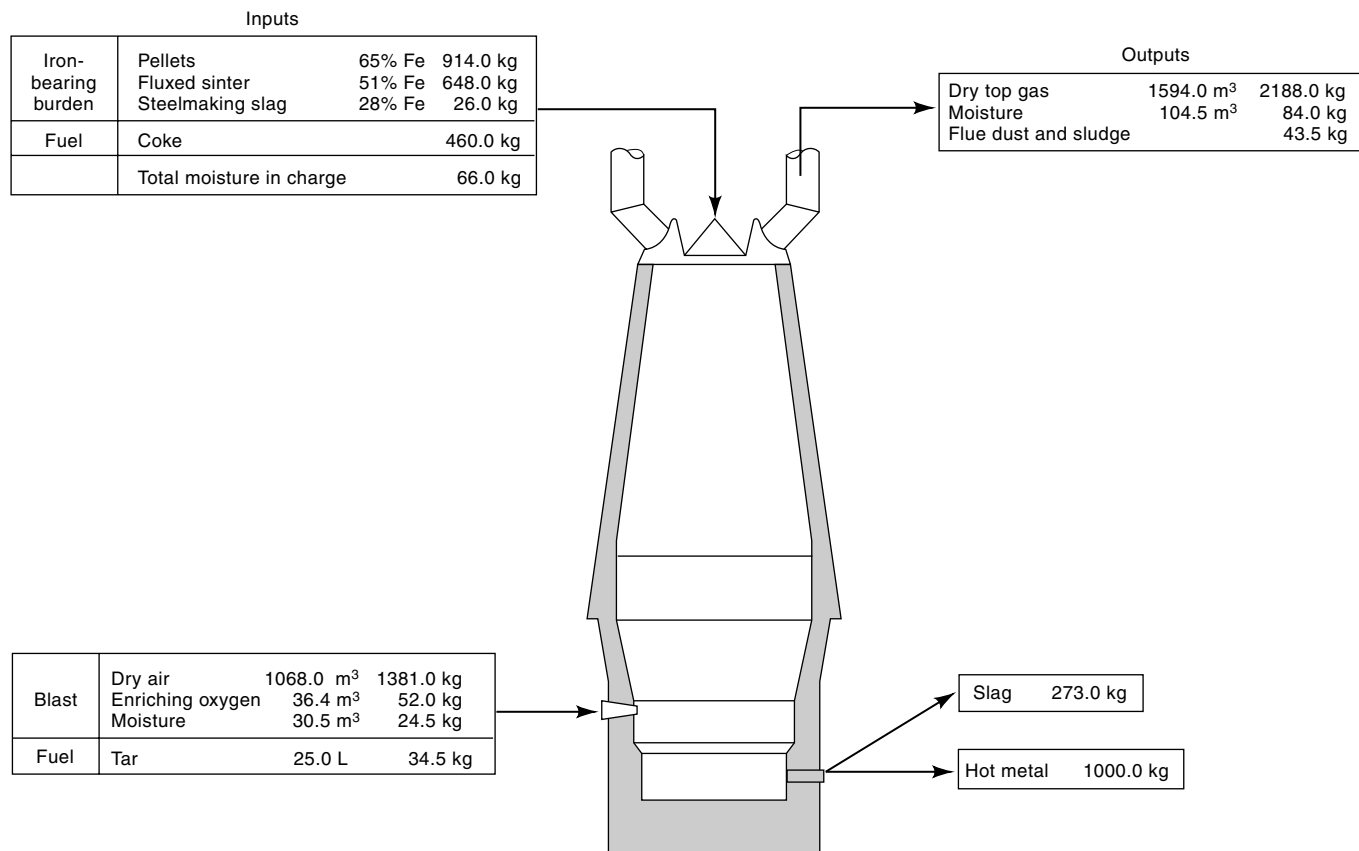
**Fig. 1.** Iron–carbon phase diagram, where  $\alpha$  is the body-centered cubic (bcc)  $\alpha$ -iron,  $\gamma$  is the face-centered cubic  $\gamma$ -iron, and  $\text{Fe}_3\text{C}$  is iron carbide(3:1) [12011-67-5] at 6.69% C. The vertical dashed line represents the demarcation between steel on the left and cast iron on the right (3).



**Fig. 2.** Schematic of a blast furnace.



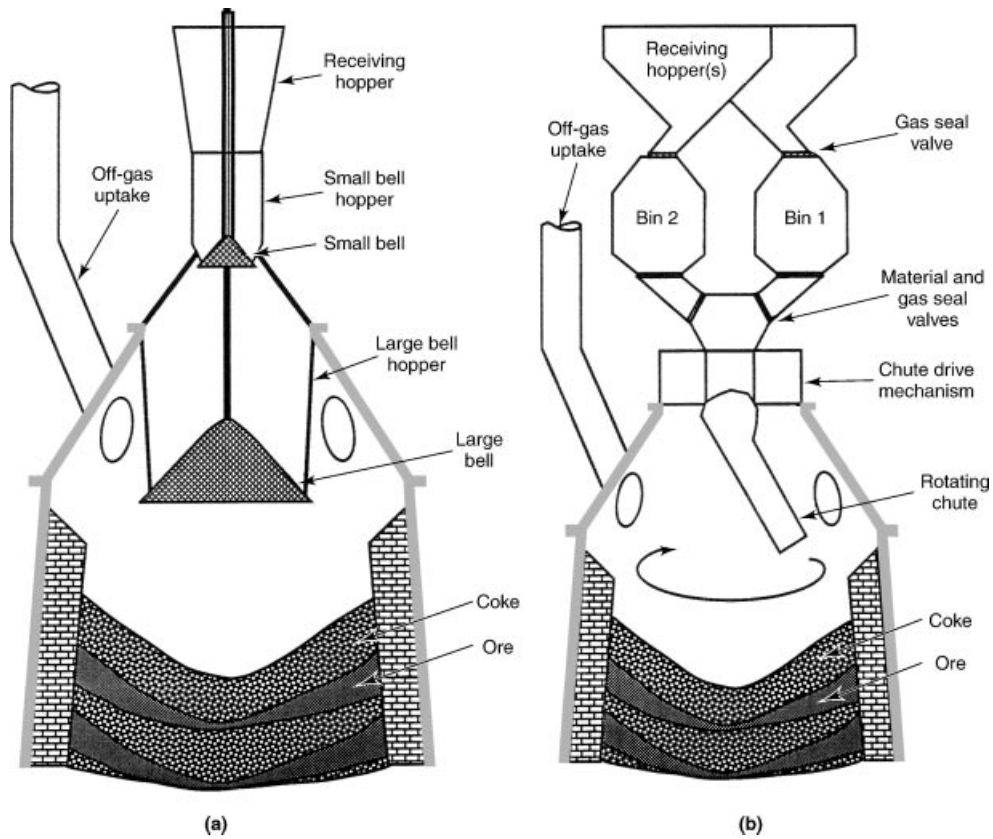
**Fig. 3.** Phase diagrams in which (—) represents FeO. (a) Fe–O–C system; (b) Fe–O–H system.



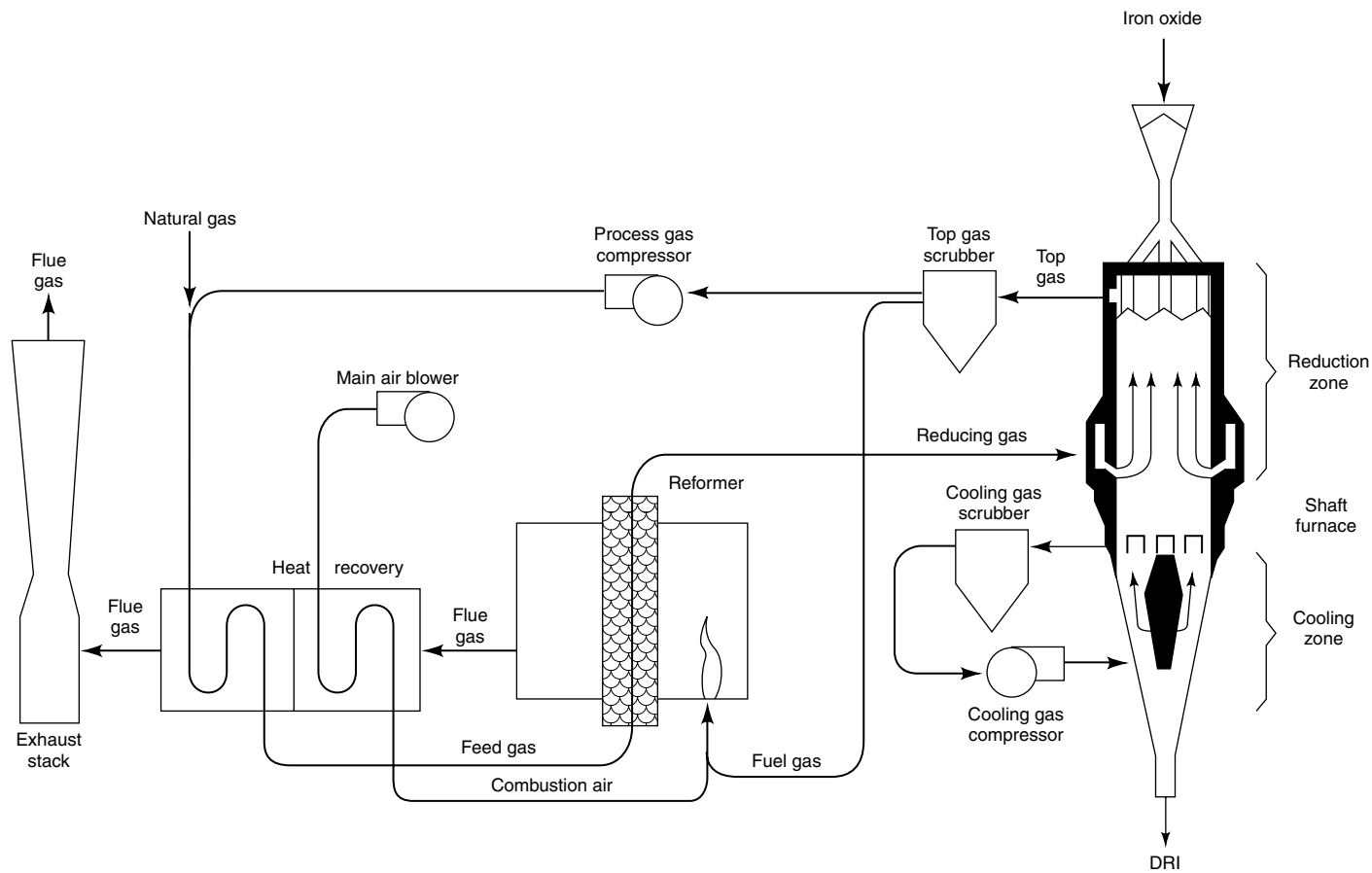
**Fig. 4.** Blast furnace material balance where all quantities represent the amount per metric ton of hot metal. The dry top gas contains 23.4% CO, 21.2% CO<sub>2</sub>, and 2.5% H<sub>2</sub>; the slag contains 38% SiO<sub>2</sub>, 9% Al<sub>2</sub>O<sub>3</sub>, 42% CaO, 10% MgO, and 1.3% S; and the hot metal contains 4.5% C, 0.48% Si, 0.59% Mn, 0.029% S, and 0.060% P (1).

**Fig. 5.** Flow diagram depicting the principal units and auxiliaries in a modern blast furnace plant, and showing the steps in the manufacture of pig iron from receipt of raw materials to disposal of pig iron and slag, as well as the methods for utilizing the furnace gases. (—), Miscellaneous raw material; (---), cold-blast air; (—■—), hot-blast air; (— — —), blast furnace gas; (—×—), steam; (— — —), hot metal; (— — —), hot slag; (— · —) flue dust; (— · · —), sludge; and (·), sinter.

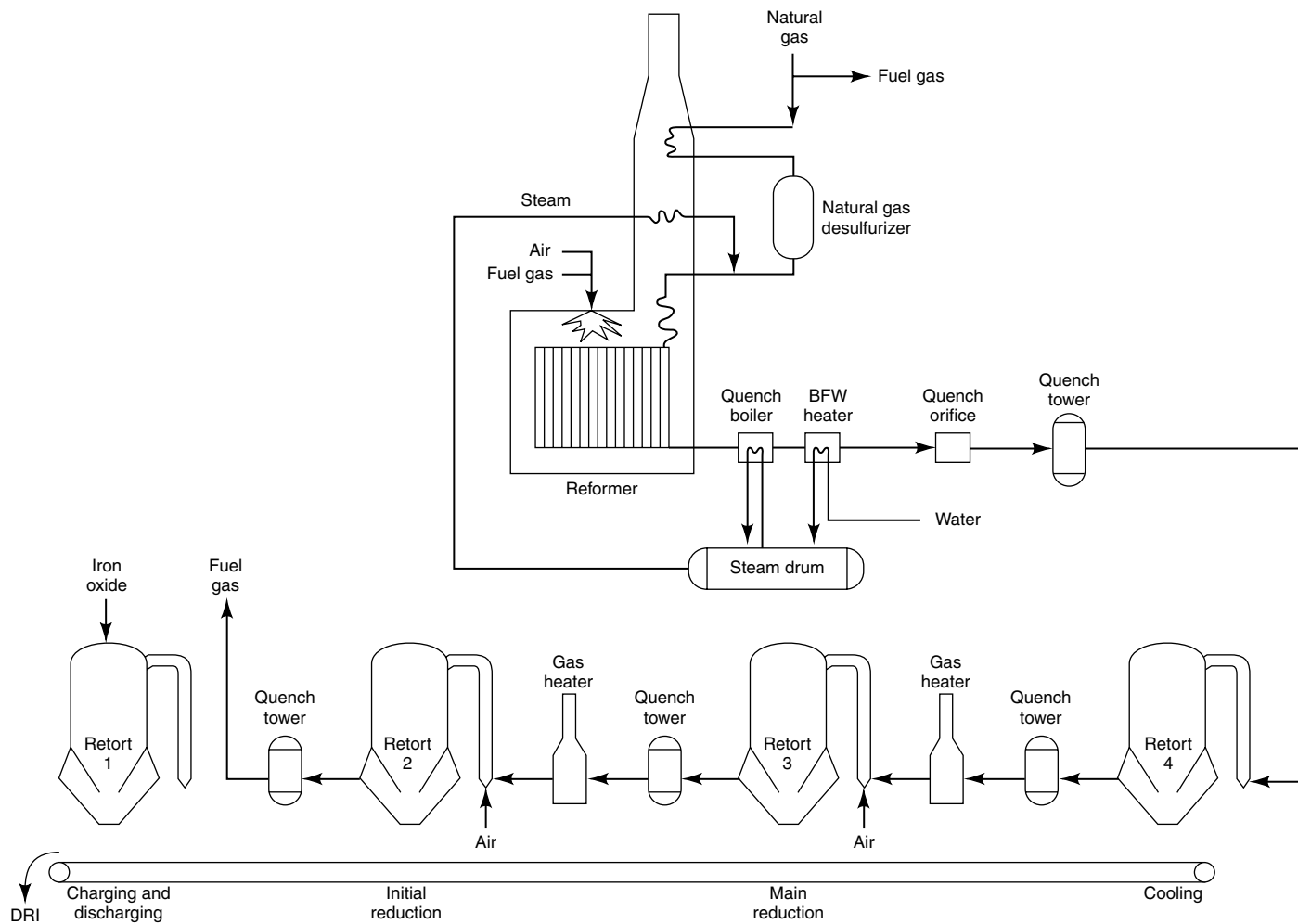




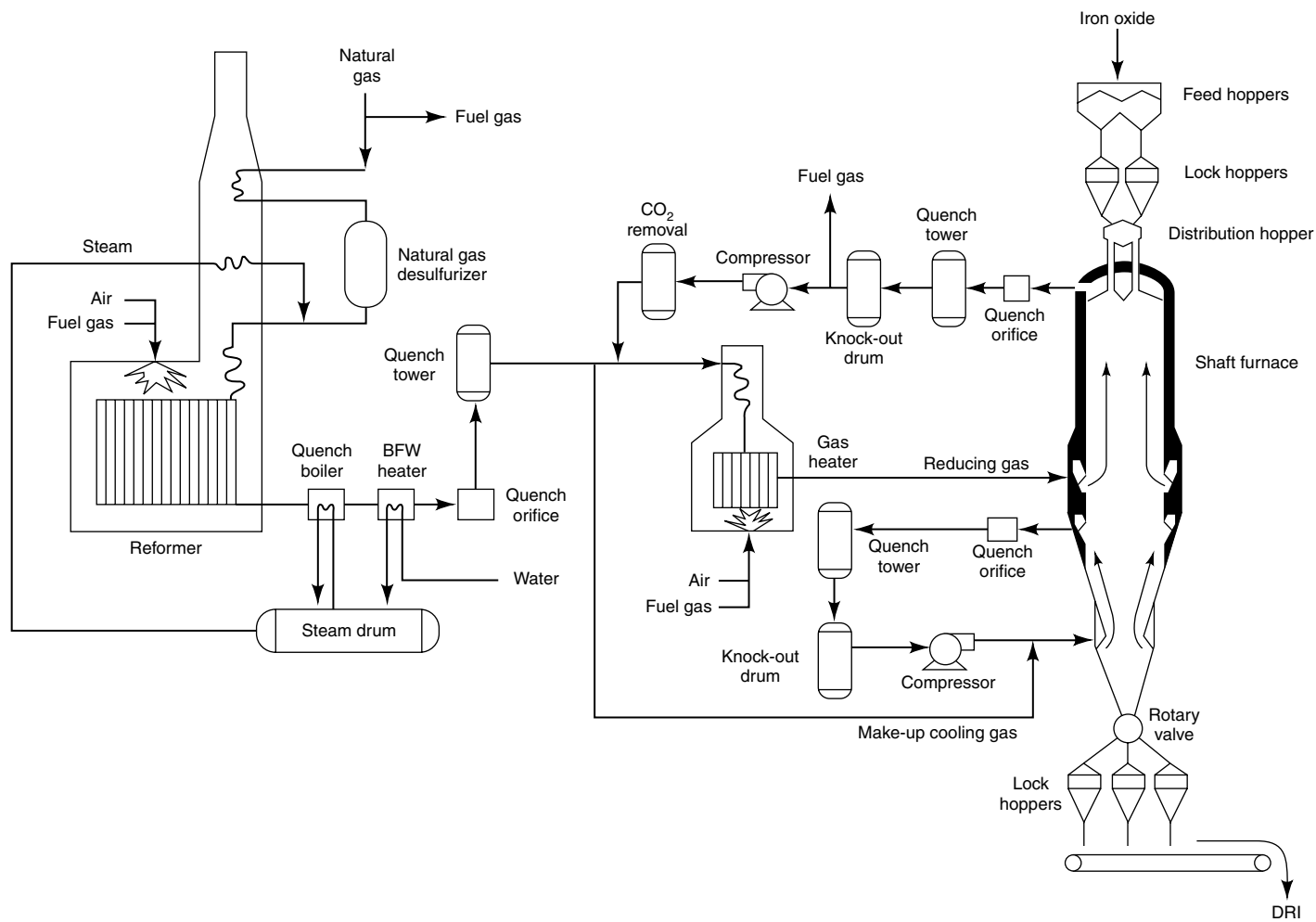
**Fig. 6.** Pressurized gas seal system at top of blast furnace: (a) two-bell top; and (b) bell-less top.



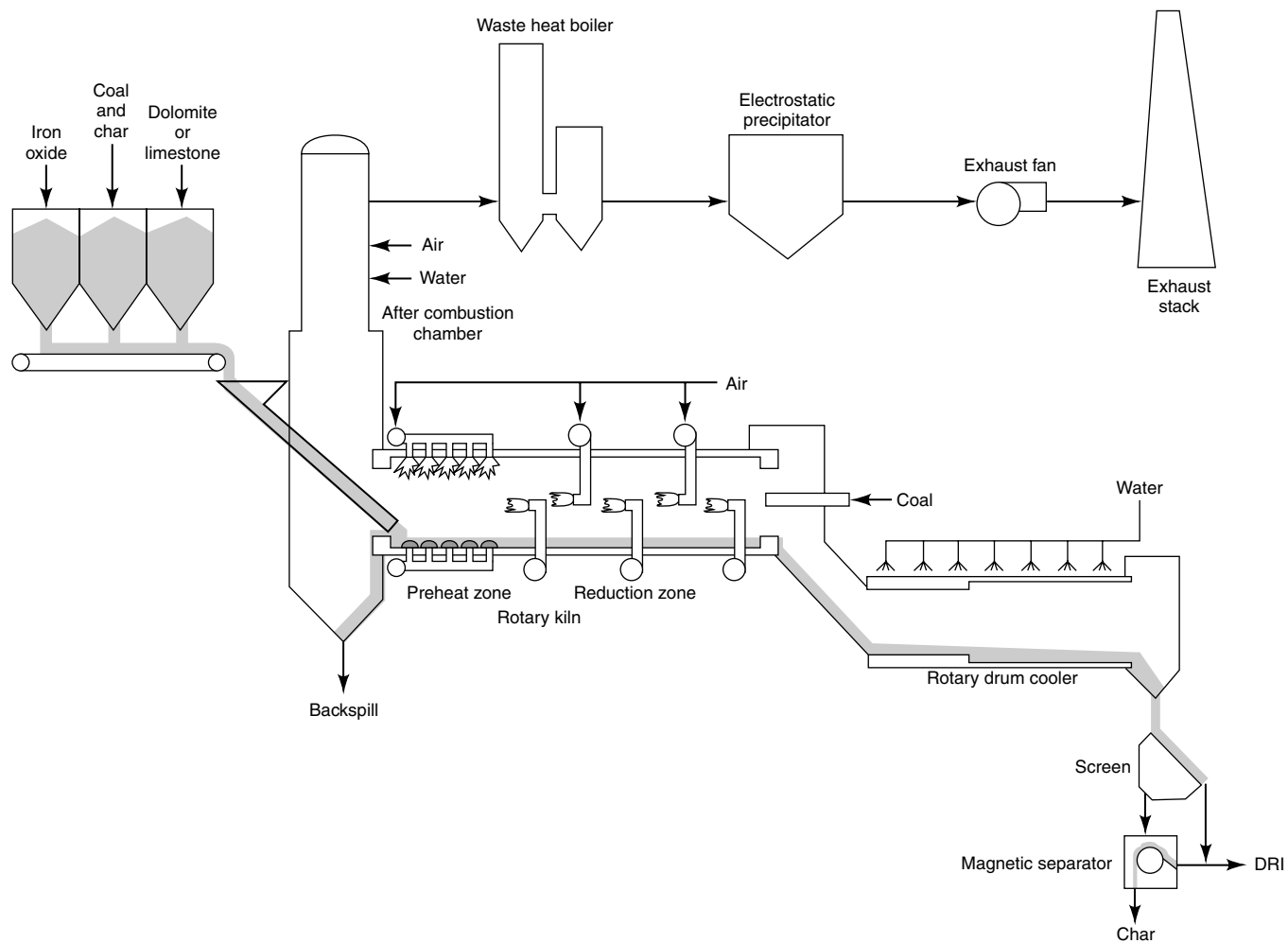
**Fig. 7.** The MIDREX process.



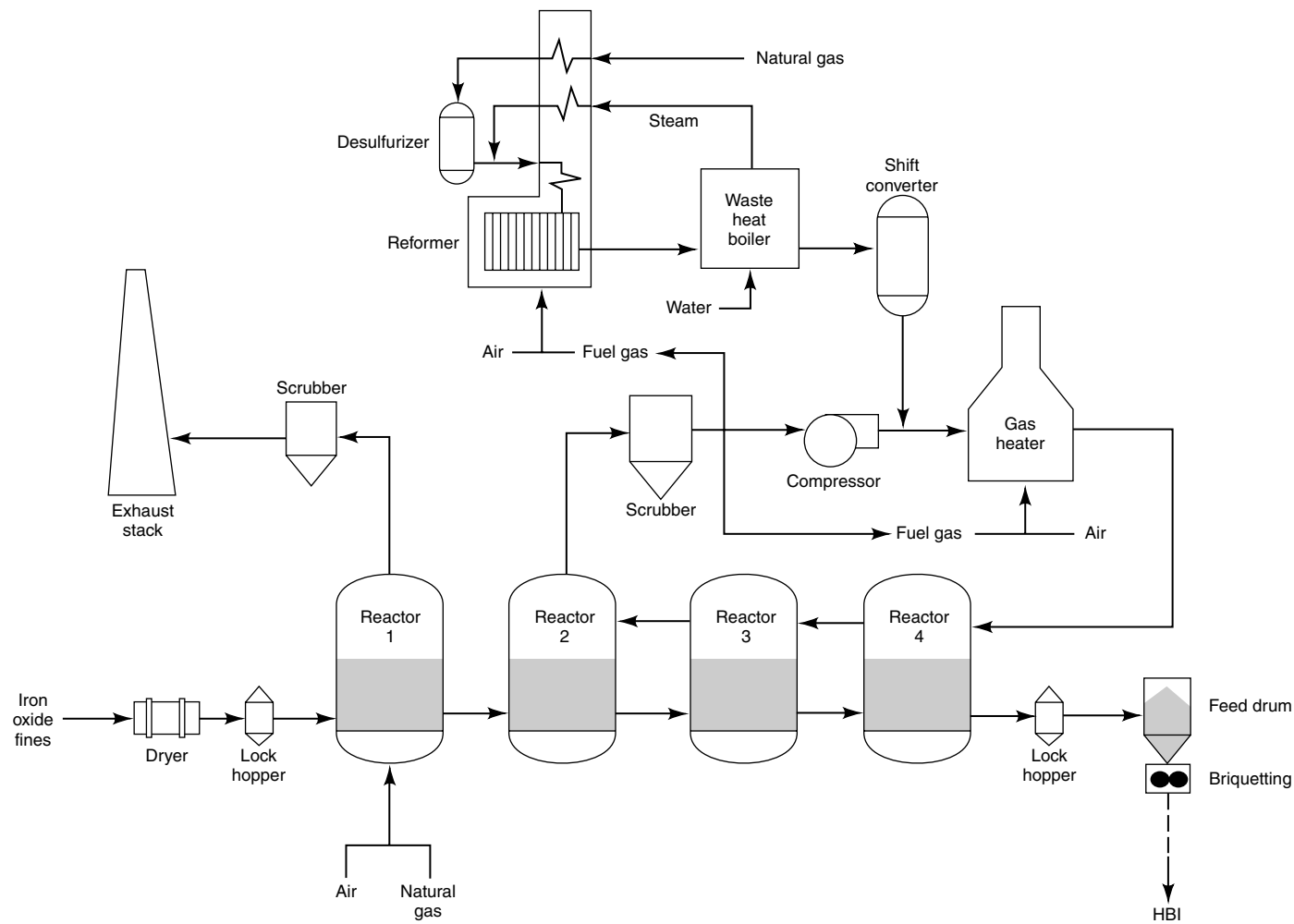
**Fig. 8.** The HYL I process, where BFW = boiling feed water.



**Fig. 9.** The HYL III process, where BFW = boiling feed water.



**Fig. 10.** The SL/RN process.



**Fig. 11.** The FIOR process.