Chapter 5

Production and Use of Industrial Gases for Iron and Steelmaking

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5.1 Industrial Gas Uses

5.1.1 Introduction

The iron and steel industry, one of the largest users of industrial gases, consumes substantial quantities of oxygen, nitrogen, argon, and hydrogen, and a small but growing amount of carbon dioxide (CO_2). Table 5.1 shows estimates of total consumption by the US industry for the most commonly used gases.

Table 5.1 Consumption of Industrial Gases by the United States Steel Industry

(Millions of Cubic Feet in Gaseous Form)

	1990	1995
Oxygen	199,420	288,105
Nitrogen	133,250	135,665
Argon	2,480	2,513
Hydrogen	830	940

Oxygen and nitrogen represent the largest volumes by far. Oxygen consumption has grown substantially in recent years while use of the other gases has remained relatively constant.

In order to provide a framework for reviewing the various uses of industrial gases, Table 5.2 summarizes the generic process functions they perform in iron and steelmaking operations.

Table 5.2 Industrial Gas Functions

Gas	Heating	Oxidation	Reduction	Stirring	Inerting	Injection
Oxygen	X	X				
Nitrogen	X (plasma)			X	X	X
Argon	X (plasma)			X	X	X
Hydrogen			X			
CO_2				X	X	X

Oxygen is used to provide process heat through various exothermic reactions which occur upon contact with hot metal and liquid steel and through combustion of fossil fuels. Injected oxygen also participates in the formation of carbon monoxide for the reduction of iron ore in the blast furnace and in some natural gas-based processes for producing direct reduced iron. Nitrogen, argon, and CO_2 are used for inerting vessels, equipment, and metal transfer streams in tapping and casting operations; to eliminate the formation of explosive mixtures in enclosed spaces; and to prevent undesirable reactions between iron and steel with oxygen and hydrogen in the surrounding atmosphere. Nitrogen and argon are also injected into molten iron and steel to provide metal stirring and slag/metal mixing, and as a carrier gas for powder injection. Additional uses for these gases include providing conditions which favor the oxidation of carbon instead of chromium in the argon oxygen decarburization (AOD) process for producing stainless and high alloy steels and as a coolant to protect oxygen injection tuyeres in various oxygen converters. The choice of gas for such inerting, stirring, injection, and steelmaking converter operations is dictated by overall cost and effect on metal chemistry and quality. Nitrogen is usually the gas of choice so long as its reactivity with molten metal and the associated increase in dissolved nitrogen or nitride formation is acceptable. Argon is used whenever a totally inert gas that does not affect metal chemistry is required. CO_2 does not result in increased nitrogen levels but can result in increased carbon, oxygen, and oxide inclusion content depending on the molten metal chemistry and extent of contact. A more detailed discussion of the use of each gas follows.

5.1.2 Oxygen Uses

The introduction of the basic oxygen furnace (BOF) for steelmaking in the 1950s also marked the genesis for tonnage supply of oxygen from on-site cryogenic air separation plants. Today, oxygen is the most widely used industrial gas due to its continued use in the BOF and its growing uses for enrichment in the blast furnace and providing supplemental chemical heat in electric arc furnace based steelmaking. Over 90% of this oxygen comes from plants that are owned and operated by industrial gas suppliers. Table 5.3 provides a summary of the more significant oxygen uses for the integrated and electric arc furnace industry segments.

Table 5.3 Oxygen Applications

	O_2 Consumption (millions of cu. ft.)		Raw Steel Production (thousands of net tons)		Specific O_2 Consumption (cf/ton* of steel)	
	1995	**1990**	**1995**	**1990**	**1995**	**1990**
Blast Furnace Enrichment	90,700	37,750	62,525	58,470	1450	645
Basic Oxygen Process	124,500	112,720	62,525	58,470	1990	1930
Electric Arc Furnaces	55,400	27,235	42,410	36,940	1305	735
Cutting, burning, etc.	17,520	15,890	104,930	95,410	165	165

*One ton equals 2000 pounds
Source: American Iron and Steel Institute, 1995 Annual Statistical Report

5.1.2.1 Blast Furnace

The use of significant quantities of oxygen for enrichment of the blast has become widespread. Table 5.3 shows that specific consumption rates have more than doubled over the last five years, and 40% of the total oxygen requirement of integrated steel mills is consumed in the blast furnace. This

increase is a result of the desire for higher furnace productivity and the growth in powdered coal and natural gas injection as a means of reducing coke consumption and lowering production costs. Typical levels of enrichment are in the range of 3–8%, but enrichment levels as high as 12% have been used in furnaces using large amounts of coal or natural gas. Oxygen enrichment increases furnace productivity by reducing the blast volume and the associated pressure drop which allows a higher total oxygen throughput rate. It is also used to compensate for the reduction in raceway adiabatic flame temperature (RAFT) that results from the injection of powdered coal and natural gas into blast furnace tuyeres, thereby maintaining smooth furnace operation and the required hot metal temperature.

Oxygen is injected through spargers into the cold blast line between the blower and stoves. While process considerations would allow the use of relatively low purity oxygen for enrichment, the need to supply high purity oxygen for the BOF and to produce nitrogen and argon usually results in the use of standard 99.5% purity plants. However, the trend to very high rates of powdered coal and natural gas injection can easily result in the use of 300 to 1000 tons of oxygen per day in a single furnace. There have been a few recent installations of on-site cryogenic plants that are dedicated to the blast furnace thereby allowing optimization concerning product purity as well as plant integration and cogeneration schemes. The pressure required depends on the operating pressure of the blast furnaces and is usually about 60 psig.

5.1.2.2 Basic Oxygen Furnace (BOF)

Oxygen is used primarily for decarburization and conversion of blast furnace hot metal to liquid steel in the BOF. This accounts for 55% of the total oxygen consumption in integrated steel mills. The heat which results from the exothermic reactions of oxygen with silicon and carbon in the hot metal and the post combustion of a portion (about 10–15%) of the carbon monoxide (CO) which is generated in the converter is sufficient to melt scrap in quantities that amount to about 25% of the total vessel charge weight. A supply system capable of providing high flow rates of up to 30,000 scfm at nominal pressures of around 250 psig for about 20 minutes is required. High purity (99.5% oxygen content) is required to achieve required low steel nitrogen contents and to maximize vessel productivity and scrap melting capability. In most vessels, all of the oxygen is injected through a water cooled top lance with tips that have four or five nozzles which generate supersonic jets that impinge on the molten bath surface. Recently, lances which also have a number of secondary subsonic oxygen nozzles have been introduced to increase the degree of CO post combustion in order to control skull formation and increase scrap melting capability. There are also several modifications to the BOF such as the K-BOP and OBM for which some or nearly all of the required oxygen is injected through hydrocarbon shrouded tuyeres located in the bottom of the converter.

5.1.2.3 Electric Arc Furnace (EAF)

Table 5.3 also shows that the total consumption of oxygen in electric arc furnaces has also more than doubled in the last five years, and that much of this increase is due to a 75% increase in specific oxygen consumption during this time period. Typical uses for oxygen in the EAF include oxy-fuel burners for scrap heating and melting; high velocity lancing for localized scrap melting, steel decarburization, slag foaming; and sub-sonic injection for post combustion of carbon monoxide. Recent trends to use more supplemental chemical energy to increase furnace productivity and reduce melting time and electric power consumption, scrap pre-heating, and the growing use of high carbon content materials such as direct reduced iron (DRI), pig iron, iron carbide, and hot metal have all contributed to this significant increase in specific oxygen consumption over the past five years. Oxygen derived chemical energy can provide 30% or more of the total energy required to make steel in a modern high productivity EAF.

The equipment used to deliver the oxygen includes water cooled burners located on furnace walls, slag doors, and pre-heat shafts to provide direct flame impingement on cold scrap; water cooled or consumable lances which are positioned through the slag door or sidewall for scrap cutting, bath decarburization, and slag foaming; and door and sidewall lances or wall mounted nozzles for post combustion.

Growth in the rate of steel production and in specific oxygen consumption at many EAF based mills have combined to increase oxygen use to levels that make an on-site plant an increasingly typical mode of supply. Cryogenic, vacuum pressure swing adsorption (VPSA), and pressure swing adsorption (PSA) type plants are all used depending on the total industrial gas requirement of the plant and surrounding local market, purity requirement, use pattern, power rate, etc. Oxygen purity is usually in the range of 90–99.5%, and supply pressure is usually in the range of 150–250 psig.

5.1.2.4 Cutting and Burning

High purity (above 98%) oxygen is also used extensively throughout integrated and EAF based mills for steel cutting and burning as well as general lancing requirements. Significant uses in this category include automatic cut-off torches on continuous casters, periodic lancing to remove skulls from the mouths of vessels and ladles, and cutting of crops, skulls, and other forms of mill scrap into pieces that can be readily fed to the BOF or EAF.

5.1.2.5 Steel Reheating

Oxygen is also sometimes used for enrichment or with oxy-fuel burners in steel reheat furnaces. Benefits associated with the use of oxy-fuel burners include a 25–60% reduction in fuel consumption and associated sulfur dioxide (SO_2) and CO_2 emissions, increased furnace productivity, up to 90% reduction in nitrous oxide (NOx) emissions, and elimination of recuperators.

5.1.3 Nitrogen Uses

Table 5.4 identifies the common uses for nitrogen in both integrated and EAF plants.

Table 5.4 Nitrogen Applications	
Integrated Plants[1]	**EAF Plants[2]**
Inerting of coal grinding and storage equipment	EAF stirring
Inerting of blast furnace charging equipment	Injecting powder for steel desulfurization
Injecting powder for hot metal desulfurization	Ladle stirring
BOF slag splashing	AOD refining
BOF stirring	Caster inerting
Annealing atmospheres	Tundish stirring
Controlling Zn thickness on hot dipped galvanizing lines	Annealing atmospheres
Instrumentation and control equipment	Instrumentation and control equipment
[1]In 1995, US plants consumed 130 billion cubic feet to produce 62.5 million tons of raw steel which is an average consumption of 2,085 scf/ton.	[2]In 1995, US plants consumed 5.2 billion cubic feet to produce 42.4 million tons of raw steel which is an average consumption of 122 scf/ton.

As noted, both overall consumption and intensity of use are considerably higher at integrated plants. Nitrogen purity for most applications is typically 99.999%. Occasionally, nitrogen with a nominal purity of around 97–99% may be used for inerting to prevent explosive mixtures in confined spaces. High purity nitrogen containing 5–10% hydrogen is used to provide a protective reducing atmosphere in batch and continuous type bright annealing furnaces for carbon steel grades.

5.1.3.1 Integrated Plants

Traditional uses of nitrogen in integrated plants include purging and inerting of blast furnace raw material charging equipment to prevent reactions of air with furnace offgas; injecting lime, lime-magnesium mixtures, or other reagents in powder form through refractory coated lances to desulfurize hot metal in torpedo cars and ladles; injection through bottom tuyeres to provide stirring and slag/metal mixing during the initial period of refining in the BOF which improves yield, reduces slag iron oxide (FeO) content, and lowers metal oxygen content; as the inert component with

5–15% hydrogen for bright annealing in continuous or batch furnaces; and as a clean and dry gas for various types of pneumatic instrumentation and process control equipment.

The adoption of powdered coal injection (PCI) in blast furnaces usually creates a new requirement for nitrogen to inert and prevent explosions in coal grinding, storage, and handling equipment. A process called slag splashing, which uses high pressure and flows of nitrogen through the top lance to coat the inside of BOF vessels and extend its refractory life, has also been recently adopted by most plants in North America. Finally, nitrogen can be used instead of air in the pneumatic knives used to control coating thickness in hot dip galvanizing lines. The benefits of nitrogen wiping include less dross formation, improved coating thickness control, and fewer coating defects such as edge build-up or entrapped oxides.

5.1.3.2 EAF Plants

Traditional uses for nitrogen in EAF plants include injection through top lances or porous plugs in ladles to provide stirring for steel temperature and composition control and to remove oxide inclusions; injecting powdered reagents containing one or more constituents such as calcium, silicon, and aluminum to desulfurize steel in ladles and ladle furnaces; preventing reaction with surrounding air of open teem streams between the tundish and molds in continuous casters; and as a clean and dry gas for pneumatic instrumentation and process control equipment.

Uses that are more site specific include injection through multi-hole elements to provide stirring in the EAF for faster melting, power savings, and improved temperature and composition control; injection through porous elements of various designs to modify flow patterns and remove inclusions in tundishes; to protect the tuyeres and promote carbon removal with minimum oxidation of chromium in the AOD process for producing stainless and other high alloy grades; and as the inert component with hydrogen for bright annealing in continuous or batch furnaces.

5.1.4 Argon Uses

Table 5.5 identifies the common uses for argon in both integrated and EAF plants. Argon purity is typically 99.998%, and it is usually supplied from liquid storage tanks at pressures up to 200 psig.

Table 5.5 Argon Applications

Integrated Plants[1]	EAF Plants[2]
BOF stirring	AOD refining
Ladle and ladle furnace stirring	Ladle and ladle furnace stirring
Injecting powder for steel desulfurization	Injecting powder for steel desulfurization
Vacuum degasser recirculation and stirring	Vacuum degasser stirring
Inerting submerged entry nozzles on casters	Inerting submerged entry nozzles on casters
Tundish inerting	Tundish inerting
[1]In 1995, US plants consumed 1.54 billion cubic feet to produce 62.5 million tons of crude steel which is an average consumption of 24.6 scf/ton.	[2]In 1995, US plants consumed 920 million cubic feet to produce 42.4 million tons of crude steel which is an average consumption of 21.7 scf/ton.

5.1.4.1 Integrated Plants

Traditional uses for argon in integrated plants include injection through bottom tuyeres to provide stirring and slag/metal mixing during the final stages of refining in the BOF which improves yield, reduces slag FeO content, and lowers metal oxygen content; injection through porous plugs to provide stirring for improved temperature and chemistry control and to promote desulfurization in ladles and ladle furnaces; injection of various powdered reagents in ladles and ladle furnaces for desulfurization; injection in vacuum degassers to facilitate carbon, hydrogen, and nitrogen removal and to provide circulating metal flow in RH type degassers; and inerting submerged entry nozzles to prevent clogging and re-oxidation or nitrogen pick-up by the steel during ladle to tundish and

tundish to mold transfers in continuous casters. Recently, argon has also been used to inert the tundish headspace during transient periods of operation to improve slab surface quality.

5.1.4.2 EAF Plants

Argon is primarily used in plants that produce stainless and high alloy grades, flat carbon steel products, and high quality long products. Traditional uses include many of those described above for the integrated plants such as ladle, ladle furnace, and vacuum degasser stirring, powder injection, and inerting of submerged entry nozzles and tundishes in continuous casters. In addition, argon is also used extensively to facilitate carbon, nitrogen, and hydrogen removal in the AOD process for producing a wide variety of stainless, tool, heat resisting, and other high alloy content grades.

5.1.5 Hydrogen Uses

Hydrogen is used in significant quantities for natural gas based production of direct reduced iron (DRI). In the Midrex process, the CO_2 and H_2O which is present in the offgas from the direct reduction shaft reactor is used to reform natural gas and produce the high temperature H_2 and CO containing reducing gas required to achieve the desired level of iron ore conversion to iron. In Hylsa's HYL III process, a conventional steam reformer is used to produce the reducing gas, and the CO_2 and H_2O in the reactor offgas is removed to allow recycle of unreacted H_2 and CO back into the reactor. The natural gas consumption is approximately 11,000 scf per ton of DRI, and the reducing gas generators are part of the overall plant installation.

The other common use for hydrogen is for annealing atmospheres. For carbon steel annealing, atmosphere compositions of 5–10% hydrogen with the balance nitrogen are commonly used in both continuous and batch furnace types. For stainless and other high alloy products, the hydrogen content is typically in the range of 75–100%. Typical hydrogen purity is 99.995%. These atmospheres serve to transfer heat, remove residual rolling oils, prevent surface oxidation, and reduce any surface oxides that may be present resulting in a bright annealed surface free from oxides, deposits, and discoloration.

A recent trend is to anneal coils in batch bell-type furnaces that have been designed to use a 100% hydrogen atmosphere. The main benefit is a shorter cycle time and increased productivity due to the higher diffusivity and thermal conductivity of pure hydrogen and improved uniformity of mechanical properties as a result of more uniform temperature distribution throughout the coil.

5.1.6 Carbon Dioxide Uses

CO_2 is sometimes used as a stirring gas in BOF vessels in place of nitrogen and argon. This option provides the ability to achieve lower steel nitrogen contents and lowers stirring gas costs by reducing or eliminating the use of argon which is more expensive per unit volume. However, since CO_2 is a reactive gas when exposed to molten steel under the conditions associated with submerged injection, increased wear of the bottom injection tuyeres and surrounding refractory materials and an inability to achieve low aim carbon contents may result. CO_2 is occasionally used for ladle stirring. As for BOF stirring, it offers a combination of lower nitrogen content and lower gas cost versus the alternatives of nitrogen or argon. However, the same potential for increased porous plug and refractory wear exists, and there is also the risk of higher oxide inclusion contents due to the reaction of the CO_2 with deoxidants such as silicon or aluminum. CO_2 has also been used in continuous billet casters for protecting the tundish to mold stream from contact with the surrounding atmosphere.

A more recent application for CO_2 is to suppress fugitive fume emissions during electric arc furnace charging and tapping operations and to lower nitrogen pick-up during EAF or BOF tapping operations. Typical practice is to inject CO_2 in snow form to eliminate air from the furnace during charging and from around the tap stream and its impact zone in the ladle. Industry experience with this type of CO_2 application is extremely limited, and more work needs to be done to optimize practices and quantify potential benefits.

5.2 Industrial Gas Production

5.2.1 Introduction

The industrial gases that are used in the steel industry are atmospheric gases (oxygen, nitrogen, and argon) or gases that are produced from hydrocarbon processing either directly or as byproducts (hydrogen and carbon dioxide.) Hydrogen is also obtained as a byproduct from a number of processes including the cracking of ethane to produce ethylene and the electrochemical process used to produce chlorine (the chlor-alkali process). The atmospheric gases are separated from air using cryogenic processes for large quantity5, pressure swing adsorption (PSA), vacuum swing adsorption (VSA), or vacuum pressure swing adsorption (VPSA) for moderate quantities of oxygen, or membranes when a moderate quantity of nitrogen is the only product desired. Hydrogen is typically produced from natural gas using steam reforming or separated as byproduct streams from hydrocarbon containing streams. The carbon dioxide that is supplied to industrial users is most often obtained as a byproduct from ammonia and hydrogen plants using an acid gas (CO_2, hydrogen sulfide H_2S, etc.) removal system. CO_2 can also be economically recovered from fermentation systems, natural gas wells, and, in some cases, from combustion systems.

Industrial gases are supplied from on-site plants that are dedicated to the needs of one steel mill, from industrial gases complexes by pipelines that serve multiple steel mills and/or other users, or as cryogenic liquid products that are trucked in from a production facility that can supply hundreds of small volume users. For atmospheric gases the process used to produce the gas will depend on which gases are needed and the quantity and quality requirements. Fig. 5.1 shows the approximate flow and purity boundaries that define the low cost supply options for oxygen. Similarly, Fig. 5.2 shows the flow/purity regions where the alternative nitrogen production processes are most economical. Argon is almost always obtained from cryogenic air separation units and supplied as a liquid.
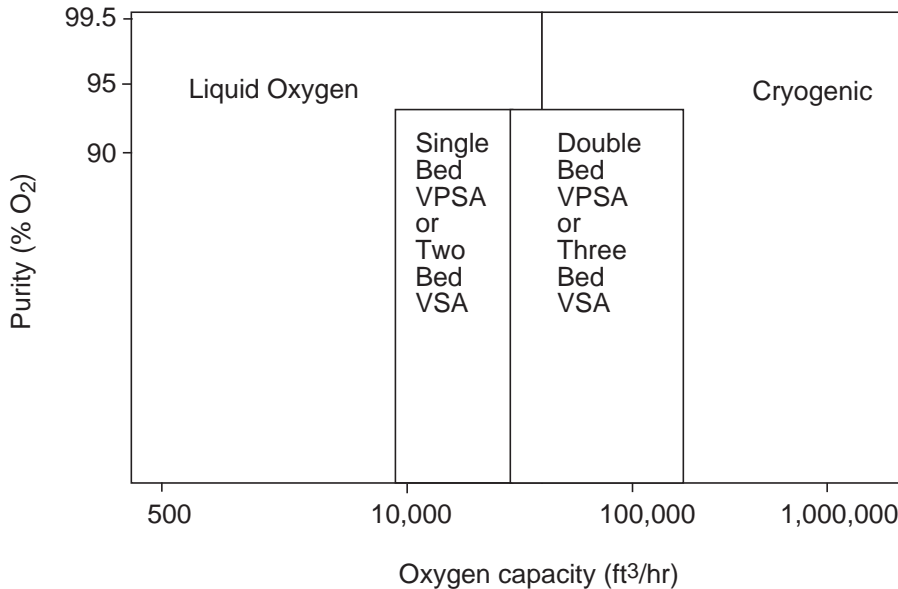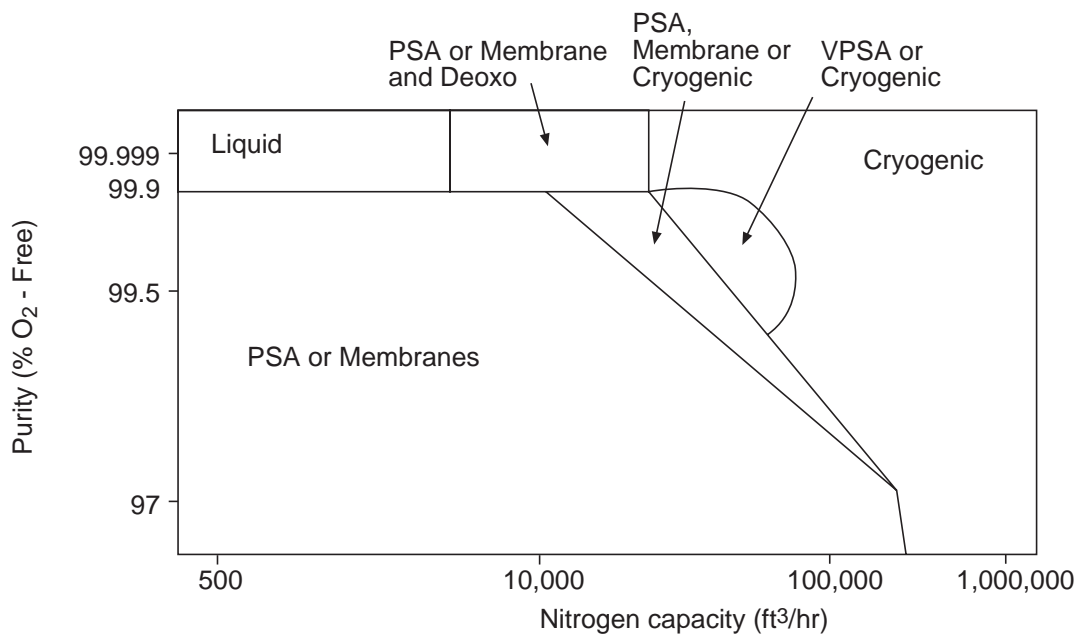

Fig. 5.1 Modes of supply for oxygen.

Fig. 5.2 Modes of supply for nitrogen.

The industrial supply options for hydrogen are presented in Table 5.6.

Table 5.6 Modes Of Supply For Hydrogen

Supply Option	Average monthly use rate, scfh
Tube trailers	>135
Liquid	120-30,000
Modular Reformers (on-site)	6,000-40,000
Custom Designed Reformers (on-site)	>40,000

The hydrogen supplied by tube trailer or as liquid is normally produced from steam reforming of methane or obtained as a byproduct, most often from chlorine production. The tradeoff between tube trailer and liquid is also affected by the location of the user relative to the production site. Tube trailer supply is favored when the distances are short (<200 miles). Modular on-site reformers are relatively new to the supply picture and are filling a void between the liquid and the custom designed reformer option.

Except for rare cases where the user is near a high quality source of CO_2, carbon dioxide is supplied as a liquid.

5.2.2 Atmospheric Gases Produced by Cryogenic Processes

Cryogenic air separation plants can be designed to produce oxygen, nitrogen, argon, or any combination of the three. Since oxygen typically is the dominant product for steel industry applications, this discussion will focus on it with nitrogen and argon treated as optional products that can be made available with system modifications.

The commercial production of oxygen in cryogenic plants is well established with hundreds of plants operating worldwide and individual capacities ranging from 20 to over 3000 tons per day. Present-day processes are basically the same as those used in the early 1900s. Although plant
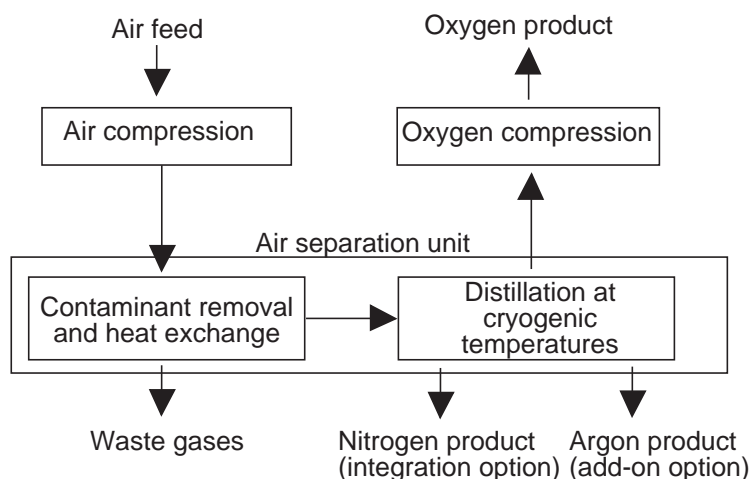
Fig. 5.3 Basic steps in cryogenic air separation plants.

capacities and efficiencies have increased dramatically and many equipment variations have been developed, the principle of distilling air to separate the oxygen from the nitrogen remains the heart of the process. This distillation technology is like that used in the petroleum and chemical industries except that air distillation requires operation at cryogenic temperatures instead of the higher temperatures used in most other applications. The four main process steps and sequence necessary to produce gaseous oxygen from air are shown in Fig. 5.3. These steps are supported by subsystems such as expansion turbines to provide refrigeration, and superheaters to recover refrigeration.

The composition of air and the characteristics of all of its constituents must be addressed in designing cryogenic separation systems. Components considered as contaminants in air separation include carbon dioxide, water, and hydrocarbons in various concentrations. The four process steps and supporting subsystems are designed to effectively remove the contaminants and separate the air into its various products.

5.2.2.1 Air Compression

Air compression, the simplest step, uses standard commercial equipment. As atmospheric air, drawn through a filter, is compressed to a pressure of about 90 psia, the heat of compression is removed by coolers and entrained water is removed by water separators. The compressed air supplied to the air separation unit contains the energy required to separate the air into oxygen and nitrogen. Power is the primary operating cost element in the production of oxygen. Since most of the power is used for compression, design of the entire air separation process must be keyed to obtaining maximum efficiency in the compression step.

5.2.2.2 Contaminant Removal and Heat Exchange

The air stream that leaves the compressor aftercooler at near-ambient temperature contains carbon dioxide, water vapor, and hydrocarbons. These contaminants must be removed, and the stream must be cooled to the liquefaction temperature before the distillation process can be started. Carbon dioxide and water freeze before the air liquefaction temperature (−278°F at 90 psia) is reached; therefore, the removal of these contaminants is critical to prevent heat exchanger plugging.

The primary method for performing contaminant removal is the pre-purifier system. Pre-purifiers use adsorbents such as molecular sieves to remove bulk and trace contaminants at ambient temperatures. The filtered air from the compression system normally is cooled to about 40°F using a refrigerant chiller to condense and remove water vapor so that smaller adsorption beds can be used. Typically, there are two beds with one on-stream while the other is being regenerated. They are

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sized to reduce the water content to 0.1 ppm and the carbon dioxide content to 0.25 ppm. These beds also reduce hydrocarbon concentrations to acceptable levels. The clean, dry process air from the pre-purifier is then cooled to the liquefaction temperature through heat exchange with the cold product and waste streams. This is accomplished in a primary heat exchanger (PHX) that is of plate-and-fin construction.

5.2.2.3 Cryogenic Distillation

The distillation process is used for separating air into its desired components of oxygen, nitrogen, etc. If the maximum amount of oxygen is recovered from the feed air stream, the feed air quantity required to produce a given amount of oxygen is minimized. Thus, the energy required for air compression (the power required for the process) is also minimized.

The distillation process is based on allowing vapor to rise through a descending flow of liquids. When a liquid mixture of two components with different boiling points is thoroughly mixed with vapors of a similar composition, the liquids and vapors reform. After the first contact, the vapor contains more of the component with the lower boiling point (nitrogen), and the liquid contains more of the component with the higher boiling point (oxygen). Thus, after one contact stage, the two components are partially separated with the vapor enriched with one component and the liquid enriched with the other. The separation becomes more complete—higher component purities are obtained—if successive vapor-liquid contacting stages are provided.

The distillation column provides many contact stages in a single vessel. Traditionally, each contact stage consisted of a single tray—a perforated plate that promotes intimate mixing of the liquids and vapors. The descending liquid spreads across the plate and contacts the vapor rising through the perforations. Part of the vapor condenses and joins the liquid which becomes progressively richer in oxygen, and some of the liquid boils off and joins the vapor which becomes progressively richer in nitrogen. Part of the fluid at the bottom of the column is withdrawn as product oxygen and the rest is heated in a reboiler to form the vapor that rises through the column. Similarly, at the top of the column, part of the fluid is withdrawn as waste-nitrogen vapor and the rest is cooled in a condenser to form the liquid that descends through the column. The components of the air are used to heat the reboiler and cool the condenser. Over the past few years packing has been used instead of trays for many air separation applications. In either case, column operation is essentially the same.

The double-column concept has been used by the air separation industry for most of this century. It enables oxygen recovery of over 95%. The key is the relationship of the boiling points of oxygen and nitrogen at different pressures. The boiling points become higher as the pressure increases. The boiling temperature of nitrogen at 90 psia is higher than the boiling temperature of oxygen at 22 psia. Under these conditions, nitrogen can be condensed by transferring heat to the boiling oxygen. The boiling of oxygen by condensing nitrogen in the double column provides the driving force for this distillation process. The double column has a combination reboiler/condenser unit (main condenser) located between the two sections of the column. Each column operates at a different pressure to exploit the boiling point variations at different pressures. By condensing nitrogen to provide reflux liquid for both the upper and lower columns, the main condenser provides vapor boil-up (gaseous oxygen) to the upper column. The lower column provides a crude product split and the upper column provides a finer separation.

The air stream that feeds the distillation column is primarily in the gaseous state. Refrigeration must be provided to cool a portion of the stream to temperatures low enough to form the liquid necessary for the distillation process. Modern plants use an expansion turbine to produce the low temperatures; the compressed air feed is expanded through a turbine and energy is recovered externally. These turbo-expanders recover energy and produce refrigeration efficiently.

5.2.2.4 Oxygen Compression

The fourth process step, oxygen compression, boosts the pressure of the product oxygen leaving the air separation unit from near-atmospheric to the desired end-use pressure. Most oxygen users

in the steel industry require pressures of 250 psig or higher. Compression of large quantities of oxygen has traditionally been accomplished by specially designed centrifugal machines that are commercially available from several suppliers.

5.2.2.5 Cryogenic Process Description

The four major process steps of a double-column air separation system integrated into a typical process arrangement for producing gaseous oxygen are shown in Fig. 5.4.
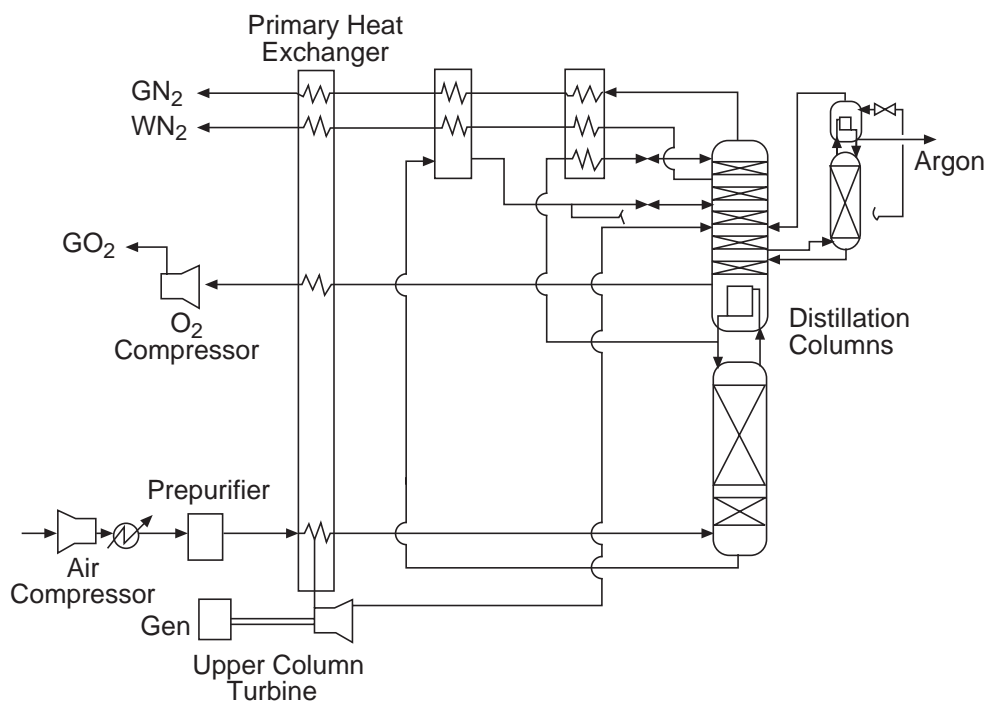

Fig. 5.4 Basic double-column plant for gaseous oxygen.

The feed air is drawn in through an inlet air filter, compressed to the head pressure of the plant, and then cooled in the aftercooler. Condensed moisture is removed in the moisture separator which also serves to smooth the flow of air to the air separation unit.

The air then passes through the switching valves into the prepurifier where the contaminants are removed. The clean air stream leaving the prepurifier is fed to the brazed aluminum heat exchanger (primary heat exchanger, PHX). The vast majority of the air (normally greater than 90%) is cooled to near its liquefaction temperature by the returning product and waste streams and flows from the PHX to the bottom of the lower column. The remaining air is removed from the primary heat exchanger at about the midpoint and fed to the air-expansion turbine which supplies the refrigeration for the process. As the vapor rises through the lower column, essentially pure nitrogen is formed. This vapor is liquefied in the main condenser and split into two streams, lower column reflux and upper column reflux. The upper column reflux is cooled against waste nitrogen gas in the nitrogen superheater. The bottoms product of the lower column, a liquid rich in oxygen, is also cooled in the nitrogen superheater before being fed to the middle of the upper column.

The bottoms product of the upper column is pure oxygen. Although a small fraction of this oxygen can be withdrawn as a liquid, the bulk of it is reboiled in the main condenser to form both the vapor that rises in the upper column and the gaseous oxygen product. The product oxygen is warmed by

a heat exchange with feed air in the oxygen superheater, and then further heated to ambient temperature as it flows through the primary heat exchanger. This product oxygen leaves the air separation unit at a pressure of about 2 psig and is compressed to the desired end-use pressure.

The overhead vapor of the upper column, the waste nitrogen stream, has the lowest temperature of any stream in the plant. The low temperature refrigeration available from this stream is recovered in the nitrogen superheater that cools the feed streams to the columns. The nitrogen is warmed to ambient temperature through heat exchange with the air stream in the primary heat exchanger before being vented to the atmosphere.

5.2.2.6 Product Options

The basic plant configuration presented in Fig. 5.4 is very versatile and can be used to provide many product variations. The product options of interest for steelmaking include gaseous oxygen, gaseous nitrogen, and argon.

5.2.2.6.1 Gaseous Oxygen Gaseous oxygen can be produced in purities varying from enriched air, slightly greater than 21 mol% O_2, to beyond standard high purity (99.5 mol%). A basic plant designed for 95 mol% purity will produce oxygen at a lower cost than a system designed for 99.5 mol% oxygen. The lower purity requires a less complete separation and, consequently, fewer trays in the upper column. Since the pressure drop caused by the trays in the upper column has a significant impact on the required compressor discharge pressure, low purity plants consume less power.

5.2.2.6.2 Gaseous Nitrogen Low purity nitrogen (~99 mol% N_2) can be obtained from the top of either the upper or lower column. Small quantities of high-purity nitrogen (99.999 mol% N_2) can be produced by increasing the number of trays in the lower column and drawing off nitrogen gas from the top of this high-pressure unit. This method of high purity nitrogen recovery has only a limited effect on the overall power requirement for oxygen production.

If substantial quantities of high purity nitrogen are required, provisions must be integrated into the original process and equipment design for the plant. Basically, this involves adding a "top hat" section on the upper column to provide the necessary separation and purification capacity. The top hat section provides additional trays which increase the pressure drop and add to the power for the air separation system. The ratio of high purity nitrogen to oxygen product can be as high as 3:1.

5.2.2.6.3 Argon All oxygen or oxygen-nitrogen plants can be designed to accommodate the add-on side column and the refinery required for argon recovery and purification. With the inclusion of the proper number of contacting surfaces in the upper and lower columns and provision for sufficient refrigeration, a relatively high percentage of the argon available in the feed air can be produced. The add-on system shown in Fig. 5.4 recovers, refines, and stores liquid argon. Argon production can range between 3–4% of the oxygen product rate.

5.2.3 Atmospheric Gases Produced by PSA/VSA/VPSA/Membranes

Cryogenic technology has been the dominant supply option for the steel industry since oxygen was first used in steel production. The development of separation systems that operate at near atmospheric temperatures and pressures have begun to supply oxygen to smaller volume users such as mini-mills (VPSA Systems). Membranes have not proven to be a cost effective method for oxygen production but can competitively produce nitrogen depending on the quantity and quality required.

5.2.3.1 PSA/VSA/VPSA Systems

Pressure swing adsorption for oxygen production involves the use of synthetic zeolites (molecular sieves) to adsorb nitrogen from a pressurized air stream in a fixed bed system. During the adsorption portion of the cycle 90–93% purity oxygen is produced while the adsorbent becomes saturated with nitrogen. When nearly all the adsorbent is at the nitrogen saturation point, the bed is removed from production service and is regenerated. Regeneration is mainly accomplished by lowering the

pressure of the bed which allows most of the nitrogen to be desorbed and released from the bed followed by purging the low pressure bed with a small portion of the product oxygen. After the bed has been regenerated, it is repressurized and placed back into service. The total cycle time (the time associated with the adsorption period through regeneration to the point in time when the bed is again making product) ranges from 1–3 minutes. PSA systems operate at feed pressures ranging from 40–80 psia and regeneration pressures near atmospheric. VSA systems use a feed pressure of one atmosphere and regeneration at 3–5 psia. VPSA systems operate with feed pressures in the 20–30 psia region with regeneration occurring at 3–10 psia. The vacuum regeneration allows for greater effective nitrogen adsorption capacity for a specific molecular sieve. VPSA systems have become the technology of choice because of their lower capital and operating costs.

5.2.3.1.1 Process Description   The number of adsorption beds used in PSA/VSA/VPSA systems have ranged from one to four depending on the choice of molecular sieve and the approach to regeneration. Fig. 5.5 shows a schematic of a two bed VPSA system.
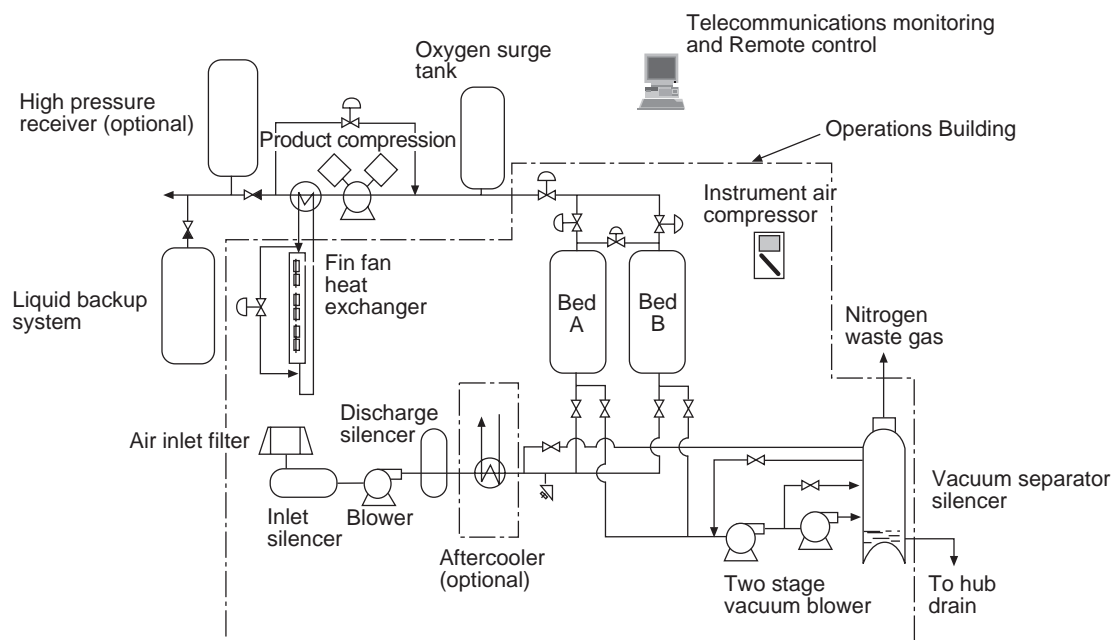

Fig. 5.5 VPSA process.

The system consists of an inlet air filter, an air blower, a feed discharge silencer, an aftercooler, switching valves, two adsorption beds, a vacuum blower, a vacuum separator/silencer, product surge tanks, an oxygen compressor, and high pressure receivers.

Air is compressed to 20–30 psia by the feed blower and cooled to near ambient temperature in the aftercooler. The air then passes through switching valves to one of the two adsorption beds, Bed A, where water vapor, carbon dioxide, hydrocarbons, and nitrogen are adsorbed. Oxygen product at 90–93% purity leaves the adsorption bed through a second series of switching valves and is fed to the product compressor. The oxygen surge tank is used to dampen pressure fluctuations at the product compressor inlet that result from the switching of the adsorption beds. The product compressor delivers oxygen at the desired pressure for use in the electric arc furnace. The high pressure receiver is used to accommodate the flow fluctuations that result from the intermittent use patterns of most EAFs.

After the sorbent in Bed A has been nearly saturated with nitrogen the feed air is switched to Bed B which had been previously regenerated. Bed A undergoes regeneration by being pumped to 5–10 psia using the vacuum blower. The nitrogen, hydrocarbons, carbon dioxide, and water vapor desorb from the sieve and are evacuated from the bed. At the end of the evacuation period a small quantity of product oxygen is used to purge the remaining desorbed material from the void spaces around the adsorbent particles prior to repressurizing the bed for use in the adsorption step.

5.2.3.1.2 Product Options PSA/VPSA systems that use synthetic zeolites as the sieve have generally been successful for the production of oxygen. The waste nitrogen from the process can contain as much as 10% oxygen as well as carbon dioxide, water vapor, and small quantities of hydrocarbons. PSA systems based on carbon molecular sieves are used to produce nitrogen (97–99.5%) in moderate quantities. The waste oxygen product from nitrogen PSAs has too much nitrogen to be of use in steel applications.

5.2.3.2 Membranes

Membranes for atmospheric gases are used exclusively for the production of nitrogen. Hollow fiber polymeric membranes use differences in permeation rates to separate nitrogen from air. Generally oxygen, carbon dioxide, and water vapor permeate faster than nitrogen so nitrogen at purities up to about 99.9% can be economically obtained at flow rates up to 10,000 scfh. The two essential characteristics of a membrane are its permeability and selectivity. Permeability defines the rate at which constituents (oxygen, nitrogen, etc.) will pass through a membrane for a given pressure drop while selectivity defines the rate that one component will flow through the membrane relative to the rate of a second component. For membranes used for nitrogen production, selectivity is the ratio of oxygen permeability to nitrogen permeability. The most cost effective membrane systems would have high permeability and high selectivity. However, membranes with high permeability usually have low selectivity and membranes that are highly selective normally have low permeability.

5.2.3.2.1 Process Description As shown in Fig. 5.6 membrane systems are relatively simple consisting of an air compressor, a membrane unit which contains bundles of hollow fiber membranes, and a control unit.
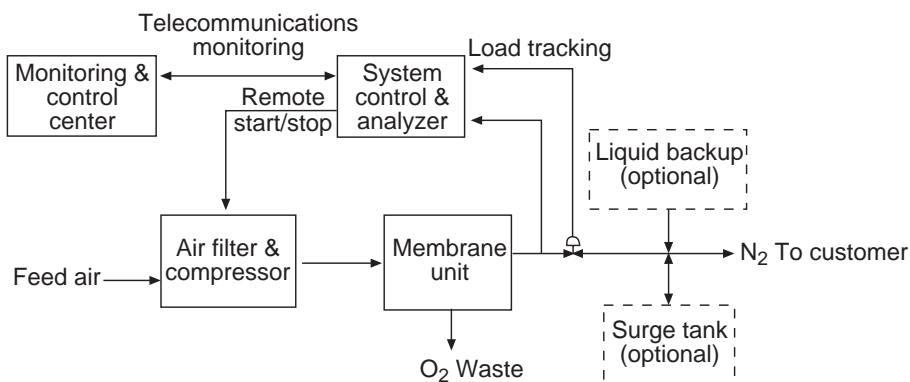

Fig. 5.6 Membrane block flow diagram.

The air compressor is used to pressurize the air to 100–150 psig. The air is then cooled and compressor oil and water are removed. The air enters the membrane unit which is composed of bundles containing more than a million membrane fibers. Each fiber is thinner than a human hair. The hollow fiber membranes are arranged in the bundles so that the unit's flow configuration is similar to that of a shell and tube heat exchanger. Bundles normally contain a fixed number of fibers having a fairly constant surface area. The number of bundles used is proportional to the desired product rate from the unit. The bundles all operate in parallel if low purity nitrogen (97%) is acceptable. If higher purities are required, then a second set or even a third set of bundles can be operated in series with the first set.

5.2.4 Hydrogen Production

Hydrogen production is dominated by the steam reforming of methane. Fig. 5.7 presents the basic schematic for a steam reformer system used to produce hydrogen. In a typical steam reformer the natural gas provides both feedstock and fuel. The feedstock portion is compressed to about 400 psia, preheated to about 750°F, and desulfurized in a zinc oxide bed. The sulfur free natural gas is mixed with steam at approximately a 3:1 steam to carbon ratio and further heated to about 925°F prior to entering the reformer. The reformer reactions proceed to near equilibrium in catalyst filled tubes that are heated from the outside by the combustion of natural gas and/or PSA tail gas. The reformed gas leaves the furnace at about 1450°F and is cooled slightly prior to entering the high temperature shift reactor (HTS). The feed gas entering the HTS has a hydrogen to carbon ratio of about 5:1. The catalyst in the HTS increases this ratio to more than 30:1. The hydrogen rich gas leaving the HTS unit is cooled to near ambient temperature and fed to a Pressure Swing Adsorption (PSA) unit. Between 80–90% of the hydrogen is recovered as product with purities of 99.999%. The unconverted CO and the unrecovered hydrogen (PSA Tail Gas) is used to fuel the reformer.
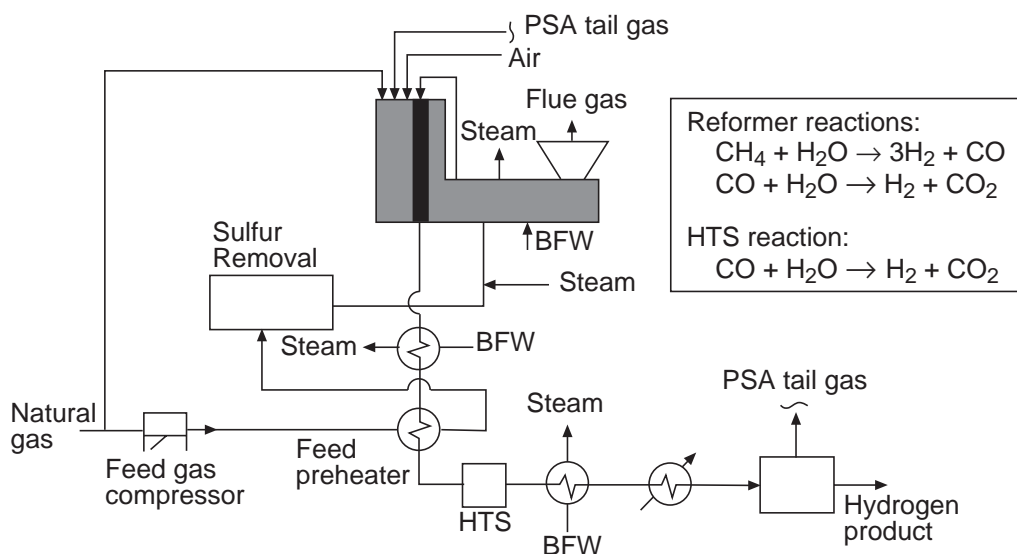

Reformer reactions:
$$CH_4 + H_2O \rightarrow 3H_2 + CO$$
$$CO + H_2O \rightarrow H_2 + CO_2$$

HTS reaction:
$$CO + H_2O \rightarrow H_2 + CO_2$$

Fig. 5.7 Steam reformer for hydrogen.

Most hydrogen needs in the steel industry are relatively small, less than 1 million scfd. Consequently, hydrogen is often supplied as liquid because the usage rate is too low to justify an on-site plant. Recently, modular reformer systems have been developed that are cost effective at flow rates as low as 150,000 scfd.

Hydrogen has also been recovered from coke oven gas which contains 40–50% hydrogen. This has been accomplished by using a PSA to adsorb all of the coke oven gas constituents except hydrogen. For this system to be effective the coke oven gas has to be compressed and nearly all of the heavy hydrocarbons have to be removed to prevent PSA fouling. This approach has been used when other sources of hydrogen have not been readily available.

5.2.5 Carbon Dioxide Production

Except for some carbon dioxide that is recovered from gas wells, most sources of carbon dioxide are dilute streams, less than about 30% CO_2, at low pressure that are very expensive to recover. Most of the carbon dioxide that is recovered for commercial use is a byproduct of another process

such as ammonia production. CO_2 removal is a requirement to make the chemical synthesis process economical and is paid for by the chemical manufacturer. Ammonia plants use either chemical absorbents (amines or hot potassium carbonate) or physical absorbents (methanol or Selexol solvent) to remove carbon dioxide from the process stream. The vent gas from these absorbent systems contains more than 90% CO_2 by volume. Normally only a portion of the CO_2 produced by these plants is converted into liquid CO_2 because more is produced than can be sold within a reasonable distribution area. Fig. 5.8 shows a common CO_2 liquefaction process.
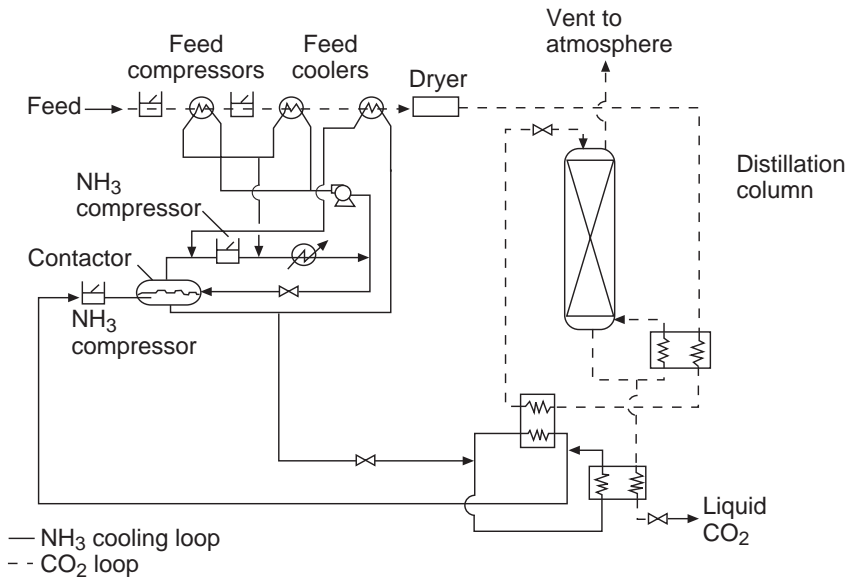

Fig. 5.8 Carbon dioxide liquefaction cycle.

A CO_2 rich stream that has been purified to remove water and other impurities is compressed to about 300 psia and dried prior to entering the heat exchangers that cool the stream to its liquefaction temperature. Part of the cooling is accomplished by boiling pure CO_2 at the bottom of the distillation column. The remainder of the refrigeration is obtained from an ammonia refrigeration loop. The distillation column provides the final purification and delivers a product that is 99.99% CO_2.

5.3 Industrial Gas Supply System Options and Considerations

5.3.1 Introduction

The choice of supply system to provide industrial gases to the steel industry depends upon several variables. The decision to supply gases by either pipeline, on-site plant or merchant liquid is determined by the number of gases required, the purity of the gases, the volume of gas, the use pressure, the use pattern, the cost of power, backup requirements and integration with other utilities.

5.3.2 Number of Gases

If oxygen, nitrogen and argon are required and the volume requirement is modest, the supply can be merchant (liquid) product delivered into tanks at the mill. If the volume of gases is large (more than 100,000 cfh oxygen) the supply will most likely be a cryogenic on-site plant. Finally, if the requirement is large for oxygen, but small for argon or nitrogen, the supply can be a combination of VPSA/VSA/PSA for oxygen and merchant for argon and nitrogen.

5.3.3 Purity of Gases

If high purity is not required for oxygen or nitrogen, the supply mode can be non-cryogenic on-site (VPSA/VSA/PSA or membrane) if the required volume is in the range of about 10,000 to 120,000 standard cubic feet per hour. These non-cryogenic supply systems deliver product purity between 90–99%. Because of separation process requirements, argon is always delivered as high purity product.

5.3.4 Volume of Gases

The amount of gas required will determine supply mode and plant size. Small users, merchant; larger users, VPSA/VSA/PSA; largest users, on-site cryogenic plants. See Fig. 5.1 and Fig. 5.2.

5.3.5 Use Pressure

The pressure requirement of the gas at the use point is no longer a variable that determines supply mode. However, it does determine requirements for compression equipment and high pressure gas storage receivers. In the case of merchant supply, high pressure tanks are used to supply high pressure product to the use point.

5.3.6 Use Pattern

The use pattern of the gases will determine the number of high pressure storage receivers required to deliver the gas when and in the volumes that are needed.

5.3.7 Cost of Power

Merchant supply requires no power to vaporize or compress the gas to use pressure. On-site supply modes require power to separate and compress the gases. The on-site supply modes have different power requirements that are dependent upon the volume and pressure requirements.

5.3.8 Backup Requirements

On-site supply systems are usually backed up with some quantity of merchant product. This quantity is determined by the process requirements of the steel mill and cost.

5.3.9 Integration

Because on-site supply systems are a steady draw on the power grid, they are good customers for the electrical company. As a major user of electrical power, the on-site supply plant should be included in an overall energy/utility strategy for the steel mill.

5.4 Industrial Gas Safety

Table 5.7 shows the boiling points and densities of the industrial gases commonly used for steelmaking. These physical properties as well as chemical reactivity are among the most important attributes that determine the potential for risk and safe handling practices for these gases.

Table 5.7 Physical Properties

	O_2	N_2	Ar	H_2	CO_2
Atomic Number	8	7	18	1	NA
Atomic or Molecular Wt.	32	28	40	2	44
Boiling Point, °F	-297	-320	-303	-423	-109**
Density NPT*, lb/ft³	0.08281	0.07245	0.1034	0.00521	0.1144

*NPT = 70°F and 14.7 psi
**Sublimation

5.4.1 Oxygen

At ambient temperature and atmospheric pressure, oxygen is a colorless, odorless and tasteless gas. For all ironmaking and steelmaking applications, oxygen is used in its gaseous form. Approximately 21% of the air we breathe is oxygen.

5.4.1.1 Chemical Properties

Ironmaking and steelmaking are processes of controlled reduction and oxidation. Oxygen in ironmaking is used to reduce iron ore by reacting with coke to form CO and to create heat by taking advantage of the chemical reaction between carbon and oxygen in the blast furnace. In steelmaking, oxygen is used to selectively oxidize carbon, silicon, manganese and phosphorus from the blast furnace iron, steel scrap and other metallic additions to the furnace. Oxygen is also combined with many different fuels to create heat which is used to increase the temperature of refractories in ladles and steel in reheat furnaces.

5.4.1.2 Safe Practices

Oxygen is not flammable, but vigorously accelerates the burning of combustible materials. Therefore, it is important to keep combustibles away from oxygen and eliminate ignition sources. Oxygen concentrations exceeding 23% by volume in air significantly increase the risk of ignition and fire. Do not smoke or use an open flame where oxygen is stored, handled or used. Do not use cleaning agents that leave organic deposits on the cleaned surfaces. Do not place oxygen equipment on asphalt surfaces or allow equipment to come into contact with grease or oil. Equipment to be used in contact with oxygen should be handled only with clean gloves or hands washed clean of oil. Any equipment that comes into contact with oxygen should be cleaned for oxygen service using the guidelines published by the Compressed Gas Association, Inc. using Pamphlet G–4.1 Cleaning Equipment for Oxygen Service and CGA Pamphlet G–4.4 Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping Systems. Read and understand the supplier Material Safety Data Sheet (MSDS) for oxygen.

5.4.2 Nitrogen

Nitrogen is colorless, odorless and tasteless. It is only slightly soluble in water and is a poor conductor of electricity. The volume percentage of nitrogen in the air we breathe is approximately 78%.

5.4.2.1 Chemical Properties

Nitrogen neither burns nor supports combustion. Although it does not react readily with most materials, at high temperatures nitrogen combines with hydrogen to from ammonia; with oxygen to form nitrogen oxides; and with some of the more active metals, such as calcium, sodium, chromium, magnesium and silicon to form nitrides. At room temperature, nitrogen reacts with lithium.

5.4.2.2 Safe Practices

The displacement of breathing air is a potential hazard when using nitrogen to purge or inert a confined space. Its density at ambient temperature is about 3% lighter than air. Nitrogen can displace normal breathing air and cause rapid asphyxiation. Therefore, the oxygen level in any enclosed space that may be entered by personnel must be maintained above 19.5% using forced-air convection, if necessary. If this is not practical, then access to the enclosed area should be locked and entry allowed only after the area has been purged with air and tested for a safe oxygen level. Read and understand the supplier MSDS for nitrogen.

5.4.3 Argon

Argon is colorless, odorless and tasteless Approximately 1% of the air we breathe is argon.

5.4.3.1 Chemical Properties

Argon is non-toxic and chemically inert. It is non-flammable, does not present a fire hazard, and in fact, inhibits combustion. Because of its properties, argon is used to provide an inert atmosphere for molten steel to prevent the reoxidation of deoxidants such as aluminum, silicon and calcium. Argon is also used as a purge gas by injecting it subsurface into liquid steel to remove dissolved oxygen, nitrogen and hydrogen.

5.4.3.2 Safe Practices

The displacement of breathing air is a potential hazard when using argon to purge or inert a confined space. As a gas at ambient temperature, argon is about 38% heavier than air. This means that in confined spaces or large containers with closed bottoms, argon will accumulate in the bottom of the space or container. Argon can displace normal breathing air and cause rapid asphyxiation. Therefore, the oxygen level in any enclosed space that may be entered by personnel must be maintained above 19.5% using forced-air convection, if necessary. If this is not practical, then access to the enclosed area should be locked and entry allowed only after the area has been purged with air and tested for a safe oxygen level. Read and understand the supplier MSDS for argon.

5.4.4 Hydrogen

Hydrogen is an element which at atmospheric temperatures and pressures exists as a colorless, odorless, tasteless, flammable non-toxic gas. It is the lightest gas with a specific gravity of only 0.0695. Its concentration in the atmosphere is only 0.0001–0.0002% by volume at sea level. Hydrogen diffuses rapidly through porous materials and through some metals at red heat. It may leak out of a system which is gas tight with respect to air or other common gases at equivalent pressure.

5.4.4.1 Chemical Properties

Hydrogen burns in air with a pale blue, almost invisible flame. The ignition temperatures of hydrogen-air and hydrogen-oxygen mixtures vary depending on composition, pressure, water vapor content, and initial temperature. At atmospheric pressure, the ignition temperature of either hydrogen-air or hydrogen-oxygen mixtures will not vary greatly from the range 1050–1074°F. The flammability limits of hydrogen-air and hydrogen-oxygen mixtures depend on initial pressure, temperature, and water vapor content. In dry air at atmospheric pressure the lower limit is 4.1% hydrogen, and the upper limit is 74.2% hydrogen by volume. In dry oxygen at atmospheric pressure the lower limit is 4.7% hydrogen and the upper limit is 93.9% hydrogen by volume. Hydrogen is fundamentally a reducing agent. Either used alone or mixed with other gases, it is used to provide a non-oxidizing atmosphere in annealing and heat treating.

5.4.4.2 Safe Practices

Hydrogen is non toxic, but it can act as a simple asphyxiant by displacing the oxygen in the air. Unconsciousness from inhaling air which contains a sufficiently large amount of hydrogen can occur without any warning symptoms such as dizziness. Still lower concentrations than those which could lead to unconsciousness would be flammable, since the lower flammable limit of hydrogen in air is only 4% by volume. All the precautions necessary for the safe handling of any flammable gas must be observed with hydrogen. Read and understand the supplier MSDS for hydrogen.

5.4.5 Carbon Dioxide

Carbon dioxide in its most common form is a gas, but depending on the temperature and pressure it may exist as a gas, liquid or solid. Carbon dioxide comprises approximately 0.038% by volume of the earth's atmosphere at sea level. It is a product of human and animal metabolism and is important to the life cycle of all types of vegetation. Gaseous carbon dioxide is about 1.5 times as heavy as air.

5.4.5.1 Chemical Properties

Carbon dioxide is nontoxic, soluble in water, colorless and normally odorless. In high concentrations, above 5,000 ppm, carbon dioxide can be detected as it dissolves in the moisture of the mucous membranes in the nasal passages. The sensation produced has been described as a pungent or irritating odor. Carbon dioxide is cooled and compressed to form a colorless liquid with approximately the same density as water. At temperatures above 87.8°F (31°C), carbon dioxide cannot be liquefied regardless of the pressure applied. Carbon dioxide is used to create an inert atmosphere for various metal working applications and for some molten metal subsurface stirring applications.

5.4.5.2 Safe Practices

Carbon dioxide can cause rapid asphyxiation if released in large quantities into a confined area lacking adequate ventilation. Carbon dioxide will replace normal air, giving no warning that a non-life-supporting atmosphere is developing. Any atmosphere that does not contain enough oxygen (19.5% by volume) can cause dizziness, unconsciousness and death. An oxygen-deficient atmosphere is created when carbon dioxide gas displaces air, causing the oxygen content to decrease. Because carbon dioxide is 1.5 times more dense than air, it accumulates in low (below grade) or confined areas. Breathable air is forced upward as the carbon dioxide concentration in a confined area increases. Continued increases in carbon dioxide concentration could force all breathable air out of an area.

Carbon dioxide is absorbed by the blood via the lungs and, to some extent, the skin. The symptoms associated with inhalation of carbon dioxide are not normally noticed until the concentration of carbon dioxide in the air is so high that there is insufficient oxygen in the atmosphere to support life. The sign and symptoms of carbon dioxide over-exposure are the same as those preceding asphyxia, namely, headache, dizziness, shortness of breath, muscular weakness, drowsiness and ringing in the ears. Read and understand the supplier MSDS for carbon dioxide.