AIR SEPARATION: OXYGEN AND NITROGEN

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1.0 SCOPE

This data sheet provides loss prevention recommendations for air separation processes. These processes are designed to separate and recover various components (nitrogen, oxygen, argon, and other trace gases) from air, either as gases or cryogenic liquids. This data sheet also provides guidance for the following support processes and equipment:

- Cryogenic storage of oxygen and nitrogen
- Vaporizers
- Argon purification

This data sheet focuses on the production of technical-grade oxygen, nitrogen, and argon. The production of ultra-pure nitrogen is not included in the scope of this data sheet. For guidance on ultra-pure nitrogen, refer to Data Sheet 7-7, *Semiconductors*.

1.1 Hazards

Atmospheric air, by itself, is fairly innocuous (see Table 1). However, when separated, its components and the physical conditions of the separation process both present significant hazards. Process (and even waste) streams in an air separation unit can contain high concentrations of oxygen, presenting the hazard of accelerated combustion, and thereby intense fires.

Unintentional vaporization of liquefied gases in cryogenic separation processes, can lead to potentially explosive events. This can result from the sudden heating of cryogenic fluids, or more slowly by heating of cryogenic tanks above their maximum allowable working pressure (MAWP). The resulting rapid phase change explosion or boiling liquid expanding vapor explosion (BLEVE) can result in significant damage to surrounding buildings or equipment.

Air separation is highly dependent on compressors driven by electric motors or steam/gas turbines, along with pumps and pressure vessels. Hazards related to large rotating equipment and their drivers are common in these facilities.

Extreme temperature hazards are present in cryogenic plants in the cold box, and in vessels storing cryogenic liquids. These extreme low temperatures can cause embrittlement of piping and equipment, leading to a potential loss of containment and subsequent rapid vaporization event. Unplanned outages can also cause large temperature swings in cryogenic processes, resulting in excessive stress on equipment.

Under cryogenic conditions, carbon dioxide, water, and other hydrocarbon contaminants in the liquid or gaseous stream(s) can freeze into deposits, leading to conditions that can cause losses.

Separated gases are a critical support utility in certain occupancies, such as steel mills and chemical plants. Extended downtimes can result from the loss of a critical air separation utility.

1.2 Changes

April 2021. This document has been completely revised. Significant changes include the following:

A. Changed the title of the standard to “Air Separation: Oxygen and Nitrogen” (from “Air Separation Processes”).

B. Moved guidance specific to high-purity nitrogen used in semiconductor occupancies to Data Sheet 7-7, *Semiconductor Fabrication Facilities*.

C. Incorporated information from Data Sheet 7-52, *Oxygen*, and made that document obsolete.

D. Incorporated information from Data Sheet 7-35R, *Air Separation Processes*, and made that document obsolete.

E. Updated construction and location guidance on bulk storage of cryogenic liquids.

F. Updated protection guidance on compressors and other rotating equipment.

G. Updated guidance on industrial control systems.

H. Updated inspection, testing, and maintenance (ITM) guidance.

I. Added guidance on contaminant management.

J. Added guidance on contingency planning and sparing.

K. Updated loss history.

L. Reorganized the document to ensure consistency with other standards.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

2.1.1 Use FM Approved equipment, materials, and services whenever they are applicable and available. For a list of products and services that are FM Approved, see the *Approval Guide*, an online resource of FM Approvals.

2.2 Construction and Location

2.2.1 Use noncombustible construction to construct air separation facilities.

2.2.2 Route waste streams that are oxygen or nitrogen enriched to safe locations. Oxygen-enriched streams present a hazard of accelerated combustion compared to ordinary air.

2.2.3 Do not position exhaust vents close to the intakes for air separation processes. This includes exhaust vents and stacks from occupancies the air separation plant is supporting.

2.2.4 Locate oxygen tanks on concrete, gravel, or other similar noncombustible materials.

2.2.4.1 Do not locate oxygen tanks on asphalt, as asphalt is a hydrocarbon that burns, and can burn and/or detonate when oxygen is spilled onto it.

2.2.4.2 Keep the ground area within 15 ft (4.5 m) of the tanks free of high weeds and grass.

2.2.5 Locate bulk oxygen storage, including fixed or portable high-pressure bulk units and/or liquid oxygen equipment preferably out of doors or in a detached noncombustible structure used solely for this purpose and separated as follows:

A. 75 ft (23 m) from the following:

- Aboveground ignitable liquid tanks or liquified flammable gases of 1,000 gal (3.8m^3) or greater capacity
- Low-pressure flammable-gas storage holders of 5,000 ft^3 (140 m^3) or greater capacity
- Unsprinklered combustible buildings
- Combustible yard storage
- Wood exterior walls

B. 25 ft (7.6 m) from the following:

- Aboveground ignitable liquid or liquified flammable gas tanks of less than 1,000 gal (3.8m^3) capacity
- Filling or vent connections to underground ignitable liquid tanks
- Low-pressure flammable-gas storage holders of less than 5,000 ft^3 (140 m^3) capacity
- Sprinklered buildings or buildings with both construction and occupancy noncombustible
- High-pressure bulk flammable-gas storage
- Ignitable-liquid unloading stations

C. 5 ft (1.5 m) from noncombustible construction having blank walls 10 ft (3 m) above and 10 ft (3 m) on each side of the equipment

2.2.5.1 If regulators and other control equipment for oxygen are located indoors, situate them in a noncombustible building that is detached or cut off from main buildings or combustible storage. A minimum 1-hour fire resistance rating is recommended for cutoffs.

2.2.6 Use gaskets, lubricants, piping, etc. that have been tested as suitable for the service.

2.2.6.1 Where oxygen is the service:

A. Do not use porous flammable materials that will absorb oxygen, hydrocarbon-based oils and greases, cork, etc.

B. Use welded joints whenever possible. If threaded joints are necessary, they are to be made of materials compounded for oxygen service.

2.2.6.2 In areas of cryogenic service, use materials and equipment with the appropriate thermal properties.

2.2.7 For argon plants or where argon is catalytically purified with hydrogen, adhere to the following:

A. Locate the reactor outside or in an area separate from other operations. If located indoors, provide natural ventilation at the roof.

B. Within 15 ft (4.6 m) of the reactor, install electrical equipment that is FM Approved for Zone 2 or Class I, Division 2.

C. Locate the hydrogen supply outside in accordance with Data Sheet 7-91, *Hydrogen*.

D. Ensure hydrogen piping and fittings are in accordance with Data Sheet 7-91, *Hydrogen*. Do not use cast iron pipe or fittings.

E. Position liquified hydrogen tanks (liquid or gaseous) in accordance with Data Sheet 7-91, *Hydrogen*.

F. Install an emergency shut-off valve downstream of the bulk storage tanks that can be operated manually and remotely from a designated control room in the event of an incident.

G. Provide a well-marked hydrogen shutoff valve, remote from the purifier, for ready access in an emergency.

2.3 Protection

2.3.1 If combustible construction is present, provide automatic fire protection in accordance with the applicable data sheets.

2.3.2 Provide noncombustible or FM Approved cooling towers per Data Sheet 1-6, *Cooling Towers*.

2.3.3 Provide automatic sprinkler protection as follows:

A. For steam turbine-driven compressors, provide fire protection in accordance with Data Sheet 7-101, *Steam Turbines and Electric Generators*.

B. For gas turbine-driven compressors, provide fire protection in accordance with Data Sheet 7-79, *Fire Protection for Gas Turbines and Electric Generators*.

2.3.3.1 Do not provide sprinkler protection for large external lubrication oil systems unless there are steam turbine drivers or other normally hot surfaces (exceeding the oil’s flash point) within 50 ft (15 m), or combustible construction is present.

2.3.4 If sprinklers are not necessary for the compressor or lube-oil hazard, but are needed to protect another hazard in the area (e.g., the building or adjacent occupancy is combustible), design automatic sprinkler protection for the surrounding occupancy. At a minimum, design the protection for a Hazard Category 2 (HC-2) occupancy in accordance with Data Sheet 3-26, *Fire Protection for Non-Storage Occupancies*.

2.3.5 Provide combination ionization/photoelectric smoke detectors for slow smoldering fires in switchgear and circuit breaker rooms in accordance with Data Sheet 5-48, *Automatic Fire Detectors*. Areas for installation include, but are not limited to, the following:

- Rooms containing switchgear and circuit breakers
- Other electrical rooms
- I/O rooms
- Control rooms
- Analyzer booths
- Motor control centers (MCCs)

2.3.5.1 Provide heat detection for compressors that are located within enclosed buildings.

2.4 Equipment and Processes

2.4.1 Eliminate dead-ended vessels, piping, or instrument lines that can accumulate oxygen-enriched liquids to prevent dry boiling and/or contaminant buildup.

2.4.2 Wherever cryogenic liquids can be trapped between closed valves, provide pressure-relief valves to account for thermal expansion.

2.4.3 Provide a continuous purge of dry nitrogen for the cold box enclosure to prevent entry of outside air/humidity, and to prevent icing or, in severe cases, perlite eruption.

2.5 Control Systems

2.5.1 Ensure the controls for the air separation process meet the recommendations in Data Sheet 7-110, *Industrial Control Systems*. If centralized control systems manage remote locations, ensure the adequacy of these controls at both locations.

2.6 Operation and Maintenance

2.6.1 Develop an asset integrity program (AIP) in accordance with Data Sheet 9-0, *Asset Integrity*. Include the following in the program:

- Equipment specification and process documentation (such as P&IDs)
- Equipment viability for the intended service
- Equipment protection strategies and Safety device adequacy
- Inspection, testing, and maintenance (ITM) methodologies
- Operating and ITM history/trends as well as current operating and environmental conditions
- Equipment breakdown scenarios and resulting impacts on production, utility and support systems, including damage to interconnected or surrounding equipment and areas
- Equipment contingency planning viability

Alternative approaches may be applied provided they meet the intent of the above guidance.

2.6.2 Maintain the following equipment in accordance with the applicable data sheet:

- Data Sheet 7-95, *Compressors*
- Data Sheet 1-6, *Cooling Towers*
- Data Sheet 13-3, *Steam Turbines*
- Data Sheet 5-17, *Motors and Adjustable Speed Drives* (large motors)
- Data Sheet 13-7, *Gears* (gear sets for integral compressors)

2.6.3 Confirm that dry nitrogen purge is flowing to the cold box on a weekly basis. Continuous oxygen concentration monitoring can be effective way of ensuring nitrogen purge.

2.6.4 Visually inspect the cold box for frost accumulations weekly, as part of the maintenance plan. Accumulations of frost on the cold box are a potential indication of a leak in the cold box or more serious condition. Schedule repairs within the next viable maintenance window due to the potential structural damage impacts from the cryogenic temperatures or rapid burning of combustibles in oxygen-enriched atmosphere.

2.7 Contaminant Management

High ambient hydrocarbon concentrations are defined as being greater than the normal levels for the trace contaminants in ambient air, as shown in Table 1 (Section 3.0). Such concentrations may exist at facilities such as oil refineries, steel mills, and chemical plants. Sudden increases in hydrocarbon levels are also possible at locations where air separation plants are also present, due to process upsets or areas subject to wildfires.

2.7.1 Establish a contaminant management program to ensure contaminants do not exceed safe operating limits. At a minimum, the following safeguards are needed at cryogenic air separation plants:

A. Monitoring on the atmospheric air intake.

B. After the pre-purification unit (PPU), provide monitoring of CO_2 levels and hydrocarbons (e.g., total hydrocarbon content [THC]). Arrange the alarm to actuate at a predetermined level for the plant conditions. Upon alarm actuation, the standby PPU is to be activated or the plant shut down. This is to occur within a short time (usually about one hour) after the alarm is sounded.

C. Reboiler sump – LOX hydrocarbon analyzer. Hydrocarbon levels not to exceed 450 ppm as THC.

D. For areas with potentially high ambient hydrocarbon concentrations, provide CO_2 and THC monitoring at the compressor inlet.

E. LOX purge: minimum of 0.2% LOX purge is provided. May be omitted if LOX product is drawn directly from the sump.

F. Provide contaminant purging by de-riming the cold box on an interval of every 3-5 years. With a risk assessment this may be extended at 1-year intervals up to a maximum of 10 years.

G. Downflow reboilers (falling film): Closely monitor CO_2 and N_20 concentrations in the LOX sump to prevent icing.

H. Thermosyphon reboilers: ensure 100% submergence is maintained.

I. For REVEX (reversing exchanger) plants, operate liquid phase adsorbers in accordance with manufacturer's instructions. This includes sampling for acetylene, typically several times per week.

2.7.2 Where contaminant concentrations are monitored, record the data to detect trends toward hazardous conditions.

2.7.3 Perform a risk assessment if there is a severe degradation of the ambient air (such as from a wildfire) to determine if a shutdown of the plant is needed.

2.7.3.1 For sudden increases in contaminants (e.g., due to a process upset), complete a risk assessment and initiate the resultant corrective actions, which may include shutting down or de-riming the plant.

2.8 Training

2.8.1 Train operators on the correct operation of the ASU, including how to handle potentially unsafe conditions. Refer to Data Sheet 10-8, *Operators*, for guidance.

2.9 Human Factor

2.9.1 Have written procedures available for response to emergency conditions or off-specification operations. Train all operators in these procedures, with refresher training at regular intervals. Include procedures and corrective actions for plant shutdowns that are short of a complete warm-up.

In short shutdown situations, hydrocarbons can concentrate in the liquid sumps and/or may desorb and pass into the process equipment containing liquid oxygen. Ensure operating procedures recognize the potential for this and provide guidance on preventative measures, such as maintaining liquid purge from sumps.

2.9.2 Prior to any hot work in the cold box, use portable gas detectors to detect the presence of oxygen from a leak or ignitable liquid leak or combustible residue.

2.9.3 Manage transient operations. This can include, but is not limited to, the following:

A. Running the plant in recycle mode for extended periods

B. Ensuring that extra liquid oxygen is purged from the system to reduce potential hydrocarbon accumulation after recycle mode has been in operation

C. Maintain contaminant levels within defined safe limits

2.10 Contingency Planning

2.10.1 Equipment Contingency Planning

2.10.1.1 If a mechanical breakdown would result in an unplanned outage to site processes and systems considered key to the continuity of operations, develop and maintain a documented, viable mechanical equipment contingency plan per Data Sheet 9-0, *Asset Integrity*.

Equipment contingency plans are to be specifically considered for:

A. Compressors (including associated drivers and gearboxes)

B. Cooling towers

C. Cold boxes

2.10.1.2 If the air separation unit provides gases that are a critical utility for the safe operation of a plant (i.e., inerting) provide a backup gas supply sufficient for safe shutdown of the host site. This is typically done in the form of a cryogenic tank and vaporizer to ensure the safe shutdown of the site.

3.0 SUPPORT FOR RECOMMENDATIONS

The three commercial air separation processes are cryogenic, adsorption, and membrane separation. All start with air that has a typical composition as shown in Table 1.

Table 1. Typical Air Composition

Component	*Volume Percent*
Nitrogen	78.1
Oxygen	20.9
Argon	0.9
Rare Gases[1]	0.002
Carbon Dioxide	0.03
Hydrocarbons	0.001-0.03

[1] Neon, Helium, Krypton, Xenon

3.1 Cryogenic Process

3.1.1 General

The cryogenic process is capable of recovering trace gases from atmospheric air as well as oxygen and nitrogen. Product gases or cryogenic liquids can be of very high purity, as much as 99.999% or better. This process is capital- and power-intensive and reportedly is economically justified only in capacities over 850 T/D (tons/day) of oxygen. Modern plants produce up to 6000 T/D of oxygen and 10,000 T/D of nitrogen.

The cryogenic process (see Figure 1) involves the following steps:

- Compressing the air
- Air contaminant removal via scrubbing, freezing, or adsorption (pre-purification)
- Cooling the air to a liquid state
- Distilling the liquefied air to separate the components
- Collection and storage of the separated components

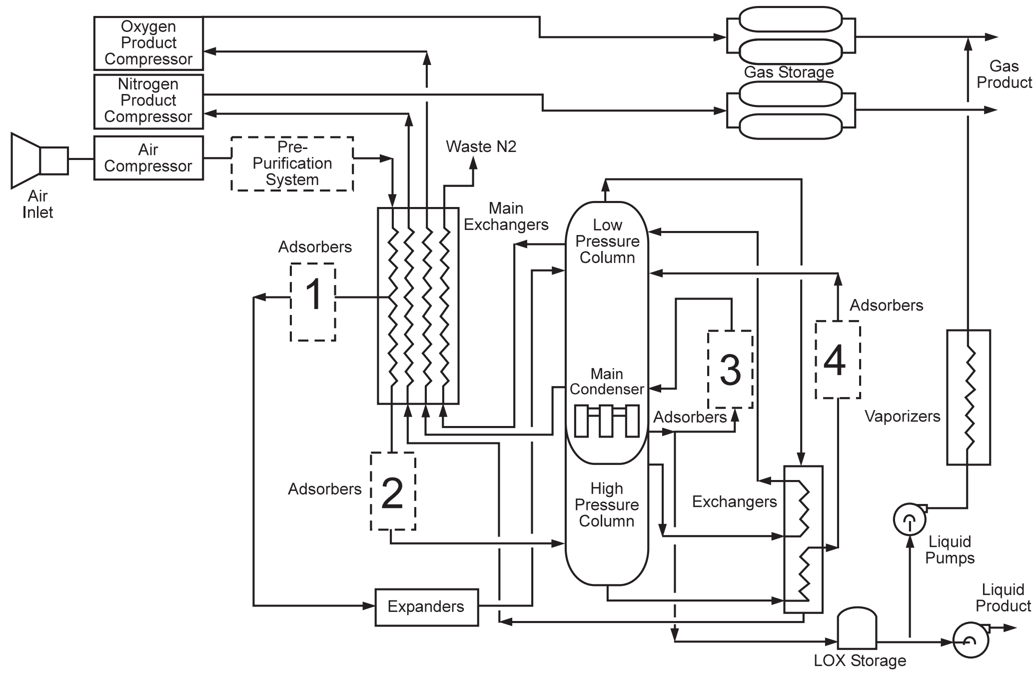


Fig. 1. Generic air separation plant flow diagram. Pre-purification and Adsorbers labeled 1 through 4 may or may not appear in a particular plant depending on design requirements. (Source: CGA P-8)

Intake air is first compressed in the main air compressor (Figure 1) to between 4atm and 10atm (58 to 147 psig). Pre-purification (if present) then occurs with the removal of contaminants, such as carbon dioxide, water and hydrocarbons from the air stream. This is done using either a pre-purification units (PPU) or in older plants a reversing exchangers (REVEX).

The air is then pre-cooled against intermediate and product streams; and there may also be expanders present to provide additional process refrigeration, before passing into the columns for separation.

High-pressure and low-pressure columns separate the oxygen and nitrogen primary components and concentrate the argon and other rare gases. Two types of distillation columns are used: either tray or packed bed. Distillation process temperatures are around -320°F (-195°C).

Products can be recovered as liquids or gases and they can either be stored (usually as liquids for later delivery) or piped directly to customers (usually as gas).

A liquid purge stream taken from the sump of the reboiler prevents high boiling components from concentrating above allowable limits.

Adsorbers can be present in numerous locations for the removal of contaminants. Typical locations are shown in Figure 1. Locations 1 and 2 are not common in large oxygen plants. Location 3 is often called the “guard adsorber,” while location 4 can be called the “hydrocarbon adsorber” or “rich liquid filter.”

Where plants are limited to nitrogen production only, a simplified process is seen where the high-pressure column is not needed, and the purity of oxygen in the low-pressure column sump, for the main condenser, is in the 50% to 90% oxygen range. This essentially eliminates the hazard of a large decomposition/explosion event involving hydrocarbons.

3.1.2 The Cold Box

Due to the low temperatures used, the process equipment (main exchangers, high- and low-pressure columns, and related adsorbers and exchangers) is enclosed in a structure called a “cold box.” Typical construction is either aluminum or steel-frame and steel-panel with perlite or mineral wool filling the spaces between the equipment. It is usually purged with dry nitrogen at 1 to 2 in Hg (3 to 7 kPa) to prevent condensation and freezing of water from the atmospheric air.

3.1.2.1 Frost Accumulations and De-Riming

Frost accumulation on the cold box is an indication of poor insulation or failure of equipment containing cryogenic liquid. These leaks could cause structural failure (from extreme cold) or ignition or explosion if small oil leaks or combustible residues are present in the oxygen-enriched atmosphere. Materials of construction should be suitable for the expected temperatures.

De-riming is the process of completely warming up the entire plant. The main purpose is to remove contaminants that may be present throughout the plant in exchangers and columns. Frequency is determined by the loss of efficiency in the exchangers or other indicators. Units with reversing exchangers can go 2 to 3 years between de-riming while PPU-based plants can go somewhat longer.

3.1.2.2 Perlite Eruptions

In air separation plants, perlite is an insulation material used as an insulating material in cryogenic enclosures such as the cold box (between the columns and the inner cold box shell) and cryogenic liquid tanks. Perlite is a nonflammable insulation material that forms a lightweight powder aggregate when expanded by heat. It is critical to maintain the perlite insulation in good condition. Failure to do so can result in icing from humidity migration, loss of insulating capability and unit efficiency, and in severe cases a perlite eruption.

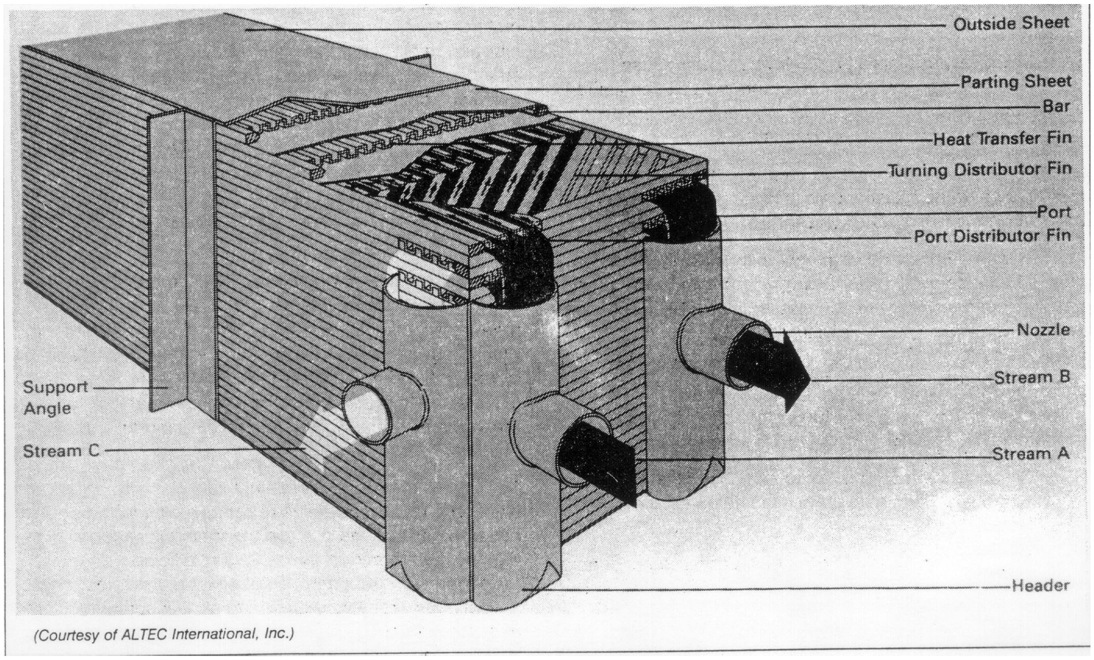
A perlite eruption occurs when pooled cryogenic liquid in the perlite is suddenly warmed, moved or physically disturbed. The resultant rapid vaporization, can overpressure the cold-box, causing the perlite to “erupt” outside of the cold-box, requiring significant repair time. These events are often caused by uneven thermal expansion or ice accumulation (expansion) causing the failure of a piping element.

Preventing humidity ingress into the cold box, maintaining a dry nitrogen purge and maintaining insulation integrity are the primary means of avoiding such an incident. External ice formation on the shell of the cold box may be an early warning of a perlite eruption and should require additional investigation.

3.1.3 Heat Exchangers

Since heat exchange with small temperature differences between exchanged streams is so critical to process economics, the heat exchangers are a major component of the process.

Plate/fin exchangers (Fig. 2) use plates/fins where corrugated flow passages are separated by thin metal sheets. Each block may have two or more separate process streams being exchanged, and several blocks may make up one exchanger. There are many variations of the basic features to provide specific efficiency improvements.



(Courtesy of ALTEC International, Inc.)

Fig. 2. Plate/fin heat exchanger

Within these units, the fluid flow passages are much smaller, and can become blocked more readily by ice accumulation (CO_2 or water) resulting in dead ends within the tubes.

Hazardous amounts of hydrocarbons can accumulate within these dead ends and precipitate out even though overall accumulations remain well above dangerous levels. The plugged passage could also lead to boiling without replenishment (dry boiling) and eventual dry spots. Preventive measures to control and remove the accumulations (mainly CO_2 and water) along with other design features can limit the formation of plugs and the dead-end boiling.

Other types of heat exchangers include:

A. Thermosyphon (flooded) exchangers

These exchangers (Fig. 3) are seen in plants where circulation is maintained by temperature differentials within the exchanger. The LOX boils and vaporizes so it rises through the exchanger. It is important to keep the LOX levels in the low-pressure column high enough to maintain submergence of the exchanger. Low levels could create dry spots and potentially increased and hazardous hydrocarbon levels in the LOX.

B. Falling film (down flow) exchangers

Falling-film exchangers (Fig. 4) allow both condensing and boiling to occur in falling films on the walls of the exchanger passes. These exchangers can be external to the low-pressure column sump, so LOX distribution is important to maintain exchanger efficiency and continuous film on the exchanger walls.

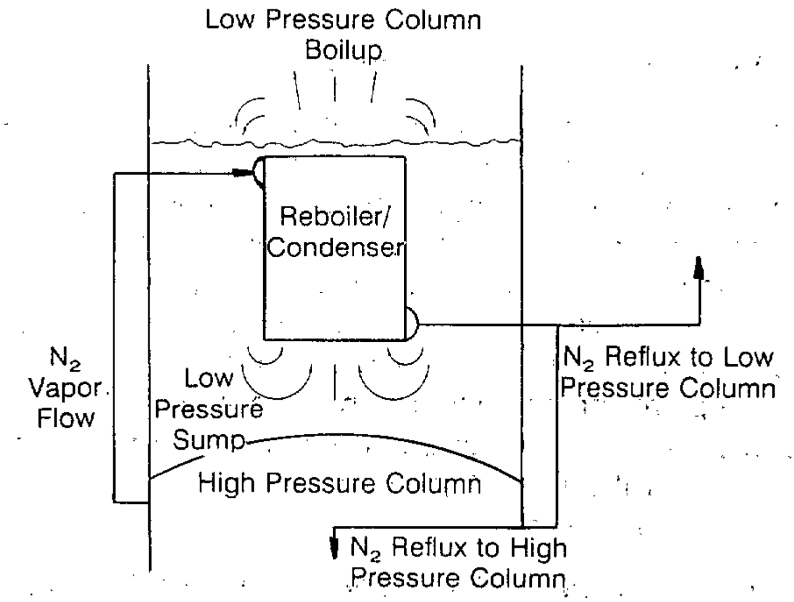


Fig. 3. Main condenser, thermosyphon design

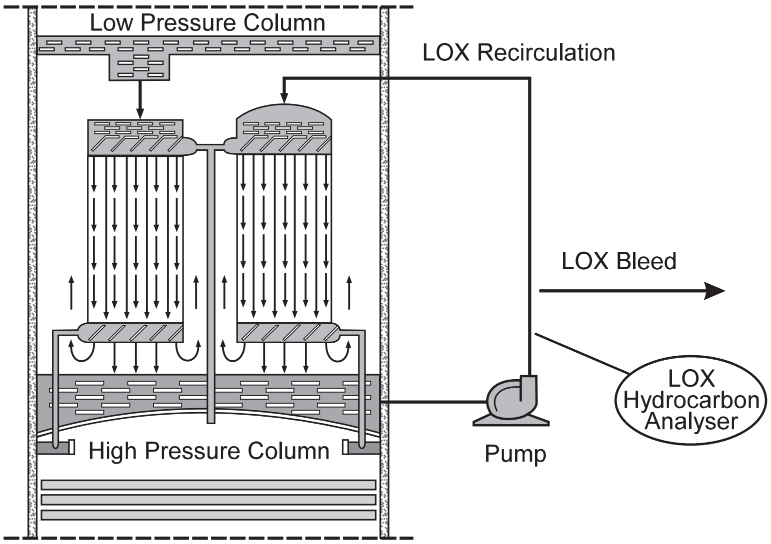


Fig. 4. Main condenser, falling-film design. Shows feed by either direct flow from the low-pressure column packing (left) or pumped recirculation from the LOX sump (right).

Reversing exchangers (REVEX) will switch as often as every two or three minutes, but more commonly every 15 minutes. Timing is strictly based on design capacity to accept plugging of the passages by frozen CO_2 or water. It is set in the early design stages and controlled by the process computer.

3.1.4 Compressors and Drivers

Large compressors are used in the ASU process. Drivers are nearly always electric motors and some are of the synchronous type. These will typically include the main air compressor, and oxygen and nitrogen compressors for pipeline delivery. Both centrifugal and reciprocating machines are used. Basic design and operational safeguards are addressed in Data Sheets 7-95, *Compressors*, 5-13, *Synchronous Motors*, and 5-17, *Large Electric Motors*.

Loss history has shown that in oxygen compressors the lubrication oil is almost never involved in the incident. Oxygen compressor fires are almost always initiated by metal-to-metal friction that results in ignition of the metal in the oxygen atmosphere. Once the oxygen supply is shut off, the fire self-extinguishes.

Nitrogen compressors present a unique problem. Fires have occurred in oil-lubricated reciprocating compressors pumping high purity nitrogen when the oxygen content has suddenly increased due to plant upset conditions. Ignition can occur in centrifugal compressors pumping nitrogen due to interference of rotating parts and in reciprocating compressors through ring or valve failure, but only in the presence of sufficient oxygen. Fuel for the reaction can be lubricating oil or accumulated organic material that has normally been exposed only to an inert atmosphere. Control of oxygen in the nitrogen stream provides the necessary protection to reduce the risk of an ignition due to increasing oxygen content.

3.1.5 Oxygen Piping

High-velocity flow of oxygen gas in a pipeline is a recognized source of ignition energy. Any dirt, metal scale, or other particle traveling with the high-velocity flow represents an energy source (impact) capable of starting a reaction.

3.1.6 Cryogenic Liquid Entrapment

Cryogenic liquid can become trapped between closed valves. Normal heat leaks can cause this trapped liquid to vaporize, generating pressure causing the piping or equipment to fail. Pressure relief valves, not designed to handle full process flows, are provided in these sections of the system to relieve the pressure generated by trapped liquid.

3.2 Adsorption Process

Adsorption processes (Figure 5) use molecular sieves (a different type from that in the cryogenic process) to adsorb and desorb a selected component from a gas stream.

Compressed air is passed through one of two parallel molecular sieve beds. The unwanted component is adsorbed on the molecular sieve, leaving the other component as a product gas stream. After the adsorption cycle, the operating beds are switched. The first bed is desorbed of the unwanted component (regenerated) while the second bed goes into the adsorption cycle.

There are two adsorption-based processes used: pressure swing adsorption (PSA) and vacuum swing adsorption (VSA, sometimes also called VSA/PSA). Figures 6 and 7 show simplified schematics of each process.

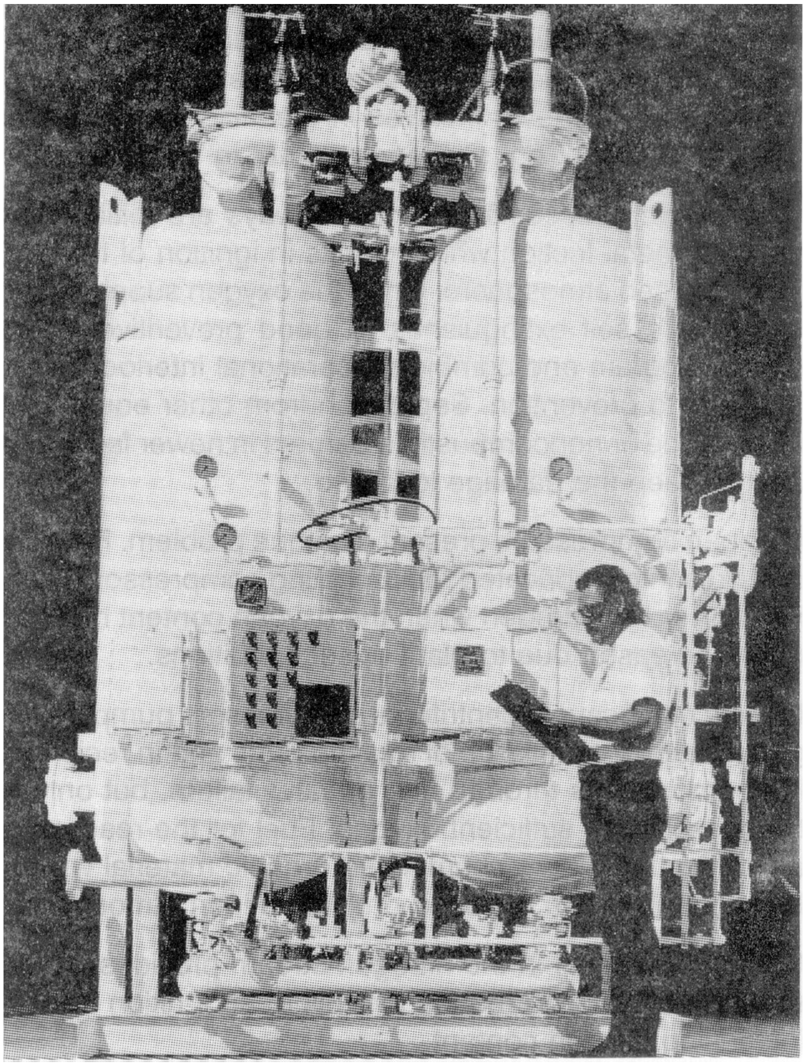


Fig. 5. Adsorption process skid

Gaseous products are typically of lower purity: 92% to 95% for oxygen and 95% to 99.9% for nitrogen and trace gases in air (such as argon and the rare gases) cannot be economically recovered by this method. The advantages of adsorption processes are lower operating costs and simpler operating requirement, making them more attractive for small users, compared to the other methods.

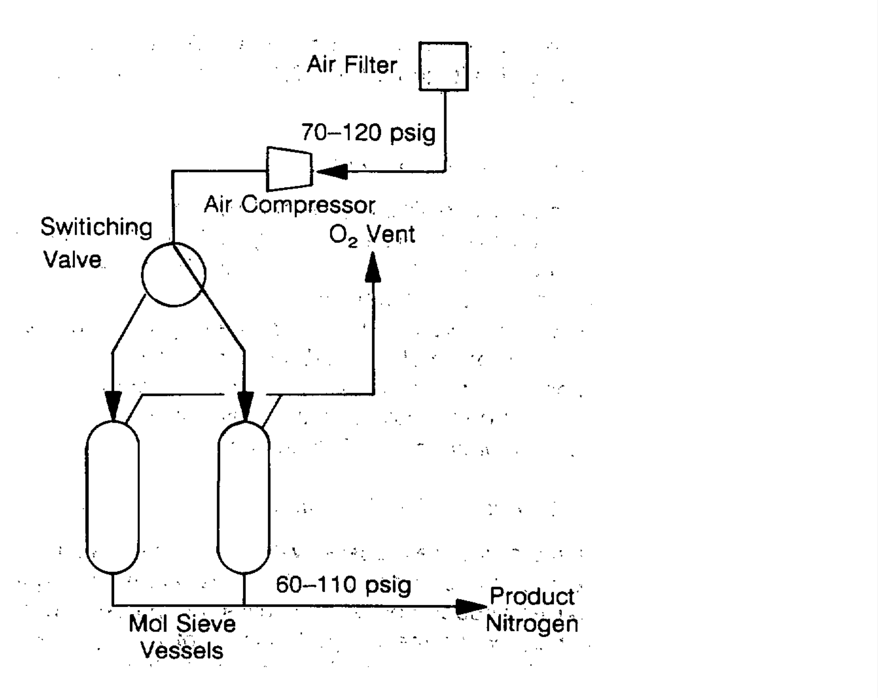


Fig. 6. Pressure swing adsorption (PSA)

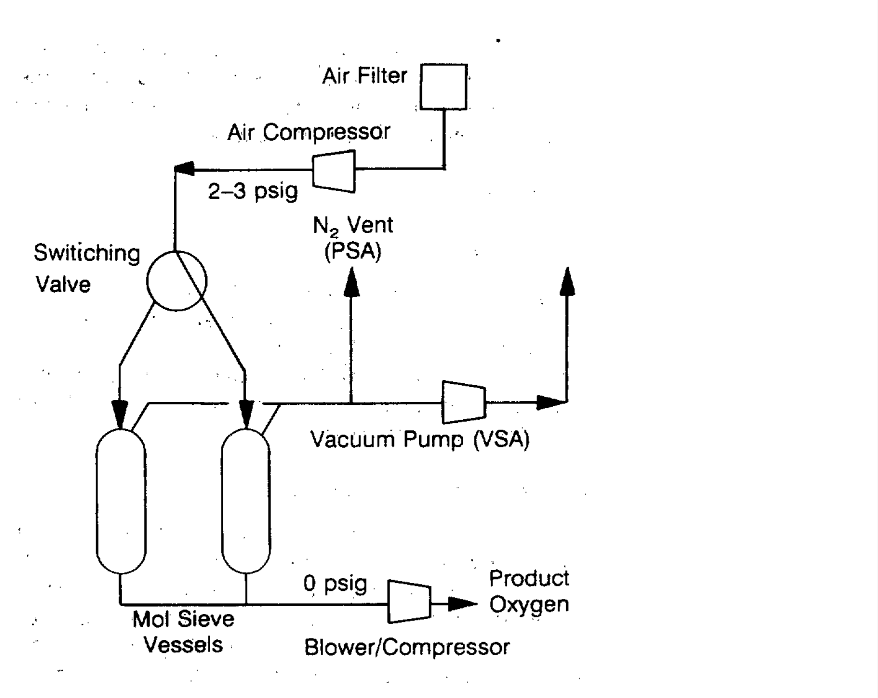


Fig. 7. Vacuum swing adsorption (VSA or VSA/PSA)

3.3 Membrane Separation Process

Similar to adsorption plants in cost and ease of operation, membrane separation plants are smaller in size. Membrane technology is only capable of producing nitrogen in the range of 95 to 99.9% purity from ambient air.

The membrane process uses semi-permeable membranes in the form of hollow tube, approximately the thickness of a human hair, These are bundled into modules and compressed air is forced down the length of these modules. Unwanted components (oxygen, CO_2 and water) selectively diffuse through the fiber walls of the membranes and are vented as waste. The remaining nitrogen-rich stream concentrates inside each fiber and is collected as product. Figure 8 shows equipment on a typical membrane process skid, while Figure 9 shows a simplified schematic of the process.

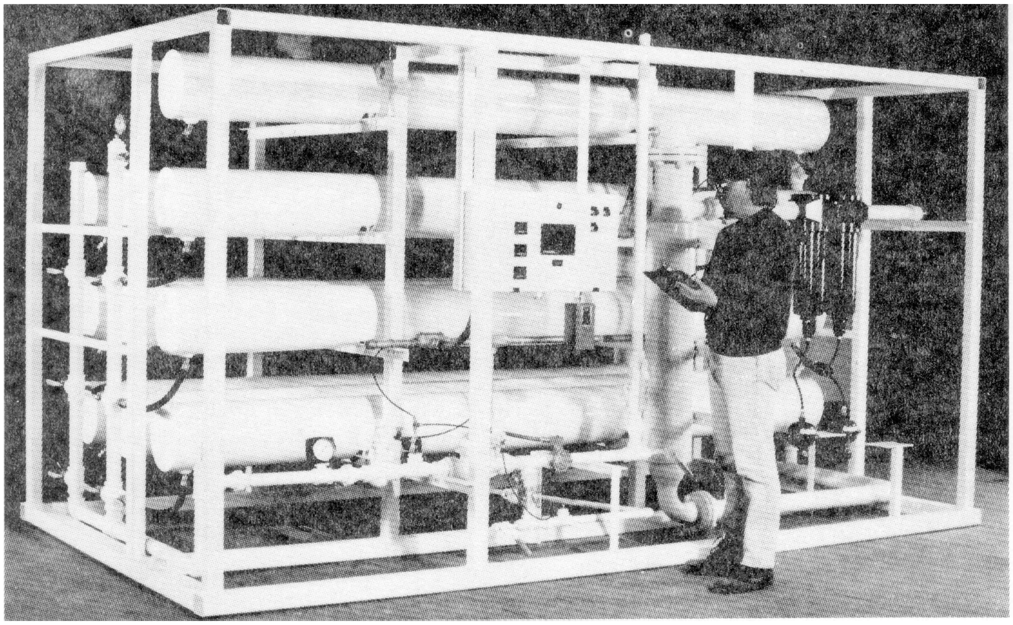


Fig. 8. Membrane process skid

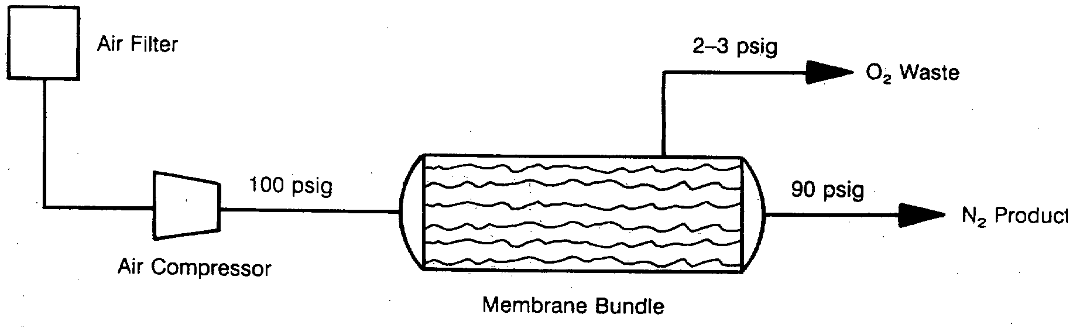


Fig. 9. Membrane process schematic

Higher purity (99.999%) can be achieved by a catalytic de-oxygenation unit. Using catalyst, the de-oxygenation unit combines trace oxygen in the nitrogen stream with hydrogen to form water.

Hydrocarbon accumulation associated with cryogenic processes and liquid oxygen does not exist in membrane processes. There is no liquefaction of the oxygen, and these processes do not increase the concentration of any trace hydrocarbons in the incoming air.

3.4 Contamination

Atmospheric contaminants, typically hydrocarbons or particulates, can enter an air separation plant through the intake air. Levels of common contaminants present in ambient air are shown in Table 2.

Table 2. Levels of Trace Contaminants in Ambient Air

Contaminant Name	*Level in Typical Air Sample (ppm per volume)*
Acetylene	0.3
Carbon dioxide	425
Ethane	1
Ethylene	0.1
Methane	5
Oxides of nitrogen	0.1
Nitrous oxide	0.35
Propane	0.05
Propylene	0.2

Sources of these contaminants can include other plants close to an ASU such as chemical plants and steel mills. Other contaminant sources can include air separation plants being located in areas subject to wildfires.

An air separation plant is designed to limit accumulations of these contaminants in the cold box. Prior to construction of a plant, air samples are taken at the proposed location, the hydrocarbon content is analyzed, and the plant's hydrocarbon removal system is tailored to the air's content and weather conditions likely in the area.

Contaminants are classified by the effects they have within an air separation unit (Table 3). There are three contaminant categories:

- **Plugging:** Contaminants of this type either precipitate out as a solid material or concentrate within the ASU. Dry or pool boiling can results concentrating these contaminants into flammable mixtures. Water, carbon dioxide and nitrous oxide are the three most common of this type.
- **Reactive:** When concentrated within the ASU these contaminants form flammable mixtures with oxygen-rich streams. Methane, ethane, Ethylene, acetylene, propane and propylene are typical examples.
- **Corrosive:** These contaminants react with piping and equipment, causing corrosion and reducing the equipment integrity. Ammonia and acidic gases are the most common.

Table 3. Common ASU Contaminants (by Type)

Plugging		*Reactive*		*Corrosive*	
Contaminant name	Symbol	Contaminant name	Symbol	Contaminant name	Symbol
Carbon dioxide	CO_2	Acetylene	C_2H_2	Ammonia	NH_3
Nitrous oxide	N_2O	Ethane	C_2H_6	Chlorine	Cl_2
Water	H_2O	Ethylene	C_2H_4	Hydrochloric acid	HCl
Oxides of nitrogen	NOx	Methane	CH_4	Hydrogen sulfide	H_2S
		Particulates from forest fires and other hydrocarbons		Sulfur dioxide	SO_2
		Oxides of nitrogen	NOx	Sulfur trioxide	SO_3
		Ozone	O_3	Sulfur compounds (other)	
		Propane	C_3H_8	Chlorides (other)	
		Propylene	C_3H_6		

Reactive hydrocarbon contaminants such as acetylene can concentrate in the liquid oxygen phase. Acetylene has a solubility limit of 5 ppm, after which solid acetylene particles settle out, either floating on the LOX surface or accumulating in the exchanger passages. Acetylene in LOX can readily detonate, although the actual mode of initiation is not clearly established. Other hydrocarbons have solubility limits exceeding 1000 ppm/v so incidents attributed to these are simply due to the high oxidation rates of hydrocarbons in LOX. Accumulations of propane and ethylene have also been responsible for explosions. Other hydrocarbons commonly present are not easily ignited.

Without steps to control hydrocarbon buildup, the hydrocarbon level in the main condenser (low-pressure column reboiler) where product (LOX) is produced, could easily reach 200 ppm/v or more.

Steps to mitigate or control contaminant buildup include the following:

A. Analyzing the intake air regularly at a frequency based on the plant's location, design, and operating conditions.

B. Designing and constructing the distillation column liquid sumps to eliminate crevices in the materials of construction.

C. Preventing ledges or shelves within the distillation column sumps where hydrocarbon crystals could accumulate. This is usually done in the design phase of the column.

D. Having pre-purification units (PPUs) to treat the incoming air.

E. Analyzing the reboiler sump liquid or product LOX to determine the hydrocarbon contamination.

F. Continuous monitoring and sampling of total hydrocarbon content of the liquid oxygen in the main condenser.

G. In plants with no liquid product, a constant LOX bleed, at least 0.1% to 0.2% of the incoming airflow rate (0.5% to 1% of oxygen production rate), is drawn from the low-pressure column to reduce hydrocarbon accumulations.

H. For carbon dioxide (CO_2), tracking the levels at the PPU outlet is an effective way to monitor the PPU performance and thus control the contamination level. CO_2 has limited solubility in cryogenic fluids and can solidify and block small exchanger passages. Levels of 1 ppm/v CO_2 are typically recognized as an alarm/unacceptable level. A continuous slip of CO_2 to levels as low as 0.2 to 0.5 ppm/v is also a danger sign as hydrocarbon contaminants such as acetylene, along with moisture, would also be bypassing the adsorber beds and corrective actions need to be taken. This, in turn, can result in dry or pool boiling of the trapped liquid and concentrating hydrocarbons. CO_2 will "breakthrough" the PPU before most hydrocarbons, thereby providing early warning of coming hazards.

At a minimum, the identification and the concentration of the individual hydrocarbons should be recorded and documented for trend analysis. Total hydrocarbon content (THC) or gas chromatography (GC) are typical methods used. Alarm levels will have been set during the design of the plant (typical levels include THC at 450 ppm as methane or GC at 10% of LEL of measured component). Records will allow for trend analysis to be conducted.

If increases in hydrocarbon contamination are appreciable, a risk assessment should be conducted that includes a review of the process and the site risk levels (consequence and probability).

If risk levels don't meet predetermined acceptability criteria, corrective actions should be taken and the solutions documented. Additional guidance on risk assessment can be found in Data Sheet 7-43, *Process Safety*. An investigation of the causes of these increases should also be conducted in a timely manner,

Corrective actions could include reduced cycle time on pre-purification units (PPUs) and adsorbers, increased severity of adsorber regeneration, and increased LOX withdrawal. Incoming air-cleaning processes (filters, PPU, REVEX) may not be capable of excluding smoke and carbonaceous aerosol materials. Under severe smoke or aerosol conditions, shutdown of the unit may be warranted to prevent combustible contaminants in the cryogenic parts of the system.

If the plant is unattended or controlled remotely and it exists in an area where levels of contamination can become dangerous for the continued operations of the plant, a remote shutdown of the plant should be performed when the hydrocarbons reach a specified high limit.

Nitrogen plants are not susceptible to the serious explosion incidents caused by hydrocarbon contaminants.

Adsorption and membrane processes are also not subject to hydrocarbon accumulation.

3.4.5 Equipment regeneration

Silica gel filters in the rich liquid or LOX circuit need regeneration based on monitoring of total hydrocarbons. Typically, the regeneration frequency is anywhere from 1 week to 1 month. Regeneration frequency could be shorter due to units designed for a smaller hydrocarbon capacity but with two units in parallel. Such a system would have one off-line (regenerating) and one online.

Where there are single units, taking the unit offline for regeneration does not present an undue hazard due to the long time for hydrocarbon buildup.

Molecular sieve beds (PPU) need regular regeneration to remove accumulated contaminants. Regeneration is usually accomplished by heating waste nitrogen in a fuel-fired, steam or electrically heated auxiliary heater. There are usually two parallel beds: one on-line, one regenerating. Regeneration frequency is set in the design phase and can range from every 15 minutes to every 12 hours and is initiated by the process control system, or manually. CO_2 levels are monitored downstream of the molecular sieves. This is the first contaminant to break through and is an auxiliary indication of a need for regeneration.

3.5 Argon Purification

Argon is recovered from air during the air separation process.

Traditionally, crude argon is passed through a catalytic reactor with added hydrogen gas. Any trace oxygen is burned, and the water vapor produced is removed in simple dryers. The intermediate stream may be re-cooled and distilled in a separate column, that may also be present in the main cold box, to remove trace nitrogen impurities and recover the argon.

In modern plants argon in enriched and purified through further distillation stages contained in columns, either within or directly attached to the main cold box. Very pure argon product, down to below 1 ppm/v (parts per million by volume) of single contaminants, can be produced in this way.

The catalytic reactor could be located indoors. Because of the small hydrogen use rates (only a few cfm [L/min]), and the high reactor temperature, special precautions for electrical equipment and construction (where indoors) are rarely practical. The location of the hydrogen supply, natural ventilation at roof level, and proper arrangement of supply piping with an easily accessible shutoff valve should be evaluated.

3.6 Routine Spares

The following are common routine spares for compressors. They should be stored in accordance with the guidance from the original equipment manufacturer to maintain viability. Compressor spares can include:

- Gears, seals and bearings
- Couplings
- Pistons and rods (reciprocating)

Additional equipment may be spared depending on the type of compressor, compressor breakdown exposure, criticality of the process, and OEM recommendations.

3.7 Loss History

In the early days of the production of oxygen and nitrogen by the cryogenic separation of air, there were numerous explosions in the cold box. Investigation of these incidents led to the discovery that small accumulations of hydrocarbons in the oxygen-rich liquid could detonate with little provocation. Hydrocarbon control procedures implemented in the air separation process have reduced the severity and frequency of the typical incident, but have not eliminated the hazard.

In 1997, an incident at the Fushun Ethylene complex in Fushun, China, destroyed the distillation column and damaged some surrounding equipment. It was reported to have had the explosive force equivalent to 1.9 T (1.7 metric tonnes) of TNT.

A second 1997 incident, at the Shell Middle Distillate Synthesis plant in Bintulu, Malaysia, destroyed the ASU and seriously damaged the adjacent user plant. It was reported to have had the explosive force equivalent to 7.3 T (6.6 metric tonnes) of TNT.

Both of these incidents are thought to have involved the same series of events:

1. Spontaneous ignition and combustion of hydrocarbon contaminants that accumulated in the passages of the braised aluminum heat exchanger (BAHX) main condenser.

2. The hydrocarbon combustion promoted ignition and combustion of a large fraction of the aluminum construction of the main condenser.

3. Flash vaporization of the LOX.

4. Explosive rupture of the distillation column and cold box.

In a 2006 survey of 47 incidents involving industrial reboiler losses, none involved nitrogen generators (Schmidt, 2006). Similar results were seen in FM loss data.

Oxygen compressor fires are usually related to metal-to-metal friction that, in the high-purity oxygen atmosphere, causes burning of metal components. Once oxygen is shut off, the fire essentially self-extinguishes. There was some involvement of released oil in the centrifugal unit in some of these losses, after the metal fire was underway.

The losses involving mechanical and electrical breakdown generally involved compressors, drivers, and electrical equipment that are only significant because they were part of an air separation plant. They could have occurred at any plant with the same equipment.

None of the losses appear to have involved the new air separation technologies, pressure or vacuum swing adsorption (PSA or VSA), or membranes.

In Table 4, 38% of the losses were specifically related to compressors. Miscellaneous equipment included motors, and valves not specific to an area within the ASU are classified as “Other.”

Table 4. Losses by Type of Equipment 2004-2020

Equipment	*Number* (1)	*% by number*	*Loss US$ M* (1)
Cold Box	4	13%	118.3
Heat Exchanger	4	13%	211.6
Compressor	12	38%	101.2
Transformer/electrical	4	13%	21.2
Purifier	3	13%	65.2
Rotating Equipment	4	11%	7.4
Other	5	14%	25.1
TOTAL	36	100%	550.0

[1] All figures are total gross loss amounts per peril indexed to 2020 values.

4.0 REFERENCES

4.1 FM

Data Sheet 1-6, *Cooling Towers*
Data Sheet 5-4, *Transformers*
Data Sheet 5-18, *Protection of Electrical Equipment*
Data Sheet 5-19, *Switchgear and Circuit Breakers*
Data Sheet 7-43, *Process Safety*
Data Sheet 7-91, *Hydrogen*
Data Sheet 7-95, *Compressors*

4.2 Others

American Society of Mechanical Engineers (ASME). Standard ANSI/ASME B31.3, *Code for Chemical Plant and Petroleum Refinery Piping*, 1990 or latest edition.

American Society of Mechanical Engineers (ASME). *Boiler and Pressure Code, Section VIII Unfired Pressure Vessels*, latest edition.

Compressed Gas Association (CGA) Standard G4.6, *Oxygen Compressor Installation and Operation Guide*, 2001.

Compressed Gas Association (CGA) Standard G4.9, *Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen*, 1996.
Compressed Gas Association (CGA) Standard G8.4 (European Industrial Gas Association [EIGA] DOC 65/99/E), *Safe Operation of Reboilers/Condensers in Air Separation Units*, 2000.

Compressed Gas Association (CGA) Standard P8, *Guideline for Safe Practices for Cryogenic Air Separation Plants* (2020).

National Fire Protection Association (NFPA). NFPA 70, *National Electric Code*, latest edition.

APPENDIX A GLOSSARY OF TERMS

Analyzer, GC (gas chromatograph): Method of analyzing a process stream for specific components and their concentration. Ability to sample many points with one instrument that cycles from one sample point to the next. Typically, any sample point gets an hourly analysis.

Analyzer, THC (total hydrocarbon concentration): Method of measuring hydrocarbon contaminants using flame ionization or combustion/infrared analyzers. Results are reported as methane equivalent.

BAHX (brazed aluminum heat exchangers): Aluminum plate fin exchangers commonly used in the air separation processes, usually as the main condenser.

Catalytic argon purification: Process in which argon-rich product gas with trace amounts of oxygen is heated, mixed with small amounts of hydrogen, and passed over a metal catalyst. The exothermic reaction removes the oxygen as water that is then removed from the argon product gas by drying.

Cold gel traps: Silica gel adsorbent beds operated at cryogenic temperatures and periodically regenerated. This is effective for removal of CO_2, acetylene, hydrocarbons with more than three carbons, and complete removal of N_2O. Can be installed as “rich liquid filters” on the product oxygen stream in pumped LOX process or recirculating systems taking LOX from reboiler sump. LOX goes through the gel traps and then back to the reboiler sump.

Dry boiling: Heat applied to a set amount of liquid will vaporize the volatile components within the liquid. The remaining less-volatile components will concentrate. Dry-boiling is when these less-volatile components form a solid after the liquid oxygen has boiled away. These solids can adhere to the equipment within the ASU. (Also see “pool boiling.”)

FM Approved: Product and services that have satisfied the criteria for FM Approval. Refer to the *Approval Guide*, an online publication of FM Approvals, and Roof*Nav* for a complete listing of products and services that are FM Approved.

Gaseous product plant: Any operation producing oxygen that is not a liquid product plant (see definition below).

Ignitable liquid: Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids, or any other term for a liquid that will burn. An ignitable liquid is any liquid that has a fire point.

Liquid product plant: Operations in which about 10% or more of the oxygen is produced as liquid. This ensures the main condenser sump is heavily purged of liquid and reduces the likelihood of hazardous contaminant accumulation.

Main condenser: Heat exchanger (reboiler/condenser) located in the base of the low-pressure column that vaporizes LOX from the low-pressure column by condensing nitrogen vapor from the high-pressure column.

Main condenser, falling film: Exchanger located in the base of the low-pressure column, with liquid coming directly from the low-pressure column or pumped from the LOX sump. This design has been in use since the mid-1990s.

Main condenser, thermosyphon: Exchanger that is mostly submerged in the LOX in the low-pressure column.

Main exchanger: First exchanger in the process train, which cools incoming feed air with outgoing oxygen and nitrogen product gases.

Perlite: A nonflammable insulation material that forms a lightweight powder aggregate when expanded by heat. It is used in cryogenic enclosures, such as the cold box.

Pool (pot) boiling: Similar to dry boiling. Concentration of the less volatile components occurs as the more volatile components are vaporized. In this case, the amount of liquid is not finite. Fresh liquid is constantly being added to the liquid present.

Pre-purification units (PPU): Vessels containing beds of activated alumina and/or molecular sieves to remove contaminants (e.g., CO_2, nitrogen oxides, hydrocarbons) from incoming compressed air. Contaminants can plug narrow passages in exchangers or create an explosion potential in the LOX. Sometimes referred to as FEP or front-end purification.

Pumped LOX plant: Air separation unit producing gaseous oxygen by withdrawing liquid oxygen from the process (low-pressure column sump) and pumping to an external vaporizer to provide product to customers.

REVEX (reversing exchanger): Heat exchangers where incoming compressed air is chilled against cold process gases to cause some contaminants to freeze out (moisture, CO_2, nitrogen oxides, some hydrocarbons). On a regular cycle, the flow of gases in the exchanger passages is reversed to "flush out" the contaminants. REVEX plants require additional hydrocarbon adsorbers in various parts of the plant to prevent hazardous accumulations. Also called RHE, reversing heat exchanger, REVEX technology has rarely been used in new plants since the late 1980s, although many older plants continue to operate.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

April 2021. This document has been completely revised. Significant changes include the following:

A. Changed the title of the standard to "Air Separation: Oxygen and Nitrogen" (from "Air Separation Processes").

B. Moved guidance specific to high-purity nitrogen used in semiconductor occupancies to Data Sheet 7-7, *Semiconductor Fabrication Facilities*.

C. Incorporated information from Data Sheet 7-52, *Oxygen*, and made that document obsolete.

D. Incorporated information from Data Sheet 7-35R, *Air Separation Processes*, and made that document obsolete.

E. Updated construction and location guidance on bulk storage of cryogenic liquids.

F. Updated protection guidance on compressors and other rotating equipment.

G. Updated guidance on industrial control systems.

H. Updated inspection, testing, and maintenance (ITM) guidance.

I. Added guidance on contaminant management.

J. Added guidance on contingency planning and sparing.

K. Updated loss history.

L. Reorganized the document to ensure consistency with other standards.

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

September 2010. Minor editorial changes were made for this revision.

June 2007. Adjusted loss data with some updated information.

May 2005. Minor editorial changes were done for this revision.

September 2004. Document was updated to include better guidance on preventing hydrocarbon contamination.

January 2000. The document was reorganized to provide a consistent format.

February 1975. Document was updated from information provided in the *Handbook of Industrial Loss Prevention* as part of Data Sheet 7-52, *Oxygen.*

April 1994. Document was updated to include new technology, PSA and VSA, as well as improvements in the cryogenic process mainly related to the control of hydrocarbon accumulation. It was also renumbered to the current designation and excluded information on liquid or gaseous oxygen storage, still in Data Sheet 7-52, *Oxygen.*

A reference document (DS 7-35R) provides an overview of several non-cryogenic oxygen and nitrogen recovery processes that have been commercialized in about the last 15 years.

Significant changes to the existing data sheet, or new information or recommendations are as follows:

1. Eliminated need for sprinklers for large compressor lube oil systems because of a lack of ignition sources and no loss history. This is consistent with the ''Exception‘‘ in Data Sheet 7-95, *Compressors.*

2. Eliminated reference to oil-type air filters and their need for sprinklers, and oil separators in the process air stream. This filter type is no longer used in new plants and compressor design has eliminated most, if not all, of the entrained oil problem.

3. Eliminated specific time period and temperature recommendations relative to hydrocarbon adsorbers and plant deriming. These features are defined in the design stages.

4. Added recommendation for fire barriers or spacing around oxygen compressors. This follows industry practice and is due to relatively frequent oxygen compressor fires. Barriers are installed to keep operating personnel away from the compressors and the possible fire exposure, as well as to reduce property exposure. Retroactivity to existing plants should be based on serious spacing deficiencies to nearby units and reasonable installation cost.

5. Added recommendation for CO_2 monitoring of air stream after passing through molecular sieves. This provides an additional level of supervision to prevent hydrocarbon carryover. With good procedures for hydrocarbon and acetylene monitoring and regular regeneration of molecular sieves, this recommendation is not retroactive.

6. Highlighted acceptable practice relative to hydrogen usage in the argon purification process.

7. Highlighted good process practices that can minimize the chance of unwanted hydrocarbon entry into the process during short shutdowns.

8. Information on the cryogenic process was updated and simplified. It highlights factors related to hydrocarbons and this material was relocated to a reference document.

9. Added description of non-cryogenic processes in the reference document.

10. Current loss history is provided as well as some historical perspectives related to the hydrocarbon explosion experience.

APPENDIX C BIBLIOGRAPHY

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