



GUIDELINE FOR SAFE PRACTICES FOR CRYOGENIC AIR SEPARATION PLANTS

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GUIDELINE FOR SAFE PRACTICES FOR CRYOGENIC AIR SEPARATION PLANTS

Prepared by AHG-3.32 of Working Group 3 Process and Equipment

As part of a programme of harmonisation of industry standards, the European Industrial Gases Association, (EIGA) has published EIGA Doc 145, *Guideline for Safe Practices for Cryogenic Air Separation Plants*, jointly produced by members of the International Harmonisation Council and originally published by the Compressed Gas Association as CGA P-8, *Guideline for Safe Practices for Cryogenic Air Separation Plants*.

This publication is intended as an international harmonised standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association, and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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Amendments from 147/20

Section	Change
2	Clarification of scope
6.2	New paragraph on siting
7.5	Additional recommendations for operation in smoke/haze conditions
12.3.2	Additional guidance for level measurement
12.10	New section on management of leaks in coldboxes
12.12.3	New text on low temperatures
12.13	New section on operation and maintenance

19.3	Additional <u>guidance on emergency procedures</u>
19.4	Additional <u>guidance on management of change</u>

Note Technical changes from the previous edition are underlined

1 Introduction

This publication provides guidance on the safe operation of cryogenic air separation plants. It is based on the experience of CGA member companies that operate cryogenic air separation units (ASUs).

Industrial cryogenic air separation has some potential hazards that must be recognised and addressed. The hazards include electricity, gases under pressure, very low temperatures, the ability of oxygen to accelerate combustion, and the asphyxiant properties of nitrogen, argon, and the rare gases [1].¹

Cryogenic air separation technology is not static; it has been progressing for decades and will continue to do so because of engineering development efforts. Consequently, plant process cycles, equipment, and operating conditions can be and are of varying kinds. Therefore, this publication includes generalised statements and recommendations on matters for which there is a diversity of opinion or practice. Users of this guide should recognise that it is presented with the understanding that it cannot take the place of sound engineering judgment, training, and experience. It does not constitute, and should not be construed to be, a code of rules or regulations.

2 Scope

This publication serves the interest of those associated or concerned with air separation plant operations and applies to safety in the design, location, construction, installation, operation, and maintenance of cryogenic air separation plants. Emphasis is placed on equipment and operational and maintenance features that are specific to cryogenic air separation processes. Limited coverage is given to plant equipment such as air compressors, which are used in other industrial applications and for which safe practices in design, installation, and use have already been established elsewhere. Further, as this publication is not intended as a universal safe practice manual for specific design and safety features, it is also important to refer to the operating manuals of the equipment suppliers.

Any new design and installation requirements contained in this edition only apply to new installations begun after the time of publication and not to existing installations. However, new requirements and recommendations may be considered by the user for existing operating units or those in the project phase.

The following are excluded from this publication:

- cylinder filling facilities;
- rare gas purification systems; and
- product transmission piping outside the plant boundaries.

3 Typical air separation unit features

Cryogenic ASUs have these features:

- air compression;
- air contaminant removal;
- heat exchange;
- distillation; and
- expansion (or other refrigeration sources).

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

Figure 1 is an example of a flow diagram for separating air by cryogenic distillation producing oxygen, nitrogen, and argon products. Air is compressed in the main air compressor (MAC) to between 4 atm and 10 atm. It is then cooled to ambient temperature. Trace contaminants such as water, carbon dioxide, and heavy hydrocarbons are removed using systems such as a pre-purification unit (PPU) or a reversing heat exchanger (REVEX). The main heat exchanger cools the air to near its liquefaction temperature before entering the high pressure distillation column. Some of the air is reduced in pressure in the expander to produce refrigeration, overcoming heat leak and process inefficiencies. Gaseous nitrogen from the top of the high pressure column is condensed by the reboiler and the liquid used to reflux both columns. Condensing nitrogen releases heat to vaporise liquid oxygen in the low pressure column sump, which is then taken as product or sent as stripping gas to the low pressure column.

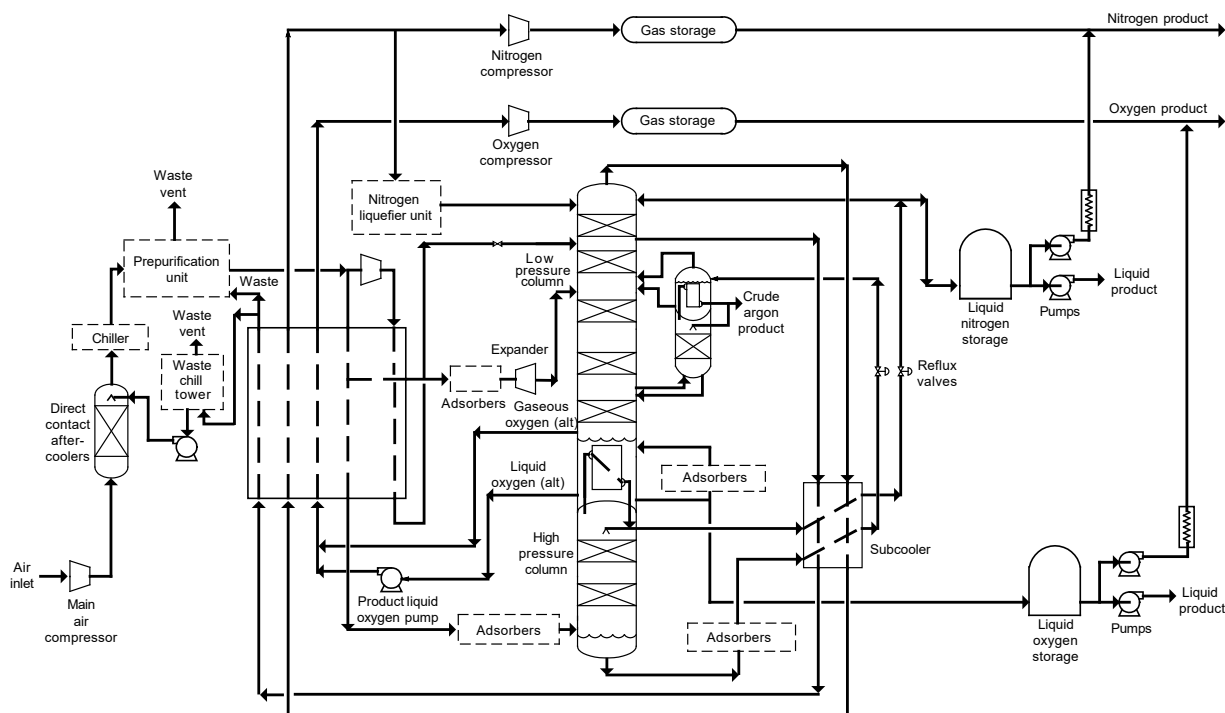


Figure 1 – Example of an air separation plant flow diagram

Oxygen has the highest boiling point of the three main components and is taken from the bottom of the low pressure column. Nitrogen is taken from the top of the low pressure or high pressure columns. An argon-rich stream can be withdrawn from the middle of the low pressure column and refined to a pure product in other distillation columns. The product streams are warmed to ambient temperature against incoming air in the main heat exchanger to recover the refrigeration. It is also possible to remove the products from the distillation system as liquid, if sufficient refrigeration is available. Producing large quantities of liquid products requires extra refrigeration, often supplied by a nitrogen liquefier unit. Liquid may be stored for pipeline backup or merchant sales.

There are two typical ASU configurations for producing pressurised oxygen. In the gas plant configuration (also called gaseous oxygen process or classic gas process), oxygen is taken as a vapour from the bottom of the low pressure column and warmed by incoming air in the main heat exchanger. If a high pressure oxygen product is needed, it is compressed to the required pressure. A liquid oxygen purge stream is taken from the sump of the low pressure column to prevent the trace contaminants from concentrating above allowable safety limits. In the pumped liquid oxygen process (also known as the internal compression process), oxygen is taken as a liquid from the low pressure column sump, pumped to the required pressure, and vaporised in the main exchanger against high pressure air from the booster air compressor. The pumped oxygen stream removes trace contaminants from the low pressure column sump, so a separate liquid oxygen purge stream from the low pressure column sump may be eliminated.

There are many other configurations of the ASU process that are specifically tailored for different products mixes and customer needs. A detailed discussion of these is beyond the scope of this publication.

4 Definitions

For the purpose of this publication, the following definitions apply.

4.1 Publication terminology

4.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

4.1.2 Should

Indicates that a procedure is recommended.

4.1.3 May

Indicates that the procedure is optional.

4.1.4 Will

Is used only to indicate the future, not a degree of requirement.

4.1.5 Can

Indicates a possibility or ability.

4.2 Technical definitions

4.2.1 Acid gas

Air contaminants such as chlorine, NO_x, and SO_x that can form acid when combined with water.

NOTE Acid gases can create corrosive conditions in brazed aluminium heat exchangers (BAHXs) and other equipment.

4.2.2 Adsorption

Purification process in which one or more components from a gas or liquid is preferentially adsorbed onto a solid desiccant or other adsorbent.

NOTE Typical adsorbents include:

- molecular sieve—granular adsorbent (typically 13X) used in air PPUs for water, carbon dioxide, and hydrocarbon removal;
- alumina—granular adsorbent typically used in air PPUs or dryers for water removal; and
- silica gel—granular adsorbent typically used in cryogenic adsorbers for carbon dioxide and hydrocarbon removal.

4.2.3 Asphyxiation

To become unconscious or die from lack of oxygen.

4.2.4 Blow out

Maintenance or commissioning procedure in which a fluid, typically dry air, is blown through piping and equipment to eliminate dirt, moisture, or other contaminants.

4.2.5 Brazed aluminium heat exchanger (BAHX)

Aluminium plate and fin heat exchanger consisting of corrugated sheets separated by parting sheets and an outer frame consisting of bars with openings for the inlets and outlets of fluids, equipped with headers and nozzles to connect to external piping.

NOTE The approximate thickness of the corrugated sheets is 0.2 mm to 0.5 mm, while the parting sheets have thicknesses between 1.0 mm and 2.4 mm. More information is provided in EIGA Doc 145, *Safe Use of Brazed Aluminium Heat Exchangers for Producing Pressurised Oxygen* [2].

4.2.6 Casing

Outside walls of a coldbox or cryogenic piping duct. The cross section can be circular or rectangular.

4.2.7 Catalyst

Material that helps promote a reaction but is not changed itself.

4.2.8 Cavitation

This phenomenon occurs when the pressure of a liquid drops to less than the vapour pressure of the liquid at a certain temperature. At this point, liquid vaporises, thereby creating vapour bubble. These bubbles can cause a pump to lose prime or suffer heavy vibration and damage.

4.2.9 Centrifugal

Dynamic compressor or pump that works by accelerating a fluid in a rotating impeller with subsequent conversion of this energy into pressure.

4.2.10 Cleanup

Removing trace contaminants from a stream or from process equipment.

4.2.11 Coldbox

Structure that contains cryogenic distillation columns, other process equipment, piping, and insulation. It can also refer to the cryogenic portion of an ASU.

4.2.12 Control system

System that responds to input signals from the process, operator, or both and generates an output that causes the process to operate in the intended manner.

4.2.13 Crude argon purification system

Warm equipment including compressors, catalytic reactors, heat exchangers, dryers, and chillers used for removing oxygen from crude argon.

4.2.14 Cryogenic liquid

Liquid that is extremely cold, less than $-90\text{ }^{\circ}\text{C}$ ($-130\text{ }^{\circ}\text{F}$).

4.2.15 Dead end boiling (pool boiling, pot boiling)

Condition occurring in thermosyphon reboilers where, due to blockages, the flow of liquid is restricted within the channels of the reboiler, thereby reducing the removal of contaminants by the flushing action of the liquid. Also known as pool or pot boiling. This phenomenon can also occur in cavities and sections of piping where oxygen-enriched liquid can be trapped and vaporised by heat leak.

NOTE This process is particularly hazardous when the oxygen-enriched liquid contains hydrocarbons that become concentrated during vaporisation.

4.2.16 Deoxidation or deoxo

Catalytic removal of trace oxygen contaminant from a gas by a reaction with hydrogen, typically in warm argon production in ASUs.

4.2.17 Deoxo unit

Catalytic-based system used in some argon refining systems to remove oxygen. Hydrogen is added to the crude argon stream and then reacts with oxygen to form water.

4.2.18 Deriming

Periodic preventive maintenance procedure where the process equipment is warmed up while simultaneously being swept with clean dry gas to remove any accumulated moisture, carbon dioxide, and atmospheric contaminants.

NOTE Also known as defrosting, de-icing, and thawing.

4.2.19 Differential temperature (ΔT)

Temperature difference between two streams in a heat exchanger, which is an indicator of the exchanger's performance and efficiency.

4.2.20 Distance piece

Extended spacer, intermediate support, or carrier frame that isolates the process end of a pump or compressor from its motor or bearings to prevent migration of process fluid, oil, heat, or refrigeration.

4.2.21 Double block and bleed

Piping or instrument arrangement that combines two block (or isolation) valves in series with a vent valve in between the block valves as a means of releasing pressure between the block valves with the intent to provide positive isolation.

4.2.22 Dry boiling

Condition occurring where oxygen-enriched liquid enters cavities and sections of piping or equipment and is totally vaporised, thereby concentrating any less volatile contaminants by extremely high factors.

NOTE Also known as dry vaporisation.

4.2.23 Exothermic

Reaction that produces heat.

4.2.24 Expander

Machine that expands a fluid from higher to lower pressure thereby removing energy (work) and creating refrigeration.

4.2.25 Failsafe

When a failure of a component of the system occurs, the resulting situation does not present a safety concern.

NOTE One example is isolation valves closing when the plant air or power supply fails.

4.2.26 Filtering device

Device that removes and retains particles from a liquid or gas stream.

NOTE The particle size removed is dependent on the actual device design. The terms filter, screen, and strainer are sometimes used interchangeably; however, they can be classified by the particle size removed as follows:

- strainer—device that removes and retains relatively coarse particles;
- screen—device that removes and retains fine particles; or
- filter—device that removes and retains very fine particles.

4.2.27 Fouling

Blockage or surface coating with any contaminants in any plant equipment (for example, heat exchanger, expanders, etc.) that can adversely affect its pressure drop or thermal performance.

NOTE In an ASU, blocking or plugging is usually caused by frozen carbon dioxide, water, or hydrocarbons in cryogenic exchangers. Fouling is also a concern with heat exchangers within the cooling system.

4.2.28 Getter

Reactive material that removes trace contaminants from a gas.

NOTE Since the contaminant is chemically adsorbed by the getter, getters can be either consumed or regenerated.

4.2.29 Inert gas / Inert liquid

Fluids that do not readily react with other materials under normal temperatures and pressures.

NOTE Nitrogen, argon, and helium are examples of inert gases.

4.2.30 Inlet guide vanes

Device on the inlet of a compressor that changes the capacity of the machine more efficiently than a suction throttling valve.

4.2.31 Inlet nozzle

Device on the inlet of an expander that is part of the expansion process.

NOTE Movable inlet nozzles can be used to adjust the capacity of the expander.

4.2.32 Instrumented system

System composed of sensors (for example, pressure, flow, temperature transmitters), logic solvers or control systems (for example, programmable controllers, distributed control systems), and final elements (for example, control valves) designed to perform a specific function.

NOTE For more information, see IEC 61511-1, *Functional safety—Safety Instrumented Systems for the Process Industry Sector—Part 1: Framework, definitions, system, hardware and application programming requirements* [3].

4.2.33 Joule–Thomson expansion

Process by which a fluid is expanded adiabatically (no work removed) from high pressure to lower pressure, usually through a valve.

NOTE—For gas applications in air separation plants, this results in a temperature drop.

4.2.34 Labyrinth

Type of gas seal that uses a series of teeth to minimise leakage of the process fluid.

4.2.35 Lockout

Condition where a device cannot be operated without a wilful, conscious action to do so to ensure safety by positively isolating energy sources (pressure, electrical, temperature, and chemical).

NOTE An example is when electricity is turned off and cannot be regained without removing a protective device such as a padlock from the actuating device. Another example is a valve where the handle is removed and stored securely until it is safe to operate the valve.

4.2.36 Lower explosive limit (LEL)

Lowest concentration of a flammable gas in an oxidant that will propagate when ignited.

NOTE LEL is sometimes referred to as lower flammability limit (LFL).

4.2.37 Net positive suction head (NPSH)

Margin of difference (measured in height) between the actual pressure of a liquid flowing into a pump and the vapour pressure of the liquid.

4.2.38 Nitrogen NF

Nitrogen that meets *United States Pharmacopeia and National Formulary (USP–NF)* requirements [4].

NOTE See CGA G-10.1, *Commodity Specification for Nitrogen*, for additional information [5].

4.2.39 Nozzle

Pipe connected to any vessel.

4.2.40 Oxygen-deficient atmosphere

Atmosphere in which the oxygen concentration by volume is less than 19.5%.

4.2.41 Oxygen-enriched atmosphere

Atmosphere in which the oxygen concentration exceeds 23.5%.

4.2.42 Oxygen USP

Oxygen that meets *USP–NF* requirements [4].

NOTE See CGA G-4.3, *Commodity Specification for Oxygen*, for additional information [6].

4.2.43 Precipitate

Formation of a solid from a liquid or vapour solution when the solubility limit for a component is exceeded.

4.2.44 Pressure relief device (PRD)

Self-contained device designed to protect a vessel or piping from achieving pressures higher or lower (vacuum) than its design to prevent failure of the piping or vessel; includes safety relief valves and rupture disks.

4.2.45 Purge

Elimination of an undesirable contaminant by displacement with another fluid.

NOTE A nitrogen purge of process equipment prevents the contact of moisture with cryogenic equipment. Liquid oxygen containing-hydrocarbons are purged from the reboiler sump with clean liquid oxygen.

4.2.46 Rare gases

Neon, krypton, and xenon are considered rare gases.

NOTE The rare gases krypton and xenon are sometimes recovered at low concentrations from cryogenic air separation plants. Krypton and xenon can be extracted from the low pressure column sump liquid through further processing.

4.2.47 Reciprocating

Positive displacement-type compressor, expander, or pump that uses pistons.

4.2.48 Regeneration

Reactivation of a spent or loaded adsorbent vessel using a hot and / or low pressure gas.

4.2.49 Safe area

Location where gases are vented safely to prevent harm to personnel or property.

NOTE In a safe area, the surrounding materials should be compatible with the exhaust gas.

4.2.50 Safety data sheet (SDS)

Documents describing a material and its associated hazards mandated by the government and made available by the material supplier.

4.2.51 Safety instrumented system (SIS)

System used to implement one or more functions necessary to prevent a hazard from arising and / or to mitigate its consequences.

NOTE A SIS is composed of any combination of sensors (for example, pressure, flow, temperature transmitters), logic solvers or control systems (for example, programmable controllers, distributed control systems), and final elements (for example, control valves). Use of the term SIS implies IEC 61511 has been used to design, operate, and maintain the safety system [3].

4.2.52 Solubility

Amount of a component that can remain dissolved in a liquid or vapour without precipitating out as a solid.

4.2.53 Structured packing

Sheets of corrugated metal arranged in a distillation column to promote intimate contact between vapour flowing upward with liquid flowing downward.

4.2.54 Sump

Bottom of a distillation column or other vessel that can contain a liquid inventory, hold-up, or reserve level.

4.2.55 Tagout

Written notification that a piece of equipment is out of service and cannot be operated without clearance from authorised personnel.

NOTE Equipment that has been tagged out typically has a paper tag attached directly to it indicating that the item is out of service.

4.2.56 Work permits

Procedural documents highlighting special safety considerations that are issued to allow work to commence in a specific location.

5 Health hazards

Some health hazards are directly associated with the compressed gas industry. Properties of certain gas products can subject personnel to extreme cold temperatures, oxygen-deficient (asphyxiating) atmospheres, or oxygen-enriched (increased fire risk) atmospheres. A basic knowledge of the gas properties and taking precautions such as wearing protective equipment minimises the risks of these hazards. Refer to the producer's safety data sheets (SDS) for specific information on materials handled in air separation plants.

5.1 Cryogenic liquids

The products of a cryogenic air separation plant have associated hazards such as:

- Cryogenic injuries or burns resulting from skin contact with very cold vapour, liquid, or surfaces. Effects are similar to those of a heat burn. Severity varies with the temperature and time of exposure. Exposed or insufficiently protected parts of the body can stick to cold surfaces due to the rapid freezing of available moisture, and skin and flesh can be torn on removal;
- Risk of frostbite or hypothermia (general cooling of the body) in a cold environment. There can be warning signs, in the case of frostbite, while the body sections freeze. As the body temperature drops, the first indications of hypothermia are bizarre or unusual behaviour followed, often rapidly, by loss of consciousness;
- Respiratory problems caused by the inhalation of cold gas. Short-term exposure generally causes discomfort; however, prolonged inhalation can result in effects leading to serious illness such as pulmonary oedema or pneumonia; and
- Hazardous concentrations and / or reduced visibility can also occur at considerable distances from the point of discharge, depending on topography and weather conditions. Cold gases are heavier than air, tend to settle and flow to low levels, and can create a dense water vapour fog.

See EIGA Doc 23.12, *Cryogenic Liquids, Spills and Vapour Clouds*, for additional details [7].

5.2 Gas products

Nitrogen and argon are simple asphyxiants and if present in sufficient quantity can reduce the oxygen in the local atmosphere to less than that required to support life. If there are any significant quantities of hydrocarbon contaminants, there can be some nausea, narcosis, or dizziness. Removal from exposure generally results in return to normal body and behavioural functions. Oxygen-enriched atmospheres increase susceptibility to ignition and combustibility rates can be many times that of normal atmospheres.

5.3 Asphyxiation

The normal oxygen concentration in air is approximately 21% by volume. Gas containing less than 19.5% oxygen constitutes a hazardous working environment as defined by Title 29 of the *U.S. Code of Federal Regulations* (29 CFR) Part 1910.146 [8]. The depletion of the quantity of oxygen in a given volume of air by displacement with an inert gas is a potential hazard to personnel, see EIGA Doc 23.12, 29 CFR and EIGA Doc 44, *Hazards of Oxygen-Deficient Atmospheres* [7, 8, 9]. Also see the U.S. Chemical Safety and Hazard Investigation Board (CSB) materials on the hazards of nitrogen asphyxiation [10, 11, 12].

When the oxygen content of air is reduced to approximately 15% or 16%, the rate of burning of combustible materials significantly decreases. The flame of ordinary combustible materials including those commonly used as fuel for heat or light is extinguished. This can be the first indication of an oxygen-deficient hazard. Somewhat less than this concentration, an individual breathing the atmosphere is mentally incapable of diagnosing the situation. The symptoms of sleepiness, fatigue, lassitude, loss of coordination, errors in judgment, and confusion are masked by a state of euphoria giving the victim a false sense of security and well-being. See Table 1 for other typical symptoms of oxygen-deficient atmospheres.

Human exposure to atmospheres containing 12% or less oxygen brings about unconsciousness without warning and so quickly that individuals cannot help or protect themselves. This is true if the condition is reached either by immediate change of environment or by gradual depletion of oxygen. The individual's condition and degree of activity has an appreciable effect on signs and symptoms at various oxygen levels. In some cases, prolonged reduction of oxygen can cause brain damage even if the individual survives.

Areas where it is possible to have low oxygen content, particularly in process buildings and control rooms, shall be well ventilated. Inert gas vents should be piped outside of buildings or to a safe area. Where an oxygen-deficient atmosphere is possible, special precautions such as installation of oxygen analysers with alarms, ensuring a minimum number of air changes per hour, implementing special entry procedures, or a combination of these procedures shall be taken. In process buildings and control rooms, warning signs shall be posted at all hazard area entrances to alert personnel to the potential hazard of an oxygen-deficient atmosphere in accordance with OSHA requirements in 29 CFR Part 1910 [8]. Oxygen analyser sensors shall be located in positions most likely to experience an oxygen-deficient atmosphere and the alarm shall be clearly visible, audible, or both at the point of personnel entry.

When an unsafe breathing atmosphere can occur, self-contained breathing apparatus (SCBA) or approved air lines and masks should be used, particularly when personnel enter enclosed areas or vessels. Breathing air should come from a verified source. A plant instrument air system shall not be used as a source of breathing air.

Personnel working in or around oxygen-deficient atmospheres shall use proper procedures including confined space entry.

DANGER: Entering an area with an oxygen-deficient atmosphere without following proper procedures can cause serious injury or death.

Table 1 – Effects at various oxygen breathing levels

Oxygen percent at sea level (atmospheric pressure = 760 mmHg)	Effects
20.9	Normal
19.0	Some adverse physiological effects occur, but they are unnoticeable.
16.0	Increased pulse and breathing rate. Impaired thinking and attention. Reduced coordination.
14.0	Abnormal fatigue upon exertion. Emotional upset. Faulty coordination. Poor judgment.
12.5	Very poor judgment and coordination. Impaired respiration that could cause permanent heart damage. Nausea and vomiting.
<10	Inability to perform various movements. Loss of consciousness. Convulsions. Death.
NOTES 1 Adapted from ANSI/ASSE Z88.2, <i>Practices for Respiratory Protection</i> [13]. 2 These indications are for a healthy average person at rest. Factors such as individual health (such as being a smoker), degree of physical exertion, and high altitudes can affect these symptoms and the oxygen levels at which they occur.	

5.4 Oxygen hazards

Oxygen concentrations greater than 23.5% create fire hazards but not asphyxiation hazards. Oxygen is not combustible, but it promotes very rapid combustion of flammable materials and some materials that are normally regarded as being relatively non-flammable. Although a source of ignition is always necessary in combination with flammable materials and oxygen, control or elimination of flammables is a precautionary step. Lubricating oils and other hydrocarbon materials can react violently with pure oxygen and the combination shall be avoided.

Personnel should not be exposed to oxygen-enriched atmospheres because of increased risks of fire. As concentrations increase above 23.5% oxygen, ease of ignition of clothing increases dramatically. Once ignited by even a relatively weak ignition source such as a spark or cigarette, clothing can burst into flame and burn rapidly. In oxygen-enriched atmospheres, the fibres on clothing and even body hair and oil are subject to flash fire that spreads rapidly over the entire exposed surface.

Areas where it is possible to have high oxygen content shall be well ventilated. Gas vents shall be piped outside of buildings or to a safe area. Where an oxygen-enriched atmosphere is possible, special precautions such as installation of oxygen analysers with alarms, ensuring a minimum number of air changes per hour, implementing special entry procedures, or a combination of these procedures shall be taken. Warning signs shall be posted at all entrances to alert personnel to the potential hazard of an oxygen-enriched atmosphere. For additional information on oxygen hazards see EIGA Doc 4, *Fire Hazards of Oxygen and Oxygen-Enriched Atmospheres* [14].

5.5 Protective clothing and personal protective equipment

Guidelines for the selection of protective clothing can be found in EIGA Doc 136, *Selection of Personal Protective Equipment* [15].

Protective clothing and personal protective equipment (PPE) serve to minimise the risk of injury due to fire hazards when working with oxygen or burns when working with cryogenic liquids or gases, but prevention of the hazard should be the primary objective.

Insulated or leather gloves (untanned and oil-free for oxygen service) shall be worn when handling anything that is cooled with cryogenic liquids and during cryogenic liquid loading and unloading activities. Gloves shall fit loosely so they can be removed easily if liquid splashes on or in them.

Personnel shall ensure that the gloves being used for handling cryogenic equipment are kept clean and free from oils, grease, or other contaminants. Personnel should have two sets of gloves—one for

handling cryogenic equipment and another for performing other tasks (for example, vehicle fuelling). Ensure that the gloves are not allowed to become wet with liquid cryogenic product. If the gloves accidentally become wet with the liquid product, personnel should immediately remove the gloves and use another pair of clean gloves. Ensure that the gloves are stored so that they do not come into contact with other tools or equipment that could have debris or other contaminants. For example, consider storing them separately in a clean, sealable plastic bag. If the gloves are wetted with liquid product, make sure that they are allowed to dry normally before storing. Training of personnel regarding proper use of gloves during handling of cryogenic equipment is essential.

Safety glasses with side shields and a face shield shall be worn at all times when handling cryogenic liquids.

There are a number of flame retardant materials available such as Nomex® for work clothing, but they can burn in high-oxygen atmospheres. There is an advantage in these materials as most of them would be self-extinguishing when removed to normal air atmospheres. All clothing should be clean and oil-free as these contaminants compromise the properties of these materials. Footwear should not have nails or exposed metallic protectors that could cause sparking.

If individuals inadvertently enter or are exposed to an oxygen-enriched atmosphere, they shall leave as quickly as possible. After exposure, avoid sources of ignition and do not smoke for at least 30 minutes. Undo or loosen their clothing and ventilate it for at least 15 min in order to remove the excess oxygen.

6 General plant considerations

6.1 Site selection

Air separation plant safety begins with a safety evaluation of the proposed plant site and the surrounding area. Generally, air separation plants are located in or near industrial areas as an adjunct to other industrial or chemical plants. A quantified risk assessment should be performed when plants are sited in proximity of hydrocarbon, corrosive, toxic, or other hazardous chemical sources. A plant installation should conform to the applicable industry consensus standards and shall adhere to all applicable local, state, provincial / territorial, and federal regulations. The plant operation should be reviewed for compatibility with the surrounding area. For example, the potential hazard of the cooling tower plume or cryogenic fog to nearby plants or vehicular traffic should be recognised. Adequate space should be provided for cryogenic liquid disposal. Environmental impacts of air separation plants are addressed in EIGA Doc 94, *Environmental Impacts of Air Separation Units* [16].

6.2 Safety factors in plant layouts

Plant layouts should be developed, reviewed, and approved to ensure safe layouts between major components such as occupied buildings, air separation unit coldboxes, bulk liquid cryogenic storage, facilities for filling road tankers, and fuel pipelines and storage. An occupied plant control room should be located a minimum of 15.2 m (50 ft) from air separation unit coldboxes and bulk liquid cryogenic storage tanks because of risk of either oxygen enrichment or deficiency as the result of a cryogenic gas or liquid release.

The use of valve pits, trenches, or both for cryogenic gas or liquid piping systems is not recommended because oxygen-enriched or oxygen-deficient atmospheres can occur very easily with such installations. If gas and liquid piping systems are installed in enclosed spaces, precautionary measures such as forced ventilation and alarm systems are recommended. Appropriate warning signs shall be posted.

Oxygen-enriched liquid drain lines should not be installed in a trench. Over time, trenches can accumulate oil, grease, and trash or other debris. If a leak in the line develops, a fire could result.

Caution should be taken to prevent liquid spills from entering floor drains or sewer systems. In areas where oxygen-enriched fluids are likely to contact the ground, asphalt ground cover shall be avoided, due to the potential for an energy release as a result of oxygen contact with hydrocarbons found in asphalt. For more information, see EIGA Doc 179, *Liquid Oxygen, Nitrogen, and Argon Cryogenic Tanker Loading Systems* [17].

Flammable, toxic, and other hazardous chemical pipe routing on the air separation plant site should be limited to those required for air separation plant operation. If it is necessary to route piping for transporting such chemicals across the air separation plant process equipment, product handling, storage and cryogenic spill / detention area, a risk assessment is required to select the appropriate installation details such as:

- above or underground routing;
- hazards from failure of the piping; and
- potential impact on the piping from air separation plant incidents.

6.3 Materials of construction

The materials used in an air separation plant are exposed to a wide range of temperatures, pressures, and purities during operation. Materials shall be selected that are compatible with the expected conditions including normal operation, startup, shutdown, and process upsets.

For an oxygen system to operate safely, all parts of the system shall be reviewed for compatibility with oxygen under all conditions they encounter [18, 19]. The system shall be designed to prevent oxygen combustion by:

- selecting compatible material;
- operating within the designed pressure, temperature, and flow limits; and
- obtaining / maintaining cleanliness required for oxygen service.

Substitution of materials should not be made without first consulting a qualified engineering source. The vendor supplying the material may also be contacted for pertinent information.

6.3.1 Handling of aluminium packing during installation

Aluminium packing for columns shall be kept clean and dry during storage, transport, and installation.

A seal should be maintained to prevent water ingress into aluminium packing when stored outdoors or installed in the column. The packed column should be pressurised for transportation and be checked for pressure at delivery.

For more information regarding aluminium-structured packing, see EIGA Doc 144, *Safe Use of Aluminium-Structured Packing for Oxygen Distillation* [20].

6.3.2 Metals

While common construction materials such as carbon steel, aluminium, and copper are used extensively in fabricating air separation plant components, it is important to remember that the use of these materials is selective and shall be compatible with the operating conditions [19]. For example, common carbon steel is not used at temperatures less than $-29\text{ }^{\circ}\text{C}$ ($-20\text{ }^{\circ}\text{F}$) because at these temperatures it loses ductility, becomes brittle, and is subject to failure under impact conditions. Some metals that can be used safely in temperatures less than $-29\text{ }^{\circ}\text{C}$ ($-20\text{ }^{\circ}\text{F}$) are austenitic stainless steel, aluminium, copper, Monel®, brass, silicon-copper, and 9% nickel (ASTM A353 steel). Reference information on the use of metals includes stainless steel, aluminium, copper, Monel®, and brass [21, 22, 23, 24, 25, 26, 27, 28, 29].

Because of cost, carbon steel is generally used in temperatures greater than $-29\text{ }^{\circ}\text{C}$ ($-20\text{ }^{\circ}\text{F}$) and at ambient temperature conditions for interconnecting process piping in air separation and liquefaction units, storage vessels, and pipelines for either oxygen, air, or any of the inert gases such as argon or nitrogen [30, 31]. In special cases such as when moisture is present, stainless steel or other equally suitable metal should be considered to prevent corrosion.

If high surface area aluminium packing contacts water, hydrogen gas is generated by oxidation. Distillation columns packed with aluminium packing can cause explosions during fabrication or erection if water has entered the column and if the hydrogen gas generated forms an explosive mixture with air.

It is recommended to maintain a good tightness regarding water ingress for aluminium packing outdoor storage and for packed column on-site assembly. It is preferred to pressurise packed column for transportation and have a pressure check at delivery. It is recommended to have vents at high points of the column in order to be able to purge the hydrogen possibly accumulated and check the hydrogen content prior to working on the column.

6.3.3 Non-metals

Non-metallic materials such as gaskets, valve packing, insulation, and lubricants shall be checked to determine if they can be used for a particular application [32]. All factors associated with their use such as temperature, pressure, etc., shall be considered in deciding if a material can be used without decreasing the design safety integrity of the system. In an oxygen system, the quantity of non-metallic materials should be kept to a minimum and, where possible, be kept out of the direct flow of the gas stream.

6.4 Insulation – other than coldbox

Interconnecting process lines between components of an air separation plant operating at low temperatures require insulation to reduce process heat leak to an acceptable minimum and to prevent exposure of personnel to extremely low temperatures. The temperature and service of the line determine the type of insulation used.

Insulation for liquid oxygen lines or other lines that can come in contact with liquid oxygen should be non-combustible to protect against a possible reaction in the event of a liquid leak. Other process lines operating at temperatures warmer than the liquefaction point of air, approximately $-192\text{ }^{\circ}\text{C}$ ($-313\text{ }^{\circ}\text{F}$), may be insulated with any commercially acceptable insulation that meets design requirements. Insulation that is non-combustible in air should be given preference. Oxygen-compatible binders, sealing compounds, and vapour barriers shall be used on lines carrying oxygen or oxygen-enriched gases or liquids.

Process lines operating at temperatures colder than the liquefaction point of air should be insulated with material compatible with oxygen. If the insulation cracks or deteriorates at these temperatures, air is diffused into the insulation, condenses against the surface of the pipe, and exposes the insulation material to oxygen-enriched liquid. For vacuum-jacketed oxygen piping, see EIGA Doc 217, *Vacuum Jacketed Piping in Liquid Oxygen Service* [33].

Personnel shall be protected from hot lines (greater than $60\text{ }^{\circ}\text{C}$ [$140\text{ }^{\circ}\text{F}$]) by either insulating the line or other barriers preventing access while the line is hot.

6.5 Cleaning

All materials for use in or interconnected with oxygen systems shall be suitably cleaned before the system is put into service. Mill scale, rust, dirt, weld slag, oils, greases, and other organic material shall be removed. An improperly cleaned line in oxygen service can be hazardous because particulates, greases, oils, and other organic materials can ignite a fire. Fabrication and repair procedures should be controlled to minimise the presence of such contaminants and thereby simplify final cleaning procedures. See EIGA Doc 33, *Cleaning of Equipment for Oxygen Service* and ASTM G93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-Enriched Environments* [34, 35].

Cryogenic process equipment and piping that handle inert fluids shall be cleaned for cryogenic service. This prevents foreign material from reaching other parts of the ASU.

6.6 Electrical requirements

Air separation plants are not typically considered hazardous locations for electrical equipment as defined by Article 500 of NFPA 70, *National Electrical Code*® [36]. Therefore, in most cases, general purpose or weatherproof types of electrical wiring and equipment are acceptable depending on whether the location is indoors or outdoors. Plants can have specific areas or equipment that necessitate special consideration due to handling of combustible or flammable materials. Such areas could include refrigeration systems using a hydrocarbon or ammonia refrigerant or an argon purification unit involving the use and handling of hydrogen.

In areas where high oxygen concentrations could be expected, electrical equipment with open or unprotected make-and-break contacts should be avoided. The simple mitigation of locating electrical equipment away from areas where high oxygen concentrations can occur eliminates potential hazards in these situations.

Design considerations specified in the appropriate national, regional, and local codes shall be followed. Industry guidelines regarding design considerations should also be considered. For further information, see NFPA 70 (in the United States) or EIGA Doc 134, *Potentially Explosive Atmospheres*, *EU Directive 1999/92/EC* (in Europe) [36, 37].

6.7 Noise

The noise produced by compressors and their drives, by expansion turbines, by high gas velocities through piping and valves, and by pressure relief valves, vents, or bypasses shall be considered from the standpoint of potential hazard of hearing damage to employees. To assess the hazard, noise surveys should be performed after initial startup and when modifications are made that could change the noise emitted [38, 39, 40, 41, 42]. Noise abatement and use of personnel ear protection shall follow government guidelines (see 29 CFR Part 1910.95 [8]). Local, state, and provincial / territorial regulations can be more restrictive and shall be investigated.

Equipment operated under varying conditions can require additional noise surveys to identify the highest noise scenario. Periodic audiometric checks of personnel can be necessary depending on exposure times and noise levels.

7 Intake air quality

Air quality can have an impact on the air separation plant site selection and shall be evaluated. The air separation plant typically is located in an industrial area and thus a degree of contamination released from industrial and / or chemical plant operations can be expected to be present in the air. Trace contaminants in the atmospheric air, particularly hydrocarbons, have a direct bearing on the safe operation of an air separation plant. It is important to identify these contaminants and their levels of concentration in the atmospheric air. Short-term air quality analyses are not representative of long-term air contaminant levels. Changing site conditions can have an impact on air quality and should be evaluated periodically or when the surrounding industries change.

7.1 Contaminants

Trace contaminants can be put into three main categories based on the potential problems they cause in the ASU (plugging, reactive, or corrosive) as shown in Table 2. See 9.1, which describes in detail how each of the contaminants in Table 2 is dealt with within the ASU process.

Plugging contaminants concentrate, precipitate out as a solid, or both in the ASU process. While plugging is an operating problem, it can also lead to dry boiling or pool boiling, which can in turn concentrate the reactive contaminants to form flammable mixtures. The plugging contaminants of most concern are water, carbon dioxide, and nitrous oxide.

Reactive contaminants can concentrate within the ASU and form flammable mixtures with oxygen or enriched air. The most important reactive contaminants in air are methane, ethane, ethylene, acetylene, propane, and propylene. The other higher boiling point hydrocarbons are typically treated together. Hydrocarbon aerosols from smoke and haze are a special type of reactive contaminant and are

discussed in 7.5. NO_x and ozone are also reactive, but are not a major concern in properly operated ASUs. For more information, see EIGA Doc 65 [43].

Table 2 – Plugging, reactive, and corrosive contaminants in air

Plugging		Reactive		Corrosive	
Chemical name	Symbol	Chemical name	Symbol	Chemical name	Symbol
Water	H ₂ O	Methane	CH ₄	Sulphur dioxide	SO ₂
Carbon dioxide	CO ₂	Acetylene	C ₂ H ₂	Sulphur trioxide	SO ₃
Nitrous oxide	N ₂ O	Ethylene	C ₂ H ₄	Hydrogen sulphide	H ₂ S
		Ethane	C ₂ H ₆	Chlorine	Cl ₂
		Propylene	C ₃ H ₆	Hydrochloric acid	HCl
		Propane	C ₃ H ₈	Ammonia	NH ₃
		Other hydrocarbons		Other sulphur compounds	
		Oxides of nitrogen	NO _x	Other chlorides	
		Ozone	O ₃		

NOTE—This table was originally developed for EIGA Doc 65, *Safe Operation of Reboilers/Condensers in Air Separation Units* [43].

The previously discussed contaminants concentrate in oxygen. Hydrogen and carbon monoxide concentrate in nitrogen, waste nitrogen product, or both and are generally not safety hazards.

Corrosive contaminants (acid gases and ammonia from sources such as ambient air or cooling water) can react with equipment and piping causing operating problems and impacting equipment life. Since this publication is primarily dealing with safety, these contaminants are not discussed in detail.

Table 3 is a typical default air quality design basis that in the absence of other data can be used as the maximum simultaneous concentrations in the air intake to an ASU. Changes to the designs of various ASU components can be required if these concentrations are exceeded. Actual data for the locality should be provided to the ASU supplier whenever such information is available.

Table 3 – Typical default air quality design basis

Contaminants	Symbol	Design air quality (ppm/v)
Acetylene	C ₂ H ₂	0.3
Carbon dioxide	CO ₂	425
Other hydrocarbons	C ₄ +	1
Ethane	C ₂ H ₆	0.1
Ethylene	C ₂ H ₄	0.1
Methane	CH ₄	5
Oxides of nitrogen	NO _x	0.1
Nitrous oxide	N ₂ O	0.35
Propane	C ₃ H ₈	0.05
Propylene	C ₃ H ₆	0.2

7.2 Reactive contaminants that concentrate in oxygen

Hydrocarbons and most other reactive contaminants have boiling temperatures higher than that of oxygen. They concentrate in the oxygen-enriched liquids found in the sumps of columns and reboilers. The primary hazard is that the hydrocarbons concentrate in liquid oxygen. If these contaminants concentrate to the lower explosive limit (LEL), a reaction with oxygen can occur. The LEL of hydrocarbons in gaseous oxygen is between 5% and 10% when expressed as methane equivalent, and the LEL in liquid oxygen is slightly higher [44].

The specific hazards of each hydrocarbon are listed in the following paragraphs:

- Methane is slightly less volatile than oxygen and is completely soluble in liquid oxygen. It is somewhat difficult to concentrate methane to unsafe levels in most ASU processes;
- Ethane's volatility and solubility in liquid oxygen, while less than methane, poses no significant potential to concentrate to unsafe levels or form a second liquid phase provided that an adequate liquid purge is maintained on the reboiler sump;
- Ethylene presents a special hazard because it can precipitate as a solid under some ASU operating conditions, primarily when boiling liquid oxygen at less than 44 psia (303.4 kPa, abs), see EIGA Doc 145 [2].² If an ethylene source is nearby, consideration should be given to plant design to ensure that ethylene remains within safe limits either by changing the process, adding analytical instrumentation, or increasing the liquid purge on the reboiler sump;
- Acetylene is a very hazardous reactive contaminant. Because acetylene has a low solubility in liquid oxygen, if it enters the coldbox it concentrates in liquid oxygen and precipitates out as a solid at concentrations as low as 4 ppm to 6 ppm (depending on the liquid oxygen pressure). The solid is relatively unstable and requires little energy to ignite. ASUs equipped with PPUs remove all of the acetylene from the air so none enters the coldbox. Plants equipped with REVEX do not remove acetylene from the incoming air and shall deal with it in the coldbox, typically by using cryogenic adsorbers;
- Propane is a relatively hazardous hydrocarbon because of its low volatility relative to oxygen and its ability to form a second liquid phase if its concentration is high enough. At low pressures, the second liquid phase forms before its concentration in liquid oxygen reaches the LEL. This second liquid phase of relatively pure propane could then react with the oxygen-rich phase, if ignited. Propane is not removed by the REVEX and is only partially removed by the PPU; the remainder shall be removed by liquid purge;
- Propylene is similar to propane in that it forms a second liquid phase in liquid oxygen if its concentration is high enough. This second liquid phase is reactive. However, propylene is removed relatively easily either by PPUs or cryogenic adsorption;
- Other hydrocarbons are the higher boiling point hydrocarbons (C4+). As the molecular weight increases, the solubility in liquid oxygen decreases. However, these are dealt with relatively easily by all trace contaminant removal systems provided that these systems are operated properly;
- NO_x can react with oxygen but are removed either by the PPU or cryogenic adsorption. NO_x compounds are primarily nitric oxide and nitrogen dioxide in atmospheric air and are the by-products of incomplete combustion. If they enter the coldbox, nitric oxide and nitrogen dioxide form increasingly higher molecular weight NO_x compounds (nitrogen trioxide, dinitrogen tetroxide, and dinitrogen pentoxide), which can then precipitate and plug equipment. At cold temperatures, NO_x compounds can react with any unsaturated dienes found in REVEXs to form explosive gums [46, 47, 48]; and

NOTE NO_x (nitric oxide and nitrogen dioxide) are different compounds than nitrous oxide.

- Ozone is unstable and decomposes to oxygen-releasing heat, which is a potential hazard. Ozone is removed either by PPU or cryogenic adsorption.

7.3 Reactive contaminants that concentrate in nitrogen

Hydrogen and carbon monoxide have boiling points less than oxygen and thus concentrate in nitrogen. The concentration factor is typically only 2 times to 10 times, so they remain at low ppm concentration.

² psi, bar, and kPa shall indicate gauge pressure unless otherwise noted as (psia, bar, abs, and kPa, abs) for absolute pressure or (psid, bar, dif, and kPa, differential) for differential pressure. All kPa values are rounded off per CGA P-11, *Guideline for Metric Practice in the Compressed Gas Industry* [45].

Hydrogen and carbon monoxide are a purity issue when ultra high purity nitrogen is produced. Carbon monoxide is also an issue when nitrogen NF is produced. They can be removed by other means such as front-end catalytic oxidation or nitrogen purification.

7.4 Plugging components

Characteristics of the specific plugging components are as follows:

- Water is very insoluble in cryogenic liquids and shall be removed before reaching the distillation columns. Water is removed in the REVEX or PPU;
- Carbon dioxide is relatively insoluble in liquid oxygen and is removed by the PPU, REVEX, or cryogenic adsorption. Reboiler liquid purge flows assist in maintaining carbon dioxide concentrations below the safe limit in the reboiler sump, see EIGA Doc 65 [43]; and
- Nitrous oxide is relatively insoluble in liquid oxygen; however, it is more soluble than carbon dioxide. Therefore, for most applications, no nitrous oxide removal is required. It is partially removed by standard PPUs but special designs of the PPU can increase the removal efficiency. It is also removed by cryogenic adsorption. Reboiler liquid purge flows assist in maintaining nitrous oxide concentrations below the safe limit in the reboiler sump [43, 49].

NOTE NO_x (nitric oxide and nitrogen dioxide) are different compounds than nitrous oxide.

The solubility limits of mixtures of nitrous oxide and carbon dioxide in liquid cryogens are less than their single component limits when both are present because they form a solid solution, see 12.4.

For more information about plugging compound accumulation, see EIGA Doc 145 [2].

7.5 Haze and smoke from fires

Haze and smoke from forest fires, burning farmland, or other biomass combustion can create higher than normal hydrocarbon concentrations in the atmosphere.

An analysis of one fire showed that emissions consisted of:

- Vapour components of n-alkanes, aromatics, and some oxygen-containing compounds of C₃ to C₂₁ hydrocarbons; and
- Aerosols composed of droplets of 0.1 µm to 2 µm diameter, mainly C₈ to C₃₆ hydrocarbons [50].

Concentrations of hydrocarbon-rich vapour and aerosols that do not exceed the design limits of the plant are not a concern for ASU safety.

Only the vapour compounds are adsorbed by a PPU; however, the aerosols are typically too small to be retained by inlet air or PPU dust filters, which typically capture particles 2 µm to 5 µm and larger. The aerosols can accumulate in the reboiler sump and become a significant hazard unless addressed.

High amounts of aerosols that are introduced into the process cannot be removed by derime and could require solvent wash to remove. If an ASU has the potential to have high amounts of aerosols in the ambient air exceeding the plant design limits for extended periods of time, the following items should be considered:

- Use a high efficiency filter to remove particles larger than 0.1 µm to 0.4 µm. The filter could be placed on the MAC inlet or on the pre-purifier outlet. Proper installation and maintenance of the high efficiency filter is critical to remove particles;
- Measure pressure drops across the high efficiency filter. High pressure drops can indicate the filter is blocked and requires maintenance. A low pressure drop can indicate bypassing of the filter (for example, improper installation, filter failure); and

- Install / use particle counters to alert operating staff to a potential hazard.

When fire events occur, the following items should be considered:

- Inform company management of the situation;
- If an ASU runs during a short period of high haze, immediately ensure that all safety measures are being followed (for example, reboiler submergence, liquid oxygen removal from the reboiler sump, etc.);
- Aerosols accumulate in the ASU over time and can be difficult to remove;
- Aerosols cannot be detected by the hydrocarbon analyser; however, an increase in the levels of lighter hydrocarbons can be detected;
- Attention should be paid to ensure that solids such as carbon dioxide and nitrous oxide are not precipitating from oxygen-rich fluids. Monitor the main compressor inlet filter, heat exchangers, and piping systems for increases in pressure drop or decreased heat transfer performance. These are indications that solids might be precipitating; and
- Operate pre-purification units so that there is no carbon dioxide breakthrough during fire / haze events;
- Consider the manufacturer's and operating company's criteria to determine if an ASU should be shut down in a high haze environment. Consult the manufacturer for guidance as to what constitutes a high haze. In the absence of any guidelines, a PM10 threshold of 150 µg/m³ may be used. PM10 is the mass of particles less than 10 µm diameter contained in 1 m³ of air. This is measured by many environmental regulating agencies throughout the world.

An overview of haze and some of the potential ASU safety problems can be found in "*Hydrocarbon Haze and ASU Safety*" [51]. Hydrocarbons from forest fire haze contributed to a large ASU explosion, as detailed in "*Investigation of an Air Separation Unit Explosion*" [50].

An indication of a haze event can be limited visibility around the plant or site. For example, when local visibility drops to less than 2 km (1.3 miles).

7.6 Contaminant sources

Airborne contaminants originate from numerous sources. Vents, stacks, flares, swampy areas, process leaks, natural gas heater emissions, exhausts from internal combustion engines, machinery lubrication system vents, landfills, and forest or field fires are the most common sources. Chemical and petroleum processes on adjoining properties and other processes within the air separation plant site shall be carefully examined as possible contamination sources.

Acetylene cylinders shall not be stored or used near the air intake of an operating MAC.

Signs should be posted near air compressor intakes prohibiting the parking and running of internal combustion engines or welding machines in the area. There have been incidents where the exhausts from nearby railroad diesel locomotives have been attributed to the appearance of acetylene in main condenser liquids.

7.7 Identification of contaminants

Contaminants can be identified by analysing the ambient air. Table 3 provides a default air quality design basis for a typical industrial environment, which can be used if no other information is available.