SAFE OPERATION OF REBOILERS/CONDENSERS IN AIR SEPARATION UNITS

AIGA 035/06

GLOBALLY HARMONISED DOCUMENT

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1 Introduction

Industrial cryogenic air separation technology used to produce oxygen, nitrogen, argon, and rare gases has an extremely good safety record. However, as with many present-day production processes, it has inherent potential hazards that must be recognized and addressed by proper design and operating practice.
The industrial gases companies have engaged, through CGA, JIGA EIGA and AIGA, in a process of developing harmonized safety practices and this publication is one of them.
Provided in this document is good general guidance on safe operation of reboilers/condensers in air separation units; two additional documents recently published by the EIGA address the specific issues of structured packing (EIGA 701/04) and brazed aluminium heat exchangers used as product vaporizers (EIGA 702/04). These and additional references are cited in Section 8.

2 Scope and purpose

2.1 Scope

This document addresses the operation of the reboilers of air separation plants. It contains a summary of current knowledge and industrial practices used in their safe application. It specifically applies to the main reboiler and oxygen product reboilers in which the oxygen concentration is above 75% in the liquid phase. Its guiding principles can be used for other reboilers within air separation plants, including auxiliary vaporizers, guard adsorber vaporizers, argon condensers, and the main reboilers in nitrogen generators.

Reboilers feeding krypton/xenon columns and the krypton/xenon distillation system are excluded from the scope of this document. These systems and their methods of dealing with hydrocarbon accumulation vary widely. Reboiler operation and safety for plants with these units should be discussed with the supplier on a plant-specific basis.

2.2 Purpose

The purpose of this document is to describe the design and operating practices that should be followed in the reboiler sections of cryogenic air separation plants. In particular, the potential hazard introduced by contamination due to hydrocarbons or other contaminants that might be present in the ambient atmosphere is addressed. It is thought that this has been the prime cause of the majority of reboiler incidents that have been reported.

This document is not intended to be a mandatory code. It is based upon the experimental data, operating experience, and design practices of major producers and operators of air separation plants. It is recognized that legislation or regulation can impose more stringent requirements for plant design and operation.

3 Definitions

The following terms are used throughout this document:

Auxiliary vaporizer: An ASU supplemental process heat exchanger that vaporizes low pressure column liquid oxygen (LOX) against a heat source, usually process air or nitrogen, to provide a thermosyphon effect or to gain hydraulic head. The thermosyphon effect can be used to ensure LOX circulation through an LOX adsorber.

Analytical Plant Derime: A derime during which some flow rates and concentration of trace components are measured, allowing the total accumulation of these components to be calculated.

Cold box: The cryogenic equipment and piping and its structural enclosure.

Cold Standby: The condition where equipment is held at cryogenic conditions for immediate service on demand.

Dead End Boiling: The 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 impurities by the flushing action of the liquid; also known as pot boiling. This phenomenon can also occur in cavities and sections of piping where oxygen-enriched liquid can be trapped and vaporized by heat leak.

Deriming: The periodic preventive maintenance procedure where the process equipment is warmed up while simultaneously being swept with clean, dry gas in order to remove any accumulated moisture, carbon dioxide, and atmospheric impurities; also known as defrosting, de-icing, and thawing.

Dry Boiling: The condition occurring in thermosyphon reboilers where, due to inadequate reboiler submergence, the liquid entering in the reboiler is totally vaporized, thereby concentrating any less volatile impurities by extremely high factors; also known as dry vaporization.

This condition can also occur in downflow reboilers where liquid is completely vaporized before reaching the bottom of the vaporizer. This can be due either to low liquid flow or inadequate distribution of the liquid.

Front-End Purification: The use of adsorbers which operate at temperatures above 0 °C to remove moisture, carbon dioxide, and the most hazardous hydrocarbons from the air feed prior to its being supplied to the cold box.

Gas Phase Adsorbers: A means to reduce concentrations of atmospheric impurities by adsorbing them cryogenically from the gas phase; also known as cold-end traps.

Internal Compression: A process in which LOX from the column is pumped to an elevated pressure and vaporized in heat exchangers external to the column system but within the cold box to produce gaseous oxygen (GOX) at pressure; also known as liquid pumping.

LOX: Abbreviation of liquid oxygen. Throughout this document, all requirements applicable to LOX are also applicable to liquids with an oxygen concentration above 70%.

LOX Adsorbers: A means to reduce concentrations of atmospheric impurities by adsorbing them cryogenically from the liquid phase of the reboiler sump; also known as guard adsorbers or LOX filters (although the action is not physical filtration, but only adsorption).

Main Reboiler: An integrated heat exchanger used to heat-couple the two primary distillation columns of an air separation unit (ASU), simultaneously condensing a high pressure fluid while vaporizing a low pressure liquid, thereby producing reflux for one column and boil-up for the other.

Plugging: The blockage of channels within the reboiler either by foreign particulates (e.g., silica gel or perlite) or by the solidification of atmospheric impurities (e.g., carbon dioxide or nitrous oxide), which can lead to dead end boiling.

Regenerators: The pre-purification process of removing moisture and carbon dioxide from ASU plant feed air by freezing them out on cold structures such as quartz stone or stainless steel.

REVEX: Abbreviation of reversing heat exchanger. The pre-purification process of removing moisture and carbon dioxide from ASU plant feed air by freezing them out within a brazed plate-fin heat exchanger, whereby the given passage is first used for feed air and then cleared of impurities by subliming the contaminants in a lower pressure, clean, dry gas flowing through the same given passage in the reverse direction.

Rich Liquid Adsorber: A means to reduce concentrations of atmospheric impurities (especially hydrocarbons) by adsorbing them cryogenically from the liquid-enriched oxygen stream flowing between the high pressure and low pressure columns; also known as hydrocarbon adsorbers.

Submergence: A measure used for thermosyphon reboilers to indicate the degree to which the *physical* reboiler is submerged in the sump as measured against the actual height of the reboiler. Therefore at 100% submergence the liquid in the sump is at the top of the reboiler.

NOTE—This measure is *not* equivalent to the *indicated* level of the sump, which indicates the relative level of the liquid interface between the upper and lower level taps. The indicated level and reboiler-submergence level, however, are interrelated by the elevations of the upper level tap, top of reboiler, lower level tap, and the height of the reboiler. For a pictorial description, please refer to Figure 1 in Appendix G.

4 Reboilers Incidents Survey

In order to raise awareness of the potential risks in operating air separation plant reboilers, the working group members surveyed known incidents related to hydrocarbons in reboilers. These incidents were categorized into three classes depending on their gravity, major explosions, limited explosions, and internal leaks. However, it should be recognized that as there is no clear delineation between small explosions limited to combustion of limited quantities of hydrocarbons and large explosions leading to extensive aluminium combustion in LOX, **it is absolutely essential to prevent any hydrocarbon accumulation within the LOX reboiler exchangers**. One purpose of this document is to help to achieve this end.

4.1 Major Explosions

Major explosions breech the cold box and cause major damage to the ASU, rendering it inoperable. There is also the possibility of off-site effects from the blast.

Under very special circumstances a violent energy release can originate in the reboiler of an air separation plant with catastrophic consequences to the plant and its surroundings. An extremely violent explosion can occur if the aluminum in the cold box becomes a fuel that reacts with oxygen in the LOX sump of the distillation column.

Two serious events of this nature were experienced during 1997. The only previous occurrence was in 1964. One of the 1997 explosions was so violent that the ASU was totally destroyed and the adjacent plant where the oxygen product was used was seriously damaged.

All three accidents are thought to have followed the same series of events:

1. Spontaneous ignition and combustion of flammable air contaminants that had accumulated within the passages of the reboiler;
2. Promoted ignition and combustion of a large fraction of the aluminum material from which the reboiler exchangers were fabricated;
3. Flash vaporization of LOX; and
4. Explosive rupture of the cryogenic distillation column and cold box casing.

4.2 Limited Explosions

Limited explosions can cause damage within the cold box but do not breech it. Damage is typically confined to the equipment within the cold box. Piping and other equipment can be damaged but are repairable during an extended plant outage. As of 1998, there were 8 incidents of this nature reported to the industry.

4.3 Internal Leaks

Internal leak incidents generally relate to minor explosions within the reboiler heat exchanger and are not seen on the outside of the cold box. They are generally only noticed by the subsequent poor operation of the distillation columns and require repair of the reboiler to eliminate the problem.

Equipment outside of the distillation column is seldom involved or affected. As of 1998, there were 36 incidents of this nature reported to the industry.

5 Air Contaminants

Safe design and operation of a cryogenic air separation plant depends on a detailed knowledge of the composition of atmospheric air and what happens to these components as they pass through an ASU. The bulk of the air and some trace components are separated to yield desired products such as oxygen, nitrogen, and argon as well as helium, neon, krypton, or xenon. Some components freeze out at cryogenic temperatures and could cause operational or safety problems. Other components can be concentrated within the air separation plant and form flammable mixtures with oxygen or enriched air. Still other components can be corrosive and lead to increased operating problems and reduced plant life.

Table 1 (refer to Appendices A through F for tables) lists many components present in air that could cause problems in air separation plants. The components are classified according to the problems they cause.

Since the main focus of this document is safety, the corrosive components will not be considered further. Plugging components, while not safety issues by themselves, can accumulate and cause dry boiling or dead end boiling and hydrocarbon build-up in reboilers.

Physical and thermodynamic property data of the components of air are necessary to understand where they can concentrate in an air separation plant and at what concentration the accumulation can become dangerous. Table 2 gives the relevant properties of many of these components.

Critical points in the air separation plant are the reboilers, since hydrocarbons or plugging components entering the cryogenic section of the plant accumulate at these locations. Table 5 lists the maximum level of contaminants in the main reboiler (thermosyphon type) allowable for safe plant operation. Table 6 lists the maximum level of contaminants in a downflow reboiler allowable for safe plant operation. See 7.4 for a more detailed review of allowable contaminant levels in the main reboiler.

It also should be noted that hydrocarbons can accumulate at other locations such as rich liquid adsorbers, LOX adsorbers, and through dead end boiling in piping dead legs.
Table 2 in conjunction with Table 3 suggests that, for a plant with adsorption-based front-end purification (FEP), the key contaminants to consider are nitrous oxide, ethane, ethylene, and propane. Carbon dioxide should also be monitored since upsets or malfunction of the adsorbers can allow carbon dioxide to enter the plant. These key components are i) not removed or only partially removed in the front end purification adsorbers; ii) have low K-values, which means very little is removed in the GOX product; and iii) have low solubility (with the exception of ethane). These and additional contaminants can be of concern in REVEX or regenerator plants. Later sections of this document describe the methods that can be used to remove or limit the build-up of these and other components.

6 Design Consideration

Unique from other process plant industries, the industrial gases industry processes ambient air to produce its final product. For this reason, the safety of air separation plants is closely related to the trace contaminants present in the air. As it is not possible to control the condition of the ambient air, an understanding of contaminant removal techniques as well as the knowledge of the site-specific air composition is imperative for safe plant design and operation.

Hydrocarbons and various other contaminants in the environment, which enter the air intake of an ASU, can cause safety and operational problems if allowed to reach the distillation equipment. These contaminants, which have higher boiling temperatures than oxygen, tend to accumulate in the oxygen-rich reboilers within the plant, most specifically in the sump of the low pressure distillation column. If their concentrations are allowed to build up, they can form flammable mixtures with oxygen or, in the case of inert contaminants, precipitate out of solution, leading to the plugging of the passages of the reboiler once their solubility limits have been reached locally. Such plugging by inert contaminants can lead to local accumulation of hydrocarbons by dead end boiling.

It is therefore essential that the more hazardous of these contaminants be removed from the feed air stream before they enter the distillation column, and that the maximum concentration for the remaining contaminants is limited to values less than those indicated in Tables 5 and 6.

6.1 Plant Surroundings

The ambient air quality is an important factor in the design and safe operation of an air separation plant (see EIGA 704/05, *Safe Practices Guide for Cryogenic Air Separation Plants*).

The air separation plant must be designed to remove components that freeze at cryogenic temperatures, components that could form flammable mixtures with oxygen or enriched air, and components that are corrosive. Since the levels of these contaminants can vary greatly from location to location, a separate review of air quality should be done for each plant site jointly by the designer and operator.

In the absence of specific data on a particular plant site, an air separation plant may be designed on the basis of a default air quality table. This would list the maximum level of each contaminant in the air of an industrial area that would be processed safely in the air separation plant without additional modifications. Table 4 defines typical maximum levels for a plant with an adsorption based FEP system.

If concentrations are reported to be higher than those in the table, the designer must analyze the impact and specify whether additional modifications to the design are necessary.

A process should be put in place to periodically review the surroundings for exposure to changes in air quality as a result of industrial development that can occur around the site following the installation of the ASU. Such new facilities can release chemicals during steady state or emergency situations (i.e., vents, flares, vehicle emissions, or other accidental release), possibly impacting operational safety of the ASU. Air quality changes due to environmental events such as fires also should be considered.

6.2 Design of Pre-purifying Systems

Various means have been used for contaminant removal. Most modern ASUs use ambient temperature FEP systems to adsorb substantially all of the moisture and carbon dioxide and the most hazardous hydrocarbons from the compressed feed air stream. These units also can partially remove certain other contaminants. Many older plants make use of REVEX plants or regenerators to freeze-out many of the contaminants as the air feed is cooled to low temperature. These plants generally require additional contaminant removal by means of vapor or liquid phase adsorbers, which operate at cryogenic temperature. A detailed explanation of the operation of these pre-purifying systems can be found in EIGA 704/05.

7 Operations

7.1 Importance of Carbon Dioxide Removal

Perhaps the most basic and important factor in maintaining air separation plant safety with respect to hydrocarbons is the operation of the pre-purifying system. Whether the plant uses an FEP or REVEXs/regenerators, ensuring that the system is properly tuned is essential in keeping carbon dioxide from entering the plant where, because of its low solubility, it can plug reboiler passages and cause localized dead end or dry boiling.

Preventing carbon dioxide breakthroughs in plants with FEP systems also is critical in controlling hydrocarbon levels in the reboiler. Some air contaminants, notably propane, ethylene, and nitrous oxide, are partially adsorbed on molecular sieve but become displaced by carbon dioxide adsorption. When carbon dioxide is allowed to breakthrough at the product end of the bed, these partially adsorbed components are desorbed and pass into the cryogenic section of the plant.

For these reasons, a breakthrough of carbon dioxide above the detectable limit at the end of the adsorption cycle should not be allowed in plants which use an FEP system. If breakthroughs are noticed, refer immediately to the operations manual for instructions on how to tune the sequencer or adsorber parameters in order to eliminate the breakthroughs, i.e., reactivation temperature, flow, times, etc.

It is recommended that the carbon dioxide concentration be monitored at the outlet of the adsorption vessel. There should be a high carbon dioxide alarm set at a level of 1 ppm/v. This indicates breakthrough of carbon dioxide and also some previously adsorbed hydrocarbons. The operator should switch to the other adsorber bed if available (i.e., adequately regenerated), maximize the liquid purge rate and, where possible, monitor sump concentrations of hydrocarbons, nitrous oxide, and carbon dioxide to assure that they do not exceed the values given in Tables 5 and 6. Where there is no sump analysis, shutdown is recommended if the adsorber cannot be switched within 30 minutes or if the carbon dioxide concentration reaches 10 ppm/v.

A low but continuous slip of carbon dioxide is just as dangerous as a significant breakthrough at the end of the cycle, because it indicates that air contaminants such as acetylene, other hydrocarbons, and moisture are also bypassing the adsorber beds. If the level of a continuous slip reaches 0.2 ppm/v to 0.5 ppm/v of carbon dioxide (according to the detection capability of the analyzer), the plant supplier should be consulted immediately. In no circumstances should the plant continue to be operated for an extended period under these conditions.

In the case of REVEX or regenerator plants, control the midpoint and cold-end temperatures of the exchanger to ensure that the exchanger correctly removes carbon dioxide and moisture. If severe upset conditions persist, a more frequent change of rich liquid adsorbers should be considered in order to prevent a buildup of carbon dioxide in the sump liquid.

7.2 Proper Reboiler Operations

Today's designers of air separation plants offer several technologies for reboilers. These include:

7.2.1 Bath-Type Reboilers

The term bath-type reboiler defines any exchanger of an air separation plant that operates submerged in liquid. Of specific interest to this document are those in which the liquid bath contains more than 75% oxygen content. This can include main reboilers (either internal or external), auxiliary vaporizers, guard adsorber vaporizers, and oxygen product reboilers.

The operating principles of these various bath reboilers are similar. In order to simplify the explanation of this operation, the main condenser bath reboiler is used as an example.

The oxygen in the bath (open passages) vaporizes against the condensing gaseous nitrogen of the high pressure column. The oxygen, in liquid phase at the lower part of the reboiler, vaporizes progressively in the passage as it flows up the core. The effect of the difference of density (higher for the liquid in the sump than for a two-phase mixture within the passages of the exchanger) generates an upward flow of the oxygen (thermosyphon effect).

As the two-phase mixture flows up and through the top of the open passages of the reboiler core, a significant amount of unvaporized liquid falls back into the bath. This is referred to as liquid recirculation.

The hydrocarbons in solution with the LOX entering the passages concentrate progressively as the LOX is partially vaporized.

If the recirculation flow rate is high, the concentration of hydrocarbons in the passages remains low, and dangerous accumulation in the passages is unlikely. On the other hand, if the recirculation flow rate is reduced or eliminated completely the local hydrocarbon concentration in the passages increases significantly. Where recirculation is eliminated completely, dry boiling occurs. Under these conditions, a second, hydrocarbon-rich, liquid phase can separate or deposits of solid contaminants can build up in the reboiler core passages.

WARNING: *Accumulation or deposition of hydrocarbons within the passages cannot be detected by analyses of the reboiler sump liquid or by any other method.*

When operating the bath below a specific level with respect to the core height, the LOX can completely vaporize as it flows up the passages. This phenomenon of no recirculation flow is called dry vaporization or dry boiling. This situation is especially dangerous since it can lead to the rapid accumulation of flammable hydrocarbons within the isolated core passages, due to lower recirculation rates.

Increasing this liquid level allows the recirculation flow to re-establish itself and eliminates the possibility of dry vaporization. The need to maintain a high liquid level is especially important for operation at reduced plant capacity.

It should be recognized that the minimum degree of submergence required for safe operation of bath-type reboilers is a function of the type of heat exchanger that is used. To ensure operational safety, the depth of the reboiler sump liquid shall be maintained at the level specified by the plant supplier. If this value is unknown, the reboiler should be operated in a fully submerged condition (100% submergence), i.e., the liquid level in the bath must reach the upper end of the reboiler core. Note that the level shown on the instrumentation does not normally correspond to the percentage submergence with respect to core height. Refer to Figure 1 for further explanation. If the correspondence between the level indication and the core submergence is not identifiable from the operation manual, the supplier shall be consulted.

Operation at levels higher than 100% submergence can give an additional margin of safety. However, care must be taken that the increased level does not adversely affect plant operation through liquid carryover into the gas lines or interference with liquid distribution or the distillation process in the bottom section of the column. An excessively high liquid level can cause mechanical damage to the internal components (distributor, trays, packing) in the lower part of the distillation column.

7.2.2 Downflow Reboilers

A downflow reboiler (also known as a film-type reboiler) is one in which the liquid to be vaporized flows in the passages from the top to the bottom of the core. The flow is generated by gravity and is delivered by a distributor at the inlet (top) to the core passages. Downflow-type reboilers are sometimes used for main or auxiliary vaporizers of ASUs. As in the case of the bath-type reboilers, the main reboiler is used as an example to illustrate the operating principles of the downflow reboiler.

LOX is fed to a distributor located at the top of the reboiler. The liquid flows by gravity in a downward direction through the oxygen passages. Vaporized oxygen flows from the bottom of the exchanger along with excess liquid. Gaseous nitrogen from the high pressure column is condensed in the nitrogen passages of the reboiler.

There are several configurations of downflow reboilers including once-through or recirculating. In all cases, it is essential to maintain the required liquid level in the distribution system using the means specified by the supplier. Also, measuring liquid flow is another equally acceptable method of ensuring adequate flow through the vaporizing side of a downflow reboiler.

As with bath-type reboilers, the hydrocarbon concentration in the LOX increases progressively as the oxygen vaporizes in the passage. A sufficient amount of LOX must flow from the bottom of the core’s passages to ensure that the maximum hydrocarbon content in the LOX does not reach dangerous levels and to ensure all passages remain wetted. Therefore, the maintenance of this liquid flow is essential.

Once-through reboiler cores are fed with liquid directly from the packing or trays of the low pressure column. The liquid contains contaminant concentrations close to the values of the purified air entering the cold box.

Some once-through-type reboilers must be supplied with an additional recirculating flow to ensure the minimum necessary amount of liquid exits the bottom of the core passages.

Recirculating reboiler cores are fed with LOX (from the sump of the low pressure column in the case of the main reboiler) that already might have been passed through a once-through core. Generally, the concentration of contaminants in this type of reboiler is higher than in the once-through core.

In all cases where recirculation is required, it is obtained by pumping liquid from the sump of the column and transferring it to the distributor at the top of the recirculating reboiler. Controlling this flow rate ensures the adequate supply of liquid to the distributor of the vaporizer.

Reaching a low flow threshold on the recirculating pump shall activate an alarm alerting the operator. The operation of the pump may then be readjusted or, if applicable, a standby pump started. If the low flow alarm remains activated beyond a 60-minute period, the unit shall be shut down.

WARNING: *The flow rate provided by the pump always shall be kept at the nominal value specified by the plant designer, even at a reduced plant capacity operating mode. If the plant can be operated above the design capacity, increasing the LOX circulating flow with the increase in air flow should be considered.*

A screen directly upstream of the distribution system feeding the downflow reboiler is recommended to prevent particles from entering the downflow reboiler distributor. Screen mesh shall be specified by the plant supplier to suit the geometry of the downflow reboiler core and its distribution system.

Because downflow reboilers are different from bath-type reboilers, they have different operating requirements. One difference in downflow reboilers is that they operate with a much higher vapor fraction at the exit of the reboiler as compared to a bath-type reboiler. Because of this higher vapor exit quality, downflow reboilers have been reported to accumulate trace components that have relatively low solubility even when the bulk concentration of these components is well below the solubility limit.

While it is impossible to completely prevent trace components such as carbon dioxide, nitrous oxide, and some hydrocarbons from accumulating within the downflow reboiler, the amount of accumulation shall be carefully controlled. Experimental work and analytical plant derimes have shown that the key variable in the accumulation rate is the component concentration in the liquid exiting the reboiler. Higher concentrations of these trace components cause higher accumulation rates. The plant operator should keep the nitrous oxide, carbon dioxide, and hydrocarbon concentrations as low as practical, and at all times the concentrations should be within the limits specified by the ASU manufacturer. Table 6 gives maximum shutdown values, but the manufacturer can mandate lower shutdown values for specific designs and operating conditions. Note that normal operating concentrations should be significantly lower than the values in Table 6. When the plant is designed for operation at high concentration factors, it can include specific protections such as cryogenic silica gel adsorbers or other appropriate protections.

Periodic deriming should be performed to remove any accumulated components. The manufacturer's recommendation for defrost intervals should be strictly followed. Solid carbon dioxide and nitrous oxide can retain hydrocarbons within the reboiler, so it is necessary to remove these components by periodic deriming.

WARNING: *Failure to remove the accumulated carbon dioxide and nitrous oxide by periodic deriming can lead to accumulating unsafe levels of hydrocarbons, which in turn can lead to an explosion.*

7.2.3 Level Instrumentation

Since control of the reboiler level and flow is important in preventing dead-end or dry boiling, proper operation of level and flow indicators as well as their alarm and shutdown set points shall be verified and recorded at regular intervals. This should be done at least annually. Where practical, observation of overflow at the vapor phase level tap, during temporary operation at the required high level, can be used to verify the calibration.

Where duplicate taps are installed to provide contingency in the case of blockage, these taps should be regularly checked and vented. Should blockage occur in one of the two taps, every effort should be made to clear the blockage using purge nitrogen or thawing during the next plant derime. If all taps are blocked or if the reboiler level cannot be determined for any other reason, the plant should be shutdown to restore level measurement.

7.3 Deconcentration of Contaminants

Regardless of the type of pre-purifying system used, some level of light hydrocarbons and potentially other contaminants reach the distillation columns and tend to collect in the sump of the low pressure column. The concentrations to which these components accumulate shall be limited to avoid hazardous operation. Methane is the only hydrocarbon that is sufficiently volatile to leave in the vapor phase of the GOX product stream. Other hydrocarbons shall be removed from the liquid phase.

There are principally two methods of maintaining a safe level of the other contaminants in the LOX:

- LOX adsorbers (see 7.3.1); and
- purging (see 7.3.2).

7.3.1 Liquid Oxygen Adsorbers

LOX adsorbers are designed to remove certain contaminants from an LOX stream drawn off from and returned to the sump of the low pressure column. Either single or paired adsorbers may be used. Using two adsorbers permits continuous adsorption during the regeneration of the spent adsorber.

Refer to Table 3 for the effectiveness of removal of the complete list of contaminants. In particular, for REVEX and regenerator plants, LOX adsorbers are effective for removal of residual acetylene, dienes, and C_4+ hydrocarbons, and are partially effective for removal of nitrous oxide. They also provide a backup to remove carbon dioxide that can reach the column, particularly during operational upsets.

7.3.1.1 Thermosyphon-driven oxygen guard adsorbers circuits

Operators of ASUs utilizing thermosyphon-driven oxygen guard adsorber circuits should follow these additional precautions:

- Adhere to the LOX circulation operating parameters specified by the plant supplier’s procedures. If the procedures specify that indicated flows or differential pressures have to be maintained by relevant plant (valve) adjustment, these indicators should be treated as important safety devices;
- Do not allow instruments to remain out of service if any become defective or give abnormal readings. These safety devices should be clearly identified as safety critical by risk assessment and maintenance procedures adapted accordingly. Under no circumstances should the plant be operated if this instrumentation is not functioning;
- Follow the manufacturer’s recommended regeneration flows to avoid fluidization and breakdown of the silica gel;
- Follow the manufacturer’s recommended regeneration temperatures and step times to ensure complete removal of adsorbed contaminants;
- Operate the guard adsorbers in accordance with the plant supplier’s procedures. Avoid excessive LOX flashing through the regenerated bed on cool down as this would have the effect of both lifting the bed and increasing attrition of the adsorbent material. Either of these

events increases the possibility of adsorbent debris accumulating in LOX return circuits or within the thermosyphon-driven exchange or main reboiler;

- Avoid introducing liquid water, which breaks down the silica gel; and
- Ensure that the guard adsorber LOX circuit vaporizer and piping are correctly derimed and recooled to operating temperature as part of the operating procedures for an ASU turn around. LOX allowed to boil in the circuit rather than drained off can both accumulate any hydrocarbons present and cause solid carbon dioxide deposition because of its low solubility. On restart, solid deposits can inhibit the liquid recirculation through the vaporizer promoting the dry boiling phenomenon.

7.3.2 Purging

Hydrocarbons that escape upstream treatment will not accumulate to high concentrations in plants that produce a significant percentage of oxygen as a liquid product, or in which the oxygen is withdrawn from the low pressure column as liquid, pumped and vaporized in exchangers external to the column system.

However, in a plant that produces only a GOX product (taken directly off the column) or a very small amount of liquid, it is necessary to deliberately remove a measurable amount of liquid from the sump of the reboiler in order to limit the concentrations of light hydrocarbons (particularly ethylene, propane, and ethane), nitrous oxide, and carbon dioxide to acceptable levels. **A minimum continuous purge rate of 0.1% to 0.2% of the incoming air is recommended.** On small plants where a continuous purge is not practical, a purge equivalent to this rate should be taken at least every 8 hours.

The following equation computes the concentration of high boiling components in the LOX:

$$\gamma_{\text{Trace contaminant}} \equiv \frac{x_{\text{Trace contaminent, LOX}}}{y_{\text{Trace contaminent, Feed}}} = \frac{F_{\text{feed}}}{F_{\text{LOX}} + K_{\text{Trace contaminent}} F_{\text{GOX}}}$$

Where:

- γ = Concentration factor, relative to the concentration in the air
- x = Mole fraction of the component in the liquid phase
- y = Mole fraction of the component in the vapor phase
- F_{feed} = Air molar flow rate to the column system
- F_{LOX} = Molar flow rate of LOX from the reboiler
- K = y/x for the component at equilibrium
- F_{GOX} = Molar GOX flow rate from the reboiler

For an internal compression cycle, where no GOX is taken from the reboiler and the LOX product flow is approximately 20% of the air from the main reboiler, the concentration factor is approximately 5 for all species. When LOX is only produced for purge (typically 0.2% of the air) and with a small *K* value, the concentration factor is 500.

NOTE—For methane, the *K* value is significant (see Table 2 in Appendix B). In this case, the concentration factor is approximately 16 and the vast majority of the methane exits in the GOX product.

7.4 Contaminant Analysis

The introduction of large quantities of hydrocarbons and other contaminants into the plant always represents a risk, regardless of the protection devices implemented in the design and operation. For this reason, it is necessary to detect when such a condition arises.

In particular, in concentrated industrial areas such as chemical, petrochemical, and metals industries, the plant operator shall maintain a good awareness of the current environment surrounding the plant. Information to be maintained should include:

- A list of nearby plant complexes liable to release significant quantities of contaminants into the air during normal operation or in the case of malfunction or accident;
- The distance between these potential sources and the air separation plant air intake; and
- Local atmospheric conditions.

Note that the potential risk of an air separation plant site is determined not only by the normal quality of the ambient air but also by the risk of contaminant releases.

If deemed necessary, the instantaneous wind direction and speed should be made available in the control room.

Depending on the characteristics of the ambient air conditions of the plant, its specific process design, as well as the potential for contaminant releases, the following continuous contaminant measurement devices should be considered:

- A carbon dioxide analyzer at the outlet of the pre-purifying system;
- A total hydrocarbon analyzer at the air inlet to detect abnormal ambient air contaminant levels;
- A total hydrocarbon analyzer in the reboiler with the highest potential concentration of contaminants. This is generally the main reboiler sump; and
- An analyzer that can detect individual hydrocarbon species in the reboiler with the highest potential concentration of contaminants.

For a REVEX or regenerator plant, routine acetylene analyses also shall be performed.

Tables 5 and 6 list the maximum allowable contaminant concentrations for the reboiler. These maximum contaminant values are much higher than the normally anticipated operating levels.

These levels are a function of parameters such as the reboiler purge rate, pre-purifier unit design, and overall process cycle as well as of the ambient air quality.

Based on these parameters, the designer shall be consulted to calculate the anticipated operating main reboiler contaminant level. In addition, the designer and operator should sample the LOX produced in the main reboiler over the design range of plant operation during commissioning to verify the anticipated normal contaminant level and to set the baseline for future measurement.

If at any point any measured contaminant exceeds 4 to 5 times its expected normal value, there should be an alarm indicating the need to investigate and understand the cause. Equally importantly, a rapid change in contaminant concentration, whether an increase or a decrease, also should be investigated.

A second alarm level should be set indicating the need to shut down the plant. This higher set point shall be provided by the manufacturer. The shutdown limits shall be set based on the manufacturer’s specific design features, operating methods, and experience. Unless specifically justified by the manufacturer, the shutdown set point values in Tables 5 and 6 shall not be exceeded.

Care must be taken to ensure that the correct reboiler operating levels (bath reboilers, see 7.2.1) and recirculating flows (downflow reboilers, see 7.2.2) are maintained. The measured average contaminant concentration in the sump can be a misrepresentation and lower than the actual local concentration within the reboiler exchanger if these liquid levels and flows are not maintained. A rapidly decreasing sump concentration can indicate an accumulation of contaminants within the exchanger.

Correct calibration of analytical equipment and level transmitters is essential to the continuous safe operation of the plant. Calibration of the analyzers at the above mentioned points shall be maintained at the frequency stated in the supplier's operating manual.

Care must be taken when sampling cryogenic liquid streams to avoid partial vaporization of the sample and inaccurate measurement of heavy components, particularly hydrocarbons.

Analytical and operational records should be maintained for an extended time to monitor for long-term changes in plant environment and operations.

7.5 Transient Conditions

Transient conditions can cause higher than normal hazards in operations. In these cases, process changes in the unit occur that are not always noticed by the operator.

Causes for transient conditions can be:

- plant load change;
- planned or unplanned shutdown of the plant;
- cold restart of the plant with or without liquid; or
- switching problems on REVEX/regenerator and FEP systems.

7.5.1 Plant Load Changes

7.5.1.1 Bath-Type Reboilers

While the liquid level in the reboiler generally increases by reducing the plant load, it can decrease while increasing the load.

According to the speed of the load increase, the sump liquid level and consequently the reboiler recirculation rate can fall very rapidly. The allowable drop of the submergence level in these reboilers shall be provided by the plant designer. If none is given, use 30% below the normal operating submergence level for a maximum period of 60 minutes.

7.5.1.2 Downflow Reboilers

The recirculation rate shall be maintained as in normal operation. The level in the distributor or the measured liquid flow to the distributor shall not fall below the allowed minimum during any plant load change. During plant load changes, the liquid level in the distributor feeding the downflow reboiler can temporarily fall below the normal operating level. This is acceptable, as long as the steady state level is above the minimum. Note that in many cases, the recirculation flow rate can be used instead of a direct level measurement.

Keep the liquid reservoir in the column under control. Special attention should be paid to the suction filters of the recirculation pumps as plugging can occur caused by freezing out of carbon dioxide and other contaminants.

7.5.1.3 Liquid Oxygen Production

Units that continuously produce significant amounts (greater than 2% of incoming air) of LOX effectively deconcentrate the contaminants entering the air separation plant. In plants without an instrumented purge line, LOX production shall be maintained at or above the minimum measurable flow rate.

7.5.2 Plant Shutdown and Cold Standby

Following a plant shutdown, the liquid contained in the packing or trays drains to the low point of the column. At this point, the level in the reboilers is well above 100% of the level indicators. This liquid is generally preserved to permit a quick restart of the plant. This mode is referred to as cold standby.

NOTE—Following a plant shutdown, level indicators might not be working reliably due to the possibility of the upper tap being filled with liquid. It may be necessary to verify and perhaps recalibrate critical transmitters.

During a one- or two-day cold standby period, continue to recirculate flow through LOX adsorbers if installed. The following guidelines shall be followed to maintain a more extended cold standby in a safe manner:

- Close inlet and outlet valves of the recirculation pumps. Drain pumps and suction filters; and
- Drain LOX adsorbers and regenerate (if applicable).

Due to the heat leak into the cold box, vaporization eventually reduces the amount of liquid in the reboiler to well below the normal operating level. When the liquid has been reduced to half of its normal level, either liquid must be added using liquid nitrogen or oxygen injection, or all liquid in the plant must be drained.

When injecting liquid into the plant, it is advisable to use liquid nitrogen rather than LOX. When LOX is used, be aware that extra hydrocarbons are added to the system.

If a hydrocarbon analyzer is available, continue monitoring hydrocarbons during the cold standby. All liquid must be drained if the contaminant levels in Table 5 or 6 (as applicable) are reached. However, since sampling during a non-operating period might not be representative, a lower result should not be used to justify a failure to adhere to other recommended actions, as mentioned earlier in this paragraph.

In the case of REVEX/regenerator plants, it is advisable to warm up the plant completely after draining the liquid. If this is not done, there is a high potential of carbon dioxide migrating into the column upon restarting.

7.5.3 Plant restart

The transient conditions described below are not always easy to separate from each other. Depending on the type of plant as well as its design, it can be difficult to determine prior to restarting a unit whether there is enough liquid. The appropriate procedure actually can be a combination of the two described in 7.5.3.1 and 7.5.3.2. When it becomes evident during a start up that the reboiler does not have sufficient liquid, purging of the remaining liquid might be required.

7.5.3.1 Cold Start after a Short Shutdown

Generally up to a period of 8 hours after a shutdown, the plant has sufficient liquid to maintain the levels in the reboilers during its restart.

In bath-type reboilers, keep the liquid level under control and at a level of at least 80% of its normal submergence value. Return the submergence level to the normal operating level as soon as possible. If available, liquid injection is recommended at this stage. A temporary drop of submergence level to 50% is allowable for a short period. If liquid injection is not available, other process steps should be considered (e.g., reduce the incoming air to the process).

In the case of downflow reboilers, control the level in the core distributor with the recirculation pump flow. Ensure that there is enough liquid in the reservoir to maintain the pump flow. Control the air intake to the high pressure column in order to maintain this level.

7.5.3.2 Cold Start after a Long Shutdown

If the liquid in the reboilers falls below 50% of the normal operating level, it is necessary to drain the liquids from the reboilers prior to restarting. The liquid present at this low level would be enriched in hydrocarbons, nitrous oxide, and possibly carbon dioxide, which can cause deposits in the reboiler core passages.

During start up from a condition that begins with a significantly lower-than-normal submergence level, it is important to first rebuild this level prior to bringing the oxygen to purity. The higher the oxygen purity in the bath, the greater the potential hazard. Maintain the GOX flow as high as possible during the start up and only reduce the flow to control the purity once the reboiler liquid level is rebuilt.

In the case of internal compression units, start the oxygen product pumps at least with the minimum flow as soon as approximately 80% of the normal level is established.

Ensure that the LOX and rich liquid adsorbers (if available) have just been regenerated. Drain the first liquid (approximately 20% to 30% of normal operating level) after producing it in the sump of the reboiler.

Problems with low liquid levels during start up can easily be overcome with a liquid assist system. As noted in 7.5.3.1, liquid nitrogen is preferred but LOX may be used if the correct precautions are taken.

7.6 Deriming

In spite of the precautions taken, the ASU shall be derimed at regular intervals in order to remove any excessive impurities such as hydrocarbons, carbon dioxide, and nitrous oxide that might have entered the plant, particularly during operational upsets. Due to the fact that the main reboiler is the component most liable to accumulate hydrocarbons, it shall be derimed with particular care.

7.6.1 Procedure

In principle, the deriming procedure should be described very accurately in the operating manual. Although the procedure differs with the various types of air separation plant, these instructions are to be adhered to.

The following points are meant to highlight the most important steps:

- Drain all liquids;
- Establish the sequence of circuits to be derimed. Derime the circuits in that sequence;
- Force the flow as far as possible through all the sections;
- Partial deriming should be avoided when proper isolation is not ensured. Experience has shown that there is a risk of shifting impurities or deposits from one section to another;
- Verify a flow from all deriming outlets;
- Open all instrument lines towards the end of the deriming process; and
- If the operating manual gives no specific instructions, deriming for a plant with FEP is typically completed when all deriming outlet temperatures are approximately 15 °C for at least 2 hours. At this point, a moisture analysis should be performed on several deriming outlets to ensure that the deriming process is successfully finished. A dew point of –40 °C to –60 °C verifies that the circuit has been successfully derimed.

A higher derime outlet temperature is desirable for plants with REVEXs and those with derime heaters. A minimum of 30 °C is preferred and temperatures up to 60 °C are acceptable. After the target temperature has been reached, deriming should be continued at that target temperature for at least 2 hours.

7.6.2 Frequency

The deriming frequency is dependent on plant design, process cycle, and its location. The normal frequency for a given plant shall be determined during the plant design and construction phase and is to be described in the supplier's operation manual. A risk assessment should be performed by qualified personnel to determine the required frequency for the particular plant in the particular location. The following factors should be included in the risk assessment:

- Design factors, e.g., FEP/REVEX, reboiler type, purge rate, LOX purity;
- Operating factors, e.g., liquid analysis arrangements, manned/unmanned, plant log;
- Environmental factors, e.g., plant location/surrounding industry, potential air contaminants, air quality; and
- Historical factors, e.g., FEP/REVEX management, plant trip frequency, condenser level variation, and previous problems.

Derime the plant every 3 years unless otherwise stated in the operating manual or unless indicated by the risk assessment.

The deriming frequency may be lengthened based on operating experience but should be shortened if any of the following abnormalities have occurred:

- abnormal pressure drops in cryogenic equipment (i.e., exchangers, distillation trays);
- high hydrocarbon level in the intake air;
- frequent switching problems with REVEXs, regenerators, or FEP systems;
- repeated instances of minor carbon dioxide breakthrough from the FEP system;
- change of the environmental conditions to other than the plant design; or
- numerous unplanned plant shutdowns, e.g., power failures.

Significant alterations of the normal operation mode (as mentioned in the previous list) could force the decision for a much higher deriming frequency.

It is further recommended that when major maintenance is carried out, a plant derime always should be considered.

7.7 Cleaning and Maintenance

Provided the plant has had a normal operating history and adequate design, no routine maintenance or cleaning requirements for the reboiler are necessary.

In some instances, however, foreign material can be introduced and can accumulate in the sumps or within the plate/fin reboilers themselves. In these cases, the foreign material is inert but must be removed as it can cause localized dead end or dry boiling and subsequent hazards.

7.7.1 Foreign Material Due to Plant Construction

Plant construction is to be undertaken under the most stringent supervision to ensure that no foreign material enters the plant during construction. This is ensured with the use of cleaned and degreased pipe, as well as by taking special care to prevent ingress of foreign matter during storage and construction. During plant commissioning, the piping is to be “blown through” to ensure any construction materials are removed from the process prior to startup. This removes any particulate such as aluminum or stainless steel shavings, aluminum oxide, rust, and welding slag.

7.7.2 Foreign Material Due to Plant Operations

During the operation of the air separation plant, the following foreign materials can be generated or introduced into the plant. These cannot be removed by routine deriming of the plant.

7.7.2.1 Adsorbent Dust

Adsorbent dust can be generated in the FEP adsorber vessels, regenerators, or in the cryogenic liquid or gas phase adsorbers. The dust is released by inadequate dust filtration or bypassing of the dust filter at its seals. In all cases, dust eventually accumulates in the LOX sump. Through boiling and circulation, this dust can pass through the fins of the reboiler core, block individual passages, and lead to dead end boiling.

7.7.2.2 Oil Contamination

Oil contamination is possible whenever oil-lubricated machinery is used as process equipment. Examples are cryogenic turbines with loss of seal gas or bearing failure. Such contamination also can occur with oil-lubricated expansion engines. Any contamination from liquid pumps is unlikely.

Oil migrating from this type of equipment certainly contaminates the cold end of the plant (exchangers) adjacent to the equipment in question and usually deposits at that point.

Progressive operation, however, allows movement of this oil to other parts of the process and possible accumulation in the LOX sump. Shutting down the plant or deriming can cause the oil/grease to become fluid and can move it to other parts of the process. Removal of this contaminant is therefore critical and can involve the use of solvents. The plant manufacturer or supplier shall be consulted if this becomes necessary (see 7.7.5).

7.7.2.3 Perlite

Incidents have been associated with plugging of reboilers with perlite. This can occur as a consequence of some component or piping failure within a perlite-insulated cold box. As with any other foreign material, the perlite finds its way to the reboilers and can cause hazardous plugging of exchanger passages. Removal of this perlite by whatever means necessary is essential prior to plant operations.

7.7.2.4 Liquid Oxygen Pump Filters

Where LOX pump filters are provided on plants with downflow reboilers, it is essential that they are not removed. The purpose of these filters is to ensure that no particles pass through the pumps and become trapped in the reboiler distributor. Should frequent blocking of these filters occur, the cause should be investigated with the plant vendor.

7.7.3 Foreign Material Due to Plant Maintenance

During plant and equipment maintenance, it is important not to introduce hydrocarbon contaminants (oil and grease) or other particles by ensuring the use of good practices for oxygen equipment. Guidance is provided by several documents listed in Section 8. Components to be installed shall be sealed and stored in plastic containers labeled DEGREASED FOR OXYGEN SERVICE. Cleaning and degreasing is achieved using a range of standard products compatible with oxygen. The use of these solvents or detergents requires strict control and it shall be ensured that they are properly removed by natural evaporation or purging with nitrogen prior to the plant being put back in service. In some cases, testing using Draeger tubes or ultraviolet lamps might be necessary.

Where oils are needed for lubrication and can come in contact with an oxygen-enriched stream, oxygen compatible oils and greases shall be used.

Particular attention should be given to the use of oxygen compatible gaskets in piping systems that can transport or come into contact with oxygen-enriched gas or liquid streams.

7.7.4 Cleaning Reboilers and Column Sumps

7.7.4.1 Heavy Hydrocarbon, Oil and Grease Removal

Heavy hydrocarbons, oil, and grease contamination can be removed only by solvent degreasing techniques. These can vary from cold liquid flushing through the cores by pumped recirculation or spraying across or through individual passages. Regular sampling of the solvent and testing for hydrocarbon is an indication of the quantity of hydrocarbon being removed and whether clean up is being achieved. To achieve the required cleanliness requires entry to the column.

Alternatively, the hot vapor recondensation technique is used. This is achieved by introducing hot solvent vapors into the equipment that, when recondensed in the equipment, dissolve the hydrocarbons, which then appear in the collected condensate. This can be achieved without entry to the column area.

Both of these methods rely on the solvent reaching all surfaces, which might not be guaranteed if some passages are blocked or if preferential flow occurs.

For either technique, it is critical to ensure that the solvent used is oxygen compatible and/or totally removed. For a listing of acceptable degreasing agents, refer to AIGA 012/04 or CGA G-4.1, both of which are cited in Section 8.

Purging of the equipment (with nitrogen) after use is critical to ensure that any liquid and vapor solvent is removed from impulse lines, drains, and dead legs before the plant is recommissioned.

7.7.4.2 Particulate and Perlite Removal

The removal of perlite and other permanent solids is critical to avoid the serious risk of dead end boiling, and can be achieved only by internal work requiring entry to the reboiler and column sump areas. Techniques include:

- rupture disc technique (for exchangers); and
- mechanical cleaning using vibration, blow through, and vacuuming.

The rupture disc technique (“Marston Excelsior” procedure) involves pressurization and rapid depressurization, creating shock and excessive velocity to dislodge and vent the perlite. A thin, scored gasket is placed over an available nozzle (flange) near to the inlet of the contaminated exchanger. A source of nitrogen (or air) slowly pressurizes the exchanger from an alternative nozzle until the gasket bursts and releases the perlite. Progressively thicker gaskets are used to increase the burst pressure (within the safe working pressure of the vessel or equipment). This continues until no further evidence of perlite is seen. This technique has been used on main exchangers (FEP dust carryover) and sub coolers (adsorber dust carryover) successfully. This technique should not be used on columns as it can result in tray collapse.

Mechanical cleaning includes the use of vibration pads on the sides of the exchangers to loosen trapped particles within the cores. Either blowing through or vacuuming can be used to remove particles.

Evidence of successful removal might be provided by using an endoscope and entering each fin through the whole length of the exchanger and visually examining that no perlite remains.

7.7.5 Gas and liquid phase adsorbers

If there is any external evidence that adsorbent has been lost in significant quantity from a gas or liquid phase adsorber such as by having to top-off the bed material on inspection during a maintenance shutdown or if the material is significantly powdered, investigate the circuit further. Determine if the missing material has accumulated in any downstream vaporizers or within the low pressure column to which the LOX return is connected. If evidence of loss of adsorbent is determined, the plant manufacturer should be contacted.

WARNING: *Operating a reboiler with particulates partially or completely blocking passages can lead to hydrocarbon accumulation and potentially an explosion.*

8 References

Unless otherwise specified, the latest edition shall apply.

[1] EIGA 704/05: *Safe Practices Guide for Cryogenic Air Separation Plants*, Compressed Gas European Industrial Gases Association, 3-5, avenue des Arts, 1210 Brussels. www.eiga.org

[2] EIGA 702/04: *Safe Use of Brazed Aluminium Heat Exchangers for Producing Pressurized Oxygen*, Compressed Gas European Industrial Gases Association, 3-5, avenue des Arts, 1210 Brussels. www.eiga.org

[3] CGA G-4.1: *Cleaning Equipment for Oxygen Service*, Compressed Gas Association, Inc., 4221 Walney Road, 5th Floor, Chantilly, VA 20151. www.cganet.com

[4] CGA O2-DIR: *2000 Directory of Cleaning Agents for Oxygen Service*, Compressed Gas Association, Inc., 4221 Walney Road, 5th Floor, Chantilly, VA 20151. www.cganet.com

[5] EIGA 701/04: *Safe Use of Aluminum Structured Packing for Oxygen Distillation*, Compressed Gas European Industrial Gases Association, 3-5, avenue des Arts, 1210 Brussels. www.eiga.org

[6] AIGA 012/04: *Cleaning of Equipment for Oxygen Service* Asia Industrial Gases Association, 298 Tiong Bahru Road, #20-01 Central Plaza, Singapore 168730. www.asiaiga.org

[7] McKinley, C., and E.S.J. Wang. "Hydrocarbon System Solubility", *International Advances in Cryogenic Engineering*, Volume 4, pp.11-25 (1958).

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[9] Houghton, Sunder, Weist, and Trexler, "Trace Component Accumulation in Downflow Reboilers," AIChE Spring Meeting, Atlanta, GA, March 2000. www.aiche.org

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[13] R.M. Hardeveld, Groeneveld, M.J., Lehman, J.-Y., and Bull, D.C., "Investigation of an Air Separation Unit Explosion," *Journal of Loss Prevention in the Process Industries*, Vol. 14, pp. 167-180, 2001. www.elsevier.com

[14] J.-Y. Lehman, Wei, X.C., Hua, Q.X., Delannoy, G., “Investigation of the Fushun ASU Explosion in 1997,” *Journal of Loss Prevention in the Process Industries*, Vol. 16, pp 209-221, 2003. www.elsevier.com

Appendix A: Table 1: Plugging, Flammable and Corrosive Components of Air

Plugging Components		**Flammable or Reactive Components**		**Corrosive Components**	
Moisture	H_2O	Methane	CH_4	Sulphur Dioxide	SO_2
Carbon Dioxide	CO_2	Acetylene	C_2H_2	Sulphur Trioxide	SO_3
Nitrous Oxide	N_2O	Ethylene	C_2H_4	Hydrogen Sulphide	H_2S
		Ethane	C_2H_6	Chlorine	Cl_2
		Propylene	C_3H_6	Hydrochloric Acid	HCl
		Propane	C_3H_8	Ammonia	NH_3
		Other Hydrocarbons		Other Sulphur Compounds	
		Oxides of Nitrogen	NO_x	Other Chlorides	
		Ozone	O_3		
NOTE—This table is duplicated in CGA P-8, *Safe Practices Guide for Cryogenic Air Separation Plants*.					

Appendix B: Table 2: Properties of Air Contaminants

	Acetylene C_2H_2	**Carbon Dioxide** CO_2	**Propylene** C_3H_6
Solubility in O2 at 90.2 K, 1.013 bar abs. (ppm/v) [1]	4 - 6	4 - 5	3600 - 6700
***K*-value** in O_2 at 90.2 K, 1.013 bar abs [2]	2×10^{-2}	10^{-3}	3×10^{-6}
Lower Flammability Limit in air at 293 K, 1.013 bar abs (%)	2.5	non-flammable	2.1
Condensed Phase (Solid or Liquid)	Solid	Solid	Liquid
Density Relative to LOX at 90.2 K, 1.013 bar abs	0.64	1.4	

	Nitrous Oxide N_2O	**Ethylene** C_2H_4	**Propane** C_3H_8
Solubility in O_2 at 90.2 K, 1.013 bar abs. (ppm/v) [1]	140 - 160	13 000-30 000	9800
***K*-value** in O2 at 90.2 K, 1.013 bar abs [2]	5×10^{-4}	2×10^{-3}	3×10^{-7}
Lower Flammability Limit in Air at 293 K, 1.013 bar abs. (%)	non-flammable	2.7	2.1
Condensed Phase (Solid or Liquid)	Solid	Solid	Liquid
Density Relative to LOX at 90.2 K, 1.013 bar abs	1.4	0.66	

	Methane CH_4	**Ethane** C_2H_6
Solubility in O_2 at 90.2 K, 1.013 bar abs. (ppm/v) [1]	Miscible	128 000-250 000
***K*-value** in O2 at 90.2 K, 1.013 bar abs [2]	0.3	2×10^{-4}
Lower Flammability Limit in Air at 293 K, 1.013 bar abs (%)	5	3
Condensed Phase (Solid or Liquid)	Does not form second liquid phase	Liquid
Density Relative to LOX at 90.2 K, 1.013 bar abs	Does not form second liquid phase	

[1] Ranges in solubility reflect different sources of experimental data. The two most comprehensive references are Karwat and McKinley. Solubility will be greater in saturated liquid at higher temperatures and pressures.

[2] *K*-value data is only accurate to approximately 1 order of magnitude. These values vary significantly with temperature and pressure.

Appendix C: Table 3: Adsorption of Air Contaminants

	No Adsorption	Partial Adsorption [1]	Total Adsorption
Alumina Front End Purification	Methane CH_4 Ethylene C_2H_4 Ethane C_2H_6 Propylene C_3H_6 Propane C_3H_8 Nitric Oxide NO n-butane nC_4H_{10}	[2]Carbon Dioxyde CO_2 Nitrous Oxide N_2O Acetylene C_2H_2	[3]Ozone O_3 Oxides of Nitrogen NO_2 N_2O_3 Moisture H_2O
Molecular Sieve Front End Purification	Methane CH_4 Ethane C_2H_6 [4]Nitric Oxide NO	Ethylene C_2H_4 Propane C_3H_8 Nitrous Oxide N_2O	Carbon Dioxide CO_2 Acetylene C_2H_2 Propylene C_3H_6 [3]Ozone O_3 Oxides of Nitrogen NO_2 N_2O_3 n-Butane nC_4H_{10} Moisture H_2O Oxygenates Chlorinated Hydrocarbons
Silica Gel Rich Liquid Adsorbers Vapour Phase Adsorbers LOX Adsorbers	Methane CH_4 Ethane C_2H_6	Carbon Dioxide CO_2 Ethylene C_2H_4 Propylene C_3H_6 Propane C_3H_8 Nitrous Oxide N_2O	Acetylene C_2H_2 Ozone O_3 Dienes

Assumptions: Contaminant at less than 10 ppm/v; carbon dioxide at 400 ppm/v
Total adsorption of heavy hydrocarbons (C_4+)

[1] Degree of removal is dependent on design and operating parameters. Total removal might be possible with adequate design.

[2] Molecular sieve is normally designed to remove carbon dioxide. Refer to Section 7 for proper operations required to prevent breakthrough.

[3] By decomposition.

[4] Nitric oxide is oxidized by air and subsequently trapped.

Appendix D: Table 4: Typical Default Air Quality Design Basis
(for adsorptive FEP system)

Component	**Design Air Quality (ppm/v)**
Methane	5
Ethane	0.1
Acetylene	0.3
Ethylene	0.1
Propane	0.05
Propylene	0.2
C_4+ hydrocarbons	1
Carbon Dioxide	425
NO_x (NO+ NO_2)	0.1
N_2O	0.35
NOTE—This table represents the maximum simultaneous concentrations in the air intake to the plant. They are assumed for design purposes in the absence of specific data. Changes to the designs of various components may be required if these concentrations are exceeded. Actual data for the locality should be provided to the supplier whenever such information is available.	

Appendix E: Table 5: Maximum Contaminant Levels in Liquid Oxygen Thermosyphon Reboiler Operation at 1.2 bar abs

Component		Maximum Allowable Concentration (ppm/v)
Methane	CH_4	500
Acetylene	C_2H_2	0.5
Ethylene	C_2H_4	200
Ethane	C_2H_6	250
Propylene	C_3H_6	35
Propane	C_3H_8	100
C_4 Hydrocarbons		5
Total hydrocarbons (THC) (as CH_4)		500
Carbon Dioxide	CO_2	4.0
Nitrous Oxide	N_2O	100
NOTE—Care must be taken in sampling cryogenic liquids to achieve accurate, consistent results. Any continuous liquid stream must be vaporized quickly to ensure that the gas phase concentration remains the same as the bulk liquid composition. Failure to do this can lead to underestimating the hydrocarbon concentration in the bulk.		

Appendix F: Table 6: Maximum Contaminant Levels in Liquid Oxygen Downflow
Reboiler Operation at 1.2 bar abs

Component		Maximum Allowable Concentration (ppm/v)
Methane	CH_4	500
Acetylene	C_2H_2	0.5
Ethylene	C_2H_4	15
Ethane	C_2H_6	15
Propylene	C_3H_6	1
Propane	C_3H_8	1
C_4 Hydrocarbons		1
Total hydrocarbons (THC) (as CH_4)		500
Carbon Dioxide	CO_2	0.5
Nitrous Oxide	N_2O	5

NOTES

1. Any significant increase in hydrocarbon component concentrations in the reboiler sump during plant load changes or shutdowns is a sign that hydrocarbon accumulation has taken place. Draining of the reboiler sump liquid or reboiler derime should be considered.
2. It should be noted that care must be taken in sampling cryogenic liquids to achieve accurate, consistent results. Any continuous liquid stream must be vaporized quickly to ensure that the gas phase concentration remains the same as the bulk liquid composition. Failure to do this can lead to underestimating the hydrocarbon concentration in the bulk.

Appendix G: Figure 1: Representation of Reboiler Core Submergence