SAFE OPERATION OF REBOILERS/CONDENSERS IN AIR SEPARATION UNITS

Doc 65/20

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Preface

As part of a programme of harmonisation of industry standards, the European Industrial Gases Association has issued Doc 65, *Safe Operation of Reboilers/Condensers in Air Separation Units*, jointly produced by members of the International Harmonisation Council.

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 (EIGA), 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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2.1	Amended with new text
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Note: Technical changes from the previous edition are underlined

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 shall be recognized and addressed by design and operating practice.

2   Scope and purpose

2.1   Scope

This publication 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 greater than 75% in the liquid phase. Its guiding principles may 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 that are used in conjunction with krypton/xenon production are typically operated with higher hydrocarbon limits than typical air separation unit (ASU) reboilers. The allowable levels of hydrocarbons as well as additional safeguards for the bath-type reboilers used in these systems are listed in Appendix A.

2.2   Purpose

The purpose of this publication is to describe the design and operating practices that shall be followed in the reboiler sections of cryogenic air separation plants. In particular, the potential hazard introduced by hydrocarbons or other contaminants that could 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 publication 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

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

3.1   Publication terminology

3.1.1   Shall

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

3.1.2   Should

Indicates that a procedure is recommended.

3.1.3   May

Indicates that the procedure is optional.

3.1.4   Will

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

3.1.5   Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Analytical plant derime

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

3.2.2 Argon condenser

Heat exchanger used to provide condensing duty for the top of an argon column in an ASU. The cooling duty for this exchanger is typically supplied via the boiling of an oxygen-enriched liquid, typically containing less than 75% oxygen.

3.2.3 Auxiliary vaporizer

ASU supplemental process heat exchanger that vaporizes low pressure column liquid oxygen 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 liquid oxygen circulation through a liquid oxygen adsorber.

3.2.4 Cold standby

Condition where equipment is held at cryogenic conditions for immediate service on demand.

3.2.5 Coldbox

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

3.2.6 Dead end boiling

Condition occurring in 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.

3.2.7 Deriming

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 other atmospheric impurities. Also known as defrosting, de-icing, and thawing.

3.2.8 Dry boiling

Condition occurring in thermosyphon/bath-type 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.

3.2.9 Front-end purification (FEP)

Use of adsorbers that operate at temperatures greater than 0 °C (32 °F) to remove moisture, carbon dioxide, and many of the hydrocarbons, either partially or fully, from the air feed prior to its being supplied to the coldbox.

3.2.10 Gas phase adsorbers

Means to reduce concentrations of atmospheric impurities by adsorbing them cryogenically from the gas phase. Also known as cold-end traps.

3.2.11 Internal compression

Process in which liquid oxygen from the column is pumped to an elevated pressure and vaporized in heat exchangers external to the column system but within the coldbox to produce gaseous oxygen. Also known as liquid pumping.

3.2.12 Liquid oxygen

Throughout this document, all requirements applicable to liquid oxygen are also applicable to liquids with an oxygen concentration greater than 75%

3.2.13 Liquid oxygen adsorbers

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 liquid oxygen filters (although the action is not physical filtration, but only adsorption).

3.2.14 Main reboiler

Integrated heat exchanger used to heat couple the two primary distillation columns of an 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.

3.2.15 Plugging

Blockage of channels within the reboiler either by foreign particulates (for example, silica gel or perlite) or by the solidification of atmospheric impurities (for example, carbon dioxide or nitrous oxide), which can lead to dead end boiling.

3.2.16 Regenerators

Prepurification 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.

3.2.17 Reversing heat exchanger (REVEX)

Prepurification 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.

3.2.18 Rich liquid adsorber

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.

3.2.19 Submergence

Measure used for thermosyphon reboilers to indicate the degree to which the reboiler core is submerged in the sump liquid 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, refer to Appendix B.

4   Reboilers incidents

The reboiler incidents are 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 liquid oxygen, it is absolutely essential to prevent any hydrocarbon accumulation within the liquid oxygen reboiler exchangers.

4.1   Major explosions

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

Under very specific conditions, 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 aluminium in the coldbox becomes a fuel that reacts with oxygen in the liquid oxygen sump of the distillation column.

Two serious events of this nature occurred in 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 incidents are thought to have followed the same series of events:

a)   Spontaneous ignition and combustion of flammable air contaminants that had accumulated within the passages of the reboiler;

b)   Promoted ignition and combustion of a large fraction of the aluminium material from which the reboiler exchangers were fabricated;

c)   Flash vaporization of liquid oxygen; and

d)   Explosive rupture of the cryogenic distillation column and coldbox casing.

4.2   Limited explosions

Limited explosions can cause damage within the coldbox but do not breech it. Damage is typically confined to the equipment within the coldbox. Piping and other equipment can be damaged but are repairable during an extended plant outage.

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 coldbox. 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.

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 can 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.

Appendix C lists many components present in air that can cause problems in air separation plants. The components are classified according to the problems they cause.

Since the main focus of this publication is safety, the corrosive components are not be considered further. Plugging components, while not safety issues by themselves, can accumulate and cause dry boiling or dead end boiling and hydrocarbon buildup 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. Appendix D 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. Appendix E lists the maximum level of contaminants in the main reboiler (thermosyphon type) allowable for safe plant operation. Appendix F 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, liquid oxygen adsorbers, and through dead end boiling in piping dead legs.

Appendix D in conjunction with Appendix G 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 not removed or only partially removed in the front-end purification adsorbers;

- have low K-values, which means very little is removed in the gaseous oxygen product; and

- have low solubility (with the exception of ethane).

These and additional contaminants can be of concern in reversing heat exchanger (REVEX) or regenerator plants. The following sections of this publication describe the methods that can be used to remove or limit the buildup 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 that 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 Appendices E and F.

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 147, *Safe Practices Guide for Cryogenic Air Separation Plants* [1].[1]

The air separation plant shall be designed to remove or reduce to less than acceptable limits the 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

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

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 table should list the maximum level of each contaminant in the air of an industrial area that could be processed safely in the air separation plant without additional modifications. Appendix H defines typical maximum levels for a plant with an adsorption based FEP system.

If concentrations are reported to be higher than those in Appendix H, the designer shall analyze the impact and specify whether additional modifications to the design and/or to the operating instructions 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 haze and smoke from forest fires, burning farmland, or other biomass combustion should also be considered.

6.2   Design of prepurifying systems

Various means have been used for contaminant removal. Most modern ASUs use 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 can also 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 vapour or liquid phase adsorbers, which operate at cryogenic temperature. A detailed explanation of the operation of these prepurifying systems can be found in EIGA Doc 147 [1].

7   Operations

7.1   Importance of carbon dioxide removal

One of the most basic and important factors in maintaining air separation plant safety with respect to hydrocarbons is the proper operation of the prepurifying system. Whether the plant uses an FEP or REVEXs/regenerators, ensuring that the prepurifying system is operating effectively is important to prevent carbon dioxide from entering the coldbox 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 is also 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 greater than the detectable limit at the end of the adsorption cycle should not be allowed in plants that use an FEP system. If breakthroughs occur, refer immediately to the operating instructions to tune the sequencer or adsorber parameters and/or the process conditions in order to eliminate the breakthroughs. If required, further investigation including ambient air analysis and process equipment performance troubleshooting should be carried out.

The carbon dioxide concentration shall be monitored at the outlet of the adsorption vessel in the ASU for oxygen production (this analyzer can be used for analysis of the reboiler sump). There shall be a high carbon dioxide alarm, typically set at 1 ppm/v. This indicates breakthrough of carbon dioxide and also some previously adsorbed hydrocarbons and other contaminants. 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 ensure that they do not exceed the values given in Appendices E and F.

There shall be a high high carbon dioxide alarm, set at 5 ppm/v or less. In case of high high alarm or where there is no sump analysis, the plant shall be shut down if the adsorber cannot be switched within 30 minutes or immediately if the carbon dioxide concentration reaches 10 ppm/v.

For plants with downflow reboilers, the maximum concentration of contaminants in the reboiler sump are less than for bath-type reboilers. Therefore, the FEP breakthrough alarm should be set at less than 1 ppm/v and the shutdown level at less than 10 ppm/v. In any case, these values shall be according to the plant manufacturer specification.

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. The plant <u>may</u> operate for an extended period under these conditions <u>provided that safe reboiler contaminant levels are not exceeded in accordance with Appendices E and F. Otherwise, the plant shall be shut down.</u>

In the case of REVEX or regenerator plants, the midpoint and cold-end temperatures of the exchanger shall be controlled to ensure that the exchanger correctly removes carbon dioxide and moisture. For more details about temperature control of REVEX plants, see EIGA Doc 147 [1]. 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

Current designs of air separation plants offer two main technologies for reboilers:

- bath-type reboilers (also known as thermosyphon reboilers); and

- downflow reboilers.

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 publication are those in which the liquid bath contains greater 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 liquid oxygen entering the passages concentrate progressively as the liquid oxygen 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. 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 <u>solid</u> deposits of <u>plugging</u> contaminants can build up in the reboiler core passages. 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.

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

Operating the bath below a specific level with respect to the core height reduces the liquid head and recirculation flow leading to complete vaporization of liquid oxygen as it flows up the passages. This phenomenon of no recirculation flow is called dry vaporization or dry boiling.

Increasing this liquid level allows the recirculation flow to re-establish itself and eliminates the possibility of dry boiling. 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 designer. 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 shall 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 Appendix B 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.

If the reboiler submergence is less than the minimum level for a period of time exceeding the recommended time by the manufacturer, the plant should be shut down. Operation at levels greater than 100% submergence can give an additional margin of safety. However, care shall 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.

Liquid oxygen 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. 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 liquid oxygen increases progressively as the oxygen vaporizes in the passage. A sufficient amount of liquid oxygen shall flow from the bottom of the core passages to ensure that the maximum hydrocarbon content in the liquid oxygen does not reach dangerous levels and to ensure all passages remain wetted. Therefore, the minimum liquid flow specified by the plant manufacturer shall be maintained.

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 coldbox.

Some once-through-type reboilers are 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 liquid oxygen (from the sump of the low pressure column in the case of the main reboiler) that already may have been passed through a once-through core. Generally, the concentration of contaminants in this type of reboiler is greater 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 process parameter that indicates 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 the period recommended by the

plant manufacturer, the ASU shall be shut down. If no recommendation is provided by the plant manufacturer, the period should not exceed 60 minutes.

WARNING: The flow rate provided by the pump shall always 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 at greater than the design capacity, increasing the liquid oxygen 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. If installed, the screen mesh shall be specified by the plant designer 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 greater vapour fraction at the exit of the reboiler as compared to a bath-type reboiler. Because of this greater vapour 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 less than 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. Greater concentrations of these trace components cause greater 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 shall be within the limits specified by the plant manufacturer. Appendix F 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 less than the values in Appendix F. 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 contaminants. The manufacturer's recommendation for derime intervals should be strictly followed. Solid carbon dioxide and nitrous oxide can retain hydrocarbons within the reboiler, so it is necessary to remove these contaminants 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/flow 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 vapour 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. Correct calibration of level and flow transmitters is essential to the continuous safe operation of the plant. Calibration of the transmitters shall be maintained at the frequency stated in the plant operating manual. If all taps are blocked or if the reboiler level cannot be determined for any other reason, the plant should be shut down to restore level measurement.

7.3   Control of contaminants

Regardless of the type of prepurifying 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 contaminants accumulate shall be limited to avoid hazardous operation and shall be removed from the liquid phase. Only methane is sufficiently volatile to partially leave in the vapour phase of the gaseous oxygen product stream.

There are principally two methods of maintaining a safe level of contaminants in liquid oxygen:

- liquid oxygen adsorbers (see 7.3.1); and

- purging (see 7.3.2).

A purge shall be taken even if liquid phase adsorber is installed to remove hydrocarbons from the reboiler sump liquid because these adsorbers may not completely remove all of the hydrocarbons. This purge shall be defined by the plant manufacturer. When none is specified, the minimum purge shall be in accordance 7.3.2.

7.3.1   Liquid oxygen adsorbers

Liquid oxygen adsorbers are designed to remove certain contaminants from a liquid oxygen 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 Appendix G for the effectiveness of removal of the complete list of contaminants. In particular, for REVEX and regenerator plants, liquid oxygen adsorbers are effective for removal of residual acetylene, dienes, and C4+ 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 using thermosyphon-driven oxygen guard adsorber circuits should follow these additional precautions:

- Adhere to the liquid oxygen circulation operating parameters specified by the plant designer'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, maintenance procedures should be adapted accordingly, and the plant should (on the basis of the introduction) not 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 designer's procedures. Avoid excessive liquid oxygen flashing through the regenerated bed on cooldown as this could 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 liquid oxygen 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 liquid oxygen circuit vaporizer and piping are correctly derimed and recooled to operating temperature as part of the operating procedures for an ASU turn around. Liquid oxygen allowed to boil in the circuit rather than being drained off can 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 dry boiling.

7.3.2   Purging

Hydrocarbons that pass through 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 and then pumped and fully vaporized in exchangers external to the column system.

However, in a plant that produces only gaseous oxygen product (taken directly off the column) or a very small amount of liquid, it is necessary to deliberately remove a sufficient 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 liquid oxygen purge rate of 0.1% to 0.2% of the incoming air is recommended. Where a continuous purge is not practical, purge equivalent to this rate shall be taken at least every 8 hours.

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

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

Where:

CF = 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 vapour phase

F_{feed} = air molar flow rate to the column system

F_{LOX} = molar flow rate of liquid oxygen from the reboiler

K = y/x for the component at equilibrium

F_{GOX} = molar gaseous oxygen flow rate from the reboiler

For an internal compression cycle, where no gaseous oxygen is taken from the reboiler and the liquid oxygen product flow is approximately 20% of the air from the main reboiler, the concentration factor is approximately 5 for all contaminants. When liquid oxygen 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 (Appendix D). In this case, the concentration factor is approximately 16 and the vast majority of the methane exits in the gaseous oxygen product.

7.4   Contaminant analysis

The introduction into the plant of quantities of hydrocarbons and other contaminants greater than the design basis always represents a risk, regardless of the protection systems and procedures 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 an awareness of the current environment surrounding the plant. Information to be maintained should include:

- 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 incident;

- distance between these potential sources and the ASU air intake; and

- local atmospheric conditions.

Note that the potential risk of an ASU 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 ASU and its specific process design as well as the potential for contaminant releases, the following continuous contaminant measurement devices shall be considered:

- carbon dioxide analyzer at the outlet of the prepurifying system;

- total hydrocarbon analyzer in the reboiler with the greatest potential concentration of contaminants. This is generally the main reboiler sump; and

- analyzer that can detect individual hydrocarbon contaminants in the reboiler with the greatest potential concentration of contaminants.

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

Appendices E and F list the maximum allowable contaminant concentrations for the reboiler. These maximum contaminant values are much greater than the normally anticipated operating levels.

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

Based on these parameters, the designer should indicate the anticipated operating main reboiler contaminant level. In addition, the designer and operator should sample the liquid oxygen 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 important, 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 greater 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 Appendices E and F shall not be exceeded.

Care shall be taken to ensure that the correct reboiler operating levels (bath-type reboilers, see 7.2.1) and recirculating flows (downflow reboilers, see 7.2.2) are maintained. The measured average contaminant concentration in the sump liquid can be a misrepresentation and less 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 is essential to the continuous safe operation of the ASU. Calibration of the analyzers at the previously mentioned points shall be maintained at the frequency stated in the plant's operating manual.

Care shall 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. If any changes are noted, consideration shall be given as specified in 6.1 to determine the impact on plant operation.

7.5   Transient conditions

Transient conditions can cause greater 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

The liquid level in the reboiler generally increases while reducing the plant load and decreases while increasing the load.

Depending on 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 and the maximum time period allowed for low submergence in these reboilers should 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 to less than 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 to less than the normal operating level. This is acceptable, as long as the steady state level is greater than 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. 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 liquid oxygen effectively deconcentrate the contaminants entering the air separation plant. In plants without an instrumented purge line, liquid oxygen production shall be maintained at or greater than 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 can be well greater than 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. In addition, liquid density may have changed that can cause inaccuracy in the indicated reboiler level.

During a one day or two day cold standby period, continue to recirculate flow through liquid oxygen adsorbers if installed. The following 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 and regenerate liquid oxygen adsorbers. The regeneration should be done soon after complete draining of the liquid and purging of the adsorber with nitrogen to avoid the release of contaminants in gaseous oxygen atmosphere.

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

When injecting liquid into the plant, it is advisable to use liquid nitrogen rather than liquid oxygen in particular for a long-term cold standby. When liquid oxygen is used, be aware that extra hydrocarbons, carbon dioxide, nitrous oxide, and contaminants in general are added to the system and could accumulate to exceed the maximum contaminant levels,

If a hydrocarbon analyzer is available, continue monitoring hydrocarbons during the cold standby. All liquid shall be drained if the contaminant levels in Appendix E or F (as applicable) are reached. However, since sampling during a non-operating period may not be representative, a lower result should not be used to justify a failure to adhere to other recommended actions.

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 in the following subsections 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 procedure can be a combination of the two described in 7.5.3.1 and 7.5.3.2. If the reboiler does not have sufficient liquid, less than 50% submergence, draining of the remaining liquid may be required to remove the contaminants concentrated in the sump. For precautions related to high or low liquid levels, refer to 7.2.

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 such as reducing the incoming air to the process should be considered.

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 to less than 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 can be enriched in hydrocarbons, nitrous oxide, and possibly carbon dioxide, which can cause deposits in the reboiler core passages. Procedures should be developed to prevent the carbon dioxide concentration from increasing to a level greater than one-half of the carbon dioxide solubility in the liquid in the reboiler (accounting for actual composition) at atmospheric pressure.

Problems with low liquid levels during start up can easily be overcome with a liquid injection system. As noted in 7.5.2, liquid nitrogen is preferred but liquid oxygen may be used if the correct precautions are taken.

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.

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 liquid oxygen and rich liquid adsorbers (if available) have been regenerated prior to start up.

For REVEX plants, drain the first liquid (approximately 20% to 30% of normal operating level) after producing it in the sump of the reboiler.

7.6   Deriming

ASUs shall be derimed at regular intervals in order to remove any excessive impurities such as hydrocarbons, carbon dioxide, and nitrous oxide that could 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 in accordance with the procedure in 7.6.1.

7.6.1 Procedure

The deriming procedure shall be described in detail in the operating manual. Although the procedure differs with the various types of ASUs, the operating manual instructions are to be adhered to.

The following points highlight the most important steps:

a) Drain all liquids;

b) Establish the sequence of circuits to be derimed. Derime the circuits in that sequence;

c) Force the flow as far as possible through all the sections;

d) 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;

e) Verify the presence of a flow from all deriming outlets;

f) Open all instrument lines towards the end of the deriming process; and

g) 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 (59 °F) 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 greater derime outlet temperature is desirable for plants with REVEXs and those with derime heaters. A minimum of 30 °C (86 °F) is preferred and temperatures up to 60 °C (140 °F) 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 plant's operation manual. A risk assessment should be performed by qualified personnel to determine the required frequency for the particular ASU in the particular location. The following factors should be included in the risk assessment:

- design factors, for example, FEP/REVEX, reboiler type, purge rate, liquid oxygen purity;

- operating factors, for example, liquid analysis arrangements, manned/unmanned, plant log;

- environmental factors, for example, plant location/surrounding industry, potential air contaminants, air quality; and

- historical factors, for example, 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, for example, 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 should always 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 shall 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 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 aluminium or stainless steel shavings, aluminium oxide, rust, and welding slag.

7.7.2   Foreign material due to plant operations

During the operation of the ASU, 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. Through boiling and circulation, this dust can pass through the fins of the reboiler core, block individual passages, and lead to dead end boiling. In all cases, dust eventually accumulates in the liquid oxygen sump. Dust generation or migration downstream can be prevented by specific design of the adsorber system or by incorporating a filter.

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.

Oil migrating from this type of equipment can contaminate the cold end of the plant equipment adjacent to the equipment in question and usually deposits at that point.

Continued operation allows movement of this oil to other parts of the process and possible accumulation in the liquid oxygen 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 7.7.4.1).

7.7.2.3   Perlite

Incidents have been associated with plugging of reboilers with perlite. This can occur as a consequence of a component or piping failure within a perlite-insulated coldbox. 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 is essential prior to restarting the plant.

7.7.2.4 Liquid oxygen pump filters

Where liquid oxygen pump filters are provided, it is essential that they are not removed while the plant is in operation. The purpose of these filters is to protect the pump itself and to ensure that no particles become trapped in the downflow reboiler distributor or in any other process equipment. If blocking of these filters occurs, the cause shall be investigated.

7.7.3 Foreign material due to plant maintenance

During plant and equipment maintenance, it is important not to introduce hydrocarbon contaminants such as oil and grease or other particles into the process piping or equipment by ensuring the use of good practices for oxygen equipment. Guidance is provided by publications listed in Sections 8 and 9. Components to be installed shall be sealed, stored, and labelled to indicate that they have been cleaned for oxygen service. Cleaning and degreasing are 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 removed prior to the plant being put back in service. In some cases, testing using analyser tubes or ultraviolet lamps may 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 come into contact with oxygen-enriched gas or liquid streams.

7.7.4 Cleaning reboilers and column sumps

Cleaning reboilers, columns, sumps, and the internals of other coldbox process equipment is a major task requiring a risk assessment and usually the technical support of the plant designer.

7.7.4.1 Heavy hydrocarbon, oil and grease removal

Heavy hydrocarbons, oil, and grease contamination can best 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 vapour recondensation technique is used. This is achieved by introducing hot solvent vapours 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.

WARNING: Both of these methods rely on the solvent reaching all surfaces, which may not be guaranteed if some passages are blocked or if preferential flow occurs. If a blockage is suspected, it shall be cleared prior to solvent washing.

For either technique, it is critical to ensure that the solvent used is either oxygen compatible or totally removed. See EIGA Doc 33, *Cleaning of Equipment for Oxygen Service* [2].

Purging of the equipment with nitrogen even if the solvent is not flammable after use is critical to ensure that any liquid and vapour 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 disk technique (for exchangers); and

- mechanical cleaning using vibration, blow through, and vacuuming.

The rupture disk technique involves pressurization and rapid depressurization and creating shock and high 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 subcoolers (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 may be provided by using a boroscope 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 liquid oxygen 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 Doc 147, *Safe Practices Guide for Cryogenic Air Separation Plants*, European Industrial Gases Association. www.eiga.eu

NOTE—This publication is part of an international harmonization program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

[2]   EIGA Doc 33, *Cleaning of Equipment for Oxygen Service,* European Industrial Gases Association. www.eiga.eu

NOTE—This publication is part of an international harmonization program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

[3]   Karwat, Ernst. "Hydrocarbons in Air Separation Plants," Chemical Engineering Progress, Vol. 54, No. 10, October 1958. www.aiche.org

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

[5]   EIGA Doc 145, *Safe Use of Brazed Aluminium Heat Exchangers for Producing Pressurized Oxygen*, European Industrial Gases Association. www.eiga.eu

NOTE—This publication is part of an international harmonization program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

9   Additional References

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

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

Lassmann and Meilinger, "Determination of Hydrocarbon Adsorption on Solid CO2 and N2O at Ambient Pressures," Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Ninth Volume, ASTM STP 1395; Steinberg, Newton, Beeson, Eds., ASTM International. www.astm.org

Lehman, J.Y., Wei, X.C., Hua, Q.X., and 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

Meneses, D., J. Thonnelier, C. Szulman, and E. Werlen, "Trace Contaminant Behavior in Air Separation Units," Cryogenics 2000 Conference, Prague, October 2000, International Institute of Refrigeration. www.iifiir.org

Miller, E. Auvil, S., Giles, N., and Wilson, G., "The Solubility of Nitrous Oxide as a Pure Solute and in Mixtures with Carbon Dioxide in Air Separation," AIChE Spring Meeting, Atlanta, GA, March 2000. www.aiche.org

Appendix A—Operation of a reboiler associated with krypton/xenon production

Production of krypton/xenon from an ASU typically requires concentration of the krypton and xenon in a supplemental thermosyphon reboiler bath prior to sending the stream to a purification unit for further processing. The supplemental reboiler can be either in a separate vessel or in the sump of the distillation column. Typically, the air separation plant will include additional equipment to remove trace quantities of carbon dioxide, nitrous oxide, and unsaturated hydrocarbons such as acetylene, ethylene, and propylene so that these components do not also have a higher than typical concentration in the supplemental reboiler bath. However, the concentration of the krypton/xenon leads to concentration of methane, ethane, and propane in the supplemental reboiler bath. The higher concentration of these hydrocarbons in the bath can lead to a rapid build-up of hydrocarbons inside of the supplemental reboiler in the event of operation at low level or a blockage in the supplemental reboiler. In addition, due to the higher levels of impurities in the supplemental reboiler during normal operation, if the purge flow is stopped, a hazardous condition could be reached more rapidly than a typical ASU reboiler bath.
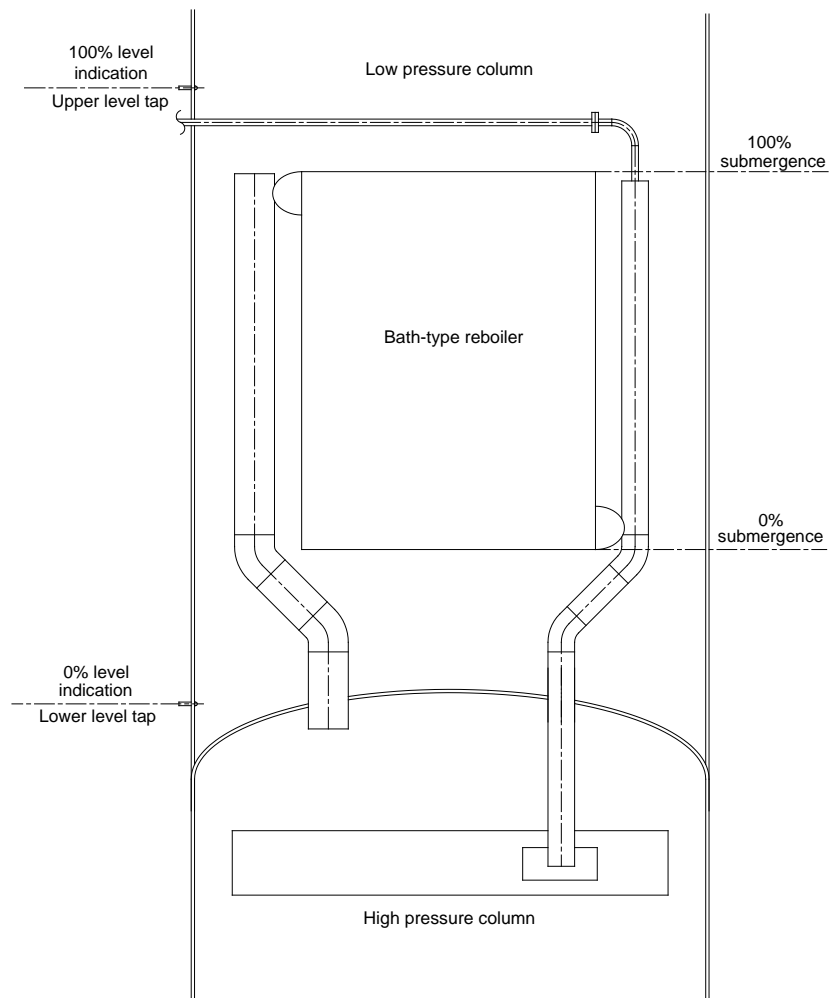
For a supplemental reboiler, Table A-1 gives recommended alarm points to indicate the need to investigate and correct the cause of the alarm as well as the maximum allowable concentration. Methane (or THC measured as CH4), carbon dioxide, and nitrous oxide shall be routinely monitored. Based on the plant design or experience, the manufacturer may recommend monitoring other contaminants listed in the table. If the maximum allowable concentrations are exceeded, the reboiler shall be shut down. Typically, the purge flow is set to keep the methane (or THC measured as CH_4), carbon dioxide and/or the nitrous oxide levels less than the alarm levels shown in the table. These are a function of plant design as well as the level of hydrocarbons in the air. Typically, there is equipment to remove carbon dioxide, nitrous oxide, unsaturated hydrocarbons, and C4+ hydrocarbons. The methane, ethane, and much of the propane in the air will concentrate in the supplemental reboiler bath. This concentration is controlled by purging liquid from the bath. The set point for alarm and shutdown for low purge flow is determined by the manufacturer based on design and operation of the equipment. The alarm and shutdown points for the bath level shown in the following table shall also be followed.

When producing krypton/xenon, the main reboiler bath may operate with higher than normal hydrocarbons. In the case that shutdown limits need to be set higher than those listed in Appendix E, the plant designer's guidelines shall be followed.

Table A-1— Supplemental Reboiler Recommended Alarm Points

Trace impurities component	Symbol	Krypton/Xenon reboiler operating at 1.2 bara	
		Alarm level (ppm/v)	Maximum allowable concentration (ppm/v)
Methane	CH_4	4500	5000 with time delay of 1 hour 7000 with time delay of 1 minute
Total hydrocarbons (THC) (as CH_4)		4500	5000 with time delay of 1 hour 7000 with time delay of 1 minute
Acetylene	C_2H_2	Typically, identical to Appendix E (See previous paragraph)	
Ethylene	C_2H_4		
Propylene	C_3H_6		
Carbon dioxide	CO_2	1.0	4 [1]
Nitrous oxide	N_2O	10	100 (no automatic shutdown required 8-hour delay acceptable) [1]
Other parameters	**Alarm level**		**Shutdown level**
Reboiler submergence See 3.2.19 and Appendix B (100% submergence is normal)	90%		80% with time delay of 1 hour 50% with time delay of 1 minute
Purge flow [2]	50% of the value established by the plant manufacturer design		25% of the value established by the plant manufacturer (1 hour time delay acceptable)

NOTES

1   Care shall be taken in sampling cryogenic liquids to achieve accurate, consistent results. Any continuous liquid stream shall be vaporized to ensure that the gas phase concentration remains the same as the bulk liquid concentration. Failure to do this can lead to underestimating the hydrocarbon concentration in the bulk.

2   The impurity concentrations will vary more quickly for a supplemental reboiler bath than for the main bath due to the   smaller inventory of liquid with the same feed of impurities.

[1]   Due to co-solubility of carbon dioxide and nitrous oxide, these maximum allowable limits may need to be adjusted.   Contact the plant manufacturer to determine the specific limits to be used.

[2]   Purge flow set point may be adjusted for startup and turndown and startup conditions based on plant manufacturer's recommendations.

Appendix B—Representation of reboiler core submergence

Appendix C—Plugging, flammable, and corrosive contaminants of air

Plugging contaminants		Flammable or reactive contaminants		Corrosive contaminants	
Chemical name	**Symbol**	**Chemical name**	**Symbol**	**Chemical name**	**Symbol**
Water	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 EIGA Doc 147 (CGA P-8): Safe Practices Guide for Cryogenic Air Separation Plants [1]					

Appendix D—Properties of air contaminants

Air contaminants	Properties				
	Solubility in oxygen at 90.2 K, 1.013 bar, abs (ppm/v) [1]	*K*-value in oxygen at 90.2 K, 1.013 bar, abs [2]	Lower flammability limit in air at 293 K, 1.013 bar, abs (%)	Condensed phase (solid or liquid)	Density relative to liquid oxygen at 90.2 K, 1.013 bar abs
Acetylene (C_2H_2)	4 to 6	2×10^{-2}	2.5	Solid	0.64
Carbon dioxide (CO_2)	4 to 5	10^{-3}	Non-flammable	Solid	1.4
Ethane (C_2H_6)	128 000 to 250 000	2×10^{-4}	3	Liquid	
Ethylene (C_2H_4)	13 000 to 30 000	2×10^{-3}	2.7	Solid	0.66
Methane (CH_4)	Miscible	0.3	5	Does not form second liquid phase	Does not form second liquid phase
Nitrous oxide (N_2O)	140 to 160	5×10^{-4}	Non-flammable	Solid	1.4
Propane (C_3H_8)	9800	3×10^{-7}	2.1	Liquid	
Propylene (C_3H_6)	3600 to 6700	3×10^{-6}	2.1	Liquid	

[1]   Ranges in solubility reflect different sources of experimental data. The two most comprehensive references are Karwat and McKinley [3, 4]. Solubility is 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 E—Maximum contaminant levels in liquid oxygen thermosyphon reboiler operation at 1.2 bar, abs

Component	Symbol	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
NOTES		

NOTES

1   Care shall be taken in sampling cryogenic liquids to achieve accurate, consistent results. Any continuous liquid stream shall 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.

2   For plants with production of pressurized oxygen by internal compression, see EIGA Doc 145, *Safe Use of Brazed Aluminium Heat Exchangers for Producing Pressurized Oxygen* [5].

Appendix F—Maximum contaminant levels in liquid oxygen downflow reboiler operation at 1.2 bar, abs

Component	Symbol	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 shall be taken in sampling cryogenic liquids to achieve accurate, consistent results. Any continuous liquid stream shall 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.

3   For plants with production of pressurized oxygen by internal compression, see also EIGA Doc 145 [5].

Appendix G—Adsorption of air contaminants

	No adsorption		Partial adsorption [1]		Total adsorption	
Alumina FEP	Methane Ethylene Ethane Propylene Propane Nitric oxide n-butane	CH_4 C_2H_4 C_2H_6 C_3H_6 C_3H_8 NO nC_4H_{10}	Carbon dioxide [2] Nitrous oxide Acetylene	CO_2 N_2O C_2H_2	Ozone [3] Oxides of nitrogen Water	O_3 NO_2 N_2O_3 H_2O
Molecular sieve FEP	Methane Ethane Nitric oxide [4]	CH_4 C_2H_6 NO	Ethylene Propane Nitrous oxide	C_2H_4 C_3H_8 N_2O	Carbon dioxide Acetylene Propylene Ozone [3] Oxides of nitrogen n-Butane Water Oxygenates Chlorinated Hydrocarbons	CO_2 C_2H_2 C_3H_6 O_3 NO_2 N_2O_3 nC_4H_1 $_0$ H_2O
Silica gel Rich liquid adsorbers Vapour phase adsorbers Liquid oxygen adsorbers	Methane Ethane	CH_4 C_2H_6	Carbon dioxide Ethylene Propylene Propane Nitrous oxide	CO_2 C_2H_4 C_3H_6 C_3H_8 N_2O	Acetylene Ozone Dienes	C_2H_2 O_3
NOTES Assumptions: Contaminant at less than 10 ppm/v; carbon dioxide at 425ppm/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 H—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
Nitrous oxide	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.	