

CGA P-8.4—2020

**SAFE OPERATION OF
REBOILERS/CONDENSERS IN
AIR SEPARATION UNITS**

FOURTH EDITION

PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has issued CGA P-8.4, *Safe Operation of Reboilers/Condensers in Air Separation Units*, jointly produced by members of the International Harmonization Council and originally published by the European Industrial Gases Association (EIGA) as Doc 65, *Safe Operation of Reboilers/Condensers in Air Separation Units*.

This publication is intended as an international harmonized 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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Work Item 17-027
Atmospheric Gases and Equipment Committee

NOTE—Technical changes from the previous edition are underlined.

FOURTH EDITION: 2020
THIRD EDITION: 2013
SECOND EDITION: 2006
FIRST EDITION: 2000

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Contents	Page
1 Introduction.....	1
2 Scope and purpose	1
2.1 Scope	1
2.2 Purpose	1
3 Definitions.....	1
4 Reboiler incidents.....	3
4.1 Major explosions.....	3
4.2 Limited explosions.....	4
4.3 Internal leaks	4
5 Air contaminants.....	4
6 Design consideration	5
6.1 Plant surroundings	5
6.2 Design of prepurifying systems	6
7 Operations.....	6
7.1 Importance of carbon dioxide removal	6
7.2 Proper reboiler operations	7
7.3 Control of contaminants.....	9
7.4 Contaminant analysis	11
7.5 Transient conditions	12
7.6 Deriming	14
7.7 Cleaning and maintenance.....	16
8 References	18
9 Additional References	19
Appendices	
Appendix A—Operation of a reboiler associated with krypton/xenon production	20
Appendix B—Representation of reboiler core submergence	22
Appendix C—Plugging, flammable, and corrosive contaminants of air	23
Appendix D—Properties of air contaminants	24
Appendix E—Maximum contaminant levels in liquid oxygen thermosyphon reboiler operation at 1.2 bar, abs	25
Appendix F—Maximum contaminant levels in liquid oxygen downflow reboiler operation at 1.2 bar, abs ..	26
Appendix G—Adsorption of air contaminants	27
Appendix H—Typical default air quality design basis (for adsorptive FEP system).....	28

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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 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 32 °F (0 °C) 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 Reboiler 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 breach 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 breach 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 CGA P-8, *Guideline for Safe Practices 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 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.

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

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 vapor or liquid phase adsorbers, which operate at cryogenic temperature. A detailed explanation of the operation of these prepurifying systems can be found in CGA P-8 [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 may operate for an extended period under these conditions provided that safe reboiler contaminant levels are not exceeded in accordance with Appendices E and F. Otherwise, the plant shall be shut down.

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 CGA P-8 [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 solid deposits of plugging 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.