

CGA G-4.9—2017

**SAFE USE OF BRAZED
ALUMINUM HEAT EXCHANGERS
FOR PRODUCING
PRESSURIZED OXYGEN**

FIFTH EDITION

PREFACE:

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has published [CGA G-4.9](#), *Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen*, jointly produced by members of the International Harmonization Council.

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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1 Introduction

Over the past twenty years, a process for producing pressurized oxygen has become the industry standard. In this process, liquid oxygen (LOX) is extracted from the separation column, pumped to higher pressure, and boiled in a heat exchanger to directly provide the elevated pressure gaseous oxygen (GOX) product. Another method still being used for producing pressurized oxygen is to remove the oxygen as a gaseous product from the separation column, warm the GOX to ambient temperature, and then raise its pressure with a GOX compressor.

Brazed aluminum heat exchangers (BAHXs) are normally used as oxygen product vaporizers. Their use creates substantial contact between high pressure oxygen (both as LOX and GOX) and aluminum material.

This publication reviews issues pertinent to the safe fabrication, installation, and operation of BAHXs used for boiling oxygen to dryness at elevated pressures.

A substantial portion of this publication is based on [CGA G-4.8, Safe Use of Aluminum-Structured Packing for Oxygen Distillation](#) [1].¹ Questions initially raised for aluminum packing were extended later by analogy to BAHXs used as product oxygen vaporizers. Therefore, a significant amount of information from [CGA G-4.8](#) is incorporated into this publication in Sections 6, 7, 8, and 10 [1].

2 Scope

This publication addresses BAHXs used for boiling product oxygen at elevated pressures. The oxygen enters the BAHX as a subcooled liquid (or supercritical fluid) and leaves as a superheated vapor. Other BAHX uses in oxygen applications are not addressed, although incidents involving aluminum in oxygen service are discussed.

This publication contains a summary of current knowledge and industrial practices used in the safe application of BAHXs for the boiling of oxygen at elevated pressures.

This publication is not intended to be a mandatory standard. It is based upon the combined experimental work, operating experience, and design practices of major producers and operators of air separation plants.

3 Summary

The industrial gas industry has used aluminum components extensively in oxygen service for more than 60 years. This has included piping, heat exchangers, vaporizers, pressure vessels, distillation trays, and packing. Overall, the safety record of aluminum in oxygen service has been very good. BAHXs have been used in cryogenic air separation service since 1950.

The information assembled for this publication provides the background to conclude that the use of BAHXs for the production of pressurized oxygen can be safely practiced. In particular, this process reduces the possibility of hydrocarbon accumulation in the main reboiler/condenser when there is a high liquid withdrawal rate from the reboiler sump.

With respect to the use of BAHXs for elevated pressure product oxygen boiling, there has been one reported combustion incident.

The experimental work (Section 9) on the flammability of BAHX samples has shown that they are flammable in boiling oxygen (9.3) and can combust with considerable intensity; however, combustion can be arrested or inhibited by fluids in alternate passages under conditions normally encountered in elevated pressure product oxygen boiling applications. Condensed or cold supercritical inert fluid or air in BAHX alternate passages is more effective than gaseous inert fluid or air from the standpoint of combustion inhibition (9.4 and 9.5). However, there are some locations in the BAHX where LOX is present and the alternate passages contain either two-phase fluid or vapor only. This is most likely in locations where the oxygen vapor fraction is high.

The safe use of aluminum-fabricated equipment in oxygen service primarily depends on excluding ignition mechanisms, including the accumulation of flammable contaminants. BAHXs also use this philosophy.

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

The procedures that have resulted in this record of safe operation with aluminum components have included following the practices described in [CGA P-8](#), *Safe Practices Guide for Cryogenic Air Separation Plants*, and proper cleaning of aluminum equipment according to standards such as [CGA G-4.1](#), *Cleaning Equipment for Oxygen Service*; [ASTM G93](#), *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-Enriched Environments*; and EIGA Doc 33, *Cleaning of equipment for oxygen service* [2, 3, 4, 5]. [CGA P-8.4](#), *Safe Operation of Reboilers/Condensers in Air Separation Units*, offers additional insights pertinent to aluminum components in air separation plants [6].

For air separation plants containing BAHXs for elevated pressure product oxygen boiling applications, continued adherence to the practices in [CGA P-8](#) and following the cleaning specifications given in Section 10 of this publication are recommended to ensure safe use [2].

The use of adsorption purification units, which prevent acetylene and other undesirable hydrocarbons from entering the plant and initiating reactions, is strongly recommended when boiling LOX at elevated pressures in a BAHX.

In summary, the information assembled in this publication supports the safe use of BAHXs in oxygen boiling applications as an alternative to oxygen compressors. Test data were obtained at pressures up to 2 180 psi (15 000 kPa) using BAHX specimens.² From current understanding, there is no step change in the risk of aluminum ignition and the combustion-propagation severity when increasing the pressure. Current industry references are up to 1 260 psi (8 700 kPa). Designers of plants operating at high pressure should perform a risk analysis to confirm that any risks related to high oxygen pressure are addressed including the margin to mechanical design limits.

4 Definitions

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

4.1 Publication terminology

4.1.1 Shall

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

4.1.2 Should

Indicates that a procedure is recommended.

4.1.3 May

Indicates that the procedure is optional.

4.1.4 Will

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

4.1.5 Can

Indicates a possibility or ability.

4.2 Technical definitions

4.2.1 Brazed aluminum heat exchanger (BAHX)³

4.2.1.1 Introduction

A BAHX consists of a block (core) of alternating layers (passages) of corrugated fins. The fins are typically 0.2 mm to 0.5 mm thick. The layers are separated from each other by parting sheets typically 1.0 mm to 2.4 mm thick and sealed along the edges by means of side bars, and are provided with inlet and outlet ports for the streams. The block is bounded by cap sheets at the top and bottom.

² kPa shall indicate gauge pressure unless otherwise noted as (kPa, abs) for absolute pressure or (kPa, differential) for differential pressure. All kPa values are rounded off per [CGA P-11](#), *Metric Practice Guide for the Compressed Gas Industry* [7].

³ Reproduced from *The Standards of the Brazed Aluminium Plate-fin Heat Exchange Manufacturers' Association* (ALPEMA standard) with permission [8].

An illustration of a multistream heat exchanger is shown in Figure 1.

The stacked assembly is brazed in a vacuum furnace to become a rigid core. To complete the heat exchanger, headers with nozzles are welded to the side bars and parting sheets across the ports.

4.2.1.2 Components of an exchanger

Figure 2 illustrates the components of an exchanger. The components are numbered for identification.

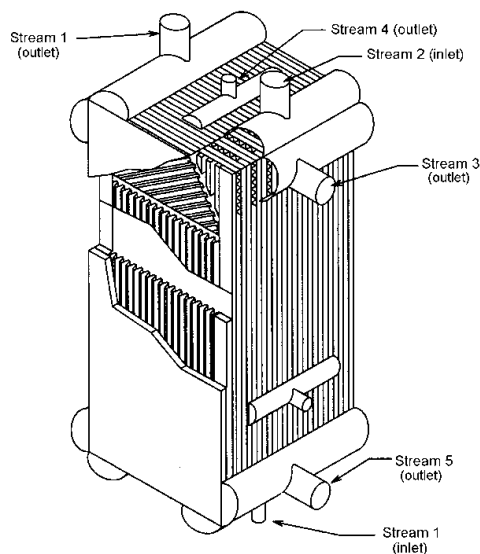


Figure 1—Illustration of a typical multistream BAHX⁴

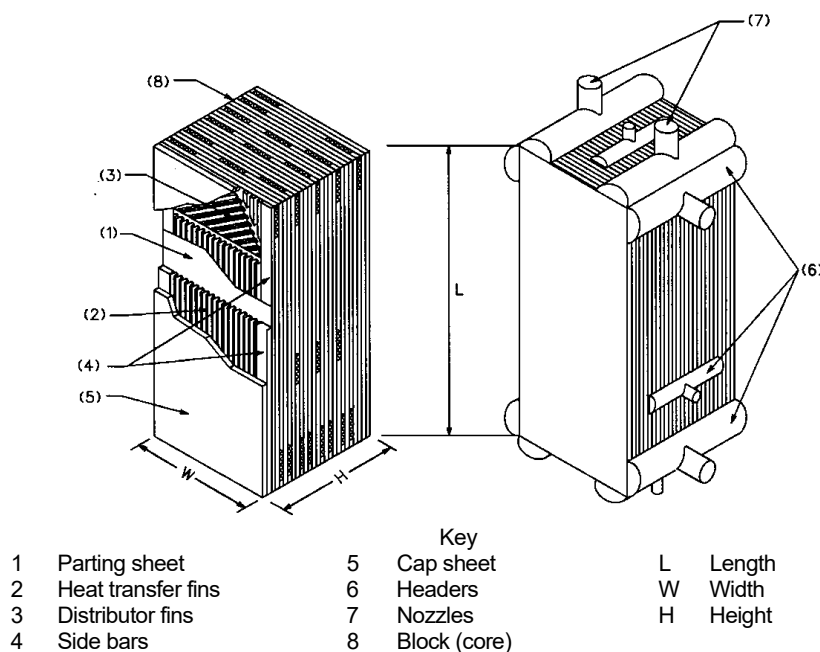


Figure 2—Components of a BAHX⁴

⁴ Reproduced from *The Standards of the Brazed Aluminium Plate-fin Heat Exchange Manufacturers' Association* (ALPEMA standard) with permission [8].

4.2.1.3 Components of manifolded exchangers

Multiple BAHXs can be connected in parallel, in series, or in parallel-series combination to form one assembly.

Figure 3 illustrates an assembly of three BAHXs connected in parallel. In this case, each individual stream enters the assembly through a manifold, is distributed to the inlet nozzles on each of the three heat exchangers, flows through the heat exchanger, and leaves the assembly through the outlet manifold.

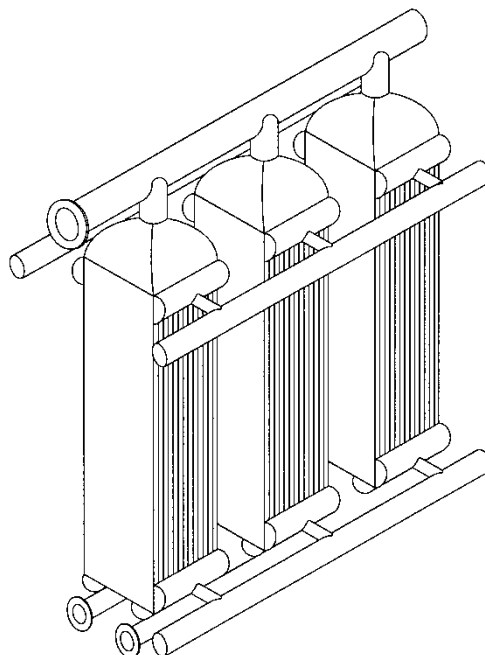


Figure 3—Typical assembly of three BAHXs in parallel⁵

4.2.2 BAHX block sample

Small segment cut from the internal heat transfer fin-parting sheet section of a BAHX ranging in weight from 170 g to 400 g.

4.2.3 BAHX specimen

Small heat exchanger with segregated passages for two streams, at least one of which has a header, ranging in weight from approximately 3000 g to 13 000 g. A 3000 g BAHX uses approximately 1000 g of thin aluminum fins and parting sheets, while a 13 000 g BAHX uses 5000 g of fin and parting sheet stock.

4.2.4 Violent energy release (VER)

Experimental result used in Section 9 in which the following indications were observed during the combustion of aluminum in oxygen: a loud report, white light, and physical destruction or substantial deformation of the specimen and/or the test vessel.

4.2.5 Supercritical fluid

Pure component or mixture of components that is at a pressure greater than its critical pressure.

NOTE—Although it can be argued that such a fluid is a compressed liquid if its temperature is less than the critical temperature of the fluid, the term supercritical fluid is used whether the fluid is greater or less than its critical temperature.

4.2.6 Pool boiling

Pool boiling occurs when heat is added to a pool or puddle of liquid to which more liquid is continually added and from which only vapor is removed. The heat causes the more volatile component to vaporize, leaving the less

⁵ Reproduced from *The Standards of the Brazed Aluminium Plate-fin Heat Exchange Manufacturers' Association* (ALPEMA standard) with permission [8].

volatile components behind. The remaining liquid becomes more and more enriched in the less volatile component until a point is reached wherein the content of the less volatile component leaving in the vapor extracted from the pool boiler equals its content entering in the added liquid. If the liquid concentration of the higher boiling component builds to a high enough level that a condensed phase forms rich in this component, the pool accumulates this condensed phase indefinitely. Pool boiling is also known as pot boiling.

Pool boiling is different from dry boiling. Dry boiling, which occurs in BAHXs as described in this publication, is where LOX is vaporized to dry out. As LOX is vaporized in the exchanger passages, the concentration of high boiling components increases in the remaining liquid. If the concentration of high boiling components is high enough, a condensed phase rich in these components can be formed at the location of the end of LOX vaporization.

NOTE—Operating with such a condensed phase is unacceptable. For boiling oxygen systems, oxygen is the more volatile component and hydrocarbons are the less volatile component(s) that are concentrated in the remaining LOX.

4.2.7 Sealed cavities

Small volume that is completely sealed by metal and weld. This becomes a potential hazard when submerged in LOX and there is a defect in the seal. LOX fills the cavity. When the plant is warmed up, the oxygen vaporizes, and the pressure rapidly increases. In other cases where there is thermal contact with a warmer temperature, hydrocarbons can accumulate because of pool boiling within the cavity.

4.2.8 Prepurification method

Method used to remove contaminants from the air before distillation. This includes both prepurification units (PPUs) and reversing heat exchangers (REVEX or RHX).

4.2.9 Prepurification unit (PPU)

System of vessels containing adsorbents used to remove contaminants from the air before distillation. These units are also called molecular sieve adsorbers, front-end purifiers, adsorption PPUs, and adsorption front ends.

5 Literature survey

Several papers are pertinent to the flammability of BAHXs for use in oxygen boiling services. A critical review of aluminum flammability data is presented by Werley, et al. [9]. Results of promoted ignition-combustion tests in oxygen-enriched atmospheres of various light metal alloys including aluminum are presented by Zawierucha, McIlroy, and Million [10]. Kirzinger, Bauer, and Lassmann and Pedley, et al., report on oil films on oxygen equipment [11, 12].

Specific to the use of BAHXs for boiling oxygen are the experiments described by Zawierucha and Million and by McNamara, et al. [13, 14, 15].

An investigation of the interaction between molten/burning aluminum and LOX is found in Barthélémy and Muller [16]. In a later investigation, Barthélémy, Roy, and Mazloumian reported the results of impact tests of aluminum in LOX and the effects of contaminants on impact behavior [17]. Present work investigates the effect of LOX purity on the probability of ignition by impact of contaminated aluminum [18].

The preparation of this publication and the general knowledge of aluminum-LOX reactions has been enhanced by a number of investigations related to the safe use of aluminum-structured packing in air separation plants. These investigations have involved flammability tests of aluminum packing, comparisons with sieve trays, studies of ignition mechanisms, and oil migration. Key investigations in these areas are those of Mench, et al.; Kirzinger and Lassmann; Dunbobbin, Hansel, and Werley; Zawierucha, et al.; Lassmann and Kirzinger; Barthélémy; Egoshi, Kawkami, and Fujita; and Fano, Barthélémy, and Lehman [19, 20, 21, 22, 23, 24, 25, 26, 27, 28].

In addition to BAHXs, pumps are a key component of pumped LOX systems. Known compatibility tests pertinent to this component involving aluminum and LOX are those of Bauer, et al. [29, 30].

Several significant incidents involving aluminum and LOX have appeared in the literature. An accident investigation involving the explosion of a LOX tank truck was reported on in a National Traffic Safety Board (NTSB) Report [31]. An aluminum-LOX reaction involving a submerged pump was reported by Kilmartin [32]. Van Hardeveld, et al. and Lehman et. al reported on explosions in air separation units (ASUs) [33, 34].

Of potential significance in aluminum-LOX reactions are trace contaminants. Lassmann reported on the enrichment of hydrocarbons in pressurized LOX evaporators [35]. Miller, et al. discussed the solubility of nitrous oxide and carbon

dioxide in air separation liquids [36]. Trace contaminant behavior in ASUs was investigated by Meneses, et al. [37]. Lassmann and Meilinger reported on the adsorption of hydrocarbons on solid carbon dioxide and nitrous oxide in LOX at ambient pressure [38]. McKinley and Himmelberger give the upper and lower flammability limits of hydrocarbons in GOX and mention that the LOX flammability range is narrower than seen in GOX [39].

In air separation plants and associated systems there are a number of components handling both GOX and LOX such as compressors, piping, tankage, and heat exchangers. Organizations such as the American Society for Testing and Materials (ASTM), CGA, European Industrial Gases Association (EIGA), and National Fire Protection Association (NFPA) have prepared standards or technical bulletins pertinent to such components [40, 41, 42, 43, 44, 45, 46, 47].

6 Industry survey on incidents of aluminum-oxygen combustion and oxygen compressor comparison

6.1 Background

Since the 1950s, when aluminum replaced copper as the preferred material of construction of cryogenic equipment, aluminum and oxygen have reacted on several occasions with varying degrees of intensity. The configuration of the aluminum involved in these reactions has varied from the very thin foil used in superinsulation to heavy plate stock that is rolled and used for elevated pressure vessels in storage tanks or LOX trailers.

Evidence of both molten aluminum and aluminum oxide can be used to determine whether or not aluminum participated in a reaction. Whereas molten aluminum might or might not be indicative of an aluminum-oxygen reaction, aluminum oxide is always indicative of this reaction.

Hydrocarbon-LOX reactions in the presence of aluminum can be divided into three categories:

- Cases of violent hydrocarbon combustion in aluminum equipment without the actual participation of the aluminum in the reaction;
- Cases in which there was evidence that a very small amount of aluminum had burned before the reaction was arrested. This has occurred in both reboilers and sealed cavities; and
- Cases where serious incidents occurred in plants involving aluminum-oxygen combustion. These were initiated by accumulated combustibles in the reboiler/condenser and resulted in extensive combustion of the aluminum reboiler. Aluminum packing was also burned in two cases as a consequence of the reboiler incidents [1, 33, 34].

A wide distribution of hydrocarbon contamination in the equipment is a probable factor for the propagation of aluminum combustion [17]. Where the contamination is localized, the high thermal conductivity of aluminum can help arrest propagation. Other factors influencing propagation are discussed in 6.4 and 6.5.

There have also been incidents in sealed cavities where the aluminum has participated, but the reaction did not propagate.

The elimination of designs with sealed cavities has reduced the number of incidents. This design improvement prevents hydrocarbon accumulation and high pressure oxygen buildup.

In one case, a serious incident occurred in a BAHX in pumped LOX service that is believed to be precipitated by the presence of a sealed cavity leading to a mechanical failure and an aluminum-oxygen reaction.

6.2 Scope of investigation

The subject under investigation is the use of aluminum in the production, compression, and distillation of air and its safety relative to environments of commercial oxygen. There is a significant body of industrial experience relating to aluminum-oxygen compatibility that was considered pertinent to the issue under investigation. Information related to rotating equipment (such as turbines, centrifugal compressors, reciprocating compressors, or LOX pumps) was considered as well as incidents associated with drain vaporizers, valves, headers, and gel traps. Certain items were excluded to reduce the scope or complexity of the undertaking to manageable proportions. The categories that remained

could be broadly classified into groups. These were reboiler/condensers, customer station storage tanks, sealed cavities in equipment, mobile transports, high-vacuum super-insulations, and auxiliary equipment handling LOX. Obviously, aluminum was a material of construction in each of these components in order for the incident to be cited.

A summary of pertinent aluminum-oxygen incidents in the industrial gases industry is shown in Table 1. In compiling this summary, only known aluminum combustion incidents were cited. Of the 34 examples cited, nine took place within the sumps of the low pressure distillation columns. Only three of these sump incidents could be described as a threat to plant personnel. The relative infrequency of such incidents is a testimonial to the safe use of aluminum in air separation equipment.

The cited pump incident involved an aluminum submerged pump operating in a mobile transport at a nominal working pressure of 45 psi (310 kPa). Failure to lubricate bearings, which resulted in a friction ignition mechanism, was identified as a contributing factor. The incident consumed approximately 8 lb (3.6 kg) of aluminum and was intense.

6.3 Survey results

Thirty-four incidents or events in an industrial environment were characterized as being representative of aluminum-oxygen reactions. These incidents are summarized in Table 1 and are listed by category and from most frequent to least frequent.

Table 1—Results of industry survey of aluminum-oxygen combustion incidents

Component	Incidents
Cavities (sealed/unsealed)	
Column junctions	4
Reinforcing pads	4
Transition joints	3
Support rings	2
Flowmeter	1
Heat exchanger ¹⁾	1
Subtotal	15
Superinsulation	
Liquid cylinders	3
Vacuum-jacketed piping	3
Subtotal	6
Customer storage tanks	2
Mobile transports	1
Reboiler/condenser	
Limited aluminum combustion ¹⁾	6
Major	3
Subtotal	9
Pumps (cited incident associated with a mobile transport)	1
Grand Total	34
¹⁾ The additional incidents were reported between 2008 and 2013.	

6.4 Interpretation of survey results

The important parameters associated with the compatibility of aluminum and oxygen are generally recognized to be oxygen purity, oxygen pressure, oxygen phase, ignition source, contamination, and aluminum configuration. Other parameters could be listed as important in some circumstances. From this survey, one new parameter that seems to be important in assessing suitability and safety is the presence or absence of LOX in the system.