



SAFE USE OF BRAZED ALUMINUM HEAT EXCHANGERS FOR PRODUCING PRESSURIZED OXYGEN

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Asia Industrial Gases Association

298 Tiong Bahru Road, #20-01 Central Plaza, Singapore 168730
Tel : +65 6276 0160 • Fax : +65 6274 9379
Internet : <http://www.asiaiga.org>



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Contents	Page
1 Introduction.....	1
2 Scope	1
3 Summary	1
4 Definitions.....	2
5 Literature survey.....	5
6 Industry survey on incidents of aluminum/oxygen combustion and oxygen compressor comparison	6
7 Ignition mechanisms.....	11
8 Ignition experiments in GOX and LOX	13
9 Experimental work on aluminum/oxygen combustion	14
10 Cleaning considerations.....	17
11 Design and operational considerations	18
12 References	24
Tables	
Table 1—Results of industry survey of aluminum/oxygen combustion incidents.....	7
Table 2—VER pressure as a function of LOX purity	15
Figures	
Figure 1—Illustration of a typical multistream BAHX	3
Figure 2—Components of a BAHX	3
Figure 3—Typical assembly of three BAHXs in parallel.....	4

1 Introduction

Over the past fifteen years, a new 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 guide 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* (EIGA Doc 701/04) [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 in 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 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 code. 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 almost 50 years. This has included piping, heat exchangers, vaporizers, pressure vessels, distillation trays, and packing. Overall, the safety record of aluminum in oxygen services 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 have been no reported combustion incidents.

The experimental work (Section 9) on the flammability of BAHX samples has shown they are flammable in boiling oxygen (9.3) and can combust with considerable intensities; 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 (see 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.

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

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

The procedures that have resulted in this record of safe operation with aluminum components have included following the practices described in AIGA 056/08, *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 G-93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-Enriched Environments*; and AIGA 012/04, *Cleaning of equipment for oxygen service* [2, 3, 4, 5]. AIGA 035/06, *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 AIGA 056/08 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 1000 psig (6900 kPa) using miniature 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 1160 psig (8000 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 considering the margin to mechanical design limits.

4 Definitions

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

4.1 Brazed aluminum heat exchanger

4.1.1 Introduction³

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.

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.

4.1.2 Components of an exchanger

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

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 These descriptions and figures are taken from *The Standards of the Brazed Aluminium Plate-fin Heat Exchange Manufacturers' Association* (ALPEMA standard) and are reprinted with permission [8].

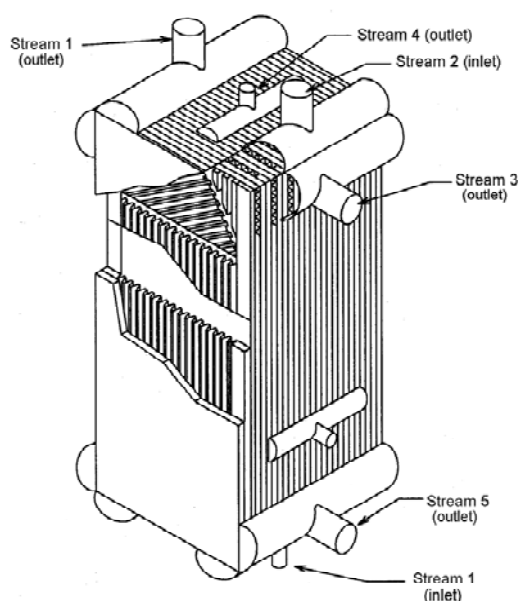
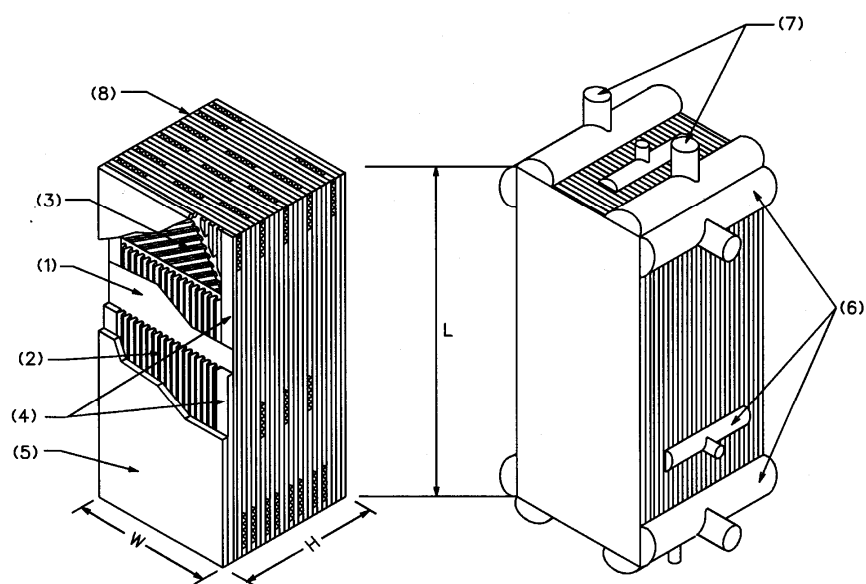


Figure 1—Illustration of a typical multistream BAHX



Key

1 Parting sheet	5 Cap sheet	L Length
2 Heat transfer fins	6 Headers	W Width
3 Distributor fins	7 Nozzles	H Height
4 Side bars	8 Block (core)	

Figure 2—Components of a BAHX

4.1.3 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.

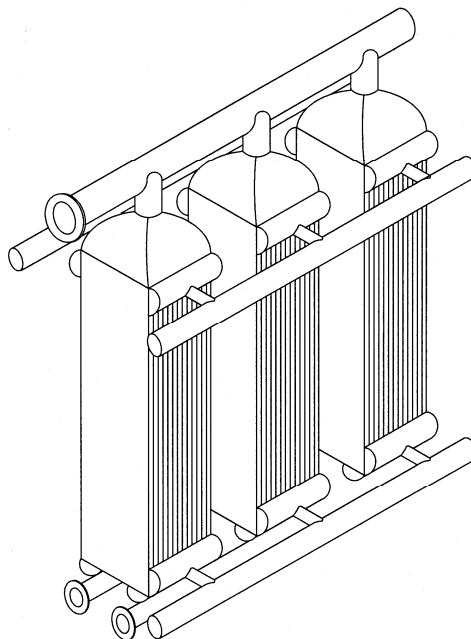


Figure 3—Typical assembly of three BAHXs in parallel

4.2 BAHX block sample

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

4.3 Miniature BAHX

A 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.

4.4 Violent energy release (VER)

An 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.

4.5 Supercritical fluid

As used in this document, a pure component or mixture of components that is at a pressure above its critical pressure.

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

4.6 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 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 ex-

tracted 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.

4.7 Sealed cavities

A 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.

4.8 Prepurification method

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

4.9 Prepurification unit

A 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, Baur, 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 [13, 14].

An investigation of the interaction between molten/burning aluminum and LOX is found in Barthélémy and Muller [15]. In a later investigation, Barthélémy, Roy, and Mazlounian reported the results of impact tests of aluminum in LOX and the effects of contaminants on impact behavior [16]. Present work investigates the effect of LOX purity on the probability of ignition by impact of contaminated aluminum [17].

The preparation of this guide 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 [18, 19, 20, 21, 22, 23, 24, 25, 26, 27].

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. [28, 29].

Several significant incidents involving aluminum and LOX have appeared in literature. An accident investigation involving the explosion of a LOX tank truck was reported on in a National Traffic Safety Board Report [30]. An

aluminum-LOX reaction involving a submerged pump was reported by Kilmartin [31]. Van Hardeveld et al and Lehman et al reported on explosions in air separation units (ASUs) [32, 33].

Of potential significance in aluminum-LOX reactions are trace contaminants. Lassmann reported on the enrichment of hydrocarbons in pressurized LOX evaporators [34]. Miller et al. discussed the solubility of nitrous oxide and carbon dioxide in air separation liquids [35]. Trace contaminant behavior in ASUs was investigated by Meneses et al. [36]. Lassmann and Meilinger reported on the adsorption of hydrocarbons on solid carbon dioxide and nitrous oxide in LOX at ambient pressure [37]. 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 [38].

In air separation plant and associated systems there are a number of components handling both GOX and LOX. Compressors, piping, tankage, and heat exchangers are examples. Organizations such as the American Society for Testing and Materials (ASTM), CGA, the European Industrial Gases Association (EIGA), and the National Fire Protection Association (NFPA) have prepared standards or technical bulletins pertinent to such components. References 39 through 46 are pertinent.

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:

- There have been many cases of violent hydrocarbon combustion in aluminum equipment without the actual participation of the aluminum in the reaction;
- There also have been some 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
- In a few cases, serious incidents occurred in plants involving aluminum/oxygen combustion. They 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, 32, 33].

A wide distribution of hydrocarbon contamination in the equipment is a probable factor for the propagation of aluminum combustion [16]. Where the contamination is localized, the high thermal conductivity of aluminum might help arrest propagation. Other factors influencing propagation are discussed in 6.4.

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.

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, a material of construction in each of these components was aluminum 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 32 examples cited, 8 took place within the sumps of the low pressure(LP) 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 psig (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-two 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
Flowmeter	1
Transition joints	3
Reinforcing pads	4
Support rings	2
Subtotal	14
Superinsulation	
Liquid cylinders	3
Vacuum-jacketed piping	3
Subtotal	6
Customer storage tanks	2
Mobile transports	1
Reboiler/condenser	
Limited aluminum combustion ¹⁾	5
Major	3
Subtotal	8
Pumps (cited incident associated with a mobile transport)	1
Grand Total	32
¹⁾ The number of reboiler incidents has increased since the 2002 edition of this publication. Only one of the limited aluminum combustion incidents occurred between 2002 and 2008. The other additional incidents occurred before 2002 and are now being reported.	

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, which seems to be important in assessing suitability and safety, is the presence or absence of LOX in the system.

6.4.1 Purity

Most of the incidents involved oxygen purities in the 99.5% to 99.9% oxygen range.

6.4.2 Configuration

Industrial incidents have been experienced with aluminum in a variety of configurations, from the thin foil used in superinsulation to the thick stock used in storage vessels and road tankers. The large number of variables affecting aluminum/oxygen combustion makes generalizations about the effect of aluminum configuration difficult, but experience shows that thick sections are more resistant to reaction at low pressures.

6.4.3 Reaction extent

The incidents listed in Table 1 are a good representation of aluminum/oxygen reactions in varying degrees and extents. Some can be characterized as violent exothermic reactions that involve significant quantities of aluminum while others were of a sufficiently limited severity that they were not detected at the time of the incident but only observed much later as a result of more or less routine inspections.

It is believed that the reaction rates for all the incidents were very rapid, but a limited amount of damage resulted because the quantity of aluminum consumed was generally rather small. The two customer storage tanks and the mobile transport vehicle are examples of violent reactions between large quantities of aluminum and oxygen. Three reboiler condenser incidents had violent reactions between large quantities of LOX and aluminum [6, 32]. The more limited reactions exemplified by evidence of molten aluminum in sealed cavities are examples of the same fundamental phenomenon but differ in the extent of the reaction and the resultant amount of energy release and damage.

6.5 Conclusions from survey

6.5.1 Effect of pressure and configuration

Those incidents that involved lower pressure oxygen usually were characterized by very thin (< 0.015 mm) aluminum geometries. The superinsulation liquid dewars and vacuum jacketed piping are examples of this type of phenomena.

Reboilers typically operate at approximately 20 psia (140 kPa) to 23 psia (160 kPa). The fins in a reboiler are typically 0.2 mm to 0.25 mm thick. While very infrequent, aluminum combustion has been observed in reboilers.

Those cases where thick aluminum cross sections were involved in extensive reactions occurred at elevated pressures, between 45 psig and 200 psig (310 kPa and 1380 kPa). These incidents include the customer storage tanks, the LOX trailer, and the submerged aluminum LOX pump.

6.5.2 Effects of oxygen phase

A somewhat surprising generalization is that practically all the industrial incidents involved LOX. The presence of liquid oxygen appears to play a much more important role than had heretofore been appreciated or understood. Mench, Haas, and Kuo have shown that the aluminum combustion rate is significantly lower in a high pressure GOX than in LOX, even when the GOX is supercritical and the GOX density approaches liquid-like values [20]. This shows that the presence of LOX increases the rate of aluminum combustion.

6.5.3 Ignition source

With rare exceptions, the source of the ignition could not be determined by remaining evidence but was only inferred from plausible mechanisms. Most incidents have not been satisfactorily replicated in the laboratory, but incidents involving superinsulation, where the palladium oxide getter or mechanical impact were viewed as likely sources of ignition and the submerged pump where friction is suspected, stand out as exceptions. In many of the incidents, circumstances indicated that hydrocarbon contamination was present, ignited, and kindled the aluminum. Acetylene is one probable ignition source since it needs only a low energy shock such as mechanical impact or static electricity to initiate a violent decomposition reaction.

6.5.4 Cavity incidents

The cavity incidents are somewhat anomalous in the severe but limited extent of the reactions. The damage was almost always localized but nevertheless gave clear indications of aluminum/oxygen reactions. In addition, there appeared to be other instances where contaminants or hydrocarbons associated with sealed cavities initiated a reaction, but did not cause the aluminum to oxidize or even melt.

6.5.5 Hydrocarbon contamination

Incidents in the reboiler/condensers of low pressure columns were, by far, the most frequent examples of incidents that were probably initiated by hydrocarbons. Generally, these incidents were extinguished before aluminum ignition. Hydrocarbon buildup was probably caused by inadequate liquid recirculation through the BAHXs, which caused the LOX to be boiled to a point where the concentration of the hydrocarbons exceeded the lower flammability limits (LFLs) for fuel in oxygen. Inadequate recirculation might have been caused by partial blockages in the LOX passages of the reboiler/condenser. There have been incidents that left egg-shaped cavities in the reboiler/condensers. In most of these incidents, there was no reported aluminum/oxygen reaction. The energy released was due mostly to hydrocarbon/oxygen reactions. In a few incidents, small amounts of aluminum combustion were detected. In others, it was difficult to closely examine the damaged areas of the reboiler, and small amounts of aluminum combustion may have been present but not detected. In all of these egg-shaped cavity cases, it is clear that the aluminum reaction, if present, was very small. In three cases, however, hydrocarbon initiation in reboilers led to extensive aluminum/oxygen reaction and severe plant damage [32]. AIGA 035/06 provides operating criteria to maintain safe reboiler operation [6].

The use of front-end air purification is preferable to the use of reversing heat exchangers. Molecular sieve adsorbents in the front-end systems have the ability to remove all traces of acetylene and other particularly hazardous hydrocarbons (C4+, dienes) from the air stream when the adsorption process is keyed on removing carbon dioxide. In other words, massive quantities of carbon dioxide break through before any significant quantity of acetylene.

Although front-end purification should reduce the frequency of reboiler incidents, its use alone is not sufficient protection against a BAHX reboiler energy release or an aluminum/oxygen violent energy release (VER). Hydrocarbons such as propane, ethylene, ethane, and methane are not removed completely in front-end purification systems and can accumulate in the oxygen-rich liquid in the reboilers of ASUs. If there is sufficient fuel present and if an energy release involving the hydrocarbon fuels and oxygen is large enough, these reactions can spread to the material of the BAHX reboiler resulting in an aluminum/oxygen VER.

Many of the incidents noted in Table 1 have been small in size and might not have involved aluminum/oxygen combustion reactions. However, BAHX reboiler energy releases of significant size, in which an aluminum/oxygen VER has caused severe damage, have occurred in ASUs equipped with front-end air purification. Furthermore, if a VER occurs in a reboiler, this might ignite the aluminum-structured packing or trays. Such propagation to packing has occurred in two instances (see 6.1). Therefore, proper cleaning, operation, maintenance, and air quality assurance are necessary to limit hydrocarbon accumulation and to reduce the frequency and severity of aluminum/oxygen reactions in ASUs. For specific guidance, refer to AIGA 056/08, AIGA 012/04, AIGA 035/06, and subsequent sections of this publication, especially Section 10 [2, 3, 6].

6.5.6 Other conclusions

Other conclusions drawn from this survey of industrial incidents are as follows:

- There were no reported incidents of ignition or combustion of aluminum sieve trays used in the distillation sections of air separation columns. One may infer that the excellent record with trays results most probably from an absence of ignition sources since experimental work has shown that trays can be flammable;
- There have been no reported incidents where an aluminum/oxygen reaction was initiated in structured aluminum packing. However, there have been two incidents where an aluminum/oxygen reaction occurred in structured aluminum packing after being initiated by a violent aluminum/oxygen reaction in the reboiler;
- There have been no reported incidents with BAHXs in pumped LOX vaporization service (see 6.6.3);
- In more than 40 years of using aluminum in oxygen service, only three of the incidents involving reboilers of distillation columns could be described as representing a threat to plant personnel;
- All industrial incidents have occurred with LOX at purities of 99.5% or higher. Experimental and theoretical work have shown oxygen purity to be an important parameter in aluminum/oxygen combustion;
- Hydrocarbons accumulated from the air in the less volatile fraction are the most commonly cited cause of aluminum reactions as the hydrocarbons are easily ignited and often kindle the aluminum reaction;
- With the exception of eight incidents, aluminum sheets of thicknesses comparable to BAHXs used for vaporizing/boiling pumped LOX have been used in plate-fin reboiler/condensers without evidence of aluminum/oxygen combustion since 1950. These heat exchangers are located in the LOX-rich LP column sump, an environment judged to be considerably more hazardous than that of the distillation sections. Unlike BAHXs used for vaporizing/boiling pumped LOX, reboiler/condensers are designed to be operated with an excess of liquid oxygen at the outlet of the vaporization section. However, improper design or operation can lead to local or global vaporization to dry out oxygen (e.g. lack of submergence of a bath type vaporizer). Due to the more favorable oxygen/hydrocarbon phase equilibria at higher pressure, the potential for hydrocarbon accumulation in a BAHX boiling oxygen at elevated pressure is lower than that in a reboiler/condenser operating at low pressure and experiencing abnormal vaporization to dry out [32]. However, improper design or operation of a BAHX in either service can result in hydrocarbon accumulation;
- There is a high degree of uncertainty as to the ignition mechanisms in the LOX storage vessels and transport incidents, although friction has been proposed as the ignition mechanism in the storage incidents. A combination of friction and impact was proposed for the transport incident;
- Elevated pressure in addition to the presence of LOX seems to be a common element in a number of the industrial aluminum/oxygen reactions. Examples are the transport, customer stations, and the postulated cavity mechanisms. However, the use of higher pressures in a BAHX used for boiling oxygen in an air separation plant equipped with properly operated molecular sieve prepurification reduces or eliminates the enrichment of airborne hydrocarbon contaminants such as acetylene, which could act as ignition promoters;

NOTE—Elevated pressures enhance both the ignition and combustion potential of aluminum.

- In the sealed cavity incidents, it can be inferred that the reaction extinguished because the pressure dropped or the oxygen purity was diluted. Experiments have shown that propagation of combustion requires that both pressure and purity be maintained above critical threshold levels for each specific geometry; and
- In reviewing incident and service histories, it is evident that before the use of BAHXs in pumped LOX services, the industry did not have significant amounts of experience with thin aluminum cross sections in elevated pressure service.

6.6 Oxygen compressor incidents, LOX pump incidents, and BAHX/LOX vaporization experience

6.6.1 Oxygen compressor incidents

Thousands of oxygen compressors are in service in the world today. These encompass a wide variety of types, designs, and materials. Task force participants estimated in a 2002 survey that more than 100 significant oxygen compressor incidents had occurred since 1965. It should be noted that this total does not include oxygen compressor incidents that might have been observed by individuals not on the task force or in facilities not operated by task force members. Including such incidents would result in a larger total. It was also noted that the compressor incident frequency has decreased as new, improved compressor designs and practices have been introduced. Significant documents relative to the preceding are CGA G-4.6, *Oxygen Compressor Installation and Operation Guide*; AIGA 055/08, *Installation Guide for Stationary, Electric-Motor-Driven, Centrifugal Liquid Oxygen Pumps*; EIGA Doc 27/01, *Centrifugal compressors for oxygen service*; and AIGA 048/08, *Reciprocating compressors for oxygen service, code of practice* [39, 40, 41, 47].

6.6.2 LOX pump incidents

Similarly, there are thousands of LOX pumps of various types, designs, and materials of construction in service throughout the world. Many of these are used in distribution equipment such as cryogenic trailers rather than air separation plants. Task force participants estimated in 2002 that more than 35 incidents had occurred at their sites on equipment owned and/or operated by task force participants since 1965. The total would probably increase if incidents from other sources were included; however, the relatively low number of LOX pump incidents in view of the large number being used is significant. There were no LOX pump incidents at plant sites using BAHXs for producing pressurized oxygen. Relative to LOX pump design and practices, AIGA 055/08, *Installation Guide for stationary electric motor driven centrifugal liquid oxygen pumps* should be consulted [42].

6.6.3 BAHX/LOX vaporization service experience at elevated pressure

Task force members estimated in 2008 that there were more than 400 air separation plants in operation that used BAHXs for producing pressurized oxygen, with a total experience of more than 2900 plant years. There have been no known incidents involving these components.

The current operating experience coupled with test data that have been generated indicates that the concept is safe.

7 Ignition mechanisms

7.1 Introduction

This section, surveys the fundamentals of aluminum ignition. Experimentation is covered in Section 8. References 8, 9, 11 through 23, and 25 through 27 include additional material on both these topics.

7.2 Conditions for ignition of aluminum

Solid and liquid aluminum are protected by a thin, dense, and flexible layer of aluminum oxide. This coating reforms immediately after damage in atmospheres containing oxygen.

Unless mechanical factors capable of removing the protective oxide layer are considered, an ignition source must heat aluminum above approximately 3632 °F (2000 °C) to initiate combustion [9]. The high thermal conductivity of aluminum means that a high heat flux and/or a very thin specimen (or very small particles) are needed to obtain high local temperatures.

7.3 Sources of ignition energy

The energy needed to achieve the ignition temperature can be supplied to the aluminum directly (by a physical mechanism) or indirectly (by the chemical reaction of a promoter).

7.4 Direct ignition

The following mechanisms were judged to be irrelevant to direct ignition of BAHXs for boiling oxygen in air separation plants:

- resonance-tube oscillations;
- reflected shock waves;
- electric arc; and
- autoignition.

Although particle impact cannot be excluded, it is judged to be unlikely in BAHXs used for boiling due to the low velocities of oxygen in normal operation. Abnormal process conditions must be examined. The use of strainers to minimize the potential for particle impact could be beneficial.

Friction, as an ignition source for a BAHX, is very unlikely due to the absence of moving equipment, but can occur in auxiliary equipment such as LOX pumps.

Adiabatic compression is an ignition mechanism that can be considered in a high pressure oxygen vaporization situation. However, this mechanism can be considered only under “dead ended” conditions, which are not normal for a BAHX. Although high pressure (well above critical pressure) is available, an oxygen pressure shock is unlikely. In addition, adiabatic conditions in a BAHX are very unlikely due to material thermal properties and its structure. Thus, this ignition mechanism is very unlikely.

It is possible through pressure or thermal cycling for small fractures to develop in the aluminum heat exchanger surface. This exposes fresh aluminum. It is theoretically possible for combustion to start on this fresh aluminum surface in the presence of LOX. However combustion has never been seen experimentally from this cause. In addition, proper design and operation as described in 11.6.5 minimizes the probability of fatigue fractures.

7.5 Indirect ignition (promoted ignition)

The ignition mechanism considered most pertinent to BAHXs in boiling oxygen service is an energy release from combustion of a secondary material. As a first step, this promoter must accumulate to its lower flammability limit or as a condensed phase; as a second step, this promoter must be ignited; and in a third step, the energy released by the promoter reaction must be able to ignite the aluminum.

Three possible types of promoters were considered:

- hydrocarbons accumulated from the air;
- lubricants used during air separation plant component manufacture and assembly; and
- foreign materials inadvertently left in the BAHX before and after installation.

7.5.1 Hydrocarbons from air

According to industry's experience, accumulation of hydrocarbons in the reboiler/condenser and in cavities where LOX was evaporating was the most common explanation offered for incidents in the bottom of air distillation columns. Such accumulation is much less probable in a pumped LOX vaporizer [34].

7.5.2 Hydrocarbons from lubricants

The amount of combustible residue remaining in a BAHX/LOX boiler after its fabrication and cleaning shall be low enough to ensure that the lower flammability limit is not reached in the LOX passages if the residue is vaporized as a consequence of unexpected heat input (see 10.2).

The hypothetical combustion of a 100 mg/m² oil film would only raise the temperature of a BAHX sheet less than 36 °F (20 °C), which is insufficient to cause the oil film to evaporate. Therefore, in the absence of a significant amount of promoter at a single point, it would be difficult to ignite a BAHX surface.

Tests and industrial experience indicate that the combustion of accumulated oil can promote the ignition of aluminum. The possibility of accumulation of oil by the following mechanisms was considered:

- cryogenic chipping of brittle oil films;
- migration at temperatures up to 140 °F (60 °C); and
- evaporation and recondensation.

Previous chipping and migration experiments reported by Kirzinger et al. showed that thin oil films (100 mg/m² corresponds to a thickness of 0.1 μm) are very stable [11].

7.5.3 Foreign materials

Solid contaminants (wood, papers, sealants, oil lumps, plastics, textiles, etc.) can be unintentionally trapped in the BAHX or they can be introduced into the BAHX during its construction or maintenance despite all precautions. Such contaminants can act as ignition promoters to ignite aluminum exchangers. The ignition of solid contaminants would need energy input either by impact or by heating energy. Heating from –292 °F (–180 °C) to the ignition temperature of the contaminant (above 392 °F to 572 °F [200 °C to 300 °C]) would be necessary.

Although frequently used as a promotion medium in experiments, a mixture of metallic aluminum and iron oxide (thermite) resulting from fabrication and corrosion processes seems an unlikely possibility because of the high temperature (melting point of aluminum) required to initiate the reaction between aluminum and iron oxide.

7.5.4 Other promoters

Other potential promoters (metal oxides, mercury, halocarbons, precious metals, and ozone) were considered but they were judged to be irrelevant to BAHX ignition.

8 Ignition experiments in GOX and LOX

8.1 Ignition promoters for use in experimentation involving BAHX block samples

Various types of promoted ignition were investigated such as thermite mixtures, pyrofuze, magnesium, and hydrocarbon grease [13]. A joule-heated nichrome wire was normally used to ignite the promoter.

NOTE—Such an ignition source obviously does not exist within a functioning BAHX.

8.2 Nichrome

At 75 psig (517 kPa), nichrome alone was unable to ignite BAHX block samples partially immersed in LOX. With a BAHX sample, at least 0.25 g of a hydrocarbon addition was required to ignite.

8.3 Nichrome/hydrocarbon versus strong metal promoters

Tests conducted in LOX indicated that either nichrome/hydrocarbon or strong metal promoters ignite BAHX block samples if suitable LOX purity and pressure are available. As mentioned previously, at least 0.25 g hydrocarbon in conjunction with a nichrome ignitor is required.

8.4 Mechanical impact

Mechanical impact tests were carried out on thin aluminum in LOX. Very thin sheets (0.01 mm) were ignited by 100 J impacts. Sheets of aluminum (0.2 mm thickness) did not ignite even when contaminated by wood or grease (which did ignite). With massive hexadecane contamination (>10 g/m²), 0.2 mm thick sheets ignited with a good reproducibility [15]. Tests performed with about 2 g/m² resulted in aluminum ignition in less than 10% of the shocks, probably due to nonhomogeneous hydrocarbon coating on the sheets.

9 Experimental work on aluminum/oxygen combustion

9.1 Reports of experimentation

Experiments on aluminum combustion have been reported in literature [9, 10]. Most of these were done in GOX. LOX tests are scarce. Detailed information on LOX tests are reported in references 13 through 25. Most of the reported LOX tests involved aluminum packing or trays [21, 22, 23, 24, 26, 27, 28, 29]. Pertinent BAHX/LOX data is described below in Zawierucha and Million [13, 14]. Molten aluminum/LOX reactions and the effects of contaminants on aluminum/LOX behavior are discussed in Barthélémy et al. [15, 16]. Flames spreading and VER processes in aluminum tubes are treated in Mench et al. [18, 19]. LOX pump combustion studies are discussed in Bauer et al. [28, 29].

9.2 Mechanical impact ignition experiments in LOX

More than 200 impact tests (100 J) have been carried out on 0.2 mm thick aluminum sheets with various levels of hydrocarbon contamination (hexadecane) and with two levels of LOX purity. The conclusion of the tests has been that the probability of aluminum ignition for a given mass of hydrocarbon is similar in standard purity LOX (99.5%) and in high purity LOX (> 99.95%) [17].

9.3 Combustion experiments in GOX with BAHX block specimens

In these experiments, 200 g BAHX blocks were ignited via nichrome with 2 g hydrocarbon promoter in high purity GOX.

Ten tests in high purity (99.9%) GOX at pressures to 200 psig (1380 kPa) resulted in no burns or VER phenomena [10].

9.4 Combustion experiments in LOX with BAHX block specimens

9.4.1 Range of tests

A total of 61 tests were conducted using BAHX block specimens in LOX [13]. BAHX blocks varied from 200 g to 400 g and fin thicknesses ranged from 0.23 mm to 0.43 mm. Fully immersed and partially immersed conditions were tested. The bulk of the tests used nichrome wire and 2 g hydrocarbon as the ignitor/promoter; however, at least four different strong metal ignitor/promoter combinations involving pyrofuze and various thermite mixes were tested. In these experiments, all passages of the BAHX specimens were exposed to LOX or supercritical oxygen; no inert fluids were present.

9.4.2 Test results

Nine tests involving high purity (99.9%) LOX at atmospheric pressure resulted in no burns or VER phenomena.

The purity of the LOX was found to affect the pressure threshold above which a VER is possible. VER pressure thresholds using a 2 g hydrocarbon promoter as a function of LOX purity are shown in Table 2.

At pressures ranging from 10 psig to 1125 psig (69 kPa to 7760 kPa), testing in high purity LOX with either nichrome/hydrocarbon or strong metal promoters resulted in 11 VERs out of 18 experiments. There were no discernible differences noted between promoter types, i.e., nichrome/hydrocarbon versus strong metal.

Surface treatment (via boehmite film treatment) or complete immersion in high purity LOX had no inhibiting effects on VER tendencies.

Table 2—VER pressure as a function of LOX purity

LOX purity	VER thresholds	
	psig	kPa
99.91 ¹⁾	~10-12	69-83
95.10 ²⁾	100-160	690-1100
91.70 ³⁾	>160	>1100
86.90 ²⁾	>160	>1100
NOTE—VER thresholds shown are valid only with the cited promoter and can vary with the strength of the promoter.		
¹⁾ Commercial mixture, balance argon		
²⁾ Binary mix, balance argon		
³⁾ Binary mix, balance nitrogen		

9.5 Experiments in LOX with miniature BAHX samples (3000 g)

9.5.1 Range of tests

The major objective of the test program was to determine whether combustion propagation after a promoted ignition in an oxygen passage would be inhibited by burnthrough into adjacent inert (air or nitrogen) passages.

Twenty-three individual experiments were conducted by Zawierucha and Million [14]. Nichrome/2 g hydrocarbon was used as the ignitor/promoter.

All experiments involved the use of high purity commercial oxygen with a range of 99.3% to 99.8% (balance argon) at pressures ranging from 10 psig to 1000 psig (69 kPa to 6900 kPa) in the oxygen passages. Most of the tests were performed at 100 psig (690 kPa) (9 tests) or above (11 tests).

Alternate or “inert” passages contained air, nitrogen, or oxygen at pressures ranging from 10 psig to 1500 psig (69 kPa to 10 340 kPa). In most tests conducted to date, the pressure ratio between the inert stream and the boiling stream was at least 1.5 and generally over 2.0. The state of the fluid was liquid or supercritical in 14 tests (12 tests with air, 1 test with nitrogen, 1 test with oxygen) and was gaseous in 9 tests (6 tests with air, 2 with oxygen and 1 with nitrogen).

9.5.2 Test results

Test results over the range of oxygen pressures from 100 psig to 1000 psig (690 kPa to 6900 kPa) did not show any detrimental effects due to an increase in pressure. However, due to the fact that only 23 samples were involved, it should be cautioned that the data base is limited at specific pressures.

These test results showed that combustion in oxygen passages stopped after burnthrough of one or more parting sheets separating the LOX passages from inert passages containing air or nitrogen. The presence of inert species in passages adjacent to liquid or supercritical oxygen might have a significant mitigating effect on combustion propagation.

Combustion propagation through an outside BAHX passage to an exterior BAHX surface never occurred if an air or inert gas stream was located within the outside passages. This was observed in 20 separate tests. In three other experiments where the inert species were replaced by oxygen, severe combustion occurred in one case only. The sample lost 50% of its weight and was completely converted to oxide, slag, resolidified metal.

It was shown that condensed liquid or cold supercritical fluid (air, nitrogen, or even oxygen) was more effective than gas in combustion propagation inhibition. In every case where liquid or cold supercritical fluid was present in adjacent passages, there was combustion only in the immediate area of the igniter and aluminum loss never exceeded 25 g. In some cases where the adjacent passages contained gas, there was more extensive combustion and melting with aluminum loss up to 300 g.

9.6 Scale-up experiments in LOX with miniature BAHX samples (13 000 g)

9.6.1 Range of tests

The major objective of the test program was to determine whether combustion propagation after a promoted ignition in an oxygen passage would be inhibited by the presence of adjacent inert (air or nitrogen) passages in a BAHX that was headered on both the LOX and inert passages. A second objective was to determine if there were any scale-up effects on using 13 000 g versus 3000 g test samples.

Six individual experiments were conducted by Zawierucha and Million [14]. Nichrome/2 g hydrocarbon was utilized in three of the experiments and nichrome/3 g hydrocarbon was used in the other three experiments as the igniter/promoter.

All experiments involved the use of high purity commercial LOX with a purity range of 99.8% to 99.9% (balance argon) at pressures ranging between 93 psig and 112 psig (641 kPa and 770 kPa).

Alternate or inert passages contained gaseous air at a pressure of 251 psig (1730 kPa) in one experiment; liquid air at pressures ranging between 246 psig and 256 psig (1700 kPa and 1770 kPa) in four experiments; or gaseous nitrogen at a pressure of 1 psig (7 kPa) in one experiment.

9.6.2 Test results

In the four tests using liquid air in the alternate passages, it was observed that the tendency for ignition and combustion propagation of aluminum was minimal.

The test samples containing gaseous air or nitrogen in the alternate passages were severely damaged in VERs. The severe damage noted in these tests and similar 3000 g BAHX tests leads to the observation that gaseous phases are not as effective as liquid or cold supercritical phases in combustion inhibition.

When the conditions for combustion inhibition were met (liquid or cold supercritical fluids in the alternate passages), no scale-up effect was observed. The combustion propagation was stopped at its beginning most probably by the heat sink effect. When gaseous fluids are used in the alternate passages, it seems that there might be a scale-up effect, the quantity of aluminum involved in the combustion being bigger on large size samples and the intensity of the VER being higher.

It should be cautioned that the 13 000 g BAHX tests involved only six tests at a nominal LOX pressure of 100 psig (690 kPa) with alternate passages of 1 psig (7 kPa) in one test and nominally 250 psig (1720 kPa) in five tests. This is a relatively small sample or data base in terms of the process conditions that might be used in this application. However, these results are considered very meaningful since they support results obtained with smaller exchanger samples.

9.7 Molten or burning aluminum in LOX

Tests were carried out in which approximately 70 g of molten aluminum was heated to approximately 2012 °F (1100 °C) and poured into LOX. No propagating reaction occurred. In addition, when 5 g of aluminum was heated to 2912 °F (1600 °C) and poured into LOX, no reaction occurred. It is believed that liquid aluminum closer to its boiling point (approximately 4172 °F [2300 °C]) might be necessary to achieve VER. It also might be necessary to ensure that an ignition source is present.

Tests that were performed indicated that the VER phenomenon involving molten or burning aluminum and LOX is very similar to the molten fuel/coolant interaction (MFCI) reactions, which have been studied for nuclear reactor safety [15]. Such reactions would not be sample geometry dependent. However, it does require the simultaneous presence of vaporizable LOX, very hot (> 1900 K) liquid aluminum/aluminum oxide, and rapid contact and mixing to get quick vaporization.

9.8 Conclusions from experimental work

9.8.1 Key factors for oxygen/aluminum combustion

The potential for aluminum and oxygen to react violently under certain conditions has been demonstrated repeatedly. The key factors in these events include the strength of promoter (a critical threshold is necessary to cause combustion), oxygen purity (a sufficiently high purity is needed to sustain combustion), oxygen pressure, and finally, a presence of oxygen in the liquid state, which seems to be essential to the occurrence of VERs.

9.8.2 Promoter strength

The minimum quantity of hydrocarbons necessary to ignite a BAHX with a 500 watt nichrome wire is 0.25 g hydrocarbon, which is equivalent to 2500 calories. The relationship of this factor to actual service contaminant levels is not known.

9.8.3 Effect of inert passages

Combustion propagation in the oxygen passages of a BAHX can be inhibited by burnthrough into adjacent BAHX passages containing inert species. Condensed or cold supercritical fluid in the alternative passages is more effective in inhibiting combustion than gas. However, there are some locations in the BAHX where LOX is present and the alternate passages contain either two phase or vapor only. This is most likely in locations where the oxygen vapor fraction is high. In particular, toward the end of a LOX vaporization zone where the potential for hydrocarbon accumulation increases, the fluid condensation in the alternate passages is only beginning.

No tests were performed with boiling oxygen in the outside passages. However, the tests that were performed indicated that combustion propagation beyond the external shell of the BAHX can be reduced by the presence of an inert species in the outside passages, and particularly if condensed or cold supercritical fluid is in the inert passages.

9.8.4 Prevention of oxygen/aluminum combustion

The safety of all oxygen equipment and systems including BAHXs depends primarily upon the exclusion of ignition mechanisms.

10 Cleaning considerations

10.1 Introduction

The high internal surface area to volume ratio of a BAHX results in a potential for introducing and accumulating surface contaminants. BAHX suppliers must take careful precautions to prevent contamination during manufacturing and shipping. BAHXs also have opportunities to become contaminated during installation, commissioning, and operation. These situations require attention on the part of installation specialists and operators. These considerations, combined with the impossibility of inspecting the inner portions of individual BAHXs blocks, result in the need to exercise control over the amount of combustible contaminants associated with BAHXs for oxygen service. AIGA 012/04 presents useful information on this topic [3].

10.2 Required cleanliness level for residual hydrocarbons

It is known that oil film levels below 100 mg/m² do not migrate in cryogenic service and do not combust *in situ*. Manufacturing of BAHXs requires much lower contamination levels than 100 mg/m². After manufacturing, the level of hydrocarbon contaminants should not exceed 100 mg/m².

10.3 Protection of cleaned BAHXs

Special attention should be taken to protect the BAHXs from recontamination during handling, transport, storage, packaging, shipping, installation, erection, commissioning, and operation of plants.

11 Design and operational considerations

11.1 General

Design, operation, and maintenance are critical factors in achieving safe and reliable performance of any system. Foremost for achieving safety of BAHXs in pressurized oxygen boiling applications is the use of good engineering design, operation, and maintenance practices that attempt to eliminate ignition sources and mechanisms. AIGA 056/08 describes the practices that have been successfully applied to these plants [2].

11.2 Hydrocarbon accumulation

11.2.1 Factors affecting hydrocarbon accumulation

The design of the ASU shall address hydrocarbon accumulation in the oxygen evaporator. Factors that affect the amount of hydrocarbon accumulation are:

- **Air quality**—The trace atmospheric hydrocarbons and plugging components such as carbon dioxide or nitrous oxide drawn into the ASU that are not totally removed in the front end air prepurification system eventually affect the hydrocarbon and plugging component concentration in the boiling oxygen. Consideration must also be given to the normal, local air quality and unusual variations in air quality caused by releases from sources of hydrocarbons near the ASU that might exceed the design removal capabilities of the front end air prepurification system;
- **Air prepurification design and operation**—Each prepurification method (adsorption and reversing heat exchange) removes trace hydrocarbons and plugging components in different amounts and in different ways, resulting in differing concentrations of residual hydrocarbons and plugging components in the boiling oxygen. The front end adsorptive prepurification method might offer an advantage in that it can be designed and operated to selectively change the type and degree of trace hydrocarbon compound and plugging component removal from the air stream;
- **Boiling pressure**—Due to the favorable gas/liquid phase equilibrium and to the increasing hydrocarbon solubility at increasing boiling pressure, the tendency to accumulate hydrocarbons from the process air decreases with increasing pressure. When boiling LOX at supercritical pressure conditions, hydrocarbon accumulation (resulting from the formation of a condensed, liquid phase) is not possible since supercritical conditions preclude formation of a distinct liquid phase. Increasing boiling pressure also increases the boiling temperature of the LOX and the solubility of the plugging components such as carbon dioxide or nitrous oxide in the oxygen gas and liquid, reducing the risk of forming solid blockages in the BAHX passages;
- **Oxygen velocity**—Increasing the velocity of the boiling oxygen in the BAHX passages reduces the tendency to accumulate a condensed hydrocarbon-rich liquid phase within the passages of the BAHX;
- **Auxiliary liquid phase adsorptive purification**—The LOX stream can be treated in a liquid phase adsorber before supplying the LOX to the BAHX. The liquid phase adsorption system can be designed and operated to remove residual trace plugging contaminants such as carbon dioxide and nitrous oxide that might not have been completely removed in the front end air pretreatment step, further reducing the risk of plugging the BAHX with solids. These adsorbers might also remove some of the hydrocarbons in the LOX;
- **Solids filtration**—Filtration of the LOX upstream of the BAHX can remove particulate matter that might inadvertently clog the finned passages in the BAHX preventing the formation of zones where pool boiling could occur;
- **Concentration of plugging components**—When inert plugging components such as carbon dioxide or nitrous oxide precipitate as solids in the BAHX passages, they can create conditions that can lead to the accumulation of hydrocarbons. Preventing solids precipitation reduces the opportunity for hydrocarbon accumulation to occur; and
- **Hydrocarbon concentration in boiling oxygen**—The amount and types of products affect the hydrocarbon concentration in the boiling oxygen. The actual values depend on the specific process and products and must be determined on a case-by-case basis.

Each ASU manufacturer shall consider all of these factors and particularly the oxygen evaporation system components in designing the ASU. The manufacturer might rely on some portion or all of these design and operating factors to adequately ensure that hydrocarbon accumulation does not result in the BAHX at the boiling pressure being used. Lassmann describes a method for minimizing hydrocarbon accumulation for a particular set of conditions [32]. Additional published information on nitrous oxide, carbon dioxide, and trace contaminants pertinent to air separation plant design and operations appear in the papers by Miller et al., Meneses et al., and Lassmann and Meilinger [35, 36, 37].

11.2.2 Mitigating the hazards of specific hydrocarbons

It is recommended to use adsorption PPUs for ASU design utilizing LOX boiling in the BAHX. Properly designed and operated adsorption PPUs remove most hydrocarbons contained in the air feed to the cryogenic processing equipment. However, methane, ethane, ethylene and propane are not typically completely removed by the PPU and therefore are potential hazards in the BAHX. Because their boiling temperatures are above that of oxygen, they concentrate in the oxygen product in the sump of the separation column. A potential safety issue is that the hydrocarbons concentrate in the LOX as the more volatile oxygen is boiled away in the BAHX. If these components concentrate to the LFL, a reaction with the oxygen can occur.

Methane is only slightly less volatile than oxygen and is completely soluble in LOX, and therefore has no significant potential to accumulate to unsafe levels.

Ethane's volatility and solubility in LOX are less than methane and higher than propane. It is possible to form a second liquid phase rich in ethane if the ethane concentration is high enough. However, the ethane concentration in LOX reaches the LFL long before forming a second liquid phase, so the LFL in LOX is typically the limiting case. To reach the LFL in LOX in a typical process, even when boiling oxygen at atmospheric pressure, requires that the ethane concentration in the air feed be at least one order of magnitude above the value recommended in AIGA 035/06 [6]. Higher pressures increase the allowable amount of ethane in the feed. Unless the local environment has a source of ethane (either continuous or intermittent) or the process recovers only a small fraction of the air as liquid from the LP column reboiler sump, ethane has a low potential to concentrate to unsafe levels or form a second liquid phase provided that the vapor and liquid flow co-currently (see 11.3.2). If there is a significant potential for ethane to reach the LFL in LOX, consideration should be given to special prepurifier design and/or adding extra instrumentation to detect abnormally high ethane concentrations.

Ethylene can present a special hazard under certain conditions. Ethylene's triple point temperature is -272°F (-169°C). If the boiling oxygen is above this temperature, ethylene cannot precipitate as a solid. The oxygen pressure that corresponds to this temperature is 340 kPa, abs (49.5 psia) for pure oxygen (low purity oxygen has a higher pressure). Therefore, if the oxygen is below 340 kPa, abs (49.5 psia) (i.e., below -272°F [-169°C]), it is at least possible that solid ethylene could precipitate should the ethylene concentration be high enough (50 ppm to 500 ppm, depending on the oxygen pressure). These concentrations are well above the normal background level of ethylene in atmospheric air, even after accounting for ethylene concentrating within the process. However, if an ethylene source is nearby, consideration should be given to plant design to ensure that ethylene remains within safe limits. This can be accomplished by special design of the PPU and/or by adding extra instrumentation to detect high ethylene concentrations before safe limits are exceeded.

Propane is potentially the most hazardous hydrocarbon that enters the coldbox because of its low volatility relative to oxygen, and it forms a second liquid phase if its concentration is high enough. At low pressures, the second liquid phase forms before its concentration in LOX reaches the LFL. This second liquid phase of relatively pure propane could then react with the oxygen-rich phase, if ignited. Higher pressures increase the solubility of propane in LOX and increase its relative volatility, which combine to reduce the tendency of propane to form a second liquid phase.

Lassmann gives a method to determine the accumulation of hydrocarbons in the boiling liquid [34]. The accumulation depends on:

- the inlet hydrocarbon concentration;
- the type and removal efficiency of the PPU;
- the enrichment factor;

- the boiling oxygen pressure; and
- the vapor and liquid must flow concurrently at high vapor fractions to prevent distillation (see 11.3.2).

ASU manufacturers should set minimum oxygen boiling pressures to minimize the risk of hydrocarbon accumulation. For the conditions assumed by Lassmann, 300 kPa, abs (43.5 psia) would be sufficient to prevent hydrocarbons from accumulating [34].

NOTE—This result is specific to the conditions used by Lassmann, and different conditions would yield different minimum pressures.

As with ethylene, if there is a propane source nearby, consideration should be given to special design of the PPU and/or adding instrumentation to detect high propane concentrations before safe limits are exceeded. Because of propane's physical properties, a total hydrocarbon analyzer measuring the LOX feed to the BAHX might not be sufficient to detect if the propane concentration exceeds its solubility limit, particularly at low pressures.

11.3 BAHX design

11.3.1 Passage arrangement

BAHXs are normally designed with inert passages located on the outside and with LOX boiling passages paired on at least one side with condensing air or inert streams. This pairing and arrangement of LOX and inert streams might be a contributing factor in the mitigation of energy releases.

11.3.2 Oxygen velocity

If a liquid, hydrocarbon-rich condensed phase forms (e.g., propane-rich liquid phase), it can accumulate in the heat exchanger. By ensuring adequate oxygen velocity and good flow distribution, the hydrocarbon-rich liquid phase can be carried further up in the passage to a location where the temperature is high enough to vaporize it completely and minimize accumulation.

Although GOX flow velocities in BAHXs that vaporize pumped LOX are normally low, consideration should be given to potential upset conditions such as loss of down-stream pressure to ensure adherence to CGA guidelines in AIGA 021/05, *Oxygen Pipeline Systems* (CGA G-4.4, EIGA Doc 13/02) [43].

11.3.3 Preventing pool boiling

It is possible, even with filtration as described in 11.5, for passages to become blocked either with debris or solids precipitated from solution. Should a blockage or partial blockage occur, it is possible for pool boiling to take place, which in turn potentially leads to hydrocarbon accumulation. Selecting fins that allow flow between the fin channels such as perforated or serrated fins can minimize this risk. Plain fins, which do not allow passage to passage flow, should be avoided.

Consideration can be given to placing space between fin pads in sections of the heat exchanger where oxygen is boiled. This prevents misalignment of the fin pads from restricting flow through individual passages (such misalignment has contributed to minor energy releases in reboiler condensers). Restricted velocity could lead to hydrocarbon accumulation as described in 11.2.1. This accumulation risk is higher at low boiling pressures. At higher pressure (typically above 1000 kPa [145 psig]), the vapor phase solubilities of the hazardous trace compounds are relatively high and if the feed to the ASU is within typical limits, consideration might be given to not using fin pad spacers in the boiling section to increase the mechanical integrity of the exchanger.

11.4 BAHX arrangement and layout

Consideration should be given to the distance between a BAHX boiling oxygen and adjacent equipment containing oxygen. The volume between adjacent equipment should be filled with a noncombustible material such as perlite, and the void space should be purged with nitrogen.

Designers might elect to use special provisions for hazard mitigation in some cases based upon hazard analysis specific to a project. In most cases, a properly designed coldbox is adequate.

Internationally recognized codes for pressure relief practices are suitable for piping and vessels associated with BAHXs that boil oxygen.

11.5 LOX and GOX piping

Installing 30 to 100 mesh strainers (openings between 0.0234 in and 0.0059 in [0.595 mm and 0.149 mm]) in the circuit between the LP column and the LOX boiling BAHXs is recommended to minimize the remote possibility that particle impact might act as an ignition source and also minimize accumulation of solid material in the core that could act as a promoter. The strainer will also remove any particles that could block portions of the passages. These blocked portions could potentially create locations for pool boiling, which could then create a flammable mixture. The materials for the strainer mesh and support shall be selected to be compatible with LOX at the operating conditions. In particular, the mesh material should be selected recognizing the enhanced flammability of thin material. One appropriate material is Nickel 200. Collapse pressure of the strainer should be considered carefully during the system design. Collapse of the strainer may result in release of large amount of accumulated particles. Either the collapse pressure should be greater than the circuit design pressure or differential pressure measurement should be installed across the strainer. The LOX pump should be shut down in case of higher than allowed differential pressure.

The use of a pressure activated shutdown device is recommended to stop LOX flow in the event of equipment rupture. A device such as a check valve also should be used to prevent backflow from the GOX pipeline.

Although AIGA 021/05 does not apply to process piping directly, it can be consulted as a guideline for the proper design and operation of warm GOX piping around the BAHX [43].

11.6 Overpressure protection

There are overpressure cases that are unique to this type of BAHX. The risk assessment shall consider the possibility of heat addition to trapped liquids, leak of high pressure fluids to low pressure circuits, and overpressurization from upstream equipment such as the LOX pump. These should be addressed during the risk assessment, and appropriate overpressure protection devices included in the design.

A risk analysis shall be performed on the cryogenic enclosure due to overpressure. Through various mechanisms, gas or liquid can be released into the cryogenic enclosure, potentially increasing the enclosure pressure above its design point. A coldbox, cold can, or other BAHX enclosure shall consider this possibility and shall be equipped with relief protection as required.

11.7 Operational issues

11.7.1 Startup

Pressurizing inert passages with air, nitrogen, or argon before introducing pumped LOX to the exchanger is recommended as a standard operation procedure to ensure availability of inert gas for arresting aluminum combustion in the event of inadvertent ignition.

NOTE—If an inert species is at an appropriate pressure in actual operation, liquefaction of the inert species in an adjacent passage occurs by heat exchange as soon as LOX is introduced and begins to boil.

11.7.2 Derime

Air separation plant deriming procedures should be carefully controlled to preclude recondensation of accumulated hydrocarbons within plant equipment and potential subsequent contamination of BAHXs.

11.7.3 Preventing embrittlement of downstream equipment

The oxygen piping downstream of the BAHX is not typically designed for cryogenic service. If either the condensing stream (typically air) to the vaporizer is accidentally stopped or the design product withdrawal rate is exceeded, an excessive heat load is placed on the BAHX. It is possible for cryogenic fluids to enter the downstream piping that can embrittle and ultimately fracture these systems. Therefore, depending on the nature of the flow and use pattern, several types of safeguards should be implemented including but not limited to low temperature shut-off devices, flow controls, trim heaters, and orifice plates. AIGA 027/06 , *Cryogenic Vaporiza-*

tion Systems—Prevention of Brittle Fracture of Equipment and Piping (CGA P-56, EIGA Doc 133/05), provides specific guidelines for system design and operation to prevent low temperature embrittlement [48]. The principles of AIGA 027/06 may be used to design a low temperature protection system (LTPS) for this service. The BAHX may be considered a continuous supply, utility driven, high thermal ballast device.

Two separate hazards are involved with embrittlement of a pipe. At the actual time of embrittlement rupture, pressure energy is released. The actual pressure energy can create a blast wave that can be a hazard, along with any projectiles such as portions of the pipe or gravel. While embrittlement can occur anywhere in the line where the materials of construction are not adequate for cryogenic service, experience has shown that a fracture most likely occurs at high stress points (e.g., elbows or welds). The second hazard associated with any embrittlement fracture is the release of oxygen to the environment, which is dealt with in AIGA 056/08 CGA P-12, *Safe Handling of Cryogenic Liquids*; and CGA P-39, *Oxygen-Rich Atmospheres* [2, 49, 50].

11.7.4 Low pressure operation

Many of the safety features discussed in this guide note that at higher pressures, hydrocarbons in the LOX are more volatile and thus less likely to concentrate in LOX. Consideration should be given to alarms and shut-downs to alert operating staff if the boiling oxygen pressure falls below the design value. Continued operation at low pressure can result in unexpected hydrocarbon accumulation.

11.7.5 High pressure operation

It is recognized that higher pressures could increase the severity of any aluminum/oxygen combustion. There is limited experimental data and operating experience above 1160 psig (8000 kPa). Plant designers operating at high pressure should perform a risk analysis to confirm that any risks of higher oxygen pressures are addressed including the mechanical design.

11.7.6 Fatigue

BAHXs in this service can be exposed to fatigue by pressure and/or temperature cycling. Pressure cycles occur on each startup and shutdown and they might occur if the operating conditions are significantly changed. Temperature cycles occur on startup and shutdown.

Because boiling fluids tend to have a relatively small change in temperature, there can be relatively large differences in temperature between the process streams in the area of the BAHX where oxygen is boiled. The location of the boiling zone moves as the operating conditions change (pressure or flowrate). Depending on the BAHX design, these flow changes can cause temperature cycles. See the Braze Aluminium Plate-Fin Heat Exchanger Manufacturers' Association (ALPEMA) standard for guidance on maximum allowable temperature difference between streams [8].

If the operating pressure changes frequently, this shall be considered in the design of the BAHX. If the exchanger is not designed for cyclic service, it shall be operated accordingly. This could require additional pressure regulation devices to allow for pressure variations in the supply pipeline.

11.7.7 High ambient hydrocarbon concentrations

If the local environment has the potential for high concentrations of hydrocarbons, consideration should be given to analyzing the oxygen flowing to the BAHX to ensure that the hydrocarbons are within the design limits. Of special concern are sources that can vent very high concentrations for short durations such as emergency vents or relief valves. Common locations to measure the hydrocarbon concentration are the main air compressor outlet, the PPU outlet, the LP column reboiler sump, or the BAHX inlet.

11.7.8 High haze conditions

Normal concentrations of hydrocarbon-rich aerosols have not been determined to contribute to ASU safety incidents. However, forest fires can release relatively high concentrations of hydrocarbons into the atmosphere as solid and liquid aerosols, for up to several weeks. Schmidt et al gives an overview of haze and some of the potential ASU safety problems [51]. Hydrocarbons from forest fire haze contributed to a large ASU explosion

[32]. If an ASU has the potential to have high amounts of particulates in the ambient air for extended periods of time, the following can reduce the risk of hydrocarbon accumulation and safety hazard.

11.7.8.1 Design measures

- Use a high efficiency filter to remove particles larger than 0.1 μm to 0.4 μm . The filter could be placed on the main air compressor (MAC) inlet or on the prepurifier outlet.
- Install particle counters on the MAC inlet or PPU outlet, to alert operating staff to a potential hazard.

NOTE—It should be recognized that filtration mitigates the hazard while particle counters only identify a potentially unsafe situation.

11.7.8.2 Operating measures

- Consult the manufacturer for guidance as to what constitutes a significant haze. In the absence of any guidelines, a PM_{10} threshold of 150 $\mu\text{g}/\text{m}^3$ may be used.

NOTE— PM_{10} is the mass of particles less than 10 μm diameter contained in 1 m^3 (35 ft^3) of air. This is measured by many environmental regulating agencies throughout the world.

- If an ASU runs during a short period of high haze, ensure that all safety measures are being followed (e.g., reboiler submergence, LOX removal from the reboiler sump, etc). Further guidance on ASU safety measures is given in AIGA 056/08 [2].
- Particular attention should be paid to ensure that solids such as carbon dioxide and nitrous oxide are not precipitating from oxygen-rich fluids. Monitor heat exchangers and piping systems for increases in pressure drop or decreased heat transfer performance. These are indications that solids may be precipitating.
- Use the manufacturer's criteria to determine if an ASU should be shut down in a high haze environment.

11.7.9 Accumulation of plugging compounds

If the boiling oxygen pressure is low enough, the vapor phase solubility of nitrous oxide and carbon dioxide is low. Consideration shall be given to PPU design, plant operation, and instrumentation to ensure that these components remain within design levels. In addition, carbon dioxide and nitrous oxide form a solid solution, which means that the carbon dioxide solubility is lower when nitrous oxide is present in appreciable quantities and vice versa [35, 36]. The allowed concentrations must take this in to account and the operating limits adjusted accordingly.

If all of the following conditions are met even if no nitrous oxide is removed in the PPU, the nitrous oxide concentration is below its solubility limit and it is impossible to precipitate solid nitrous oxide. Therefore, no special considerations would need to be applied.

- The oxygen purity is above 98%;
- The boiling oxygen pressure is above 300 kPa, abs (43.5 psia);
- The oxygen product is 20% of the air;
- The atmospheric concentration of nitrous oxide is 310 ppb (as is typical in most locations); and
- The carbon dioxide concentration is low, i.e., the PPU removes essentially all of the carbon dioxide. (The required removal level must be determined during the design, and this varies with boiling oxygen pressure.)

11.7.10 Corrosion

Air passages in a BAHX can experience corrosion if condensate films are allowed to form in the passages of a BAHX. Normal atmospheric constituents such as carbon dioxide and water in conjunction with site-specific industrial pollutants such as sulfur dioxide can produce acidic condensates that are corrosive to aluminum. Effective prepurification eliminates or minimizes corrosion. It is recommended to use PPU for ASU design utilizing LOX boiling in the BAHX.

11.7.11 Leaks

Consideration shall be given to the consequences of leaks between streams and into the cryogenic insulation enclosure. Leaks will cause flow from the high to the low pressure stream, and can have the following effects:

- The purity of the low pressure stream will change, due to the inward flow of different molecules;
- The pressure of the low pressure stream can increase; or
- Leaking cold liquids or gases into the cryogenic enclosure can cool structural members below normal operating temperatures.

To mitigate these effects, a risk assessment shall be performed to understand the magnitude and consequence of the leak. The most significant safety items are:

- Leaking oxygen into a lower purity stream can increase the oxygen concentration to unsafe levels;
- A high pressure stream can raise a low pressure stream above its design pressure; and
- Structural members can lose their strength or become brittle if cooled excessively.

Possible detection and mitigation measures include material selection, design pressure selection, purity analysis, temperature measurement, pressure measurement, or pressure relief devices.

11.8 Auxiliary equipment

Industry practices currently applied to equipment in LOX service are adequate for auxiliary equipment associated with BAHX-LOX high pressure vaporization cycles. References 4 through 6 and 39 through 44 are pertinent.

12 References

Unless otherwise specified, the latest edition shall apply.

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