



SAFE USE OF BRAZED ALUMINIUM HEAT EXCHANGERS FOR PRODUCING PRESSURIZED OXYGEN

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Preface

As part of a programme of harmonization of industry standards, EIGA has adopted the Compressed Gas Association (CGA) publication, G-4.9, *Safe Use of Brazed Aluminium Heat Exchangers for Producing Pressurized Oxygen*.

This publication is intended as an international harmonized publication for the worldwide use and application by all members of Asia Industrial Gases Association (AIGA), Compressed Gas Association, CGA, EIGA, and Japan Industrial and Medical Gases Association (JIMGA). The EIGA edition has the same technical content as the CGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Also, any references to regional regulatory requirements have been replaced with the relevant European requirements.

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Amendments to 145/14

Section	Change
5	Addition of new reference [15]
9.1	Addition of new reference [15]
9.5.1	Additional text following inclusion of new reference
9.5.2	Additional text following inclusion of new reference
12	New reference [15] added

Note: Technical changes from the previous edition are underlined

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 aluminium 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 aluminium 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 EIGA Doc 144 *Safe Use of Aluminium Structured Packing for Oxygen Distillation* [1]¹. Questions initially raised for aluminium packing were extended later by analogy to BAHXs used as product oxygen vaporizers. Therefore, a significant amount of information from EIGA Doc 144 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 vapour. Other BAHX uses in oxygen applications are not addressed, although incidents involving aluminium 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 aluminium 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 aluminium 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 vapour only. This is most likely in locations where the oxygen vapour 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 aluminium-fabricated equipment in oxygen service primarily depends on excluding ignition mechanisms including the accumulation of flammable contaminants. BAHXs also use this philosophy.

The procedures that have resulted in this record of safe operation with aluminium components have included following the practices described in EIGA Doc 147, *Safe Practices Guide for Cryogenic Air Separation Plants* and proper cleaning of aluminium 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]. EIGA Doc 65 *Safe Operation of Reboilers/Condensers in Air Separation Units*, offers additional insights pertinent to aluminium 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 EIGA Doc 147 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 15000 kPa (2180 psi)² using BAHX specimens. From current understanding, there is no step change in the risk of aluminium ignition and the combustion-propagation severity when increasing the pressure. Current industry references are up to 8700 kPa (1260 psi). 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.

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]

4.2 Technical definitions

4.2.1 Brazed aluminium 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.

An illustration of a multi-stream 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.

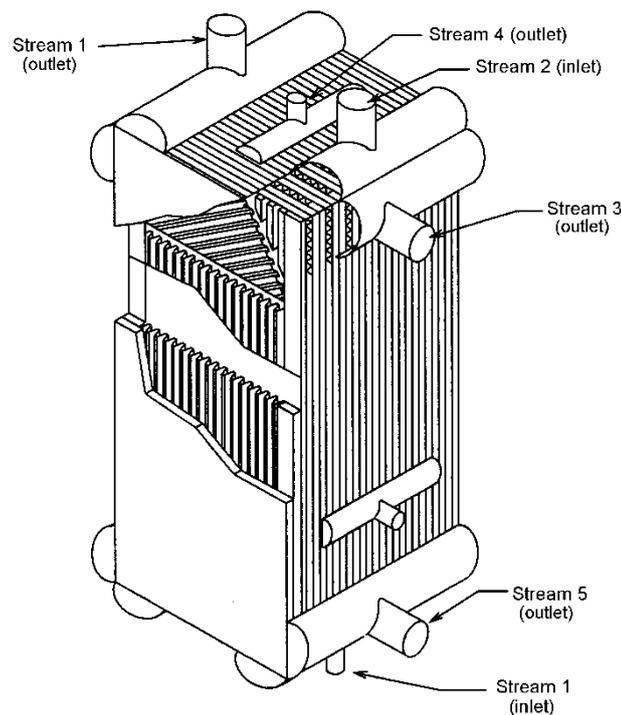
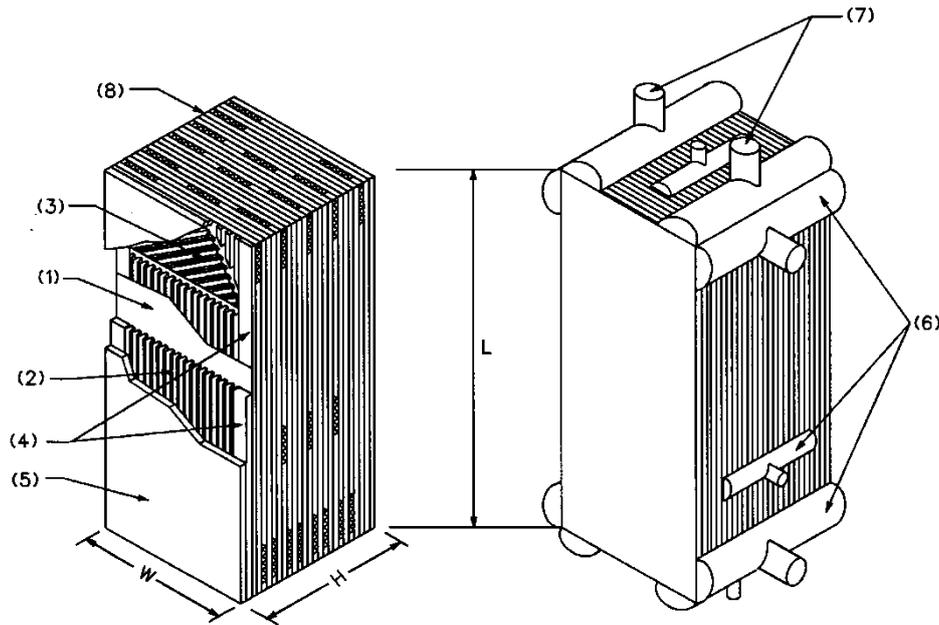


Figure 1 Illustration of a typical multistream BAHX

4.2.1.2 Components of an exchanger

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

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]



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

Figure 2 Components of a BAHX

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.

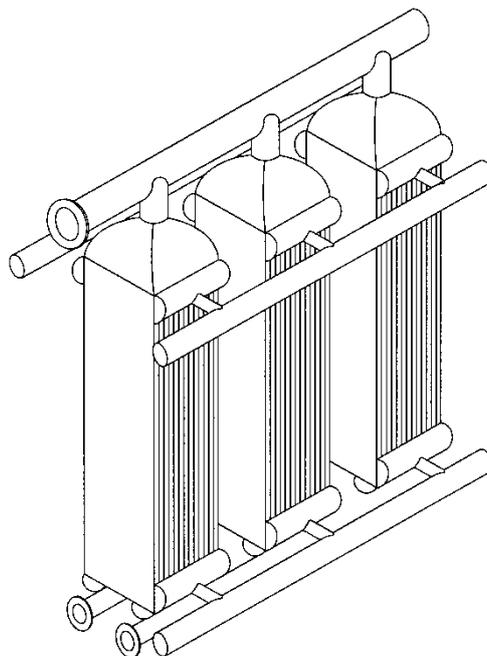


Figure 3 Typical assembly of three BAHXs in parallel

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 13000 g. A 3000 g BAHX uses approximately 1000 g of thin aluminium fins and parting sheets, while a 13000 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 aluminium 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 vapour 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 vapour 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 Pre-purification method

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

4.2.9 Pre-purification 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 PPU's, 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 aluminium 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 aluminium 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 aluminium and LOX is found in Barthélémy and Muller [16]. In a later investigation, Barthélémy, Roy, and Mazlounian reported the results of impact tests of aluminium in LOX and the effects of contaminants on impact behaviour [17]. Present work investigates the effect of LOX purity on the probability of ignition by impact of contaminated aluminium [18].

The preparation of this publication and the general knowledge of aluminium LOX reactions has been enhanced by a number of investigations related to the safe use of aluminium structured packing in air separation plants. These investigations have involved flammability tests of aluminium 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 aluminium and LOX are those of Bauer et al. [29, 30].

Several significant incidents involving aluminium 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 aluminium 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 aluminium 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 behaviour in ASUs was investigated by Menesees 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 aluminium/oxygen combustion and oxygen compressor comparison

6.1 Background

Since the 1950s, when aluminium replaced copper as the preferred material of construction of cryogenic equipment, aluminium and oxygen have reacted on several occasions with varying degrees of intensity. The configuration of the aluminium 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 aluminium and aluminium oxide can be used to determine whether or not aluminium participated in a reaction. Whereas molten aluminium is not always indicative of an aluminium-oxygen reaction, aluminium oxide is always indicative of this reaction.

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

- Cases of violent hydrocarbon combustion in aluminium equipment without the actual participation of the aluminium in the reaction;
- Cases in which there was evidence that a very small amount of aluminium 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 aluminium/oxygen combustion. These were initiated by accumulated combustibles in the reboiler/condenser and resulted in extensive combustion of the aluminium reboiler. Aluminium 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 aluminium combustion [17]. Where the contamination is localized, the high thermal conductivity of aluminium 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 aluminium 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 build-up.

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 aluminium oxygen reaction.

6.2 Scope of investigation

The subject under investigation is the use of aluminium 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 aluminium/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 aluminium was, a material of construction in each of these components in order for the incident to be cited.

A summary of pertinent aluminium/oxygen incidents in the industrial gases industry is shown in Table 1. In compiling this summary, only known aluminium combustion incidents were cited. Of the thirty-four 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 aluminium in air separation equipment.

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

6.3 Survey results

Thirty four incidents or events in an industrial environment were characterized as being representative of aluminium/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 aluminium/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 aluminium 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 aluminium and oxygen are generally recognized to be oxygen purity, oxygen pressure, oxygen phase, ignition source, contamination and aluminium 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.

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 occurred with aluminium 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 aluminium/oxygen combustion makes generalizations about the effect of aluminium 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 aluminium/oxygen reactions in varying degrees and extents. Some can be characterized as violent exothermic reactions that involve significant quantities of aluminium 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 aluminium consumed was generally rather small. The two customer storage tanks and the mobile transport vehicle are examples of violent reactions between large quantities of aluminium and oxygen. Three reboiler condenser incidents had violent reactions between large quantities of LOX and aluminium [6, 33]. The more limited reactions exemplified by evidence of

molten aluminium 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.

The one heat exchanger sealed cavity incident involved considerable aluminium combustion and physical damage, including breaching of the coldbox as well as damage outside the coldbox, although there were no injuries.

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) aluminium geometries. The superinsulated liquid dewars and vacuum jacketed piping are examples of this type of phenomena.

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

Those cases where thick aluminium cross sections were involved in extensive reactions occurred at elevated pressures, between 310 kPa (45 psi) and 1380 kPa (200 psi). These incidents include the customer storage tanks, the LOX trailer, and the submerged aluminium 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 LOX appears to play a much more important role than had been appreciated or understood. Mench, Haas, and Kuo have shown that the aluminium combustion rate is significantly lower in high pressure GOX than in LOX, even when the GOX is supercritical and the GOX density approaches liquid-like values [21]. This shows that the presence of LOX increases the rate of aluminium 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 aluminium. 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 typical 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 aluminium/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 aluminium to oxidize or even melt.

The heat exchanger cavity incident reported in Table 1 was likely precipitated by the presence of a sealed cavity immediately below the LOX inlet distributor. The cavity was formed by a small gap between two horizontal transverse bars, where the small gap was sealed at the exchanger side bars. Overpressure within the sealed cavity led to the mechanical failure of this heat exchanger, which allowed for the high velocity impact of particles on thin aluminium fin material as well as the exposure of fresh aluminium metal.

6.5.5 Hydrocarbon contamination

By far, incidents in the reboiler/condensers of low pressure columns were the most frequent examples of incidents that were probably initiated by hydrocarbons. Generally, these incidents were extinguished before aluminium ignition. Hydrocarbon build-up 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 (LFL) for fuel in oxygen. Inadequate recirculation could 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 aluminium/oxygen reaction. The energy released was due mostly to hydrocarbon/oxygen reactions. In a few incidents, small amounts of aluminium combustion were detected. In others, it was difficult to closely examine the damaged areas of the reboiler, and small amounts of aluminium combustion may have been present but not detected. In all of these egg-shaped cavity cases, it is clear that the aluminium reaction, if present, was very small. In three cases, however, hydrocarbon initiation in reboilers led to extensive aluminium/oxygen reaction and severe plant damage [33]. EIGA Doc 65 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 aluminium/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 aluminium/oxygen VER.

Many of the incidents noted in Table 1 were small in size and might not have involved aluminium/oxygen combustion reactions. However, BAHX reboiler energy releases of significant size, in which an aluminium/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 can ignite the aluminium-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 aluminium/oxygen reactions in ASUs. For specific guidance, refer to EIGA Doc 144, EIGA Doc 65 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 aluminium 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 aluminium/oxygen reaction was initiated in structured aluminium packing. However, there have been two incidents where an aluminium/oxygen reaction occurred in structured aluminium packing after being initiated by a violent aluminium/oxygen reaction in the reboiler;
- There has been one reported incident with BAHXs in pumped LOX vaporization service (see 6.6.3);
- In more than fifty years of using aluminium 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 greater. Experimental and theoretical work have shown oxygen purity to be an important parameter in aluminium/oxygen combustion;
- Hydrocarbons accumulated from the air in the less volatile fraction are the most commonly cited cause of aluminium reactions as the hydrocarbons are easily ignited and often kindle the aluminium reaction;

- Since 1950, with the exception of nine incidents, aluminium sheets of thicknesses comparable to BAHXs used for vaporizing/boiling pumped LOX have been used in plate-fin reboiler/condensers without evidence of aluminium/oxygen combustion. These heat exchangers are located in the LOX rich low pressure (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 LOX at the outlet of the vaporization section. However, improper design or operation can lead to local or global vaporization to dry out oxygen, for example, lack of submergence of a bath type vaporizer. Due to the more favourable oxygen/hydrocarbon phase equilibria at higher pressure, the potential for hydrocarbon accumulation in a BAHX boiling oxygen at elevated pressure is less than that in a reboiler/condenser operating at low pressure and experiencing abnormal vaporization to dry out [34]. 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 aluminium/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 pre-purification 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 aluminium.

- 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 aluminium 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. In a 2002 survey task force participants estimated 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*; EIGA Doc 148 *Installation Guide for Stationary, Electric-Motor-Driven, Centrifugal Liquid Oxygen Pumps*; EIGA Doc 10 *Reciprocating Compressors for Oxygen service* and EIGA Doc 27, *Centrifugal Compressors for Oxygen Service* [40, 41, 42, 43].

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. In 2002, task force participants estimated 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. See EIGA Doc 148 for information on LOX pump design and practices [41].

6.6.3 BAHX/LOX vaporization service experience at elevated pressure

There are hundreds of air separation plants in operation today that use BAHXs for producing pressurized oxygen with a total operating experience of thousands of plant years. There has been only one known incident involving these components, see Table 1.

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

7 Ignition mechanisms

7.1 Introduction

This section, addresses the fundamentals of aluminium ignition and Section 8 addresses experimentation [8, 9, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 26, 27, 28].

7.2 Conditions for ignition of aluminium

Solid and liquid aluminium are protected by a thin, dense, flexible layer of aluminium 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 aluminium to greater than approximately 2000 °C (3632 °F) to initiate combustion [9]. The high thermal conductivity of aluminium 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 aluminium directly (by a physical mechanism) or indirectly (by the chemical reaction of a promoter).

7.4 Direct ignition

The following mechanisms were considered 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 considered to be unlikely in BAHXs used for boiling due to the low velocities of oxygen in normal operation. Abnormal process conditions shall be examined. The use of strainers to minimize the potential for particle impact could be beneficial.

Mechanical failure of a BAHX can generate many particles and high velocities. Impact of the high velocity particles upon other particles and thin fin material along with exposing fresh aluminium material can cause ignition.

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 aluminium heat exchanger surface which exposes fresh aluminium. It is theoretically possible for combustion to start on this fresh aluminium 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 11.7.6 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, the ignition promoter has to accumulate to its LFL or as a condensed phase; as a second step, this promoter has to be ignited; and as a third step, the energy released by the promoter reaction has to be able to ignite the aluminium.

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 [33].

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 LFL 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 20 °C (36 °F), 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 aluminium. The possibility of accumulation of oil by the following mechanisms was considered:

- cryogenic chipping of brittle oil films;
- migration at temperatures up to 60 °C (140 °F); 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 0.1µm) 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 aluminium exchangers. The ignition of solid contaminants would need energy input either by impact or by heating energy. Heating from -180 °C (-292 °F) to the ignition temperature of the contaminant (above 200 °C to 300 °C [392 °F to 572 °F]) would be necessary.

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

7.5.4 Other promoters

Other potential promoters such as 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 517 kPa (75 psi), 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 aluminium in LOX. Very thin sheets (0.01 mm) were ignited by 100 J impacts. Sheets of aluminium (0.2 mm thickness) did not ignite even when contaminated by wood or grease (which did ignite). With massive hexadecane contamination ($>10 \text{ g/m}^2$), 0.2 mm thick sheets ignited with a good reproducibility [15]. Tests performed with about 2 g/m^2 resulted in aluminium ignition in less than 10% of the shocks, probably due to non-homogeneous hydrocarbon coating on the sheets.

9 Experimental work on aluminium/oxygen combustion

9.1 Reports of experimentation

Experiments on aluminium 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, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25. Most of the reported LOX tests involved aluminium packing or trays [21, 22, 23, 24, 25, 27, 28, 29]. Pertinent BAHX/LOX data is described in Zawierucha and Million and McNamara [13, 14, 15]. Molten aluminium/LOX reactions and the effects of contaminants on aluminium/LOX behaviour are discussed in Barthélémy et al. [16, 17]. Flames spreading and VER processes in aluminium tubes are treated in Mench et al. [19, 20]. LOX pump combustion studies are discussed in Bauer et al. [29, 30].

9.2 Mechanical impact ignition experiments in LOX

More than 200 impact tests (100 J) were carried out on 0.2 mm thick aluminium sheets with various levels of hydrocarbon contamination (hexadecane) and with two levels of LOX purity. The conclusion of the tests were that the probability of aluminium ignition for a given mass of hydrocarbon is similar in standard purity LOX (99.5%) and in high purity LOX (greater than 99.95%) [18].

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 GOX (99.9%) at pressures to 1380 kPa (200psi) 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 69 kPa to 7760 kPa (10 psi to 1125 psi), 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	
	psi	kPa
99.91 ¹⁾	Approximately 10 to 12	69 to 83
95.10 ²⁾	100 to 160	690 to 1100
91.70 ³⁾	Greater than 160	Greater than 1100
86.90 ²⁾	Greater than 160	Greater than 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 BAHX specimen samples (3000 g)

9.5.1 Range of tests

The major objective of the test programme was to determine whether combustion propagation after a promoted ignition in an oxygen passage would be inhibited by burn through 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 69 kPa to 6900 kPa (10 psi to 1000 psi) in the oxygen passages. Most of the tests were performed at 690 kPa (100 psi) (9 tests) or greater (11 tests).

Alternate or inert passages contained air, nitrogen, or oxygen at pressures ranging from 69 kPa to 10340 kPa (10 psi to 1500 psi). In most tests conducted to date, the pressure ratio between the inert stream and the boiling stream was at least 1.5 and generally greater than 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).

The testing was extended to greater oxygen pressures, super critical fluid conditions, using a similar test setup and BAHX specimen as previous tests. High purity commercial oxygen was tested at pressures up to 2 250 psi (15 600 kPa). Of the total of ten tests, eight tests were at 14 700 kPa to 15 600 kPa (2 129 psi to 2 263 psi) and two at 10 400 kPa to 10 500 kPa (1 503 psi to 1 519 psi) oxygen pressure. The alternate or inert passages contained air at supercritical pressure, ranging from 8 300 kPa to 16 400 kPa (1 200 psi to 2 380 psi). Of the total of ten tests, six were carried out with air at greater pressure than oxygen and four were carried out with air at a pressure less than oxygen [15].

9.5.2 Test results

Test results over the range of oxygen pressures from 690 kPa to 6900 kPa (100 psi to 1000 psi) 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 burn through 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 can 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 only one case. The sample lost 50% of its weight and was completely converted to oxide, slag and 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 aluminium loss never exceeded 25 g. In some cases where the adjacent passages contained gas, there was more extensive combustion and melting with aluminium loss up to 300 g.

Additional testing was completed at greater oxygen pressures with super critical conditions on both sides. Ten tests were completed at these conditions. In two of these ten tests, there was extensive combustion with aluminum loss exceeding 2000 gm (out of 3000 gm to 4000 gm BAHX specimen), indicating unmitigated VER [15]. The complexity of the application and number of parameters involved require further consideration when interpreting the test results.

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

9.6.1 Range of tests

The major objective of the test programme 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 used 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 641 kPa and 770 kPa (93 psi and 112 psi).

Alternate or inert passages contained gaseous air at a pressure of 1730 kPa (251 psi) in one experiment; liquid air at pressures ranging between 1700 kPa and 1770 kPa (246 psi and 256 psi) in four experiments; or gaseous nitrogen at a pressure of 7 kPa (1 psi) 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 aluminium 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 could be a scale-up effect, the quantity of aluminium involved in the combustion being greater on large size samples and the intensity of the VER being greater.

It should be cautioned that the 13000 g BAHX tests involved only six tests at a nominal LOX pressure of 690 kPa (100 psi) with alternate passages of 7 kPa (1 psi) in one test and nominally 1720 kPa (250 psi) in five tests. This is a relatively small sample or database in terms of the process conditions that might be used in this application. However, these results are considered meaningful since they support results obtained with smaller exchanger samples.

9.7 Molten or burning aluminium in LOX

Tests were carried out in which approximately 70 g of molten aluminium was heated to approximately 1100 °C (2012 °F) and poured into LOX. No propagating reaction occurred. In addition, when 5 g of aluminium was heated to 1600 °C (2912 °F) and poured into LOX, no reaction occurred. It is believed that liquid aluminium closer to its boiling point (approximately 2300 °C [4172 °F]) and/or in vapour phase 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 aluminium 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 (greater than 1900 K) liquid aluminium/aluminium oxide, and rapid contact and mixing to get quick vaporization.

9.8 Ignition energy

Ignition of aluminium foils in gaseous oxygen was experimentally tested by using a diode laser as the energy source, which provided a well-controlled, accurate, and reproducible method of ignition. These tests were conducted under different conditions of oxygen pressure, oxygen purity, aluminium thickness and gas velocity. The aluminium foils tested had thickness between 0.2 mm and 0.45 mm, a range typical of fins contained in BAHXs used in ASUs.

The experimental results showed that the oxygen pressure has no significant effect on the ignition energy of aluminium over the pressure range tested (10 bara to 120 bara). This conclusion holds for both standard commercial grade oxygen purity (99.8%) and high purity oxygen (99.99%), and also for gas velocities greater than typically encountered in ASU BAHX. See "Ignition of Aluminium in High Pressure Gaseous Oxygen" for more information [48].

9.9 Conclusions from experimental work

9.9.1 Key factors for oxygen/aluminium combustion

The potential for aluminium 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 or supercritical state, that seems to be essential to the occurrence of VERs.

9.9.2 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.

9.9.3 Effect of inert passages

Combustion propagation in the oxygen passages of a BAHX can be inhibited by burn through 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 vapour only. This is most likely in locations where the oxygen vapour 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.

9.9.4 Prevention of oxygen/aluminium 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 shall take precautions to prevent contamination during manufacturing and shipping. BAHXs can also 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. CGA G-4.1 presents information on this topic [3].

10.2 Required cleanliness level for residual hydrocarbons

It is known that oil film levels less than 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

Specific 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. EIGA Doc 147 describes the practices that have been successfully applied to these plants [2]. The design parameters should be combined with an operation system to result in

the necessary layers of protection required for the safety robustness in ASU operation consistent with manufacturer's and/or operator's practices.

11.2 Hydrocarbon accumulation

11.2.1 Factors affecting hydrocarbon accumulation

The design of the ASU shall address hydrocarbon accumulation in the BAHX. 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 that are drawn into the ASU but are not totally removed in the front end air pre-purification system eventually affect the hydrocarbon and plugging component concentration in the boiling oxygen. Consideration shall 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 could exceed the design removal capabilities of the front end air pre-purification system;
- **Air pre-purification design and operation**—Each pre-purification 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 pre-purification method can 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 favourable 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 pre-treatment step, further reducing the risk of plugging the BAHX with solids. These adsorbers can also remove some of the hydrocarbons in the LOX;
- **Solids filtration**—Filtration of the LOX upstream of the BAHX can remove particulate matter that can inadvertently clog the finned passages in the BAHX preventing the formation of zones where pool boiling can 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 shall 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 may 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 [35]. 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 [36, 37, 38].

11.2.2 Mitigating the hazards of specific hydrocarbons

It is recommended to use adsorption PPUs for ASU designs using 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 greater than 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 greater than propane. If the ethane concentration is high enough it is possible to form a second liquid phase rich in ethane. 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 greater than the value recommended in EIGA Doc 65 [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 vapour 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 pre-purifier 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 $-169\text{ }^{\circ}\text{C}$ ($-272\text{ }^{\circ}\text{F}$). 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 less than 340 kPa abs (49.5 psia) (i.e., below $-169\text{ }^{\circ}\text{C}$ [$-272\text{ }^{\circ}\text{F}$]), it is 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. 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 because 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. 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 analyser 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.

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

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

- boiling oxygen pressure; and
- vapour and liquid have to flow co-currently at high vapour 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) is sufficient to prevent hydrocarbons from accumulating [35].

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

The pressure of the condensing or dense fluid air or inert stream can be a contributing factor in the mitigation of energy releases or VER.

11.3.2 Oxygen velocity

If a liquid, hydrocarbon-rich condensed phase forms for example., 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, see EIGA Doc 13, *Oxygen Pipeline and Piping Systems* [44].

11.3.3 Preventing pool boiling

Even with filtration as described in 11.5, it is possible 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 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 greater than 1000 kPa (145 psi)), the vapour phase solubilities of the hazardous trace compounds are relatively high. If the feed to the ASU is within typical limits, consideration may 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 non-combustible material such as perlite, and the void space should be purged with nitrogen.

Designers may 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 0.595 mm and 0.149 mm (0.0234 in and 0.0059 in)) in the circuit between the LP column and the LOX boiling BAHXs is recommended to minimize the remote possibility that particle impact can act as an ignition source and also to minimize accumulation of solid material in the core that could act as a promoter. The strainer can also remove any particles that could block portions of the passages. These blocked portions could potentially create locations for pool boiling, that 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 during the system design. Collapse of the strainer can result in a release of large amounts 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 greater than allowed differential pressure.

The use of a pressure activated shut-down 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 EIGA Doc 13 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 [44].

11.6 Overpressure protection

There are overpressure cases that are unique to the type of BAHX used to produce pressurised oxygen. A risk assessment shall consider the possibility of heat addition to trapped liquids, leak of high pressure fluids to low pressure circuits, and over pressurization 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 assessment 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 to greater than its design point. A coldbox, coldcan, or other BAHX enclosure shall consider this possibility and shall be equipped with relief protection as required.

11.7 Operational issues

11.7.1 Start-up

Pressurizing inert passages with air, nitrogen, or argon before introducing pumped LOX to the exchanger is recommended as a standard operating procedure to ensure availability of inert gas for arresting aluminium 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 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. EIGA Doc 133, *Cryogenic Vaporization Systems—Prevention of Brittle Fracture of Equipment and Piping*, provides specific guidelines for system design and operation to prevent low

temperature embrittlement [49]. The principles of EIGA Doc 133 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, for example., elbows or welds. The second hazard associated with any embrittlement fracture is the release of oxygen to the environment, which is dealt with in EIGA Doc 147; CGA P12, *Safe Handling of Cryogenic Liquids*; and EIGA Doc 09; *Fire Hazards of Oxygen and Oxygen Enriched Atmospheres*, [2, 49, 50].

11.7.4 Low pressure operation

Many of the safety features discussed in this publication 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 shutdowns 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 aluminium/oxygen combustion. There is limited experimental data and operating experience greater than 8000 kPa (1160 psi). Plant designers operating at high pressure should perform a risk assessment to confirm that any risks of higher oxygen pressures are addressed including the mechanical design.

11.7.6 Fatigue

BAHXs producing pressurized oxygen can be exposed to fatigue by pressure and/or temperature cycling. Pressure cycles occur on each start-up and shutdown and they can occur if the operating conditions are significantly changed. Temperature cycles also occur on start-up 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 analysing the oxygen flowing to the BAHX to ensure that the hydrocarbons are within the design limits. Sources that can vent very high concentrations for short durations such as emergency vents or relief valves are of special concern. 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 incidents. However, forest fires can release relatively high concentrations of hydrocarbons as solid and liquid aerosols into the atmosphere, for up to several weeks. Schmidt et al gives an overview of haze and some of the potential ASU safety problems [52]. Hydrocarbons from forest fire haze contributed to a large ASU explosion [33]. 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 hazards.

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 pre-purifier outlet; or
- 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 PM10 threshold of 150 $\mu\text{g}/\text{m}^3$ may be used.

NOTE PM10 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 regulatory agencies throughout the world.

- If an ASU runs during a short period of high haze, ensure that all safety measures are being followed for example., reboiler submergence, LOX removal from the reboiler sump, etc.. Further guidance on ASU safety measures is given in EIGA Doc 147 [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 could be precipitating; and
- 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 vapour 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 than when nitrous oxide is present in appreciable quantities and vice versa [36, 37]. The allowed concentrations shall 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 less than 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 greater than 98%;
- The boiling oxygen pressure is greater than 300 kPa abs (43.5 psia);
- The oxygen product is 20% of the air;
- The atmospheric concentration of nitrous oxide is 310 parts per billion (ppb) which is typical in most locations; and
- The carbon dioxide concentration is low, for example., the PPU removes essentially all of the carbon dioxide. The required removal level shall 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 aluminium. Effective pre-purification eliminates or minimizes corrosion. It is recommended to use a PPU for an ASU design using 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:

- Purity of the low pressure stream will change, due to the inward flow of different molecules;
- Pressure of the low pressure stream can increase; or
- Leaking cold liquids or gases into the cryogenic enclosure can cool structural members to less than 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 to 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 (PRDs).

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. [5, 6, 7, 40, 41, 42, 43, 44, 45].

11.9 Mechanical considerations

Mechanical design shall not allow the presence of a sealed cavity. For example, avoid the use of dual transverse bars sealed at the ends that would create a sealed cavity.

If dual transverse bars are unavoidable, there shall be a minimum gap of 5 mm between the bars and the gap shall be vented on at least one end.

12 References

Unless otherwise specified, the latest edition shall apply.

[1] EIGA Doc 144 (CGA G-4.8), *Safe Use of Aluminium Structured Packing for Oxygen Distillation*, www.eiga.eu

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

[2] EIGA Doc 147 (CGA P-8), *Safe Practices Guide for Air Separation Plants*, www.eiga.eu

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- [6] EIGA Doc 65 (CGA P-8.4), *Safe Operation of Reboiler/Condensers in Air Separation Units*, www.eiga.eu
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