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SAFE USE OF ALUMINUM-STRUCTURED PACKING FOR OXYGEN DISTILLATION

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1 Introduction

As a part of a programme of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has adopted the Compressed Gas Association (CGA) standard G- 4.8.

This international harmonized document is intended for use and application by all IHC member associations. The AIGA edition has the same technical content as the CGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Also, references to regional regulatory requirements have replaced US regulations.

Many air separation plants use aluminum sieve trays in their distillation columns. Most plants built after 1990 have used structured packing in place of trays. The low pressure-drop and good mass transfer effectiveness of packing make it attractive for some air separation applications, particularly for columns operating at near-atmospheric pressure.

2 Scope

This publication addresses the use of aluminum-structured packing in oxygen distillation. Other materials that can be used in this service such as brass, copper, or stainless steel are not addressed.

A summary of current knowledge and industrial practices used in the safe application of aluminum-structured packing in columns for the distillation of oxygen is included.

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

Aluminum components have been used extensively in oxygen service since the late 1950s. This has included piping, heat exchangers, vaporizers, pressure vessels, distillation trays, and packing. Overall, the safety record of aluminum in oxygen service has been very good.

Structured packing was introduced during the 1980s as an alternative to sieve trays for distillation. Three major investigations regarding the safety of aluminum-structured packing have been reported in the literature [1, 2, 3].¹ The first of these references concludes that copper packing should be used in those sections of the distillation column where aluminum packing might be flammable. The latter two, which included tests conducted under simulated operating conditions, conclude that aluminum can be used safely in all column sections. The information assembled for this publication provides the background to conclude that the use of aluminum-structured packing in all sections of the low pressure column of an air separation plant introduces no additional risk relative to that associated with aluminum sieve trays, provided that similar care is taken to clean equipment adequately and to lessen the presence of combustible contaminants.

Aluminum sieve trays have been used throughout the industry since the 1960s with no reported combustion incidents. Experimental work has shown that trays and packing require approximately equal energy levels for ignition (see 8.1), are flammable under some conditions that might be encountered in oxygen distillation columns (see 9.3), and combust with comparable intensities (see 9.3). Together these facts indicate that the safety of oxygen distillation columns fabricated from aluminum depends on the exclusion of ignition mechanisms and preventing accumulation of flammable contaminants in the flammable regions of the column. This is true for both trays and packing.

The procedures that have resulted in this record of safe operation with aluminum components have included following the practices described in CGA P-8 and AIGA 056, *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, *Cleaning of equipment for*

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

oxygen service [4, 5, 6, 7, 8]. CGA P-8.4 and AIGA 035, *Safe Operation of Reboilers/Condensers in Air Separation Units*, offer additional insights pertinent to aluminum components in air separation plants [9, 10]. To ensure safe use for columns containing aluminum-structured packing, follow the procedures in CGA P-8 and AIGA 056 and the cleaning specifications given in Section 10 of this publication [4,5]. The use of adsorption prepurification units, which prevent acetylene from entering the plant and initiating reactions, is also recommended.

In summary, the information assembled in this publication supports the safe use of aluminum-structured packing in oxygen distillation service. However, some air separation unit (ASU) suppliers may choose to use alternative materials in distillation columns.

It should be noted that most of the tests and data supporting this conclusion were limited to pressures less than 10 psig (69 kPa), packing sheets of 0.2 mm thickness, and oxygen purities up to 99.9%.² ASU suppliers should consider on a case-by-case basis the implications of operating at conditions outside this range. In general, higher oxygen pressures, higher oxygen purities, and thinner structures tend to increase the flammability of metals. Refer to "The Flammability of Aluminum Alloys and Aluminum Bronzes as Measured by Pressurized Oxygen Index" [12].

4 Definitions

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

4.1 Structured packing

Engineered structure consisting of numerous layers of thin, vertically oriented, corrugated metal sheets to facilitate intimate contact between liquid and vapor for mass transfer [13].

4.2 Violent energy release (VER)

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

5 Literature survey

Several papers address the flammability of structured packing for use in oxygen service. Dunbobbin et al. report flammability data for aluminum, brass, copper, and stainless steel, while Zawierucha et al. and Barthélémy report on aluminum packing under simulated operating conditions [1, 2, 3]. Dunbobbin et al. concluded in 1991 that only copper packing should be used under those conditions where aluminum packing is flammable [1]. Zawierucha's and Barthélémy's works, conducted and published later, concluded that aluminum was a satisfactory material for all sections of an oxygen distillation column [2, 3]. A critical review of aluminum flammability data is presented by Werley et al. [14]. Kirzinger et al. report on oil films on packing at cryogenic conditions [15]. In 1995, Barthélémy proposed that the violent energy release (VER) phenomenon involving molten or burning aluminum with liquid oxygen (LOX) can be similar to molten fuel/coolant interaction reactions, which have been studied for nuclear reactor safety [16]. F. Crayssac and P. Houghton et al report that the energy level required to ignite aluminum sheets/fins is not fundamentally affected by pressure [17].

Also in 1995, Kirzinger et al. compared the flammability of aluminum sieve trays and aluminum packing in ASUs [18]. A companion paper by Lassmann et al. evaluated ignition mechanisms for aluminum trays and packing in the low pressure column of ASUs [19]. Egoshi et al. discussed oil migration on structured packing by evaporation and recondensation during the defrosting operation in ASUs [20]. Fano et al. describe tests on the flammability of aluminum-structured packing and trays under column operating conditions including irrigation [21].

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

6 Industry survey on incidents of aluminum/oxygen combustion

6.1 General

Since the 1950's, when aluminum replaced copper as the preferred material of construction for 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 reboiler/condensers 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/condenser. Aluminum packing was also burned in two cases as a consequence of the reboiler/condenser incidents [22, 23].

A wide distribution of hydrocarbon contamination in the equipment is a probable factor for the propagation of aluminum combustion [22]. 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.

Two serious incidents occurred in 1997 in plants involving aluminum/oxygen combustion due to abnormal contaminants in the intake air. Both were initiated by accumulated combustibles in the reboiler/condensers and resulted in extensive combustion of the aluminum heat exchangers. Aluminum packing was also burned in both cases as a consequence of the reboiler/condenser incidents [9, 22, 23].

6.2 Survey scope

The phenomenon under investigation is the use of aluminum-structured packing in the distillation of air and its safety relative to environments of high-purity oxygen. A significant body of industrial experience relating to aluminum/oxygen compatibility was not deemed relevant to this issue. Information related to rotating equipment such as turbines, centrifugal compressors, reciprocating compressors, or LOX pumps was not considered. To reduce the scope or complexity of the undertaking to manageable proportions, incidents associated with drain vaporizers, valves, headers, and gel traps were excluded. The categories that remained could be broadly classified into five groups: reboiler/condensers, customer station storage tanks, sealed cavities in equipment, mobile transports, and high-vacuum superinsulations. Obviously, in order for the incident to be included as part of the study, aluminum was a material of construction in each of these components.

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 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 aluminum in air separation equipment provided that safe operating procedures are followed, especially prevention of contaminant buildup.

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-four incidents or events in an industrial environment were characterized as representative of aluminum/oxygen reactions. These incidents are summarized in Table 1.

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 parameter that seems to be important in assessing suitability and safety is the presence or absence of LOX (oxygen phase) in the system.

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

Industrial incidents have been experienced with aluminum in a variety of configurations, from the thin foil used in super insulation 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.

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. Others were of a sufficiently limited severity that they were not detected at the time of the incident, but observed much later as a result of 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 [9, 22]. The more limited reactions exemplified by the evidence of molten aluminum in sealed cavities are examples of the same fundamental phenomena but differ in the extent of the reaction and the resultant amount of energy release and damage.

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

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

6.5 Conclusions from survey

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

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

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.

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, Hass, and Kuo have shown that the aluminum 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 [24]. This shows that the presence of LOX increases the rate of aluminum combustion.

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; the incidents involving superinsulation, where the palladium oxide getter or mechanical impact were viewed as like-

ly 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. In plants with incomplete acetylene removal, acetylene may be viewed as a probable ignition source since it needs only a low energy shock such as mechanical impact or static electricity to initiate a violent decomposition reaction.

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. 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 brazed aluminum plate-fin heat exchangers, 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 may 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/condensers, 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 reboiler/condensers has led to extensive aluminum/oxygen reaction and severe plant damage [22, 23]. CGA P-8.4 and AIGA 035 provide operating criteria to maintain safe reboiler/condenser operation [9,10].

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/condenser incidents, its use alone is not sufficient protection against a brazed aluminum heat exchanger (BAHX) reboiler/condenser energy release or an aluminum/oxygen 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/condensers of the 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/condenser, resulting in an aluminum/oxygen VER.

Many of the incidents noted in 6.4 have been small in size and may not have involved aluminum/oxygen combustion reactions. However, BAHX reboiler/condenser 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/condenser, 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 CGA P-8, CGA G-4.1, CGA P-8.4 and AIGA 056, AIGA 012, AIGA 035 and subsequent sections of this publication [4,6, 9, 5,8,10].

Other conclusions that have been 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 can infer that the excellent record with trays results from an absence of ignition sources, since experimental work has shown that trays can be flammable (see 9.3);
- There have been no reported incidents of combustion starting in aluminum packing in oxygen service. There have been two incidents of packing burning as a result of reboiler/condenser explosions [9,10, 22, 23];

- Most industrial incidents have occurred with LOX at purities of 99.5% or higher. Experimental and theoretical work has 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 promotion medium leading to reactions between aluminum and oxygen;
- 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 several of the industrial aluminum/oxygen reactions. Examples are the transport, customer stations, and the postulated cavity mechanisms; and
- 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 at characteristic levels for each specific geometry.

7 Ignition mechanisms

7.1 General

This section surveys the fundamentals of aluminum ignition. Experimentation is covered in Section 8. “Compatibility of Aluminum Packing with Oxygen Environments under Simulated Operating Conditions,” “Compatibility of Aluminum Packing with Oxygen Test Results under Simulated Operating Conditions,” and “Critical Review of Flammability Data for Aluminum,” include additional material on both these topics [2, 3, 14].

7.2 Conditions for ignition of aluminum

Solid and liquid aluminum are protected by a thin, dense, and tenacious 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 as shown in the paper titled “A Critical Review of Flammability Data for Aluminum” [14]. 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 aluminum packing in distillation columns:

- adiabatic compression;
- resonance-tube oscillations;
- shock waves;
- autoignition by heating to the melting point;
- fracture (creation of fresh surface);
- electric arc; and
- particle impact.

Although mechanical impact cannot be excluded, it is judged to be less likely as an ignition source in packed columns than in trayed columns because of the flexibility and the thinness of packing material.

Friction as an ignition source is very unlikely due to the absence of rotating equipment in the distillation column. Friction caused by thermal contraction can occur during startup but before oxygen purity is established.

7.5 Indirect ignition (promoted ignition)

The ignition mechanism considered most pertinent to packed and trayed columns is an energy release from combustion of a secondary material. As a first step, this promoter must accumulate to its LFL 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 promoter were considered:

- hydrocarbons accumulated from the air;
- lubricants used during air separation plant component manufacture and assembly, including packing; and
- foreign materials inadvertently left in the column after fabrication.

According to industry 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. In the distillation section, where accumulation of hydrocarbons from the air feed is not possible, ignition initiation has never been observed.

If oil is left behind on the packing due to the manufacturing process and it is not removed, the risk of ignition is increased. The amount of combustible residue remaining on the packing after its fabrication and cleaning should comply with the recommended values in section 10. In general, the selected values are intended to keep the vaporized residue below its LFL in the volume between the packing sheets. Vaporization of the residue could occur as a consequence of unexpected heat input.

N-hexadecane was chosen as a worst-case model substance for lubrication oil with respect to vapor pressure and lower flammability limit. For structured packing having a specific surface area of $500 \text{ m}^2/\text{m}^3$, the lower explosive limit of an N-hexadecane vapor-gaseous oxygen (GOX) mixture was calculated to correspond to an oil film concentration of 96 mg/m^2 .

“Fire and Explosion Hazards in Compressed Air Systems” estimates that a shock wave would be able to ignite and detonate N-hexadecane if its concentration exceeded 390 mg/m^2 [25].

The lowest oil concentration ever reported to ignite was 65 mg/m^2 , on average. Refer to “Ignition of Contaminants by Impact of High Pressure Oxygen” [26]. The ignition source was a 1000 psi (6900 kPa) oxygen impact.

The hypothetical combustion of a 100 mg/m^2 oil film would raise the temperature of aluminum packing less than 36°F (20°C). Thus, it would be impossible to ignite aluminum packing in the absence of any other promoter.

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

- cryogenic chipping of brittle oil films;
- migration by gravity at temperatures up to 140°F (60°C); and
- evaporation and recondensation of oil films that move as a result of deriming operations.

With the exception of deriming operations, none of these mechanisms, however, were found to result in any accumulation of oil on packing or trays. For chipping and migration by gravity, this result was confirmed by experiments that showed that such thin oil films (on average, 100 mg/m^2 corresponds to a thickness of $0.1 \mu\text{m}$) are very stable according to the paper “The Behaviour of Oil Films on Structured Packing under Cryogenic Conditions” [15].

During the deriming operation, the migration and accumulation of oil can occur by evaporation and recondensation. Simulation results showed that light oil such as hexadecane can accumulate locally during deriming, but can disappear after completion of the derime [20]. Deriming procedures should avoid the migration and accumulation of oil and other contaminants in the columns.

Despite all precautions, solid contaminants (wood, papers, sealants, oil lumps, plastics, and textiles) can be unintentionally trapped in the packing or between trays, or they can be introduced into the column during its construction or maintenance. Such contaminants can act as promoters to ignite either packing or trays. 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 (200°C) to 572°F (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 source of promoted ignition because of the high temperature (melting point of aluminum) required to initiate the reaction between aluminum and iron oxide. Other potential promoters (metal oxides, mercury, halocarbons, precious metals, and ozone) were considered, but they were judged irrelevant to packing ignition.

7.6 Ignition by adjacent equipment

Depending on the energy released in an incident, such as a reboiler explosion, packing might ignite and increase the severity of the incident. Recommendations on safe reboiler operation are covered in CGA P-8.4 and AIGA 035 [9,10].

8 Ignition experiments

8.1 Ignition promoters for use in experimentation

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

The following applies to thermite-based promoters [1, 2, 3, 18]:

- Thermite mixtures ($\text{Fe}_2\text{O}_3/\text{Al}$) in the range of 1 g to 3 g were successfully used to ignite both packing material (0.2 mm) and tray material (1.0 mm) in GOX. A promoter comprising 1 g thermite and 0.24 g magnesium was widely used for packing tests;
- Studies to determine the minimum quantity of promoter able to cause ignition were not carried out. Rather, the quantity needed to obtain reliable ignition was determined. For packing, it was found to be 1 g thermite plus 0.24 g magnesium, or 3 g thermite. For a piece of dry tray material, 1 g thermite was found to be reliable; and
- The addition of hydrocarbon grease to a thermite promoter had no discernible effect on the ignition of aluminum packing.

8.2 Lubricating oil

Experiments have shown that complete combustion of a layer of lubricating oil of 5000 mg/m^2 did not ignite packing in the test configuration examined [19].

8.3 Accumulated hydrocarbons

Tests were conducted to simulate the effect of accumulated hydrocarbons on packing and trays. Ignition of aluminum packing and trays occurred with combustion of 5 g to 8 g of hydrocarbons in ambient temperature, atmosphere pressure GOX [19].

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 ($>10 \text{ g/m}^2$), 0.2 mm thick sheets ignited with a good reproducibility. Tests performed with about 2 g/m^2 resulted in aluminum ignition in less than 10% of the tests, probably due to nonhomogeneous hydrocarbon coating on the sheets. Refer to "Ignition of Aluminum by Impact in LOX – Influence of Contaminants" and "Reaction of Molten/Burning Aluminum with Liquid Oxygen" [16, 27].

9 Experimental work on aluminum/oxygen combustion

9.1 Reports of experimentation

Many experiments on aluminum combustion have been reported in the literature [10]. Five companies carried out experiments to verify the basis for this publication. Detailed information on many of these tests is reported in references 2, 3, 16, 18, and 21.

9.2 Propagation investigations on small samples

Tests were performed on packing and tray samples in GOX partially immersed in LOX and with LOX flowing over them as for normal operation.

Experiments in which molten/burning aluminum could fall into a pool of LOX frequently resulted in VERs. No VER occurred in tests where LOX was not present or when it was present merely as a film on the packing's surface.

Trays and packing exhibited similar degrees of flammability and abilities to produce VERs even though trays were thicker.

The VER mechanism is not yet fully understood, but it appears to result from a situation in which very hot molten/burning aluminum contacts LOX. Refer to "Reaction of Molten/Burning Aluminum with Liquid Oxygen" [16].

9.3 Propagation investigations on large samples

All these tests were performed at atmospheric pressure using promoters, as described in 8.1, located in the upper part of the samples. Refer to "Tests of Combustion of Aluminum Packing and Trayed Columns" [21]. These tests were performed with LOX of high purity (99.99%+) and normal purity (99.8%).

Tests performed on dry packing samples (60 cm x 15 cm x 15 cm) showed that combustion propagated from the upper part towards the bottom, rather than sideways or upward. When an LOX pool was situated under the packing during a flammability test, a VER occurred.

Tests were performed on 7 columns containing packing (columns 30 cm diameter x 2 m high) with LOX irrigation at roughly 30% of actual operation. No LOX was present below the packing. The promoter was placed near the top of the packing.

These tests showed that the irrigation of aluminum packing is able to terminate propagation of aluminum combustion, provided that irrigation occurs within a few centimeters of the ignition zone. But, if propagation continues beyond this distance before it reaches an irrigated zone, complete combustion of irrigated packing can occur.

Tests were also performed on 6 columns containing tray samples (columns 30 cm diameter x 2 m high with 20 aluminum trays) in conditions similar to actual operation. LOX was supplied from the top and GOX flow from the bottom. The GOX/LOX flows were both 40% of the normal flows in air distillation columns. Although LOX was present on all trays except the top one, no LOX pool was present below the trays. The promoter was placed on the upper tray. When the trays were ignited, propagation occurred, occasionally producing VERs with projections of metal fragments to more than 300 m. Combustion propagation was more severe than with the packed columns.

9.4 Molten aluminum in liquid oxygen

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. Refer to "Evaluation of Ignition Mechanisms for Aluminum Trays and Packing in the Low Pressure Column of Air Separation Units" [19]. 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 temperatures closer to the boiling point of liquid aluminum (4172 °F (2300 °C)) are necessary to achieve a VER. Other tests suggest that temperatures close to the melting point of alumina (approximately 4892 °F (2700 °C)) are required to achieve a VER [15].

9.5 Conclusions from experimental work

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 the promoter (a critical threshold is necessary to cause combustion), oxygen purity (a sufficiently high purity is needed to sustain combustion), and finally, the presence of a LOX pool, which seems to be essential to the occurrence of VERs.

Irrigation of packing samples, when the initial ignition energy is low enough, inhibited ignition and early propagation. If a sufficient quantity of aluminum burns before the combustion zone encounters an irrigated area, the combustion propagation will continue.

The minimum quantity of thermite necessary to reliably ignite aluminum packing or trays is of the same order and equal to 1 g to 3 g thermite (ignited by electric filament wire).

Combustion propagation in trayed columns was observed to be more severe than in packed columns [21].

10 Cleanliness

10.1 General

The very high surface area of structured packing results in a potential for introducing a higher total quantity of surface contaminants into packed column plants.

Both packing and trays have many opportunities to become contaminated, not only during manufacturing, but also during shipping, storage, installation, commissioning, and operation.

These considerations, combined with the difficulty of inspecting the inner portions of individual packing blocks, result in the need to exercise control over the amount of combustible contaminants associated with structured packing for oxygen service. CGA G-4.1 and AIGA 012 presents useful information on this topic [6, 8].

10.2 Required cleanliness level for residual lubricating oil

The information presented in 7.5 indicates that oil contamination levels below 100 mg/m² on average will not migrate if proper plant operating procedures are followed and will not combust at the original location.

It has been demonstrated that ultraviolet (UV) light inspection techniques are capable of the reliable detection of some oils at contamination levels of 50 mg/m² and above.

A practical and reasonable level for the oil film limit should be in the range of 50 mg/m² to 100 mg/m². It is recommended that 100 mg/m² be specified as the maximum level for any localized area of packing and that 50 mg/m² be specified as the average level for a whole area of packing.

These levels can preclude the packing from reaching the lower flammability limit of the oil vapor-oxygen mixture under any conditions. They also preclude the accumulation of residual oil, and they can be practically verified by UV light inspection.

Any accumulated oil or other containment that can be detected by visual inspection under white light shall be removed. Depending on the nature of the contamination, it may be appropriate to use UV light to verify the cleanliness of all affected packing.

10.3 Protection of cleaned packing

Special attention should be taken to protect the packing from recontamination during handling, transport, storage, packaging, shipping, installation, and especially erection and commissioning of the plant.

10.4 Quality control

Packing cleanliness should be verified by visual and UV light inspection before its placement in a column. After installation, each layer of packing should be visually checked again to ensure that no combustible impurities have entered the packing.

11 Design and operational considerations

Design, operation, and maintenance are critical factors in achieving safe and reliable performance of any system. CGA P-8 and AIGA 056 describe the procedures that have been successfully applied to ASUs with distillation columns [4, 5].

12 References

Unless otherwise specified, the latest edition shall apply.

- [1] Dunbobbin, B.R., J.G. Hansel, and B.L. Werley, "Oxygen Compatibility of High Surface Area Materials," ASTM STP 1111, Vol. 5 1991, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [2] Zawierucha, R.A., J.F. Million, S.L. Cooper, K. McIlroy, and J.R. Martin, "Compatibility of Aluminum Packing with Oxygen Environments under Simulated Operating Conditions," ASTM STP 1197, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 6, 1993, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [3] Barthélémy, H.M., "Compatibility of Aluminum Packing with Oxygen Test Results under Simulated Operating Conditions," ASTM STP 1197, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 6, 1993, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [4] CGA P-8, *Safe Practices Guide for Cryogenic Air Separation Plants*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com
- [5] AIGA 056, *Safe Practices Guide for Cryogenic Air Separation Plants*, Asia Industrial Gases Association, 3 HarbourFront Place, #09-04 HarbourFront Tower 2, Singapore 099254. www.asiaiga.org
- [6] CGA G-4.1, *Cleaning Equipment for Oxygen Service*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com
- [7] ASTM G-93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-Enriched Environments*, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. www.astm.org
- [8] AIGA 012, *Cleaning of Equipment for Oxygen Service*, Asia Industrial Gases Association, 3 HarbourFront Place, #09-04 HarbourFront Tower 2, Singapore 099254. www.asiaiga.org
- [9] CGA P-8.4, *Safe Operation of Reboilers/Condensers in Air Separation Units*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com
- [10] AIGA 035, *Safe Operation of Reboilers/Condensers in Air Separation Units*, Asia Industrial Gases Association, 3 HarbourFront Place, #09-04 HarbourFront Tower 2, Singapore 099254. www.asiaiga.org
- [11] CGA P-11, *Metric Practice Guide for the Compressed Gas Industry*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com

- [12] Benning, M.A., J.S. Zabrenski, and N.B. Le, "The Flammability of Aluminum Alloys and Aluminum Bronzes as Measured by Pressurized Oxygen Index," ASTM STP 986, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, 1988, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [13] Fair, J.R., et al., "Distillation Columns Containing Structured Packings." *Chemical Engineering Progress*, January 1990, American Institute of Chemical Engineers, Three Park Ave., New York, NY 10016. www.aiche.org
- [14] Werley, B.L., H. Barthélémy, R. Gates, J.W. Slusser, K.B. Wilson, and R.A. Zawierucha, "Critical Review of Flammability Data for Aluminum," ASTM STP 1197, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 6, 1993, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [15] Kirzinger, A., K. Baur, and E. Lassmann, "The Behavior of Oil Films on Structured Packing under Cryogenic Conditions," ASTM STP 1197, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 6, 1993, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [16] Barthélémy, H. and C. Mueller, "Reaction of Molten/Burning Aluminum with Liquid Oxygen," ASTM STP 1267, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 7, 1996, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [17] Werlen, E., F. Crayssac, O. Longuet, and Willot, F, "Ignition of Contaminated Aluminum by Impact in Liquid Oxygen – Influence of Oxygen Purity," *Journal of ASTM International*, Vol. 6, Iss. 10, November 2009, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [18] Kirzinger, A. and E. Lassmann, "Comparison of the Flammability of Aluminum Sieve Trays and Aluminum Packing in Air Separation Units," *Separation and Purification Technology*, Vol. 9, November 1, 1995, EMDOCS Document Delivery Service, 3801 E. Florida Ave., Ste. 200, Denver, CO 80210. www.elsevier.com
- [19] Lassmann, E. and A. Kirzinger, "Evaluation of Ignition Mechanisms for Aluminum Trays and Packing in the Low Pressure Column of Air Separation Units," *Separation and Purification Technology*, Vol. 9, November 1, 1995, EMDOCS Document Delivery Service, 3801 E. Florida Ave., Ste. 200, Denver, CO 80210. www.elsevier.com
- [20] Egoshi, N., H. Kawakami, and I. Fujita, "Oil Migration on the Structured Packing by Evaporation and Recondensation During the Defrosting Operating in the Air Separation Unit," ASTM STP 1319, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 8, 1997, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [21] Fano, E., H. Barthélémy, and J.Y. Lehman, "Tests of Combustion of Aluminum Packing and Trayed Columns," ASTM STP 1395, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol. 9, 2000, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org
- [22] van Hardeveld, R.M., M.J. Groeneveld, J.Y. Lehman, and D.C. Bull, "Investigation of an Air Separation Unit Explosion," *Journal of Loss Prevention in the Process Industries*, Vol. 14(2001), pp. 167-180, Elsevier Science Limited, The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB England. www.elsevier.com
- [23] Lehman, J.Y., Wei, X.C., Hua, Q.X., Delannoy, G., Investigation of the Fushun ASU Explosion in 1997, *Journal of Loss Prevention in the Process Industries*, Vol. 16, (2003), pp. 209 - 221. www.elsevier.com
- [24] Mench, M. M., J. Haas, and K. K. Kuo., "Combustion and Flame Spreading of Aluminum Tubing in High Pressure Oxygen," The Fifth International Symposium on Special Topics in Chemical Propulsion: Combustion of Energetic Materials, K. K. Kuo and L. DeLuca, Eds., June 2000.
- [25] Burgoyne, J.H. and A.O. Craven, "Fire and Explosion Hazards in Compressed Air Systems," 1973 Seventh Loss Prevention Symposium, American Institute of Chemical Engineers, Three Park Ave., New York, NY 10016. www.aiche.org

[26] Pedley, M.D., J Pao, L. Bamford, R.E. Williams, and B. Plante, "Ignition of Contaminants by Impact of High Pressure Oxygen," ASTM STP 986, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, 1988, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org

[27] Barthélémy, H., D. Roy, and N. Mazloumian, "Ignition of Aluminum by Impact in LOX—Influence of Contaminants," ASTM STP 1395, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, Vol.9, 2000, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428. www.astm.org