Safe Design and Operation of a Cryogenic Air Separation Unit

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ABSTRACT

Cryogenic Air Separation Units (ASU’s) frequently supply oxygen and nitrogen to chemical, petroleum and manufacturing customers. Typically, the ASU is located remotely from the use point, and the products are supplied via a pipeline. This paper provides the basic design and operating methods to safely operate an ASU. The four primary hazards associated with an ASU are (1) the potential for rapid oxidation, (2) interfaces between the ASU and the downstream systems, (3) pressure excursions due to vaporizing liquids, and (4) oxygen enriched or deficient atmospheres. The important requirements for safely handling oxygen within the air separation facility and also at the product use point are also discussed in this paper.

INTRODUCTION

Technology for separating air into its primary components (oxygen, nitrogen & argon) by cryogenic distillation has been practiced for over 100 years. Figure 1 is a basic flow diagram for the separation of air by cryogenic distillation. Air is compressed in the Main Air Compressor (MAC) to between 4 and 10 atm. It is then cooled to ambient temperature and passed through the Pre-Purification Unit (PPU). This consists of a pair of vessels containing a fixed bed of adsorbent, typically either or both activated alumina or molecular sieve. As the air passes over the adsorbent, many of the trace contaminants are removed, especially water, carbon dioxide, and the heavy hydrocarbons. The purified air then enters the main heat exchanger, where it is cooled to near its liquefaction temperature (approximately 100°K) before entering the distillation system. The products are produced from the Low Pressure (LP) column (the top column in Figure 1). The high pressure column’s main function is to allow thermal integration by producing the boil-up and reflux for the low pressure column.

Oxygen is the highest boiling of the three main components, so it is taken from the bottom of the low pressure column. Nitrogen is taken from the top of the low pressure column. (Argon splits between the oxygen and nitrogen, and can be recovered as a pure product by adding a third distillation column.) The product streams are warmed to ambient temperature against incoming air to recover the refrigeration. It is also possible to remove the products from the distillation system as liquid if sufficient refrigeration is provided. Liquid may be retained (for back-up or merchant sales).

There are two primary configurations of the air separation process (See Figure 1). In the “GOX process”, oxygen is taken as a vapor from the bottom of the low pressure column, and warmed against incoming air. If a high pressure product is needed, this oxygen can be further compressed. As will be discussed in detail later, a liquid purge stream must be taken from the sump of the reboiler, to prevent high boiling components from concentrating above allowable limits. In the “Pumped LOX Process”, the oxygen is taken as a liquid from the bottom of the LP column, pumped to the product pressure, and vaporized against incoming air in the main exchanger. This eliminates the need for product oxygen compression, and the LOX purge stream may be eliminated from the LP column sump, because the product oxygen stream ensures an adequate purge rate.

The reboiler/condenser which thermally integrates the distillation system is typically a brazed aluminum heat exchanger. This type of heat exchanger provides a large amount of surface area which increases the plant efficiency by allowing the heat to be transferred with a small temperature difference. Two types of reboilers are used for this service:

- The thermosyphon type is submerged in a pool of liquid oxygen which circulates naturally when heat is provided by the condensing nitrogen.
The downflow reboiler vaporizes oxygen as it flows downward through the reboiler. The downflow reboiler requires more detailed piping and distribution systems to introduce the liquid oxygen and may require additional equipment for start-up and operation. However, the downflow system allows for higher heat transfer coefficients associated with the vaporization of thin liquid films and hence tighter temperature approaches and a more efficient plant.

Air contains many trace components that must be dealt with to avoid safety problems. The problems that the trace contaminants can cause are grouped into three categories: corrosion, plugging, and reactions. Table 1 gives a list of the trace contaminants in air, their associated potential problems, the design basis used by APCI for ASU's, and the typical removal of these components in the PPU.

The vendor of the ASU typically does not know the environment in which the plant will be operating. Defining this environment is the responsibility of the owner/operator. However, getting an accurate air quality analysis can be difficult for several reasons:

- Changes in neighbors may change the air quality at a later date.
- The ambient air quality can depend on such things as weather conditions and wind direction, which require a long-term test, which can be very expensive.
- Intermittent vents can radically change the air quality, and these may occur very infrequently.

The air quality can be determined by one of three methods:

- Site survey, where the neighbors are defined, and any normal or intermittent vents are identified. The general weather conditions and wind direction are also taken into consideration.
- If the site survey results warrant, a direct measurement of the air quality can be made. Care must be taken to ensure that the test is long enough to cover the expected situations, and also that the instrumentation used has enough sensitivity to measure the required components and concentrations.
- Where these two are not practical, a general air quality design basis can be used. Air Products' design basis is given in Table 1. These values are typically higher than normal sites, and provide a conservative design basis.

Whichever method is used, the customer and ASU supplier must agree on a design basis to ensure that the ASU can be operated safely. The vendor should design the ASU to operate safely, as long as the air quality specification is met. It is operator's responsibility to note any changes in ambient conditions, and if these exceed the plant design basis, they should contact the vendor for advice.

Most of the problem components in the air separation process boil at temperatures above oxygen, and hence will tend to concentrate in the oxygen product unless otherwise removed. Two general rules are followed in the management of trace compounds.

- The total hydrocarbon concentration in the bulk liquid oxygen is limited to 450 ppm as “methane equivalent”. This methane equivalency accounts for carbon atoms present in the hydrocarbon molecules, so the limit imposed allows for more methane to be present than heavier organic molecules (see Table 2). 450 ppm is about 1% of the Lower Explosive Limit (LEL) of hydrocarbons in oxygen, providing a margin of safety for any further concentration in local zones.
- Limit the concentration of plugging compounds in the bulk liquid or vapor to 50% of their solubility. This allows a margin for uncertainties in flow imbalances, the thermodynamic data, and any other non-idealities.
Air Products has reported that CO$_2$ and N$_2$O form a solid solution (9), and this has recently been confirmed by others (10). This means that the CO$_2$ solubility is lower when N$_2$O is present in appreciable quantities and vice-versa. The computation of solubility must take this into account, and the operating limits reduced accordingly.

GENERAL APPROACH TO PROCESS SAFETY

The remainder of this paper discusses Air Products’ approach to safety in Air Separation plants. This approach is similar to other industrial gas companies, but there are some differences from company to company. Air Products’ practices and procedures have resulted in an outstanding safety record. The most recent CMA statistics (1999) show Air Products has the lowest recordable accident rate of any major chemical company. (Note that while this paper covers the important aspects of safely designing and operating an ASU, but it should be recognized that there are many necessary details that are beyond the scope of this paper.)

There is a simple three-step process to deal with safety issues:

- Identify the hazard
- Put actions in place to abate the hazard
- Verify that the abatement is effective

If followed, this three-step process is effective for dramatically reducing any safety risks. On a high-level view, this process is applied in the following manner:

- As part of the overall plant design, each project has a formal, documented Design Hazard Review (DHR) to identify any hazards and develop abatement and verification methods.
- Individual equipment items have specific requirements to abate specific hazards (these will be discussed in some detail later).
- Operate the equipment properly by following written procedures. Thoroughly investigate any incidents that may happen, to prevent their recurrence.

DHR - Every project has a formal, documented Design Hazard Review (DHR) to identify any hazards. To ensure that all hazards are addressed, each project uses the HAZOP technique, which is a formal, structured process to ensure that all aspects of the plant are addressed, including startup, shutdown, normal operation, materials of construction, etc. Because ASU’s are very similar from plant to plant, a standard knowledge-based HAZOP has been performed for general use by individual projects. This increases the speed at which the HAZOP can be performed, but more importantly, ensures that no items are overlooked. Each project then can focus on the differences and changes from the “typical” ASU.

During the HAZOP, a Quantitative Risk Assessment (QRA) is performed if either (a) an area of specific concern is identified, or (b) the public-at-large could be affected. A QRA is a more detailed analysis of the hazard that ultimately quantifies how often a specific outcome can be expected and guides the design team in developing methods to abate the hazard and verify that the abatement is performing as designed. QRA’s have been performed for many specific pieces of ASU equipment as part of the knowledge-based HAZOP.

Individual Equipment Items – The specific design requirements of individual equipment items is discussed in detail later in the paper.
Operation Practices - Prior to starting up each plant, a formal, documented Operation Readiness Inspection (ORI) is performed to ensure that all aspects of the DHR have been incorporated and that the plant is ready for operation. Once the plant is operational, proper documented practices assure safety. Regular training sessions and safety meetings keep safety in the forefront. Formal management of change procedures ensure that any additions or deletions to procedures or equipment do not overlook a safety item. There are periodic operating hazard reviews to ensure that plants operate to current standards and practices. If there is an accident or serious near-miss, a formal root-cause analysis is performed. Any incident that occurs is communicated world-wide to ensure that all sites are aware of hazards and can prevent a reoccurrence.

PROCESS HAZARDS

The remainder of this paper will deal with the four major hazards in a cryogenic air separation plant:

- Rapid Oxidation
- Embrittlement
- Pressure Excursions due to vaporizing liquids
- Oxygen enriched or deficient atmospheres

RAPID OXIDATION

Rapid oxidation releases a great deal of energy, either as pressure or heat, which create significant safety hazards. In the familiar fire triangle, oxidation requires: a fuel, oxygen, and an ignition source. Many process fluids in an ASU can contain high levels of oxygen, either in normal or upset conditions. For these streams, either the fuel or the ignition source must be eliminated. The two primary sources of fuel are trace atmospheric hydrocarbons that concentrate at various points in the ASU process or the materials from which the ASU equipment is manufactured. It is more common for the oxidation to occur in the process fluids due to hydrocarbon enrichment, but the more rare case of the materials combusting can be much more energetic.

Atmospheric air contains ppm levels of many trace impurities (see Table 1). The high boiling hydrocarbons are completely removed in the PPU. This is verified by monitoring the outlet of the PPU for CO2, and if the CO2 is completely removed, the high boiling hydrocarbons are also completely removed. However, some low boiling hydrocarbons (propane, ethane, ethylene, and methane) will enter the coldbox. Once these components enter the coldbox, they can concentrate by the following mechanisms, because they all boil at temperatures above oxygen:

1) **Dry boiling** occurs if heat is applied to a pool or puddle of liquid, to which no more liquid is added. The heat causes the more volatile components to vaporize, leaving behind the less volatile components in a concentrated form.

2) **Pot-boiling** is similar to dry-boiling, but is distinguished by the continued addition of fresh liquid to the “pot”. Again the less volatile components are concentrated as the more volatile components are vaporized.

3) **Distillation** the less volatile components are concentrated in a liquid, as it countercurrently contacts vapor. The less volatile components of the vapor end up in the liquid.

Through a combination of pot-boiling and distillation, the low boiling hydrocarbons will concentrate in the low pressure column sump, in the oxygen rich liquid around the reboiler condenser. These hydrocarbons are removed primarily with a liquid oxygen purge. (In the GOX process, much of the
methane and small quantities of other components leave the process in the GOX product.) The purge rate is set as the maximum of

- Flowrate sufficient to keep the total hydrocarbons concentration below 450 ppmv as methane equivalent.
- Flowrate sufficient to keep all components at less than 50% of their liquid phase solubility
- Flowrate equal to 0.2% of the air feed (except when special instrumentation and equipment are present, in which case it can be lowered to 0.1%)

The purge flowrate is measured, to verify that the proper flowrate is maintained. There is a low flow alarm if the purge rate falls below the required value, and the plant must be shutdown if the flow cannot be restored. Note the in the Pumped LOX process, the product O₂ stream acts as the reboiler purge flowrate.

In many plants, a total hydrocarbon (THC) analyzer is also used as further verification that the hydrocarbons are less than the maximum allowable level. The THC analyzer is preferable to an analyzer capable of measuring the concentrations of individual hydrocarbons for two reasons:

- The analysis is much simpler, because only the total number of carbon atoms is measured. To measure individual components requires a more expensive and complicated analyzer.
- As shown in Table 2, while the LEL of individual hydrocarbons varies significantly, when expressed as THC, all values are between 50,000 and 100,000 ppmv. The conservative value of 50,000 ppmv is used. Therefore, it is possible to detect an unsafe level of a component, even if one is not specifically looking for that individual component.

Thus, a simple, robust device may be used to ensure that the hydrocarbon concentrations are within safe levels. In some plants, procedures are put in place to obtain periodic batch samples of the liquid oxygen in the sump. This provides further verification that the abatement procedures (PPU, liquid purge) are working as designed.

Other trace non-hydrocarbon components in the air will also concentrate in the reboiler. Of particular concern are CO₂ (carbon dioxide) and N₂O (nitrous oxide). These are only slightly soluble in the liquid and vapor oxygen and can precipitate as a solid. The precipitation can cause operating problems by blocking equipment and piping. However, the precipitation can also partially block flow areas, leading to pot boiling, which can in turn concentrate hydrocarbons. The abatement methods for CO₂ are the PPU and the liquid purge. Since trace quantities of CO₂ do enter the coldbox, the liquid oxygen in the reboiler is periodically sampled for CO₂ concentration, to ensure that the proper limit is maintained. N₂O is partially removed in the PPU, and the remainder is removed with the liquid purge. Typically, little or no N₂O removal is needed, so real time concentration analysis is not required. However, monitoring the purge rate does ensure that N₂O will not concentrate to unacceptable levels in the reboiler sump. However, where further N₂O removal is needed, this can be accomplished by using a special proprietary adsorbent in the PPU(1, 8). This proprietary adsorbent removes 95% of the N₂O when the PPU is run to CO₂ breakthrough, and by slightly shortening the onstream time, the N₂O removal can be increased to over 99%.

The liquid purge rate is very important for ASU safety, as proven by years of safe ASU operation. An adequate purge rate ensures that neither the plugging compounds (CO₂ and N₂O) nor the trace hydrocarbons concentrate above their proper levels. Air Products has also specified that the purge rate shall never be less than 0.2% of the air, regardless of ambient air concentration, process conditions, or LOX composition. (The only exception is if special instrumentation and equipment are present, in which case the minimum purge can be lowered to 0.1% of the air.) The purge rate must be measured, either directly with a flowmeter, or indirectly by measuring changes in liquid level. If an adequate purge rate cannot be maintained, the plant must be shutdown.
REBOILER SAFETY

The reboiler condenser presents special hazards, because in this piece of equipment, liquid oxygen is partially boiled away, leaving behind liquid enriched in hydrocarbons. The hazard is increased because the reboiler has many separate passages or channels operating in parallel. It is impossible to verify that each individual passage is operating properly, so care must be taken in system operation to minimize the risk.

As stated above, there are two types of reboilers: thermosyphon, where the fluid boils in an upward direction, and downflow (or falling film) reboilers, where the liquid flows downwards as it is evaporated. Safety features of the thermosyphon focus on ensuring that liquid oxygen is able to circulate through all passages:

- Special design features dramatically reduce the possibility of blocking an individual passage through manufacturing defect.
- The reboiler must operate fully submerged to ensure adequate circulation through all passages.
- The reboiler is designed for positive defrost to ensure no blockages of frozen components.

Special considerations for a downflow reboiler are:

- The reboiler is designed to ensure that countercurrent flow of vapor and liquid is not possible, which prevents enrichment by distillation.
- As with thermosyphon reboilers, the chance of blocking an individual passage by a manufacturing defect is dramatically reduced by specific design features.
- Positive defrost features are designed into the reboiler to prevent blockage by frozen components.
- Extra attention is given to flow distribution to ensure even flow through the each passage.
- Special filtration eliminates debris which could plug reboiler passages, which could in turn lead to pot boiling.
- Periodic defrost at specified intervals to remove accumulated inert components.
- The N₂O and CO₂ concentrations must be maintained at very low levels (1% and 6% of their solubilities, respectively).

The last two requirements are due to extensive work (6) that has shown that downflow reboilers will accumulate small quantities of inert trace impurities (i.e., N₂O and CO₂), even when CO₂ and N₂O are present in the reboilers at only small fractions of their solubility. As stated above, these impurities are not in themselves a safety hazard; they are only a problem if they cause hydrocarbons to accumulate to unsafe levels. Work has shown that these compounds can act as an adsorbent and accumulate trace levels of hydrocarbons (7). However, Air Products' testing has never shown more than trace levels of hydrocarbons in operating plants (6). Therefore, by proper design, operation, and periodic defrost, accumulation is never allowed to reach unsafe levels.

The industry has developed general guidelines for the safe operation of reboiler condensers (2).

PUMPED LOX EXCHANGER

If the Pumped LOX process is used, special consideration must be given to the brazed aluminum heat exchanger in which the product oxygen is boiled. The potential hazard is different here than in a reboiler:
• The oxygen is boiled in a once-through manner, leading by its very nature to dry-boiling
• The pressure is higher than in the LP column sump, increasing the risk of ignition and propagation.

To abate these hazards, the following design and operating features are used. Many of these focus around preventing local or widespread accumulation of hydrocarbons, which could act as an ignition source.

• The CO₂ and N₂O concentrations must be 50% of the solubility limits to prevent precipitation which could lead to local pool boiling. To achieve these concentrations at low O₂ boiling pressures (less than approximately 3 bara), the N₂O and CO₂ concentration entering the coldbox must in be the low ppb range. This requires careful PPU design and operation. Special PPU adsorbents are effective in reducing the N₂O going into the coldbox (1, 8).
• The O₂ velocity must be high enough to entrain small liquid droplets to prevent recirculation and distillation
• The system is free draining to prevent hydrocarbon accumulation on shutdown.
• Special design features ensure proper distribution from passage to passage and across a passage
• The inlet LOX is filtered to remove any debris, which will prevent local blockages.
• Passage arrangement and process conditions are set to minimize chance of propagation
• Equipment enclosure is designed to minimize exposure and risk to personnel

The Pumped LOX process has some inherent safety features:

• The liquid purge from the LP column reboiler is approximately 20% of the air. This limits the concentration buildup in the reboiler sump to no more than approximately 5 times the concentration entering the coldbox.
• There is often no oxygen compressor, eliminating many potential hazards.
• If the oxygen is boiled at a supercritical pressure, there is no vapor/liquid interface, making it impossible to create a hydrocarbon-rich phase.

These safety features more than offset the low risk of the ignition of the aluminum heat exchanger in which oxygen is boiled, provided that the core is designed and operated correctly. Further discussion of Pumped LOX BAHX safety is given in (3).

OXYGEN COMPRESSORS

In most applications, the oxygen pressure must be boosted above those in the Low Pressure column. When the GOX process is used, the product oxygen is typically raised with a product oxygen compressor. The two basic types of oxygen compressors are centrifugal and reciprocating. An oxygen compressor is a potential hazard, because

• By it's very nature, it contains high pressure, high purity oxygen
• The only practical materials of which many components must be made are combustible in oxygen
• Compressors have moving parts, which can provide friction ignition sources
• The possibility of particle contamination (weld slag, rust particles, dust, sand blasting residue, etc.) can never be completely eliminated, especially in new installations and after major maintenance. The high velocity of the gas (350 m/sec) in some areas of the compressor mean that particle impact is a potential ignition source.
The air separation industry has recognized that these are special hazards requiring special attention. The basic philosophy is that personnel are not exposed to the consequences of an oxygen compressor fire, and as a second priority, equipment damage is minimized. The general methods used to meet these requirements for oxygen compressors are described in references (11) and (12), of which some highlights are below:

**Barrier** - A “Hazard Area” is defined as an area around the compressor in which injury to personnel and damage to equipment is most likely to occur in the event of a compressor fire. Components that could be involved in a fire are placed within a fire resistant barrier. Equipment needed to shutdown or isolate the compressor in the event of a fire is placed outside of the barrier, where it cannot be damaged by a fire. Any equipment that might need adjustment or maintenance while the compressor is running is placed outside the barrier, as is the lubricating oil reservoir. Personnel are not allowed within the barrier whenever the compressor is running and compressing oxygen.

The barrier design guidelines ensure that it provides adequate protection to contain the fire while the compressor is shut down and isolated from oxygen sources. Additionally, the barrier prevents any molten metal from being projected outside of the barrier. The barrier is not designed to contain the fire indefinitely, only to allow adequate time to secure the compressor.

Typically barriers are placed on compressors which pressurize oxygen to 4 barg or higher. For lower pressure compressors, Air Products designates approximately 8 m around the compressor as the Hazard Area, and personnel are restricted from entering that area, except to perform necessary tasks. (German codes require barriers when compressing O₂ above 1 barg).

**Seals** – Centrifugal oxygen compressors have labyrinth seals minimize the contact of rotating parts. The seal systems are designed to minimize loss of product oxygen, to prevent oxygen from migrating from the process chambers to unsafe areas (e.g. bearing housings), and to prevent oil from migrating into the process areas. Air or inert gases are used as buffering seal gases. Special instrumentation prevents the compressor from starting if the seal gas is not available at the proper pressure, and the compressor is shutdown if seal gas is lost. To further reduce the probability that oil will enter the process, oil seals are separated from the buffered gas seal by an atmospheric space.

For reciprocating compressors, the compressor cylinders are non-lubricated, and the distance piece is vented so that oxygen cannot enter the lubricated gear casing. Dry compartment drains that are piped outside the safety barrier to allow for positive verification that oil is not migrating to an oxygen enriched area.

**Materials of construction** - These are specially selected for each component of the compressor. Specific attention is paid to materials that do not readily combust, conduct heat readily (minimizing heat buildup in the case of contacting moving parts), and have high heat capacity (limiting the heat buildup). This is in addition to the normal mechanical requirements as dictated by service and operating conditions. Clearances between stationary and rotating components are relatively large in oxygen compressors to prevent contact in all be the most extreme circumstances.

**Cleaning** - The compressor must be carefully cleaned for O₂ service as it is constructed and installed. Care must be taken to keep the compressor clean, once it has been cleaned. Suction filtration is needed to prevent particles from entering the compressor and potentially acting as ignition sources.

**Startup/Shutdown** – Startup and shutdown operations increase the chance of moving parts contacting other components, especially as centrifugal compressors pass through any critical speeds. Therefore, it is desirable to start the compressor on air or an inert gas until it reaches stable pressures and temperatures. Oxygen is then introduced. On controlled shutdowns, it is desirable to
replace oxygen with air/inert gas before shutting the unit down. This is obviously not possible for emergency shutdowns. Personnel are forbidden to enter the barrier whenever the compressor is pressurizing oxygen. If personnel need to examine the machine while it is running (e.g., to troubleshoot instrumentation), the compressor must be compressing another less hazardous gas.

Whenever the compressor is shutdown, the gaseous inventory must be bled down in 20 seconds to less than 1 barg. This minimizes the mass of oxygen present in the compressor, which in turn minimizes any damage if the compressor is shutdown due to a fire.

**Instrumentation** - In addition to instrumentation used for normal compressor monitoring, special instrumentation is placed on oxygen compressors to provide maximum safety. Of particular importance is instrumentation used to detect a fire if it should occur and quickly shutdown and isolate the compressor. Rapid response temperature elements are installed in discharge piping of centrifugal compressors and in suction and discharge piping (or compressor valves) on reciprocating machines. If a high temperature is detected the machine is tripped, vented (as described above) and isolated by a quick closing valve located in the suction line. These are described in more detail in (11) and (12).

**SUMMARY OF PROCESS SAFETY FEATURES**

There are many operating practices necessary to run an ASU safely. However, there are seven key features discussed above, and they are summarized here for the convenience of the reader:

<table>
<thead>
<tr>
<th>ACTION</th>
<th>REASON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyze CO₂ at PPU Exit (a)</td>
<td>Verify Proper PPU Operation</td>
</tr>
<tr>
<td>LOX Purge &gt; 0.2% of the air, and it must be measured (b)</td>
<td>Ensure no contaminant buildup in the reboiler sum</td>
</tr>
<tr>
<td>HC Analyzer &lt; 450 ppm as C₁ equivalent</td>
<td>Ensure no hydrocarbon buildup in the reboiler sump</td>
</tr>
<tr>
<td>Batch Analysis</td>
<td>Verifies each component is present at acceptable levels.</td>
</tr>
<tr>
<td>Periodic Defrost</td>
<td>Remove trace components from low flow areas</td>
</tr>
<tr>
<td>Downflow reboiler exit CO₂ concentration &lt; 6% solubility, N₂O &lt; 1% solubility</td>
<td>Ensures that CO₂ and N₂O do not accumulate at too high of a rate</td>
</tr>
<tr>
<td>Full Submergence of Thermosyphon reboiler (a)</td>
<td>Ensure adequate circulation to prevent locally high concentrations</td>
</tr>
</tbody>
</table>

(a) Plant shutdown required after time delay
(b) With special instrumentation and equipment, the minimum purge can be reduced to 0.1% of the air

**MATERIAL SELECTION**

The metals from which an ASU is manufactured have several requirements. Carbon steel is used for most warm equipment and piping. The cryogenic portion of the plant must be capable of withstanding temperatures down to 77°K while still being economic. Almost all parts of the ASU will see enriched oxygen, either during normal operation or upsets. Copper, aluminum, and stainless steel are all good for the cryogenic temperatures.
<table>
<thead>
<tr>
<th></th>
<th>Carbon Steel</th>
<th>Copper</th>
<th>Aluminum</th>
<th>Stainless Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suitable for Low Temps</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Relative Strength(^{(a)})</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Very High</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Ignitability w/ O(_2)(^{(b)})</td>
<td>Moderate</td>
<td>N/A(^{(d)})</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Intensity of Burning(^{(c)})</td>
<td>Moderate</td>
<td>N/A</td>
<td>High</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

Notes:  
(a) This is a relative measure of the strength of the materials, 1=highest, 4=lowest  
(b) Difficulty of initiating combustion of the metal with O\(_2\)  
(c) Once started, a relative measure of energy released  
(d) Copper is not flammable in O\(_2\)

The ignitability of any material is a function of the O\(_2\) purity, O\(_2\) pressure, and material geometry. Ignitability generally increases with higher pressure, higher purity, and thinner materials. Aluminum in particular is very sensitive to O\(_2\) purity, with just fractions of percent impurities decreasing the ignitability very significantly.

A three-tier methodology is used to select a material for a given O\(_2\) service and to minimize the risk to personnel:

- If possible, all ignition sources are removed. Without ignition, the material cannot combust. A good example of this is the careful cleaning of carbon steel pipe in high pressure O\(_2\) pipelines. By eliminating the ignition source, carbon steel is an acceptable material.
- In some cases, it is not possible to remove all ignition sources. However, the material may still be used safely, if it is used where the combustion will not propagate. An example of this is aluminum pipe. Aluminum/O\(_2\) ignition is not completely understood, so it is difficult to eliminate all ignition sources. However, by only using aluminum pipe in services where propagation does not occur, it is possible to safely use aluminum pipe, as the long history of safe service of aluminum pipe has shown. (Note that when aluminum is used in O\(_2\) service, it is cleaned to eliminate as many ignition sources as possible.)

There are a few cases where the ignition source cannot be removed, and the process operates in a region where the only available practical materials can possibly ignite and propagate. In these cases, design features, instrumentation, and administrative controls are used to ensure that personnel are not put at risk. This approach is used for oxygen compressors, which are discussed in more detail above.

IGNITION SOURCES AND CLEANING

Two of the most common ignition sources are particle impact and promoted ignition. In particle impact, a small foreign object impinges on the surface of a material, and the energy is sufficient to ignite the material. For promoted ignition, a combustible material reacts with the oxygen, and the reaction energy is sufficient to ignite the primary material of construction.

In both of these cases, removing the ignition source by careful and thorough cleaning of the system prevents combustion. This “cleaning for oxygen service” removes oils, greases, solvents, weld slag, dust, dirt, sand, and other materials. The Compressed Gas Association (CGA) provides some basic guidance for oxygen cleaning and recommends that systems must be cleaned for O\(_2\) service if the concentration exceeds 25% O\(_2\) (14, 15). (At the time that this paper was written, this limit was under discussion. The reader should check the current version of the reference 14 to obtain the current recommended limit.)

Of particular interest is structured packing used in the distillation column. In the manufacturing process, lubricants are often needed in the pressing, stamping, and cutting steps. These lubricants must be carefully removed, because the packing is thin material, making it relatively easy to ignite,
and being thin, the combustion would propagate more easily. Air Products cleans the packing so that lubricants are removed to less than 50 mg/m², with the maximum measurement plus three standard deviations less than 100 mg/m². While there is not agreement in the industry, the reactivity of aluminum with O₂ is high, and aluminum packing has been shown to be highly reactive in liquid oxygen (5). Air Products takes a conservative approach and installs copper packing in regions in a distillation column where the normal oxygen concentration is above 99%. As copper is not combustible, this eliminates the risk of combusting the packing in these sections of the column. Further discussion on the safe use of aluminum structured packing for air separation service is given in (4).

Oxygen pipelines must be carefully designed and constructed:

- Both metallic and non-metallic materials of construction in the line should be evaluated carefully for O₂ compatibility at the operating conditions of the pipeline. As well as the pipe material itself, this includes all other components in contact with the O₂, e.g., gaskets and valve seats.
- The pipeline should be carefully cleaned to remove and combustibles any foreign particles.
- Depending on the materials of construction, the oxygen gas velocity in the pipe should be limited to avoid entraining foreign particles in the oxygen, which could impact on the pipe and lead to combustion.
- Impingement areas (bends, valves, and elbows) must be designed so that any impingement of particles will not lead to combustion. This may mean changing the materials of construction to more oxygen compatible materials, or in some cases, further limiting the piping velocity.
- High-pressure oxygen lines should be designed so they can be pressurized slowly to avoid adiabatic compression of the gas that can lead to higher fire potential. Theoretical calculations show that if O₂ is adiabatically compressed from 1 to 35 atm, the final O₂ temperature is over 800°K (527°C).

The CGA has developed guidance documents for the design of oxygen systems (17)

INTERFACES WITH THE ASU

Oxygen and nitrogen systems are typically treated as utility systems by the customer once they leave the cryogenic air separation facility. Two potential hazards which must be addressed during the DHR are:

- The pressure ratings of the house systems must match the pressure rating of the ASU, or alternatively, pressure relief systems must be put in place to ensure that the house lines are not pressurized above their safe limit.
- Most house systems are not designed for cryogenic service. It is possible for cryogenic fluids to enter the downstream systems, which can embrittle and ultimately fracture these systems. Therefore, depending on the nature of the flow and use pattern there are several types of safeguards that can be implemented including, but not limiting to, low temperature shutoff devices, flow controls, trim heaters, and orifice plates.

Embrittlement failures have most commonly occurred is immediately downstream of a cryogenic liquid vaporizer. Either the heat source to the vaporizer is accidentally stopped or the design product withdrawal rate is exceeded, placing an excessive heat load on the vaporizer.

There are two separate hazards that 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 material of construction are not adequate for cryogenic service, experience has shown that a fracture most likely will occur at high stress points (e.g., elbows or welds.) The second hazard associated with any embrittlement fracture is the release of cryogenic fluid which can create an oxygen rich or oxygen deficient atmosphere. The hazards associated with atmospheres are described further in other sections of the paper.

OVERPRESSURIZATION DUE TO TRAPPED CRYOGENIC LIQUIDS

Any place in a line where there is a potential to trap cryogenic liquid in a line, there is a need to provide overpressure protection. The vaporization of the trapped liquid can cause a considerable overpressure. For example, with no pressure relief, vaporizing liquid oxygen with no increase in volume generates pressures as high as 3500 atm. Therefore thermal relief protection is a standard part of cryogenic line design. Similar to embrittlement there are the two hazards: the pressure energy release and then the release of cryogen. Overpressure can cause a catastrophic failure, but more likely would start a small leak or tear. The resulting cryogenic fluid release rate would also be small. Still, pressure relief devices are needed whenever there is a possibility of trapping cryogenic liquids.

At times the thermal sizing case can be quite large depending on the amount of liquid that can be trapped into the system and how fast the heat transfer into this liquid can be. This is a concern around heat exchangers including utility driven heat exchangers, such as product vaporizers.

OXYGEN ENRICHED OR DEFICIENT ATMOSPHERES

There are inherent hazards with oxygen rich and oxygen deficient atmospheres. These are different than other process hazards, because they typically occur outside of the normal process operation, either by product spills and vents or by working on process systems. Oxygen, nitrogen and argon are colorless, odorless and tasteless and cannot be detected at ambient temperatures. Spills of cryogenic vapors or liquids involving oxygen, nitrogen or argon are visible due to the fog formed by condensing water vapor in the air around the cold gas or liquid. The visible fog should be assumed to contain the possible hazardous concentration of the gas. Hence escape upwind from the visible fog is the recommended course of action for persons outdoors.

Personnel are allowed to work in atmospheres only when the atmosphere is between 19.5 and 23.5% O2. If work must be done outside of these concentrations, breathing air must be provided.

OXYGEN ENRICHED ATMOSPHERES

An oxygen-enriched atmosphere can cause materials not usually susceptible to burning in air to burn. If hair and clothing become saturated with oxygen, they may burn violently if ignited.

There have been very few major accidents with significant consequences outside the ASU battery limits involving oxygen releases to the atmosphere. This can be directly attributed to the high standards adopted for these types of installations. There are only a relatively small number of companies involved in the industrial gases industry; they work closely on safety issues (through trade associations such as CGA, European Industrial Gas Association [EIGA], British Compressed Gas Association [BCGA], etc.) resulting in high standards throughout the industry.

The British Compressed Gas Association studied the hazard of being exposed to an oxygen rich environment (13). The risk of fatal or serious injury is quantified by multiplying three probabilities:
• Probability of Ignition Source Being Present
• Probability of Igniting Clothing
• Probability of Fatal or Serious Injury

Smoking is the most obvious ignition source; others are open flames, use of electrical equipment, and internal combustion engines (such as motor vehicles). The BCGA report concludes that the probability of clothing being ignited in an oxygen rich atmosphere increases with increasing total oxygen concentration and gives values for these probabilities. Based on this analysis of ignition probability, burning rate and reaction time, conservative values which could be adopted for probability of fatal or serious injury are:

Probability of Fatality or Serious Injury if Accidentally Exposed to O₂ Enriched Environment

<table>
<thead>
<tr>
<th>O₂ Concentration</th>
<th>Probability of Off-site Populations</th>
<th>Probability for On-Site Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%</td>
<td>0.0175%</td>
<td>0.0085%</td>
</tr>
<tr>
<td>30%</td>
<td>0.17%</td>
<td>0.085%</td>
</tr>
<tr>
<td>35%</td>
<td>0.53%</td>
<td>0.265%</td>
</tr>
<tr>
<td>40%</td>
<td>2.8%</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

The Major Hazards Assessment Unit of the United Kingdom Health and Safety Executive, on the basis of the work in the BCGA report reported above, has defined the dangerous dose to the public for liquid oxygen spills as 35% total oxygen concentration in the air. Logically the same criteria could be used for a large release of oxygen gas. It is suggested that the probability figures noted above can be used directly in risk and consequence analysis to predict individual or societal risk for persons outdoors as a function of the total oxygen concentration to which they are exposed.

Breathing high oxygen concentrations can produce harmful effects in people. OSHA has defined the maximum O₂ concentration that personnel can be exposed to as 23.5%. At concentrations above this, procedures need to be in place to protect personnel. Breathing pure oxygen can cause coughing and chest pains in 8-24 hours. At partial pressures above 2 atm, the central nervous system is affected, including tingling of fingers and toes, confusion, and seizures.

Abatement measures to reduce on-site and off-site risks for high oxygen releases include:

• Control of sources of ignition on-site, (no smoking or open flames, control of vehicles, etc.)
• Use of remotely operated or automatic emergency shut off systems to reduce the duration of foreseeable oxygen releases
• Avoidance of oxygen piping or vessels in confined spaces where personnel can enter.
• Hot work/Vessel/pit entry procedures
• Use of oxygen enrichment monitors
• Careful design and location of oxygen vent systems
• Fire fighting equipment
• Good housekeeping to avoid accumulation of combustible material
• On-site and offsite emergency plans

OXYGEN DEFICIENT ATMOSPHERES

Workers have lost their lives or been overcome by high concentrations of nontoxic, inert gases such as nitrogen or argon. A very large proportion of the fatalities and near misses involving asphyxiation concern persons being in, or entering, confined spaces, enclosures or buildings.
containing an oxygen deficient atmosphere. The release of asphyxiant gases into the open air is a very rare cause of fatalities or asphyxiation near misses.

As the oxygen concentration in the air is reduced by increasing the asphyxiant gas concentration, for example due to a liquid nitrogen or liquid argon spill or argon or nitrogen gas release, certain physiological effects take place in the human body.

<table>
<thead>
<tr>
<th>Oxygen Concentration</th>
<th>Affect on Personnel</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-19.5%</td>
<td>Loss of coordination</td>
</tr>
<tr>
<td>&lt;12-15%</td>
<td>Respiration rate increase, loss of coordination, perception, and judgment are pronounced</td>
</tr>
<tr>
<td>10-12%</td>
<td>Further increase in respiration, poor judgment, blue lips.</td>
</tr>
<tr>
<td>8-10%</td>
<td>Mental failure, nausea, vomiting, unconsciousness</td>
</tr>
<tr>
<td>6-8%</td>
<td>8 minute exposure, 100% fatal</td>
</tr>
<tr>
<td></td>
<td>6 minutes exposure, 50% fatal</td>
</tr>
<tr>
<td></td>
<td>4-5 minute exposure, recovery with treatment</td>
</tr>
<tr>
<td>4%</td>
<td>Coma in 40 seconds, respiration ceases, death</td>
</tr>
</tbody>
</table>

In O₂ deficient atmospheres, symptoms or warnings are generally absent or, if present, the victim’s condition prevents him or her from helping themselves. Typical accidents as a result of nitrogen use fall into two categories:

- Accidental leaks into an area where personnel are not expecting a nitrogen atmosphere
- Lack of awareness that nitrogen is flowing into a purged area where an entrant walks in to do work.

Small leaks can be difficult to detect, so, depending on the area, it may be appropriate to use safeguards such as ambient oxygen deficiency monitoring. This is especially important to consider in small, poorly ventilated spaces that have the potential for leaks.

Purposeful venting of oxygen and nitrogen must be done with care so as not to create hazardous atmospheres. Even small low-pressure vents can create a hazardous atmosphere. It is important to pipe process vents and bleeds outside enclosures or buildings whenever possible, avoiding potential ventilation intake points.

Abatement measures to reduce on-site and offsite risks for asphyxiant releases include:

- Forced ventilation inside enclosures with fan failure alarms
- Oxygen deficiency monitors
- Vessel/pit entry procedures. A good practice is to treat any confined space entry as having potential for O₂ deficient atmosphere, and strictly defining a confined space to included any area with potential for improper circulation into which one can insert even just one’s head.
- Breathing apparatus
- Back up personnel, harnesses, etc
- Careful design and location of asphyxiant vent systems
FIGURE 1
CRYOGENIC AIR SEPARATION PROCESS
Table 1  
Trace Contaminants in Air (1)

<table>
<thead>
<tr>
<th>Species</th>
<th>Class</th>
<th>Typical Design Basis</th>
<th>Typical % removal in PPU(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>for concentration air(a)(ppm)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>P</td>
<td>400</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>SO₂</td>
<td>C, P</td>
<td>0.1</td>
<td>100%</td>
</tr>
<tr>
<td>HCl</td>
<td>C</td>
<td>0.05</td>
<td>100%</td>
</tr>
<tr>
<td>H₂O</td>
<td>P</td>
<td>10,000 (approx.)</td>
<td>100%</td>
</tr>
<tr>
<td>N₂O</td>
<td>P</td>
<td>0.3</td>
<td>30-70%</td>
</tr>
<tr>
<td>NO₃ (NO+NO₂)</td>
<td>P, R</td>
<td>0.05</td>
<td>100%</td>
</tr>
<tr>
<td>O₃</td>
<td>R</td>
<td>0.2</td>
<td>100%</td>
</tr>
<tr>
<td>CH₄</td>
<td>R</td>
<td>10</td>
<td>0%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>R</td>
<td>0.1</td>
<td>0%</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>R</td>
<td>0.3</td>
<td>50%</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>R</td>
<td>1.0</td>
<td>100%</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>R</td>
<td>0.05</td>
<td>67%</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>R</td>
<td>0.2</td>
<td>100%</td>
</tr>
<tr>
<td>C₄</td>
<td>R</td>
<td>1.0</td>
<td>100%</td>
</tr>
</tbody>
</table>

Notes:  
(a) This is a typical design basis. For most components, the actual value will be lower.  
(b) Approximate breakthrough order for conventional PPU’s (first to last):  
CH₄ >C₂H₆ >NO >C₃H₈ >N₂O >C₄H₁₀ >CO₂ >> C₅H₁₀, NO₂, HCl, SO₂, C₂H₂, C₄ > H₂O  
(c) Any CO and H₂ which enter the process follow N₂. They are not removed by the PPU and they do not concentrate in the LP column sump.

Table 2  
LEL of Hydrocarbons in GOX (16)

<table>
<thead>
<tr>
<th>Component</th>
<th>LEL (ppmv)</th>
<th>LEL (ppmv CH₄ Equivalent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>50,000</td>
<td>50,000</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>30,000</td>
<td>60,000</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>21,200</td>
<td>63,600</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>18,600</td>
<td>74,400</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>14,000</td>
<td>70,000</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>11,800</td>
<td>70,800</td>
</tr>
<tr>
<td>C₇H₂₀</td>
<td>8,300</td>
<td>74,700</td>
</tr>
<tr>
<td>C₁₀H₂₂</td>
<td>7,700</td>
<td>77,000</td>
</tr>
<tr>
<td>C₈H₄</td>
<td>27,500</td>
<td>55,000</td>
</tr>
<tr>
<td>C₉H₆</td>
<td>20,000</td>
<td>60,000</td>
</tr>
<tr>
<td>C₁₀H₈</td>
<td>16,500</td>
<td>66,000</td>
</tr>
<tr>
<td>C₁₀H₂</td>
<td>25,000</td>
<td>50,000</td>
</tr>
<tr>
<td>C₁₀H₈ (toluene)</td>
<td>12,700</td>
<td>89,000</td>
</tr>
<tr>
<td>C₁₀H₆ (benzene)</td>
<td>14,000</td>
<td>64,000</td>
</tr>
</tbody>
</table>
REFERENCES


(2) “Safe Operation of Reboilers/Condensers in Air Separation Units”, European Industrial Gases Association, IGC Document Doc 65/99/EFD.


(4) CGA G-4.8, Safe Use of Aluminum Structured Packing for Oxygen Distillation


(12) “Centrifugal Compressor for Oxygen Service”, European Industrial Gases Association, IGC Document Doc 27/93/E.


