Property Risk Consulting Guidelines

A Publication of AXA XL Risk Consulting

PRC.17.2.4

AIR SEPERATION PLANTS

INTRODUCTION

Air separation plants separate air by distilling it into its individual components. Air separation technology is widely used in many major industries in the world today. The two main products are oxygen and nitrogen. Some facilities also produce carbon dioxide, argon, neon, krypton, xenon and helium. Air separation processes can be designed to yield liquid or gaseous products and can be customized to produce only specific fractions, discarding the rest. Air liquefaction plants are normally located near the customer to reduce transportation costs and to supply large volumes to the customer via pipelines. Typical occupancies requiring large oxygen/nitrogen supplies include chemical/petrochemical plants, steel mills and other large metal workers. High purity nitrogen is also used in the electronics industry.

The first plants that prepared oxygen by liquefying and distilling air were subject to frequent explosions. Because of this, the vessel containing the boiling liquid was often located behind barricades or in a pit. Gradually, safer design and operating procedures made explosions rare. These early plants produced low-pressure, high-purity oxygen, which was then compressed and bottled for use in oxyacetylene welding.

Newer plants usually operate at 200 psi – 3000 psi (1,380 kPa – 20,680 kPa). This permits withdrawing the oxygen as a cryogenic liquid, which could be stored in heavily insulated low-pressure tanks or vaporized and compressed into high-pressure cylinders.

During and after World War II, several processes were developed that are economical only when cheap oxygen is available. Among these are:

- the Sachsse process for manufacture of acetylene by partial oxidation of natural gas followed by immediate shock cooling of the products of combustion;
- the Texaco process for producing hydrogen by partial oxidation of a hydrocarbon in the presence of steam;
- the Oxo Process for making synthesis gas (syngas) by incomplete oxidation of natural gas;
- the more efficient production of pig iron by enriching the air blast to a blast furnace;
- the more efficient production of steel by the use of oxygen in top blown converters instead of air in Bessemer converters.

Although the need for oxygen was the driving force behind the development of air liquefaction plants, it must be noted that nitrogen is a by-product of increasing value. In fact, some plants are being used solely to produce nitrogen with the oxygen being discarded.

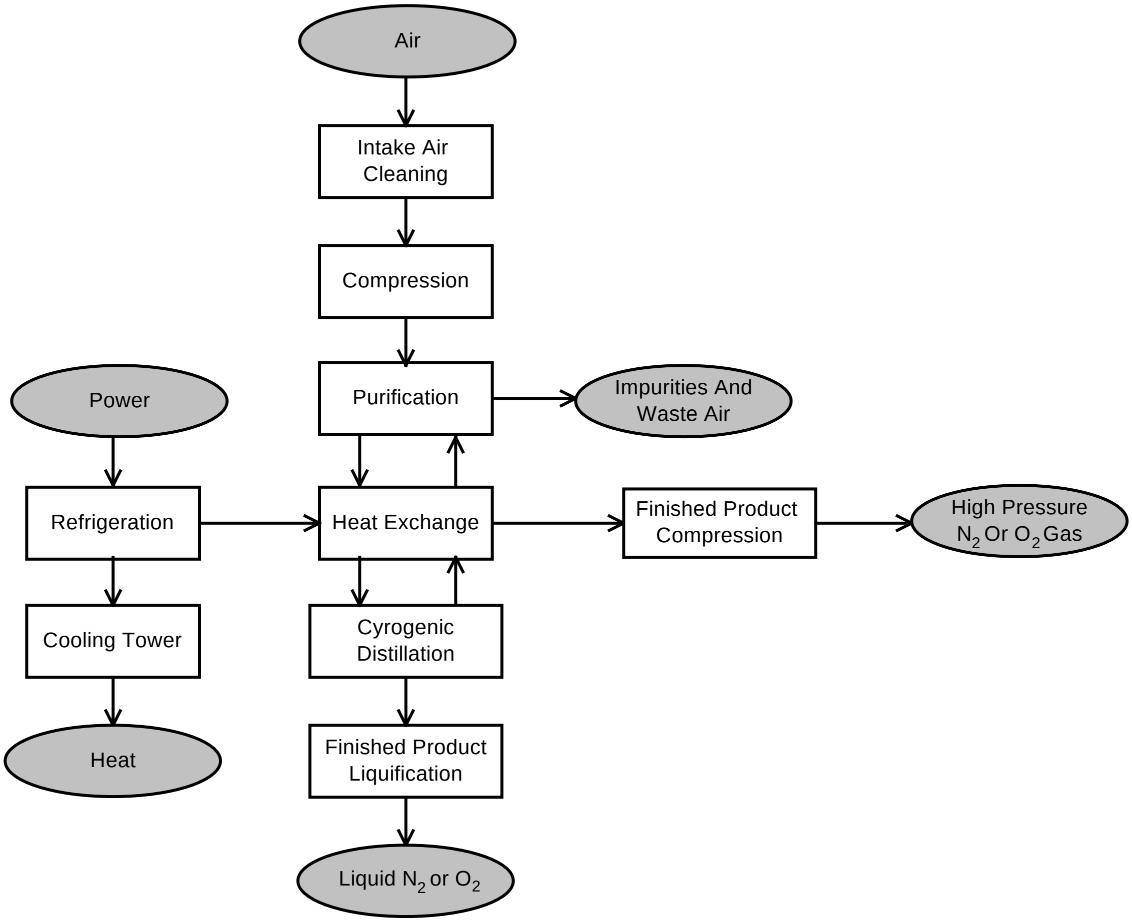

Figure 1. Air Separation Plant Process Flow.

PROCESSES AND HAZARDS

The usual method of separating air into its constituent fractions is by liquefaction. This method is the most cost efficient, particularly for very large installations.

Liquefaction or liquid air plants separate air by means of the differing boiling points of the constituent gases. These plants clean and compress air, then cool it by either a gas stream or cooling water. The cooled air is expanded through an orifice or expansion engine, cooling it further. The various fractions of the cold air then condense at different levels in what is essentially a distillation column. The oxygen or nitrogen can be drawn off as a cryogenic liquid or can be vaporized by heat from the incoming air stream. Gases can be piped directly to the point of use or compressed and stored in cylinders. Trace gases, such as argon or neon, are generally discarded but can be sent in crude form to a specialized unit which distills them again to achieve high purity. Figure 1 shows a block diagram of the above process.

Older liquification plants suffered explosions with distressing frequency. The cause was generally traceable to acetylene, which gradually crystallizes inside the liquid air distillation column and then decomposes explosively. With few exceptions, these explosions do not cause extensive physical damage. Even minor mechanical damage will cause major business interruption. One reason for this is that the equipment operates at very low temperatures inside a heavily insulated “cold box.” Hence, after even a small explosion, it may take several days to warm up the equipment so it can be opened, a day or two to repair physical damage, several days to reinsulate, and as long as a week to get the equipment down to operating temperature. Thus, an explosion that damages just one valve could conceivably cause a large plant to lose as much as three weeks production. Acetylene buildup remains a hazard to this day although more modern instrumentation and better operating procedures have reduced the danger somewhat.

Intake Air Cleaning

The first step in processing air is removing contaminants from the air stream. Failure to do this results in the buildup of these contaminants in the liquid air distillation column inside the cold box. The worst of these is acetylene, which can decompose explosively. However, any hydrocarbon is hazardous because it can be exposed to pure oxygen in parts of the system. Mixing any hydrocarbon with pure oxygen creates a combustion explosion hazard.

Avoiding Contaminants

The best way to deal with the hazards posed by contaminants is avoid the problem altogether. The simplest way to do that is to install hydrocarbon analyzers on the air intake and shut down the liquid air plant whenever dangerous concentrations of hydrocarbons are detected.

Some plants have multiple air intakes and switch from one to another based on wind conditions, plant operations and the results of air analyses. The need for multiple intakes depends on the location of possible sources of air contamination from processes in the vicinity of the air plant.

Spraying With Water

Spraying air with water cleans the air of water-soluble substances, dusts and vaporized air compressor lubricants. Caustic scrubbers, if used to remove CO_2, also remove acidic compounds like H_2S and oxides of nitrogen. Adsorptive dryers remove compressor lubricant mists and heavy hydrocarbon vapors, as well as, water vapor. When working under high pressure, they will also remove lower boiling-point contaminants.

Filtration

When oils are used in compressors, means are generally taken to remove oil fog and vapor from the air. Oil fog particles as small as three microns in size have been removed by ultra filters. Wool felt also removes the fog or changes it to a vapor. By adding cooled water vapor, the oil vapors can be removed more easily. Both alumina and activated carbon are also used to remove oil vapor.

Oxidation

A relatively new safeguard is catalytic oxidation of hydrocarbons (particularly acetylene). The unit is installed after the last compression stage before any cooler, as it must operate at temperatures in excess of 300°F (149°C). The unit is preceded by a filtration unit, which should be arranged with two filters in parallel. If the gases contact the catalyst for 0.2 s at 375°F (191°C), all unsaturated hydrocarbons are eliminated. Higher temperatures of up to 500°F (260°C) would be necessary to oxidize saturated hydrocarbons but are not used on these installations. The catalyst is a combination of MgO and CuO, which decomposes ozone in addition to oxidizing unsaturated hydrocarbons. Plants where these systems have been in use report no acetylene on the downstream side of these units. Any plant subject to severe acetylene contamination should consider installing such a unit.

Adsorption

Silica gel, generally in pellet form, adsorbs acetylene and has been widely used for many years for this purpose.

Adsorbers are usually installed in the liquid line passing from the bottom of the high-pressure column to the low-pressure column. These adsorbers are paired so one may be regenerated while the other is in use.

Some plants have additional "guard adsorbers" that circulate liquid oxygen by pump or thermal siphon to remove any trace of acetylene from the primary adsorbers or the low-pressure column. Thermal siphon systems are not as reliable as pumping systems.

Plants that use expansion engines for cooling a portion of the air generally introduce this air into the upper column directly. However, it is standard practice to install paired adsorbers before the expansion engine to remove CO_2 and acetylene.

All these adsorbers do an excellent job in removing acetylene provided they are not overloaded. Each unit has a definite acetylene adsorption capacity. When this amount has been taken up, the unit becomes ineffective and any additional acetylene will pass through. Therefore, it is important to have periodic regeneration. This is usually accomplished by passing hot nitrogen through the unit, thereby heating the silica gel to a temperature in excess of 200°F (93°C). Without sufficient heat, the unit will not be fully regenerated. A minimum of 180°F (82°C) is necessary. Some plants monitor the regeneration gas from the adsorbers and regenerate until analysis shows that all acetylene and other contaminants have been removed.

Tests have shown only a slight reduction in adsorber efficiency after several years of use provided adequate regeneration is practiced. However, as a result of tests, some plants with severe contamination problems have established two years as the life of the adsorbent. Regeneration is seldom done more often than every week but there should never be longer than six months between regenerations.

These adsorbers pick up miscellaneous hydrocarbon contamination in the streams and also CO_2; however, it appears that acetylene is preferentially adsorbed and the amount of other substances adsorbed will not materially affect the acetylene removal capacity.

In summary, silica gel is the first and most important safeguard to prevent explosions in liquid air plants. No gas or liquid should enter the low-pressure column unless it has passed through a silica gel adsorber.

Failure of filtration could lead to a build-up of contaminants in the liquid oxygen holdup, causing a severe explosion.

Compression

Filtered ambient air is drawn into air compressors and compressed to various pressures depending on plant design. The most typical pressures are in the 75 psig – 100 psig (517 kPa – 689 kPa) range. Compressors are generally large multistage units of reciprocating, centrifugal, or turbine type. Sizes range from 25 tons/day to 2000 tons/day (23 to 1800 tonnes/day). In addition, plants that sell high-pressure gaseous oxygen need one or more compressors to compress the pure oxygen.

Lubricating oil for the compressors is stored in consoles from which the oil is circulated with primary and auxiliary pumps. These consoles are generally located adjacent to the compressor or outside the compressor building. The lube oil is usually combustible. Accidental release of this oil from pump seals, piping, etc., may be ignited from adjacent hot surfaces and cause a severe fire. Casings or moving parts of compressors can also suffer metal fractures. This can result in the simultaneous release of lubricating oil and the generation of sparks causing ignition.

Most lubricating oils burn spontaneously in an oxygen rich atmosphere, so if oil is released in conjunction with an oxygen leak, such as a ruptured oxygen compressor, a severe fire will result. Phosphate ester lubricating oils are less prone to this problem. The latest technology involves compressors equipped with magnetic bearings used in conjunction with dry-type seals, eliminating the need for lubricating oil.

Compressors in these plants are specialized units for this process. They are expensive and take a long time to replace.

Cold Boxes

A cold box is an enclosure for the distillation column and is normally insulated with perlite. Other noncombustible insulation may be used. The cold box internals are made up of low- and high-pressure separators that are part of the same distillation system. Air enters into the high-pressure section of the column. Liquid oxygen pools at the bottom while liquid nitrogen is recovered at the top.

In the low-pressure column, the boiling oxygen is at a temperature below the boiling point of nitrogen in the high-pressure column. Therefore, nitrogen from the high-pressure column, passing through tubes cooled by liquid oxygen in the low-pressure column, will partially liquefy. The liquefied nitrogen is used as a reflux in both distillation sections. Pure nitrogen gas is recovered at the top of the low-pressure column. Liquid oxygen is extracted at the bottom of the low-pressure separator.

Hydrocarbons present in the intake air may condense in the low-pressure column and could lead to an explosion if critical concentrations are reached or if the temperature rises. Temperature rise could occur during shutdown for service. Ignition temperatures could easily be reached even while the unit is still relatively cool. Acetylene can form crystals floating on the liquid oxygen and these crystals could eventually detonate. On-line instrumentation is usually provided to detect hydrocarbon buildup. The oxygen pool, where hydrocarbon build-up is more likely to occur, is typically constantly purged.

Cold box insulation is noncombustible, as an oxygen leak could lead to a severe fire if the material were combustible. The fill areas are often purged with nitrogen as an additional precaution.

The following example illustrates the importance of using noncombustible cold box components. During a normal shutdown of a 150 ton/day (136 tonnes/day) oxygen plant for routine inspection, it was found necessary to make repairs in the cold box. The repairs required welding. This particular cold box had a wood floor sheathed with sheet iron. The maintenance crew, noting the metal sheathing, took no particular precautions. It is postulated that welding sparks started an undetected smoldering fire in the wood floor. Upon completion of the repairs, the plant began its startup cycle, during which time a liquid oxygen spill occurred in the cold box. The oxygen found its way to the charcoal formed from the partially burned wood flooring. This caused an explosion that completely destroyed the plant.

An investigation into the cause of this disaster showed that porous materials, such as charcoal, softwoods and even hardwoods are capable of rapid adsorption of liquid oxygen. Oxygen-soaked charcoal burns so fast that it is equivalent to a powerful explosive. Under ordinary circumstances, liquid-oxygen-soaked wood does not burn fast enough to become explosive. However, if confined so that the gaseous products of combustion cannot dissipate, explosive pressures can develop.

Cold boxes operate at very low cryogenic) temperatures. (Special alloys and construction techniques are used to fabricate such equipment. Inadequate alloys could lead to brittle fracture of the metal. Even an explosion and/or fire from some other cause would most likely result in a large loss due to the special metallurgy and construction techniques needed for the repairs.

Cooling

Large quantities of refrigeration are needed to cool the compressed air to a temperature that will cause it to partially liquefy when expanded. Most of this cooling is obtained from the cold product and waste streams coming from the low-pressure column. However, even though all cold equipment is in a heavily insulated cold box, heat transfer is not 100% efficient. Additional heat may be removed by cooling the compressed air directly or indirectly, using water. This cooling is sometimes supplemented by mechanical refrigeration.

The heat exchange between the cold gases leaving the column and the compressed air is accomplished in various types of equipment. Initially, conventional tube bundle exchangers were used. These were subject to plugging with solid CO_2 and with ice. Ice plugging, because of the expansion of water when it freezes, would also damage the exchanger. Consequently, it was necessary to remove as much water vapor and CO_2 as possible, before the air reached the exchangers. Cooling the air with water lowered the dew point, scrubbing with caustic soda solution removed CO_2 and more water, and still more water could then be removed by cooling, using refrigeration or by the use of adsorptive dryers, such as activated alumina. Nevertheless, the exchangers had to be warmed periodically to remove the ice and solid CO_2 that still collected because 100% prior removal was not practical. Therefore, the exchangers were installed in pairs so that while one was cooling air, the other was being de-iced.

Another development in air cooling was using paired regenerators instead of exchangers. In a regenerator, cold exit gas flows through a tank containing metal rings, stone pebbles or some similar material having high heat capacity and capable of withstanding large temperature changes without damage. When the fill is cold, the cold gas flow is switched to a parallel unit and air to be cooled flows through the cold generator. Periodically, each regenerator is de-iced by blowing warm air through it.

For various reasons, many plants do not use regenerators. For example, cooling a regenerator requires a long time because of the high heat capacity of a large mass of packing. Therefore, if a plant is to operate on an intermittent basis, exchangers are preferred.

The exchangers now used are seldom of the older shell and tube type. Instead, they are paired copper or aluminum tubes wound together on a supporting frame. Cold gas flows through one tube and warm gas through the other. Alternatively, they may be "extended surface" units, such as those in which corrugated metal sheets (usually aluminum) are welded together to form a honeycomb structure. Cold gas then flows through one set of cells and warm air to be cooled flows the other way through the adjacent set. The metal in these units is usually as thin as is consistent with safe design, in order to keep the mass small. As a result, strict de-icing schedules have to be followed to avoid exchanger damage by ice. Furthermore, an explosion in the system can easily damage these relatively fragile units. Because they are usually of special design, replacement after damage may be quite time-consuming.

The exchangers may be of the reversing type with air normally flowing in one direction through any given passage. Operation of an automatic reversing valve then sends cold product through the same passage in the opposite direction. Because the cold product contains no water vapor or CO_2, it is reasonably effective in de-icing the passage. Alternatively, the exchangers may be deiced by periodic warm-up, without use of reversing valves. In such a case they have to be installed with spares if the plant runs continuously without periodic shutdowns.

Due to the wide difference in freezing points, it is theoretically possible to remove water vapor first in one set of coolers, which could be designed to resist damage by freezing, then CO_2 in more fragile units. In practice, this idea is not very feasible because of the low temperature of the gases used for cooling and the difficulty of controlling heat flow through an ice film of changing thickness.

At this point, major design variations appear depending on the ratios of product desired (gaseous or liquid, N_2 or O_2). These variations use the fact that a compressed gas can be cooled by making it do work. Obviously, the cooling produced by doing work plus expanding is greater than the cooling produced by expansion alone, so practically all oxygen plants have an expansion engine somewhere in the cycle. In the case of high pressure (500 psi – 3000 psi. [3,350 kPa – 20,680 kPa]) plants, it is customary to split the cold air stream in or before the exchangers. Part enters the lower column through the expansion valve while another part enters the same column through an expansion turbine. By varying the ratio of air through the two cooling devices, it is possible to regulate the temperature in the column. In the case of low-pressure tonnage plants, the air is usually compressed to 100 psi (689 kPa). or less. In some plants when the portion of the cold air passing stream through the engine is fed into the upper column, and only that portion eventually goes through an expansion valve feeding into the lower column.

With a low-pressure tonnage plant, considerations of heat efficiency often make it desirable to draw off the oxygen as a gas by vaporizing it, so that the heat of vaporization of the oxygen can be used for refrigeration with maximum efficiency. This system allows any contaminants present to become concentrated in the pool of liquid oxygen in the upper, low-pressure column.

In one system, the liquid oxygen circulates by thermal siphon through an auxiliary reboiler. By heat exchange with waste nitrogen, sufficient oxygen is boiled so that the mixture leaving the unit is a gas, carrying liquid drops. These drops are collected in a separator and this collected liquid (containing the impurities) is the product stream.

This method keeps putting what might be called double distilled oxygen back into the upper column so any trace of acetylene entering with the liquid air is automatically diluted. The liquid oxygen from the separator is pumped to a separate vaporizer where it is converted to gas in the course of high velocity flow through heated tubes. Any dissolved acetylene is gasified along with the oxygen. It cannot separate out because of the high velocity and the high temperature gradient.

In another system, an auxiliary condenser acts like the auxiliary reboiler. However, the gasified oxygen, after passing through the liquid separator, is taken off as product instead of being returned to the column. A higher proportion of the initial liquid is vaporized and the liquid collected in the separator is relatively rich in acetylene and other contaminants. This liquid is discarded to dispose of the contaminants.

Some plants use flat-bottomed reboilers, most use round or elliptical ones. The flat bottom equipment could have dead spaces where solids might collect; the others should not be subject to this condition.

Cooling Towers

Usually, wooden cooling towers with wood or PVC fill are located on site. Electrically operated fans are provided at the top of the tower.

Wooden construction with combustible fill makes cooling towers fire hazards. During shutdowns, cooling towers become extremely dry and can burn easily. Maintenance work, if not properly monitored, can provide an ignition source. Even during operation, the towers have dry spots, which can be ignited by faulty electric motors or other ignition sources.

Cryogenic Distillation

Preventing explosions in oxygen plants requires understanding the distillation column design. Figure 2 shows the basic double column. The double column, or two equivalent separate columns, using expansion for cooling and the change of boiling point with pressure for boiling, is the basic unit in all modern oxygen plants. Cooled air enters the high-pressure column near the bottom or at one of the lower plates in the column. Nitrogen boils at a lower temperature than oxygen, so the nitrogen boils and the liquid in the bottom of the high-pressure (lower) column becomes richer in oxygen.

The higher the pressure, the higher the temperature at which liquids boil. In the bottom of the low-pressure (upper) column, the boiling oxygen is at a temperature below the boiling point of nitrogen in the high-pressure column. Therefore, high-pressure nitrogen, rising through sealed tubes in the top of the high-pressure column, gives up heat and partially liquefies. The heat is given up to the liquid oxygen in the low-pressure column, causing it to boil and distill in the upper column. Part of the liquid nitrogen runs back down the lower column as reflux and part is trapped in an annular trough and taken to the low-pressure column as reflux. The oxygen-enriched liquid air from the bottom of the high-pressure column goes to the upper column where it is separated by distillation into oxygen and nitrogen. Oxygen is taken off at point "A" (see Figure 2) as a gas or at point "B" as a liquid.

In some oxygen plants, air enters the high-pressure column through an expansion valve. Expansion of a gas causes cooling and results in some liquefaction taking place with the rest of the liquefaction coming from nitrogen reflux. If the expansion valve is in the liquid air line going to the upper column, the same amount of cooling takes place by boiling liquid air at reduced pressure. In such a case, all cooling for liquefaction in the lower column comes from the nitrogen reflux.

PRC.17.2.4.A discusses air components and contaminants, and how they affect the distillation process.

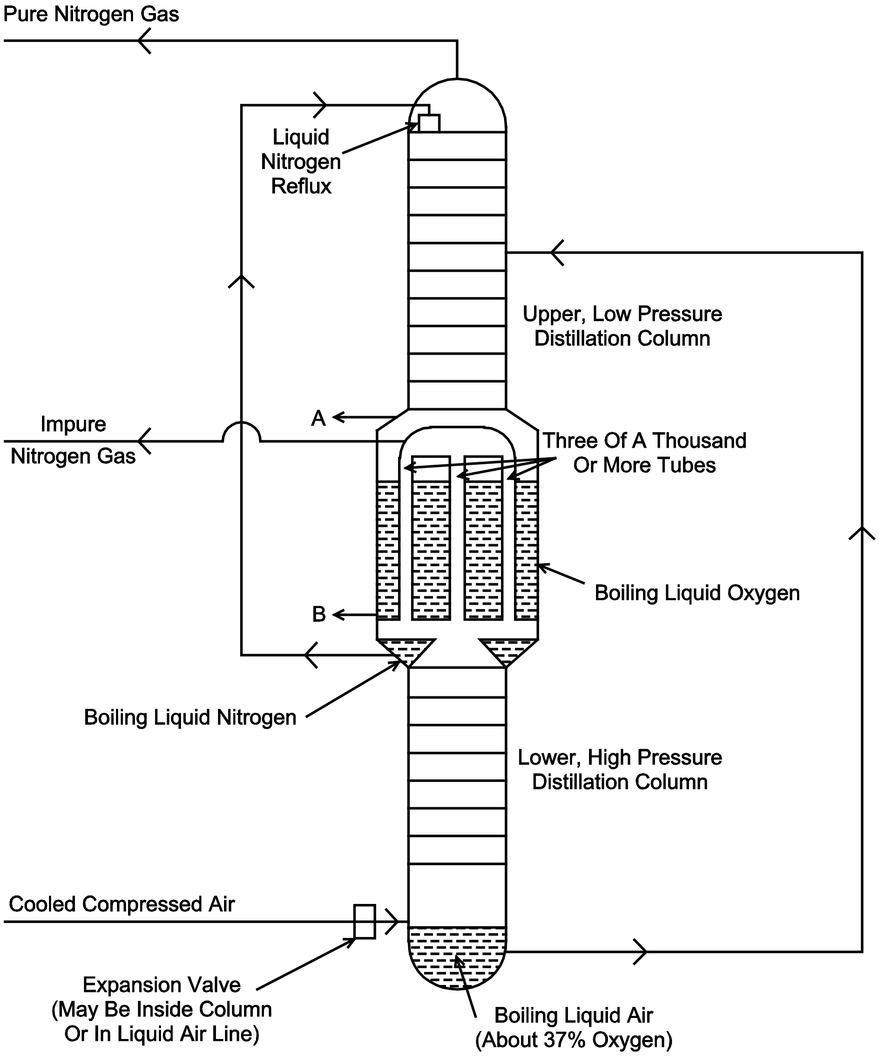

Figure 2. Typical Liquid Air Distillation Column.

Handling and Storage

Oxygen is noncombustible, but will greatly promote combustion if a fuel and ignition source are present. Also, fires in oxygen-rich atmospheres will burn intensely.

Normal operational sequences for an oxygen plant periodically require the disposal of quantities of liquid oxygen, ranging from a large-scale disposal when draining a low-pressure column and condenser of tonnage plants during defrost, to lesser amounts when draining small plants or vessels, cooling down liquid oxygen pumps, draining liquid daily from small plants for acetylene control, etc. It is important that the hazard involved in operations of this nature be recognized.

It is very common to locate small, unattended air liquefaction plants near customer sites. Some larger plants are occupied 24 h/d by only a few operators. Lack of personnel puts a premium on automatic systems for the prevention of losses.

LOSS PREVENTION AND CONTROL

These protection guidelines are not all inclusive. They discuss only hazards or construction features that are unique to air separation plants. Use judgement in applying the protection guidelines given, since they were written with an "average" hazard level in mind. Increased levels of hazard warrant increased protection. Consult the protection standards cited in the Reference section.

Management Programs

Structure management programs so that administrators report to top management through the minimum number of steps. Institute adequate loss prevention inspection and audit programs to communicate program effectiveness to top management. This management feedback is a key feature of *OVERVIEW*, AXA XL Rsik Consulting's total management program for loss prevention and control. In developing a program, pay particular attention to the following important areas:

Process Hazards Evaluation

Research the pertinent physical and chemical properties of liquid air fractions, potential contaminants, and any other materials used or present. List conditions that best represent the possible operating conditions.

Establish routine procedures for testing physical and chemical properties of all equipment to confirm that it is constructed of materials required for safe operating conditions.

Determine the safe operating and potential upset conditions of the air plant.

Design the air plant with as much inherent safety as possible by using instrumentation, adhering to written operating procedures, and installing adequate pressure relieving devices. Interlock processes to shut down automatically and safely in event of operator error, equipment failure, or unsafe conditions. Provide intermediate alarms to allow operators time to take corrective action.

Provide redundant instrumentation for all critical controls. In redundant loops, include **both** separate signal transmitters and signal receivers. In most cases, install a comparator to notify operators when control and redundant signals differ significantly.

When designing safety features, assume a minimum of two consecutive errors, one of which may be misinformation because of a faulty instrument or a misunderstanding of instructions.

Design and specify equipment considering all possible operating conditions, both normal and abnormal. Give particular attention to suitability of the equipment to handle the process stream and to withstand external environmental influences.

Operator Training

Educate all operators in the hazards involved and in functions of the safety control equipment. Forbid operators to run the air plant when any of this equipment is out of order. Train operators in manual emergency shut-down procedures. Forbid deviations from the written procedures.

Schedule periodic re-education and training at least annually. Include testing to assure proper performance of all assigned duties with particular emphasis on emergency shutdowns.

Pre-Emergency Planning

AXA XL Risk Consulting's "PEPlan," the pre-emergency plan from *OVERVIEW*, may be used to develop a customized plan. This customized plan should include the following features:

- A fire and disaster alarm system.
- An emergency communications system, including radio where needed.
- A planned program of cooperation with neighboring plants and with public firefighting and disaster control organizations.

Business Interruption Planning

A program to analyze the interruption of business that may result from potential incidents and to develop plans for minimizing loss of production during rebuilding.

Preventive Maintenance and Inspection

Inspect and maintain process equipment, piping, instrumentation, electrical equipment and pressure relief devices according to a schedule established with proper consideration of design and service conditions. Include all appropriate types of modern nondestructive testing, IR scanning and vibration analysis in the inspection techniques. Establish a detailed record-keeping system which includes equipment retirement forecasts.

Management of Change

Apply all management programs to any changes made to the facility's physical arrangements or procedures. Pay particular attention to the following areas:

- Repeat the process hazards evaluations program for any modification to the process. Determine the need for new or different safety equipment or measures.
- Whenever equipment is changed from one service to another, or when process changes are made, examine the inspection and maintenance program and modify as necessary. Monitor daily operating changes.
- Verify new construction materials and all maintenance parts and supplies as conforming to original (or modified) design specifications.
- Apply the program for handling new construction, including the control of outside contractors.
- Update operations procedure manuals after each modification which results in a change in operating procedure.
- Review and follow through expeditiously on all inspection recommendations from insurance agencies.

Other Management Programs

Incorporate these features into the comprehensive management program for loss prevention and control:

- Welding, cutting and other "hot work" permit programs.
- A program of supervision of impairments of fire protection equipment using AXA XL Risk Consulting's "RSVP" program.
- Smoking regulations.
- Plant security and surveillance.

Duplication of Facilities

Provide multiple process trains rather than a single larger train. Design each unit to facilitate prompt repair using readily obtainable or pre-purchased parts. Where neither approach is feasible, store the liquid air fractions in sufficient quantity to permit normal operations until repair or replacement is complete.

Install spares of equipment that is highly susceptible to loss or very important for continued operations. If this is not possible, keep readily available spare parts and maintain them ready for use. Physically separate or compartmentalize duplicated equipment. Carefully maintain spare parts for equipment known from loss experience to be critical.

Location

Locate the air plant (or at least the air intakes) upwind of as many of the potential sources of contaminants as possible. Where necessary, install multiple air intakes.

Construction

Construct buildings of noncombustible materials.

Use only cooling towers that are rated noncombustible by a nationally recognized testing laboratory.

Exclude all combustible materials from the cold box. Restrict insulation materials to those containing no more than 0.5% by weight of combustible material (for example, oil or synthetic resin). Purge the insulation fill volume of the cold box continuously with nitrogen.

Do not support any process equipment with wood blocks. Use cement or some type of concrete for this purpose.

Do not use aluminum as the packing material for liquid oxygen distillation columns.

Sprinklers

Protect compressors with water spray or deluge sprinklers as outlined in NFPA 15 and PRC.12.2.1.2.

Protect combustible cooling towers with waterspray or deluge sprinklers in accordance with NFPA 214.

Provide buildings with sprinkler protection in accordance with NFPA 13 and PRC.12.1.1.0.

Supervision

Relay all process instrumentation abnormal conditions signals and all fire protection supervisory signals and alarms to a constantly attended location. If the site is unoccupied, arrange for the availability of local personnel who can be dispatched in the event of a trouble signal.

Supervise the intake air and the process stream continuously with nondispersive infrared analyzing systems.

Operations

Air Intakes

Interlock the monitoring systems to automatically open the air intake receiving the cleanest air and to close all others.

Compressors

Reduce the buildup of hydrocarbons from the breakdown of lubricating oils used in the air compressors by any or all of the following means:

- Use only high-grade oil.
- Use oil in minimum quantity.
- Use glass fiber reinforced Teflon rings.
- Use compressors with low compression ratios (less than 4 to 1) and provide intercoolers between each compression stage to keep gas temperatures low, but not below the dew point of the gas.
- Clean the discharge piping from the compressors periodically to remove any oil film, using soap, not solvents.
- Use synthetic lubricants of the phosphate ester type, such as tricresyl phosphate.

Filtration

If oils are used in an air compressor, install an oil removal system of the alumina or carbon bed type immediately downstream.

Adsorption

Install paired silica gel adsorbers with automatic regeneration at the following points.

- In the line moving liquid from the bottom of the high pressure column to the low pressure column.
- In a line recirculating liquid oxygen from the bottom of the low pressure column.
- Upstream of any expansion engine.

Size the adsorbers so that either half of each pair can handle the full flow rate while the other is being regenerated.

Establish regeneration and replacement frequencies based on the measured concentration of contaminants so as to prevent saturation of the silica gel.

Oxidation

In the event that contamination is particularly heavy, leading to overloading of the silica gel adsorbers, install a catalytic oxidizer between the last compression stage and the first cooler.

Cold Boxes

Design and construct cold boxes so that any auxiliary vaporizer or acetylene separator is housed in a separate, easily accessible section.

Provide all cold boxes with interlocked systems to purge and drain the unit as needed.

Shutdowns

Monitor the unit continuously for the presence of potentially explosive contaminants in accordance with Table 1. Install interlocks to sound an alarm and increase the liquid oxygen removal rate, if safe levels are exceeded by 100%. Arrange the interlocks to shut down, purge, and drain the unit if these levels are exceeded by 1000%. To prevent the concentration of potentially explosive contaminants as cryogenic liquids evaporate, maintain continuous monitoring of the liquid oxygen in the low pressure column during normal shutdowns unless and until it is brought up to room temperature or completely purged. In the event that the detected concentrations approach dangerous levels, purge and drain the unit.

TABLE 1

Contaminant Monitoring Parameters

Contaminant	Safe Level	Alarm	Shutdown
Total hydrocarbons	50 ppm	100 ppm	500 ppm
Acetylene	0.01 ppm	0.02 ppm	0.1 ppm
Ozone	0.2 ppm	0.4 ppm	2.0 ppm
Oxides of nitrogen	0.01 ppm	0.02 ppm	0.1 ppm

Oxygen Storage

Locate oxygen storage tanks at least 50 ft (15 m) from buildings and other process equipment.

Oxygen Disposal

Never drain large quantities of liquid oxygen into the operating area. Use one of the following disposal schemes instead:

- If a large natural area such as a lake, large field, etc. exists nearby and an inspection indicates it to be free of combustible materials, run a drain line to the area. Locate the drain line outlet at least 100 ft (30 m) so that clouds of cold oxygen vapors will not drift back into the operating area. Do not pipe the drain through an oily trench or adjacent to other piping that could present a hazard if a liquid leak occurred.
- Vaporize the liquid oxygen in a heat exchanger or by direct contact against steam or water, as it drains by gravity from the low-pressure column and condenser. Pipe the gaseous outlet from this exchanger at least 25 ft (8 m) upward to prevent fogging and concentration of oxygen at ground level. Establish an adequate flow of steam or water prior to the draining operation.
- Drain the liquid by gravity into an uninsulated storage tank of sufficient capacity to contain the inventory from the low-pressure column and condenser. Locate this tank at least 50 ft (15 m) from the operating area.

If it becomes necessary to drain a plant because the maximum allowable operating limit for acetylene or hydrocarbon in the reboiler has been reached, use one of the first two methods only. Contaminants can be further concentrated in a drain tank.

AIR COMPONENTS AND CONTAMINANTS

COMPONENTS OF AIR

The major problems in air liquefaction systems come from the fact that air is not a mixture of only nitrogen, oxygen and the rare gases. It also contains appreciable amounts of water vapor and carbon dioxide and contaminants. Materials other than nitrogen, oxygen, carbon dioxide, water vapor, and the noble gases are considered contaminants. Table 1 lists physical data on the normal constituents of air and air contaminants.

In a moist, warm climate, water vapor can be as much as 4% of the volume of air. Carbon dioxide concentration averages about 300 parts per million (ppm) in open country. This may increase to 700 ppm – 800 ppm in industrial areas. Another normal constituent of air is hydrogen. This, however, is normally present in a concentration of about only 5 ppm.

The removal of residual water vapor and CO_2 in regenerators or exchangers also removes all but traces of compounds that boil above 90°F and freeze above -270°F (-168°C). The net result is that hydrocarbons such as butane and butylene and those of lower molecular weight (except butadiene and methyl acetylene) would pass through the exchangers as would CO, NO, O_3, N_2O, and traces of CO_2. At this stage, the "simple" system for separating nitrogen and oxygen is working on a gas that may contain as many as 20 different components.

In addition to gaseous components, the stream may also contain frozen mists of ice, dry ice, and high-boiling contaminants such as lubricating oil.

In the absence of additional means for separating all the possible components of the air stream, the course they take is easy to follow. Helium, hydrogen, neon, some of the carbon monoxide and a little of the argon go along with nitrogen. Some of the carbon monoxide, most of the argon and essentially all of the other components go with the oxygen and wind up in the pool of boiling oxygen at the bottom of the upper column. Since air is approximately ⅕ oxygen and a ⅘ nitrogen, the concentration of components in this boiling oxygen is five times greater than the concentration of the same components in the cold air entering the columns.

The components concentrated in the boiling oxygen pose various degrees of danger: argon, krypton and xenon are inert and present no hazard. Carbon monoxide that does not go with the nitrogen from the lower column goes off with the nitrogen from the upper column because its boiling point is above that of liquid oxygen. Carbon dioxide, if present, probably exists as solid dry ice. The organic materials, oxides of nitrogen, and ozone exist in a dissolved and diluted state except as discussed later.

Table 1 gives the solubilities of various contaminants in liquid oxygen. Some of these are low. This is important because if organics precipitate out, the resulting mixture of solid organic material with liquid oxygen is explosive. Acetylene is the only organic material with sufficiently low boiling and freezing points and low solubility in liquid oxygen to cause this problem even though found in air in trace amounts only.

TABLE 1

Properties of Components of Air

Material	Formula	Normal Boiling Point °F[2]	Freezing Point °F[2]	ppm Solubility In Liquid Oxygen At -297°F
Helium[1]	HE	-452	----	
Hydrogen[1]	H_2	-423	-431	
Neon[1]	NE	-411	-416	
Nitrogen[1]	N_2	-321	-346	
Carbon Monoxide	CO	-313	-341	
Argon[1]	A	-303	-309	
Oxygen[1]	O_2	-297	-361	
Methane	CH_4	-259	-296	980,000
Krypton[1]	KR	-244	-251	
Nitric Oxide	NO	-241	-263	
Ozone	O_3	-169	-314	
Xenon[1]	XE	-163	-169	
Ethylene	C_2H_4	-155	-272	23,000
Ethane	C_2H_6	-128	-298	220,000
Nitrous Oxide	N_2O	-127	-132	70
Acetylene	C_2H_2	-119(Sublimes)	-115	5.6
Acetylene	C_2H_2	-119(Sublimes)	-115	1.7[3]
Carbon Dioxide[1]	CO_2	-70(Sublimes)[4]	-70[4]	
Carbon Dioxide[1]	CO_2	-109	-110	
Hydrogen Sulfide	H_2S	-75	-122	50[3]
Sulfide	COS	-58	-218	28
Propylene	C_3H_6	-54	-301	2,500[3]
Propane	C_3H_8	-44	-306	56,000
Formaldehyde	CH_2O	-6	-180	
ISO-Butane	C_4H_{10}	11	-256	180
ISO-Butylene	C_4H_8	20	-221	125
Butene -1	C_4H_8	20.7	-303.43	1,000
1,3 Butadiene	C_4H_6	24	-164	20
N-Butane	C_4H_{10}	31	-217	150[3]
Oxide	C_2H_4O	51	-168.3	50.0
ACETaldehyde	CH_3CHO	70	-191	0.4[3]
Dioxide	NO_2	70	16	15
N-Pentane	C_5H_{12}	97	-204	20[3]
Pentene	C_5H_{10}	88	-	220
Acetone	CH_3COCH_3	134	-137	1.5[3]
Methanol	CH_3OH	147	-144	12[3]
N-Hexane	C_6H_{14}	156	-138	2[3]
Ethanol	C_2H_5OH	173	-178	15[3]
Benzene	C_6H_6	176	42	4[3]
N-Decane	$C_{10}H_{22}$	345	-24	12

SI UNITS: °C=5(°F-32)/9

NOTES:
1. Normal Components
2. To Nearest Degree
3. At –320°F
4. At 5.2 Atmospheres Pressure

ACETYLENE CONTAMINATION

Although most of the solubilities given in Table 1 have been determined rather recently, it was reasoning along these lines that gradually placed the blame for early oxygen plant explosions on the presence of trace amounts of acetylene in the intake air. Since the early use of oxygen was mostly in connection with welding, oxygen plants were frequently installed close to acetylene plants so that both oxygen and acetylene could be bottled and sold on the same premises. Accordingly, the first steps taken to prevent explosions were to provide air intakes for the oxygen plants at points where they would be unlikely to draw in acetylene.

When followed, these precautions were usually adequate to prevent explosions in high-pressure plants. Infrequently, however, plants exploded when there was no acetylene leakage nearby. After much searching, it was believed that acetylene was still the cause. In these cases, however, it may have originated inside the air plant. The theory is that the air compressors were to blame. When they ran hot enough they could cause the lubricating oil to break down and one product of oil cracking is acetylene.

With a low-pressure tonnage plant, considerations of heat efficiency made it desirable to draw off the oxygen as a gas so that the heat of vaporization of the oxygen could be used for refrigeration with maximum efficiency. This meant that any dissolved impurities would gradually concentrate in the liquid. Since the solubility of acetylene in liquid oxygen at the normal temperature in the upper column is approximately 5 ppm, exceeding this concentration in the upper column would cause a build-up of solid acetylene as a slurry in the oxygen or as particles floating on it. In fact, an acetylene concentration less than this could cause trouble because a solution of acetylene in liquid oxygen behaves like a solution of ordinary salt in water. Even though the solution is not saturated, solid forms at the gas-liquid interface where the liquid surface touches the walls of the container and solid crystals gradually creep up and encrust the container walls.

Crystals of 100% acetylene are lighter than liquid oxygen and, consequently, float on the surface. Crystals of 100% nitrous oxide (N_2O) are heavier than liquid oxygen and will sink. Also, nitrous oxide can cocrystallize with acetylene and if these cocrystals contain sufficient nitrous oxide they will also sink. For example, a mixed crystal of 70% N_20 and 30% C_2H_2) will sink. Such a mixed crystal can detonate in liquid oxygen if it contains enough acetylene. It was also found that on long contact with liquid oxygen, nitrous oxide leaches out preferentially, making the mixed crystal richer in acetylene. In an investigation following an explosion in the reboiler of a low-pressure oxygen column, it was found that the mixed crystal containing 60% nitrous oxide and 40% acetylene could explode with extreme violence even though accumulated in only a thin layer at the bottom of the reboiler. Such a mixed crystal would be heavier than liquid oxygen.

It is also known that cocrystals of carbon dioxide and acetylene can be heavier than liquid oxygen but any such crystal which sinks in liquid oxygen cannot be exploded in contact with liquid oxygen and crystals containing 40% CO_2 float in liquid oxygen. It was specifically noted in the investigation that mixed crystals containing 40% or more CO_2 failed to explode in liquid oxygen.

Examples of all these properties are given in Tables 2, 3, and 4.

The other route that might admit acetylene to the system is into the upper column from the air stream cooled by expansion engines. This cooling may be direct, air expanding through the engine and entering the upper column; or indirect, waste nitrogen from the top of the lower column expanding through the engine and cooling the air by heat exchange. This latter system has the advantage of eliminating all worry about expansion engine lubricant getting into the liquid oxygen. This is discussed later.

TABLE 2

Relative Density Of Nitrous Oxide
Acetylene Mixtures And Liquid Oxygen (LOX)

Mixture			
% N_2O	% C_2H_2	Temp. C.	Observation
100	0	-183	Sank in LOX Additional pure solid C_2H_2 added floated to the surface leaving clear liquid between heavy N_2O & light C_2H_2.
50	50	-183	Some floated and some sank in LOX
30	70	-183	Floated in LOX
70	30	-183	Sank in LOX
100	0	-196	Sank in LOX
75	25	-196	Sank in LOX
67	33	-196	Sank in LOX
58	42	-196	Suspended in LOX
50	50	-196	Floated in LOX
67	33	-183	Sank in LOX
58	42	-183	Sank in LOX
50	**50**	**-183**	**Suspended in LOX**

TABLE 3

Detonation Of Nitrous Oxide
Acetylene Mixtures In Liquid Oxygen (Lox)

% N_2O in Mixture	Ignition Source	Explosion
50	Squibb	Detonation
75	Squibb	Failure
75	Squibb	Detonation
56	Squibb	Detonation
70	Squibb	Detonation
80	Squibb	Failure
0	Squibb	Detonation
LOX only	Cap	Failure

NOTE: This table shows that N_2O - C_2H_2 mixtures containing less than 75% N_2O can detonate when immersed in liquid oxygen.

TABLE 4

Relative Densities Of Carbon Dioxide
Acetylene Mixtures And Liquid Oxygen

Mixture		
% CO_2	%C_2H_2	Observation at-183°C
0	100	Floated in LOX
100		Sank in LOX
50	50	Suspended
29	71	Floated in LOX
71	29	Sank in LOX

NOTE: The data in this table help explain explosions in reboilers of oxygen columns when it is found that the explosion took place at or near the bottom of the reboiler.

It is common practice to pass the air through adsorbers before it goes to the engine and the upper column. The major purpose is to remove CO_2, which would foul up the expansion engine. At this stage, the air has been cooled in the exchangers or regenerators so the adsorbers are very efficient and remove most acetylene as well as the CO_2. However, these adsorbers are working on gas rather than liquid and more acetylene undoubtedly gets into the upper column by this route than by way of the liquid air route. When air is cooled by interchange with the exhaust from an expansion engine operating on nitrogen, the supercooled air is usually introduced into the high-pressure column.

Now consider further the case where the air goes through an expansion engine and into the upper column. To insure that this stream will liquefy promptly in the column and that too great a proportion will not go off as gas, particularly when starting up, a side stream of gas from the lower column is often added to the stream going to the expansion engine. Although this side stream comes from a point in the process where the air has been partially liquefied by expansion and/or by giving up heat to boil the liquid oxygen in the upper column, experience has been that it can still contain acetylene. Practice has been to take this side stream from a point low on the lower column where the gas is relatively rich in oxygen. However, it appears that acetylene is not completely dissolved at this point and that it is safer to take gas richer in nitrogen from a point high on the lower column, where the gas has been washed free from acetylene by nitrogen reflux.

CONTAMINANTS OTHER THAN ACETYLENE

Other than acetylene, there are few dangerous compounds that boil below 90°F (32°C), and have low solubility in liquid oxygen. These include butadiene, acetaldehyde and possibly formaldehyde, about which solubility data are lacking. However, all of these have higher molecular weights than acetylene and should be removed even better than acetylene by silica gel adsorbers.

Turning to the hydrocarbons that are fairly soluble in oxygen, experiments show that these mixtures have definite explosive limits just as flammable vapors do in air. In other words, there is a lower limit concentration that must be reached before an explosion can be initiated. Similarly, an upper limit mixture, too rich to explode, can be prepared with methane in liquid oxygen, or, under pressure, with ethane in liquid oxygen.

Table 5 gives the flammability limits of various gases and vapors in air. The first column shows these limits expressed as "mole %"; the second as "mole %" with the assumption that the hydrocarbon exists as methane (methane basis). This concept is valuable since analysis of total hydrocarbon content, by combustion methods, can be readily related to theoretical methane content.

The experiments made to determine the explosive limits of hydrocarbons dissolved in liquid oxygen showed about 11 mole % as the lower limit for methane and about 4 mole % (8 mole % on a methane basis) as the lower limit for ethylene. The lower limits are higher in liquid oxygen than in air. This is probably because a portion of the heat of combustion, in the case of liquid oxygen, must be used in raising the temperature of the cold mixture to a point where it can react. In any case, it would appear that use of the gas phase limits would provide a margin of safety. On this basis, using the approximation that the lower limit expressed as methane is at least 5 mole %, a value of 500 ppm of soluble hydrocarbons expressed as methane in the liquid oxygen represents a safety factor of at least 100 to 1.

TABLE 5

Flammability Limits Of Various Gases In Air

Compound	Formula	Lower limit (mole %)	Lower limit (mole %, methane basis)
Methane	CH_4	5.00	5.00
Ethane	C_2H_6	3.00	6.00
Propane	C_3H_8	2.12	6.36
Butane	C_4H_{10}	1.86	7.44
Pentane	C_5H_{12}	1.40	7.0
Hexane	C_6H_{14}	1.18	7.08
Nonane	C_9H_{20}	0.83	7.47
Decane	$C_{10}H_{22}$	0.77	7.7
Ethylene	C_2H_4	2.75	5.5
Propylene	C_3H_6	2.0	6.0
Butene-1	C_4H_8	1.65	6.6
Acetylene	C_2H_2	2.30	5.0
Toluene	$C_6H_5\text{-}CH_3$	1.27	8.9
Benzene	C_6H_6	1.4	6.4

Besides hydrocarbons of varying solubility, other substances have been tested for their explosion hazard in liquid oxygen. Lubricant mists solidify and form slurries. Slurries of ordinary lubricating oil, tri-cresyl phosphate lubricant (Pydraul or Cellulube) and polyethylene glycol lubricant (Ucon) were all explosive although these synthetic lubricants are normally considered low hazard fluids. A fluorocarbon lubricant slurry, however, was non-explosive. N_2O and NO_2 gases can be exploded but were not explosive when slurried with liquid oxygen. However, a complex of N_2O and acetylene forms an explosive slurry. Ozone gas can be exploded at concentrations above about 9 mole %. Solutions of ozone in oxygen cannot be exploded but at concentrations above 17.6 mole % a second phase consisting of ozone dissolved in oxygen separates out. This ozone-rich phase is explosive. Chances of accumulating this much ozone in an air liquefaction plant are negligible. However, traces of ozone will cause explosion of an acetylene-oxygen slurry and ozone in appreciable quantities might cause some lowering of the lower explosive limit of hydrocarbon oxygen mixtures. Traces of ozone do not cause explosion of a slurry of ethylene in liquid oxygen.

COUNTERMEASURES

The low-pressure column contains a pool of liquid oxygen at the bottom. Therefore, as noted previously, hydrocarbon contamination, particularly acetylene, presents a hazard. Despite all safeguards and controls placed in the system prior to this point, some contamination and, therefore, some hazard may exist. To run the plant and keep it from being severely damaged or destroyed by explosion, it is imperative to know the extent of contamination.

Recording nondispersive infrared analyzers can determine a particular hydrocarbon, such as acetylene, or measure total hydrocarbons on a continuous basis. Generally, for air intakes, a sample of air is catalytically oxidized to convert all hydrocarbons to CO_2. As CO is a much stronger absorber of infrared radiation than hydrocarbons and, since a mole of hydrocarbon heavier than methane will produce two or more moles of CO_2, a much more accurate determination of total hydrocarbons in the air can be made. If the air contains some CO_2, a sample can be taken and passed through a reference cell in the analyzer without oxidation. In this way only the increase in CO_2 due to hydrocarbon contamination in incoming air is recorded. This valuable tool can then be used to monitor the level of hydrocarbon contamination entering the plant. Better decisions can then be made about when to shut down, which air intake to use (if there is a choice) and how much purge from the column in the form of liquid oxygen is needed to keep the system safe.

Other methods of analysis prove valuable, such as the Ilosvay calorimetric test for acetylene—a very accurate but fairly time-consuming test (about 30 min). Also, chromatography is being used in some plants to obtain a very accurate analysis of all contaminants in the liquid oxygen. Analyzing a sample with this method takes at least an hour. A frequency of 8 analyses per hour has been reported for an automatic hydrocarbon analyzer using a hydrogen flame ionization detector that is able to detect hydrocarbons, including acetylene, has been reported. In addition, mass spectrometry is often used, but generally as a check for other more rapid means of analysis.

The question naturally follows: If one knows the level of contamination in the liquid oxygen, at what level is action taken and what action is taken?

Some plants operate at 50 ppm total hydrocarbons and less than 0.01 ppm acetylene. If either of these safely low figures rise 50% to 100%, the contamination is reduced, generally by increasing the removal rate of liquid oxygen from the low-pressure column. If this does not reduce the level of contamination, the plants are shut down and liquid oxygen drained.

It is generally accepted that a concentration of acetylene of 0.5 ppm or a total hydrocarbon concentration of 500 ppm is the maximum safe operating level. Many use lower figures and a few slightly higher, but most agree that if acetylene and/or hydrocarbon concentrations rise rapidly and cannot be reduced just as rapidly, it is unwise to continue operating the plant. Every plant should have a specific figure of contamination which, when reached, requires mandatory plant shutdown.

In case of a planned shutdown not due to contamination, there is a very wide divergence of opinion as to how long the unit should be allowed to remain cold before purging. The variation is from 15 min to 5 weeks; however, a majority feels that a shutdown of less than 8 h does not require purging of liquid but one in excess of 24 h does. During a cold shutdown, nitrogen from the trays in the upper column drains down into the liquid oxygen pool at the base. This dilutes the oxygen and raises the liquid level. As time passes, the nitrogen in the liquid will evaporate again, enriching the liquid in oxygen and lowering the level. When the plant is restarted, the liquid level drops sharply as the trays are refilled. During this process, if contaminants (particularly acetylene) with fairly low solubilities are present, they may be deposited as solids on the walls of the column and could then explode. Therefore, the time a plant can remain shut down with liquid in it is a function of the degree of contamination, hence routine analysis of the liquid oxygen in the low-pressure column must continue during each shutdown.

Ozone, if present in sufficient concentration, could serve as a sensitizer and initiator for an explosion of hydrocarbons present in the oxygen. However, appreciable quantities have not been detected in air plants, specifically in the liquid oxygen reservoir. The effect of the oxides of nitrogen is not very predictable. They can sensitize and also inhibit explosions. Generally if present in concentrations of from 0.2 to 2 parts per million, it is not believed any hazard is present. Nitric oxide (NO) and dienes have been known to react with explosive violence. It is believed that reduction of NO content to less than 0.1 ppm will prevent any difficulty.

Until recently the hazards of combustible materials inside the column was assumed to be limited to hydrocarbons and other materials that entered the column as part of the incoming air stream. However, aluminum packing has recently become part of column interiors. Although it was known that aluminum would burn in the presence of pure oxygen, it was assumed that there was not sufficient initiation energy available to start the fire. Several fires have proven that this is not true.