

ASU REBOILER/CONDENSER SAFETY

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1. ABSTRACT

This paper presents the principles to safely operate reboilers within Air Separation Units (ASU's). Two types of reboilers are used in ASU's: thermosyphon and downflow. The features of each are discussed, focusing on the safety aspects. The vast majority of ASU reboilers are Brazed Aluminum Heat Exchangers (BAHX's), because of their high performance.

The general potential reboiler hazards are

- accumulating trace contaminants in the oxygen enriched liquids processed by the reboiler
- the possibility that the BAHX itself may react with the oxygen.

The specific hazards that may occur within an ASU are identified, along with the simple methods to abate these hazards. Good operating practice is to verify each abatement method during operation.

This history of reboiler incidents is summarized.

Following the abatement and verification methods described in this paper will enable safe operation of both thermosyphon and downflow ASU reboilers.

2. ASU PROCESS DESCRIPTION

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 simplified 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 adsorbent bed, 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. A few trace contaminants, however, do get through the PPU. These can create potential safety hazards, and will be discussed in much more detail throughout this paper.

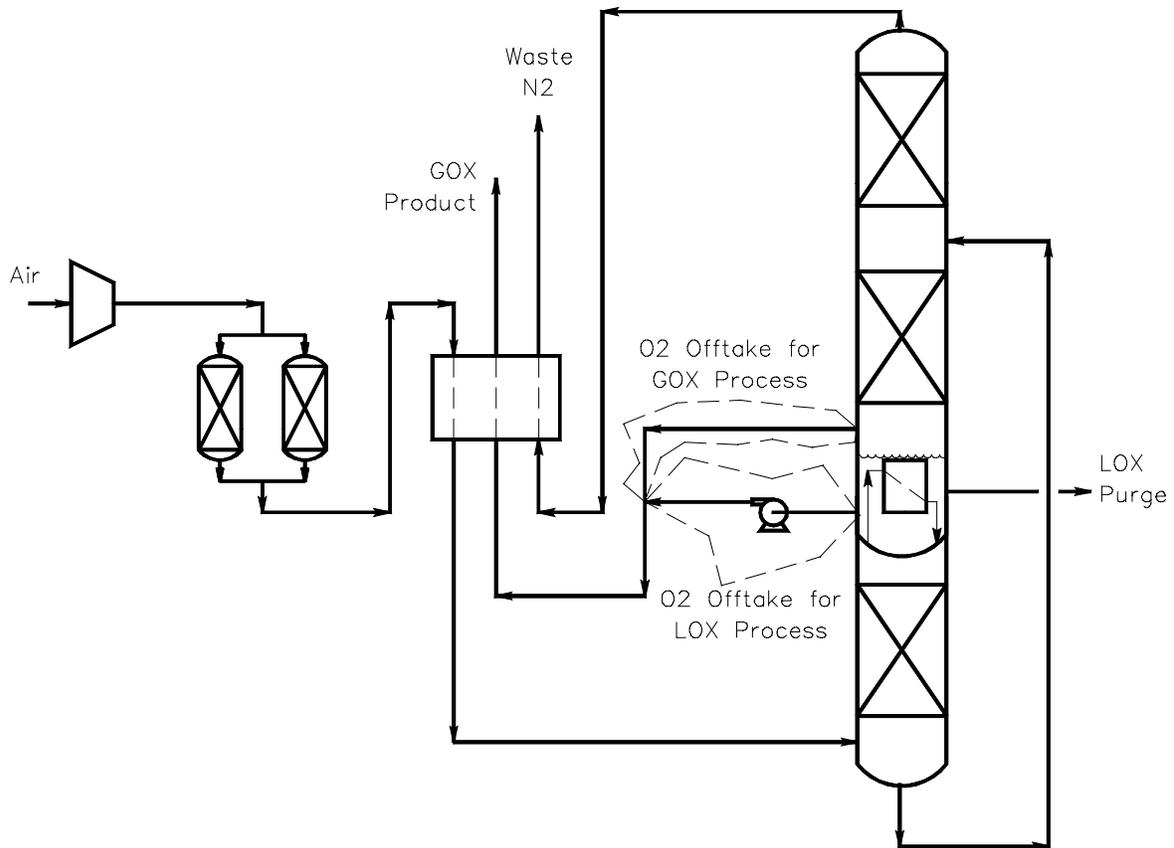


Figure 1
Simplified ASU Flowsheet

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).

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", gaseous oxygen (GOX) 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 liquid oxygen (LOX) is taken 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. There are some specific hazards associated with boiling O_2 in BAHX's at high pressure. These are discussed in detail in reference 1.

When only N_2 is desired as a product, a simpler process is used (Figure 2). Gaseous nitrogen (GAN) is taken directly from the top of the HP column. The LP column is removed, and the liquid from the bottom of the HP column is reduced in pressure, and it is boiled against condensing N_2 from the HP column. Because there is no LP column, the waste stream from the reboiler is approximately 40% O_2 . (In other configurations of N_2 generators, a partial LP column is added. In these plants, the maximum waste O_2 purity is approximately 70%.) The advantage of using N_2 generator cycles is that they are more capital efficient and produce N_2 at elevated pressures (3 to 15 bara), with the disadvantage of not producing high purity O_2 .

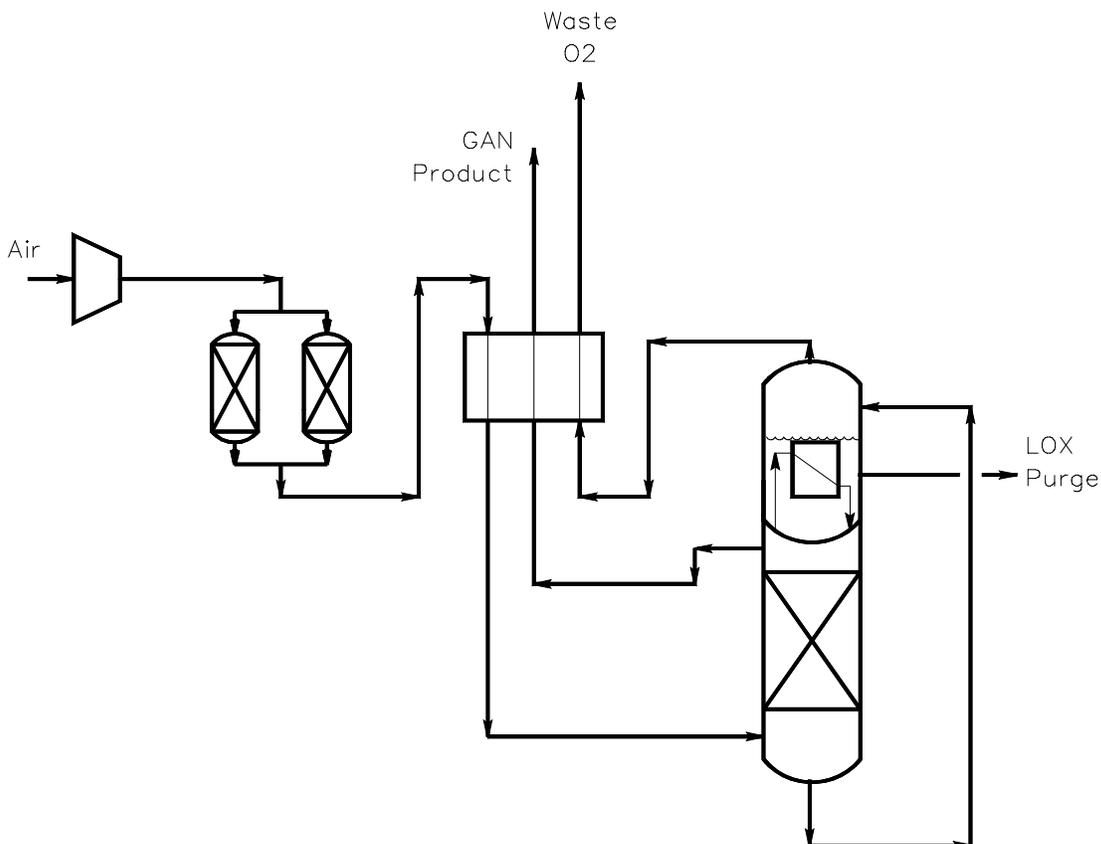


Figure 2
Nitrogen Generator Flowsheet

The processes above use adsorption based PPU's to remove water, carbon dioxide, and many hydrocarbons. PPU's have been used for over 25 years. Another technology for removing these trace components is the Reversing Heat Exchanger (REVEX). This technology is not used in plants designed today; however there are

many of them still in operation. The special features of those plants are discussed in Appendix 1.

3. COMPOSITION OF AIR

3.1 Categories of Contaminants

Air contains three basic components: oxygen, nitrogen, and argon. However, there are many trace contaminants in air. These have been categorized into the potential problems that they create in an ASU (Table 1, ref 2):

Plugging Contaminants: These can precipitate out of either vapor or liquid phases, creating solids which can block process equipment.

Reactive Contaminants: These components, if they concentrate to sufficient levels, can react with oxygen, each other, or components within the process.

Corrosive Contaminants: These will react with the process equipment, and can weaken equipment items until they cannot contain the process pressure. These are dealt with in other equipment items, and will not be discussed further in this paper.

Light Contaminants: These components concentrate in the nitrogen or waste products. They are typically not a safety problem, and will not be dealt with in this paper.

Table 1
Trace Contaminants in Air

Main Components	Plugging Contaminants	Reactive Contaminants	Corrosive Contaminants	Light Contaminants
O ₂	H ₂ O	CH ₄ , C ₂ H ₂ , C ₂ H ₄ ,	SO ₂	H ₂
N ₂	CO ₂	C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ ,	SO ₃	He
Argon	N ₂ O	C ₄ ⁺ , O ₃ , NO _x	H ₂ S	Ne
	NO _x	Haze from forest fires (ref 3,4)	Cl ₂	
			HCl	
			NH ₃	

3.2 Special Hazards of Specific Contaminants

Four contaminants deserve special mention due to their specific hazards:

Acetylene (C₂H₂) – Acetylene is only slightly soluble in LOX. At typical reboiler conditions, a solid will precipitate out of solution if the concentration exceeds about 4 ppm. Solid acetylene is shock sensitive, and requires only a slight amount of energy to ignite. Fortunately, the adsorbents within PPU's remove 100% of the acetylene in the air, eliminating this contaminant as a hazard within ASU's. However, in reversing heat exchanger plants (REVEX), acetylene enters the coldbox, and must be removed by a combination of liquid phase adsorption and LOX purge (see Appendix 1). While in principle it would be acceptable to have up to 2 ppm acetylene (50% of its solubility in LOX), Air Products takes action whenever acetylene reaches 0.3 ppm, which is slightly above the Lower Detectable Limit (LDL). This is because the normal operation of an ASU should keep acetylene below these values, and if the concentration rises, the ASU is running abnormally, and action should be taken.

While beyond the scope of this paper, acetylene has been reported to form a solid solution with N_2O , which can explode, and one serious ASU incident has been attributed to this compound (ref 5).

Propane (C_3H_8) – Propane has a very low relative volatility when compared to O_2 , so it can rapidly concentrate in LOX. At reboiler operating conditions, it will form a second liquid phase at approximately 15,000 ppm. This second liquid phase is very propane rich, and can react with the bulk liquid oxygen. Propane is only partially removed by a PPU, so ASU design and operation must consider how to deal with propane. Also, the general neighborhood of an ASU should be surveyed for any propane sources, including propane powered equipment and heaters.

CO_2 and N_2O – These are plugging compounds, with relatively low solubility in LOX (7 and 250 ppm, respectively, at typical reboiler operating conditions.) If these compounds exceed their solubility, they will form a solid. This solid is inert in LOX, so it is not directly a safety hazard by itself. However, if the solid forms within reboiler passages (as it is possible to do, because that is where the liquid concentrates), then the passage can become partially or totally blocked. These can create conditions for pool or dry boiling, which can in turn, lead to hydrocarbon concentrations above the allowed limit.

Experimental work has shown that CO_2 and N_2O can create a solid solution, when both are present in relatively significant quantities (when expressed as a % of solubility). (ref 16 and 7) This is significant in operating plants, because when both CO_2 and N_2O are present, a solid will form more readily than if either was present in the same concentration by itself. This must be taken into account when setting the allowable concentration limits of these components.

4. TRACE CONTAMINANT REMOVAL WITHIN THE ASU PROCESS

As mentioned above, there are many trace contaminants within air. These are typically present at less than a few ppm. However, given the large volume of air processed within a typical ASU, up to several kg per day of some of these components will pass through the ASU. It is therefore vital to deal with these components to prevent safety and/or operating problems (ref 8, 9)

It is important in the design and operation of an ASU that the background composition of the air is known. Special care must be taken to identify any sources of potentially hazardous contaminants within a few kilometers of the ASU, and also if new sources are built after the ASU is operating. Typical “worst case” ambient concentrations are given in ref 2, which may be used for design.

Modern ASU's use adsorption PPU's to remove most contaminants prior to the air entering the coldbox. The typical adsorbents remove all of the trace contaminants in the air, except the following:

<u>Component</u>	<u>Amount Removed by PPU</u>
CH ₄	0%
C ₂ H ₆	0%
C ₂ H ₄	30-70%
C ₃ H ₈	30-70%
CO ₂	99.99+%
N ₂ O	30-100%

The variation in amount removed depends on the specific PPU design and operation.

Once the trace contaminants enter the coldbox, they can concentrate by the following mechanisms, because they all boil at temperatures above oxygen (except for the light contaminants: H₂, He, and Ne, which leave in a N₂ or waste stream):

- **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. The most hazardous situation here is if the less volatile components form a solid when the oxygen is boiled away, because solids tend to adhere to equipment and remain within the ASU process.
- **Pool-boiling** is similar to dry-boiling, but differs because fresh liquid is continually added to the “pool”. The less volatile components are concentrated as the more volatile components are vaporized. This is also called “pot boiling”.
- In **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.

As air is distilled into O₂ and N₂ products, the trace contaminants eventually enter the low pressure column, and concentrate in the oxygen rich liquid around the reboiler condenser. The degree of concentration is controlled by the amount of liquid oxygen production removed from the reboiler sump. To prevent the trace contaminants from concentrating to unsafe concentrations, a liquid stream must ALWAYS be taken from the low pressure column sump, even if liquid production is not required for any other reason. Equation 1 describes the concentration of high boiling components in the liquid oxygen in terms of a concentration factor (γ).

$$\gamma_{\text{Trace contaminant}} \equiv \frac{x_{\text{Trace contaminant, LOX}}}{y_{\text{Trace contaminant, Feed}}} = \frac{F_{\text{feed}}}{F_{\text{LOX}} + K_{\text{Trace contaminant}} F_{\text{GOX}}} \quad (1)$$

where

- x = mole fractions of the indicated component in liquid phase
- y = mole fractions of the indicated component in vapor phase
- F = the molar flow rate
- K = equilibrium ratio y/x for the indicated component.

For the pumped LOX process, the entire oxygen product is taken as liquid ($F_{GOX} = 0$ and $F_{LOX} = 20\%$ of the air), so the concentration factor is about 5 for all species. However, for the "GOX" process, where LOX is only produced for purge, it is necessary to consider the species separately. For typical process, where $GOX = 20\%$ and the LOX purge is 0.2% of the air, and the equilibrium constant K is essentially 0, the concentration factor is 500, which is significantly higher than for the pumped LOX process. The concentration factors for the most common contaminants of air are given in Table 2 at the end of this paper (see also ref 8). Note that methane has a relatively high K -value of 0.3, so it is the only hydrocarbon which will leave in substantial quantities with the GOX.

5. GENERAL SAFETY CONSIDERATIONS

Air Products has a simple three-step philosophy for handling process safety risks:

Identify the Potential Hazard - This is accomplished through rigorous procedures, including design HAZOP's and Operational Readiness Inspections.

Abate the Hazard - Install one or more countermeasures to ensure that the potential hazard does not actually occur.

Verify the Abatement - Have a process or procedure in place which verifies that the abatement is working as intended.

This methodology is applied in ASU reboilers to minimize the safety risks.

5.1 General Safety Guidelines

Two general guidelines are used in setting up abatement methods:

1) *The maximum allowable total hydrocarbon concentration is 450 ppm, when expressed as CH_4 equivalent.* (CH_4 equivalent is the sum of each component, multiplied by the number of carbon atoms in the molecule. For example, 20 ppm of propane is 60 ppm of CH_4 equivalent). This rule is used for two reasons:

- Total Hydrocarbon (THC) analyzers are used to monitor hydrocarbon concentration in the reboiler sump. THC analyzers are relatively simple instruments to operate and maintain. The alternative is to use gas chromatographs, which while they give the breakdown of individual components, are more difficult to operate.
- All hydrocarbons have the approximately the same LFL (Lower Flammability Limit), when expressed as CH_4 equivalent, i.e., between 5 and 10% (50,000 and 100,000 ppm). This makes it easy to know when one is approaching an unsafe concentration, without knowing exactly which species is present. (See Table 3, which is taken from reference 10)

Table 3
LEL of Hydrocarbons in GOX (ref 10)

Component	LFL (ppmv)	LFL (ppmv CH ₄ Equivalent)
CH ₄	50,000	50,000
C ₂ H ₆	30,000	60,000
C ₃ H ₈	21,200	63,600
C ₄ H ₁₀	18,600	74,400
C ₅ H ₁₂	14,000	70,000
C ₆ H ₁₄	11,800	70,800
C ₉ H ₂₀	8,300	74,700
C ₁₀ H ₂₂	7,700	77,000
C ₂ H ₄	27,500	55,000
C ₃ H ₆	20,000	60,000
C ₄ H ₈	16,500	66,000
C ₂ H ₂	25,000	50,000
C ₇ H ₈ (toluene)	12,700	89,000
C ₆ H ₆ (benzene)	14,000	64,000

Note that the limit of 450 ppm gives a safety factor of approximately of 100 on the LFL.

2) *The maximum allowable concentration of any component in a fluid is 50% of its solubility.* This ensures that the component does not precipitate as a solid or create a second immiscible liquid phase, which could then concentrate or collect, creating safety problems. The 50% limit allows for uncertainties in thermodynamic data or variations in the process operation, relative to design.

6. REBOILER/CONDENSERS

The reboiler/condenser thermally integrates the distillation system. It condenses nitrogen vapor from the high pressure column, while boiling O₂ from the low pressure column.

6.1 Brazed Aluminum Heat Exchanger (BAHX)

The reboiler is typically a Brazed Aluminum Heat Exchanger (BAHX). A BAHX consists of alternate fluid passages (See Figure 3). The passages are separated by parting sheets. Within each passage are corrugated fins, which serve two purposes:

- They separate the parting sheets, while providing the mechanical integrity to hold the heat exchanger together.
- They promote heat transfer between the fluids.

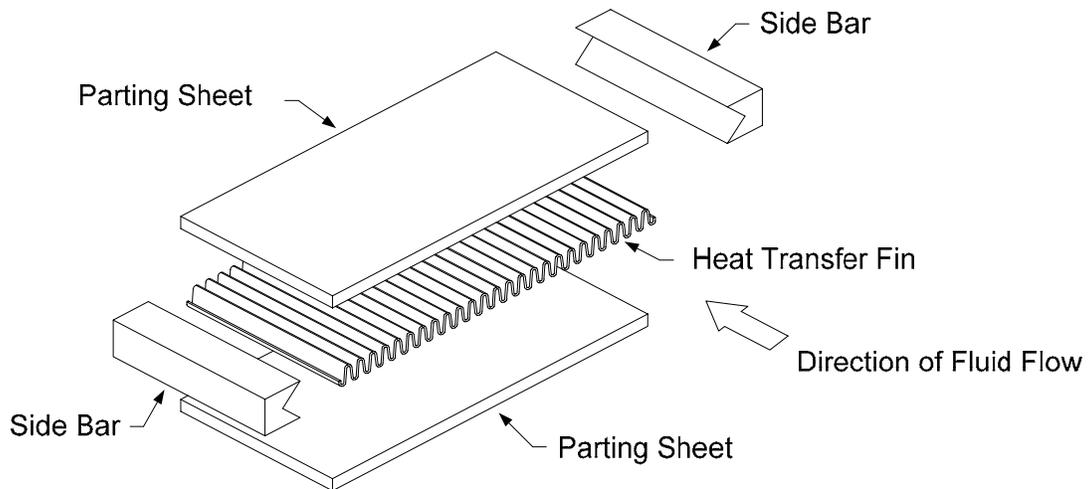


Figure 3
BAHX Passage Construction

The BAHX is built up like a sandwich with alternating passages of differing fluids. To introduce and remove the streams from each passage, at the feed and product end of the exchanger, the fins are angled towards a specific point. A half-pipe header is welded over the opening to collect the fluid. For a reboiler, however the oxygen end is open and does not have header tanks or distributors. While ASU reboilers only have two fluids, BAHX's can be used to exchange heat between many streams. Some BAHX's contain 7 or more different process fluids (ref 11).

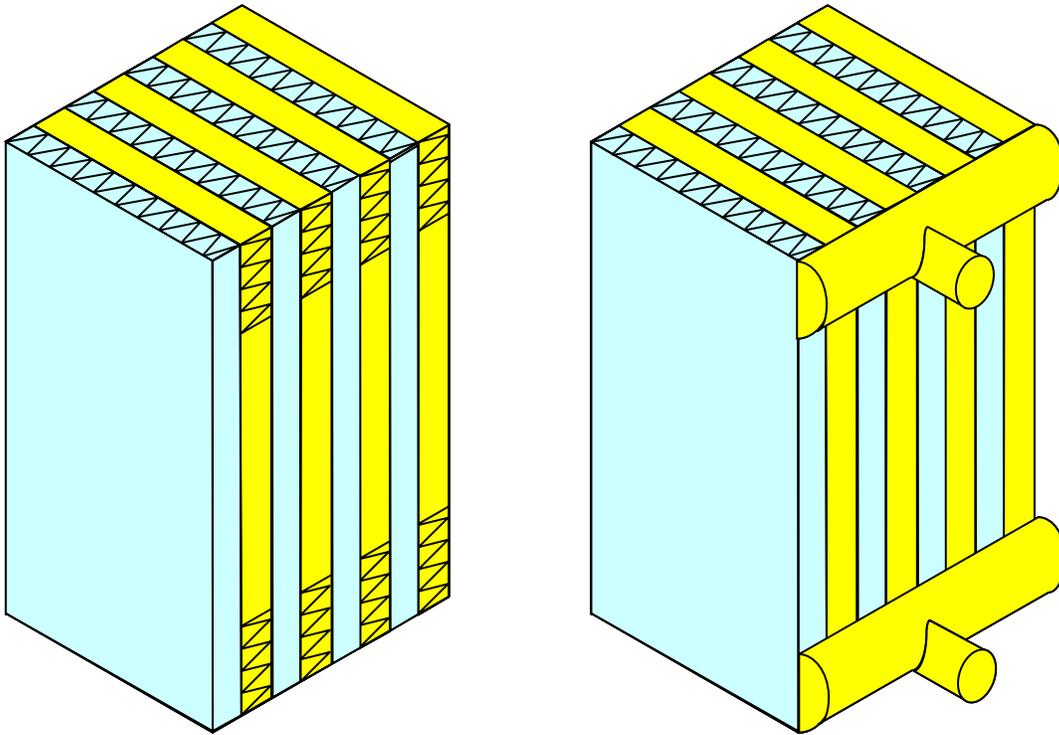


Figure 4
BAHX Construction

(Block on the right has distributor headers attached)

Figure 4 shows a schematic reboiler. The O_2 passages are open at both ends. The N_2 passages are shown open on the sides in the left hand sketch. The right hand sketch shows the header tanks attached. The actual passage heights are 5 to 10 mm. A full size reboiler can be up to 1.4 by 1.4 m in cross section and 2 to 5 m long. Figure 5 shows a single reboiler being installed into a column during manufacture.



Figure 5
Reboilers in Construction

BAHX's provide a large amount of surface area which increases the plant efficiency by allowing the heat to be transferred with a small temperature difference. Compared to other Chemical Processing heat exchangers, the ASU reboiler temperature differences are very small: typically 1 to 4°C.

6.2 Reboiler Types

Two types of reboilers are used in ASU service:

- A thermosyphon reboiler is submerged in a pool of liquid oxygen which moves upwards through the reboiler when heat is provided by the condensing nitrogen.
- A 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 different internal pressure profiles. These give downflow reboilers a smaller temperature approach and a more efficient plant.

6.3 Thermosyphon Reboiler/Condensers

A thermosyphon reboiler/condenser is a countercurrent exchanger that is submersed in a pool of liquid (See Figure 6). Saturated nitrogen vapor enters at the top of the core, flows downward and is condensed, leaving the bottom of the core as liquid. The boiling fluid, which enters at the bottom of the core, is partially vaporized in an upward direction, carrying with it a large amount of liquid which is recirculated.

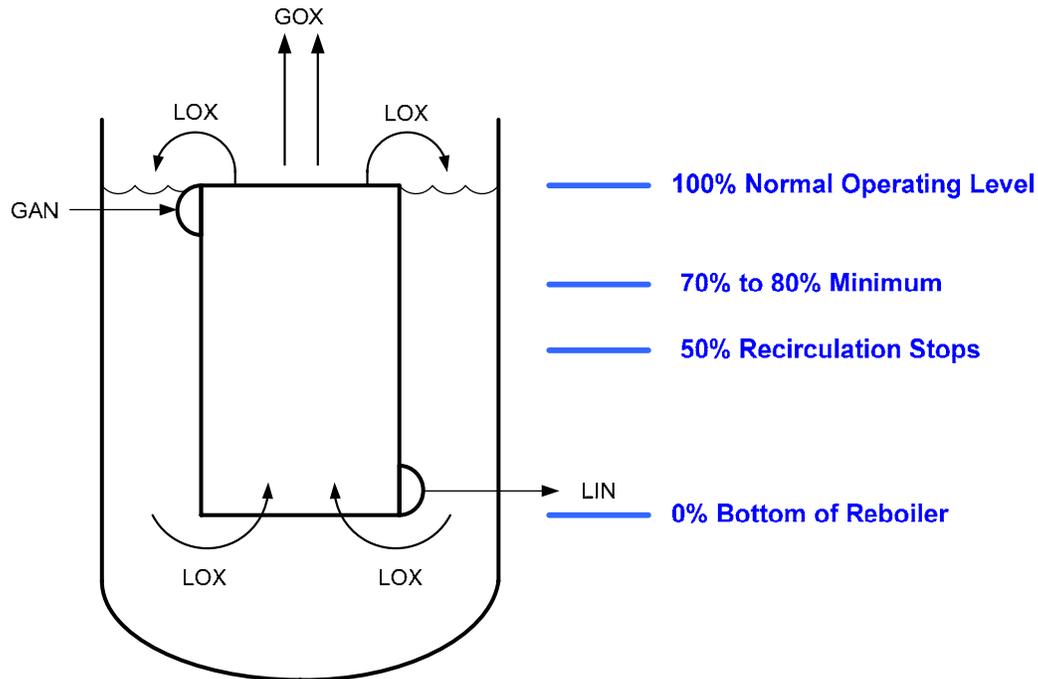


Figure 6
Thermosyphon Reboiler Schematic

This recirculation is generated when the liquid in the reboiler passages is partially vaporized. The bulk density is reduced, lowering the static head inside the reboiler. The greater static head of the single phase liquid outside the exchanger then forces the two-phase stream out of the top of the core.

The recirculation rate can be varied by changing the liquid level outside the exchanger. A lower the liquid level reduces the driving force, in turn lowering the recirculation. If the level is too low, the recirculation stops, and the reboiler will pool boil.

Reboiler submergence defines the location of the liquid level outside the reboiler core as a percent of the exchanger length (Figure 6). At 100 percent reboiler submergence, the liquid level is at the top of the core, and at zero percent reboiler submergence, the liquid level is at the bottom of the core. Industry practice is to operate all reboilers at 100% submergence (ref 2).

Note that most liquid level instruments list the “% liquid level”, the percent of level measurement height. The “% liquid level” is almost always different from the “% reboiler submergence”, i.e., 100% submergence typically occurs at a less “% liquid level”. The proper reading for the thermosyphon reboiler level must be obtained from the ASU manufacturer.

Figure 7 represents a typical reboiler/condenser cooling curve for boiling pure oxygen and condensing pure nitrogen. For reboiler-condensers operating with impure fluids, the operating lines will be somewhat different. However, the underlying principle of operation is the same.

Liquid oxygen enters at the bottom of the core (A), subcooled by its own liquid head. As the liquid flows up through the core, its temperature increases and density decreases due to heat transfer from the nitrogen. Its pressure decreases due to pressure drop and increased elevation. This de-subcooling zone takes typically a third of the exchanger length.

At elevation (B), the oxygen reaches its bubble point. Boiling does not begin at this point however, and the liquid becomes superheated. In the liquid superheat region the temperature difference between the LOX and GAN streams becomes less than 0.1 °C.

At elevation (C), the requirements for boiling and bubble initiation are achieved and boiling begins. The oxygen continues through the exchanger at its bubble point determined by the local pressure, leaving the top of the reboiler (D) saturated at the reboiler sump pressure. The typical top end ΔT associated with this type of exchanger is about 1 to 3°C, depending on the duty, fin type, and the number of the exchangers.

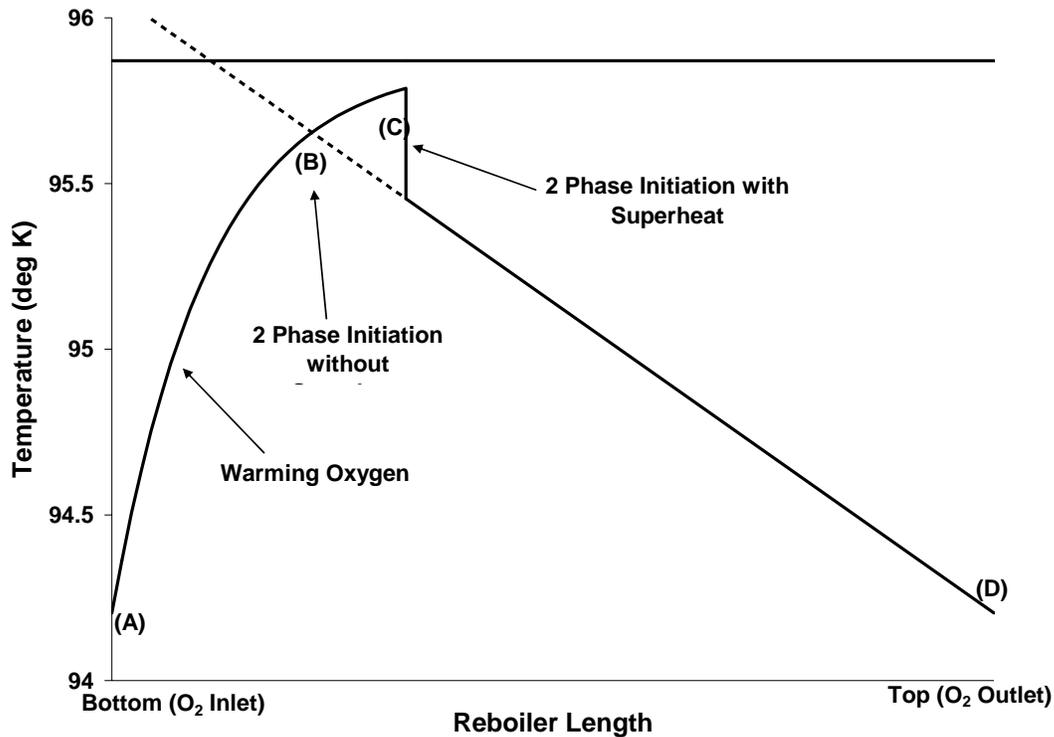


Figure 7 - Thermosyphon Reboiler Cooling Curves

Reboiler submergence in excess of 100 percent reduces plant efficiency, because the increased liquid static head raises the bubble point temperature and hence the condensing side pressure.

6.4 Downflow Reboiler/Condensers

The Downflow Reboiler/Condenser (DFRC) is a cocurrent exchanger, with both the boiling and condensing fluids entering at the top of the exchanger. The DFRC system consists of liquid collection, a means to increase pressure (i.e. a head tank), liquid filtration, liquid introduction and the exchanger itself (see Figure 8). In many cases, a liquid pump recirculates liquid, and a liquid phase adsorber is sometimes placed in the recycle line to remove trace CO₂ and N₂O.

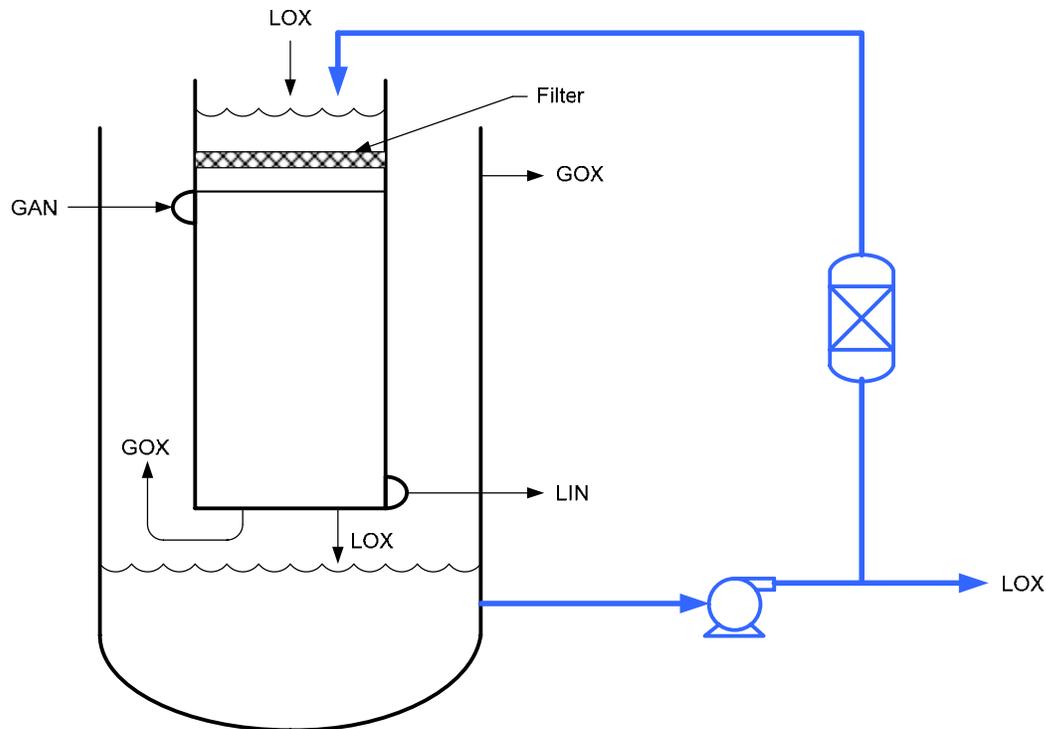


Figure 8
Downflow Reboiler Schematic

The liquid must be collected from the original source, whether it is a sump from another vessel or distillation trays or packing above. This is fed into a feed tank. A liquid level will be established in the feed tank, which gives the liquid enough pressure to overcome the pressure drop of the core.

The liquid is then distributed among the multiple exchangers, if there are more than one, and then introduced into the core itself. Within a single heat exchanger, special design features ensure even distribution to all of the passages. The proprietary details of this distribution system vary from manufacturer to manufacturer. The liquid boils as it flows downward through the exchanger, and a two phase mixture exits the DFRC. The liquid is collected in the bottom of the column and withdrawn, and the vapor either goes up the column or is withdrawn through a side nozzle as GOX product.

The condensing side of a DFRC is similar to thermosyphon reboiler design.

The benefit of using a DFRC can be seen in comparing the temperature profiles for each exchanger along the length of the exchanger. Because the liquid entering the bottom of a thermosyphon reboiler is in a subcooled state, due to static head, approximately 1/3 of the thermosyphon reboiler length is used to de-subcool this liquid (Figure 8). Boiling is initiated at the pinch in the curve and the fluid continues to boil as it travels up the exchanger.

In a DFRC, the de-subcooling region is negligible (see Figure 9). Since the boiling fluid enters the exchanger near its saturation point, and is distributed to be in film flow, evaporation can occur very quickly. The boiling curve is relatively flat, due to low static head, and the ΔT associated with the reboiler is much lower, usually about 0.5 to 1°C (Figure 9). This becomes about 0.5 to 2 % savings in power, depending on the process.

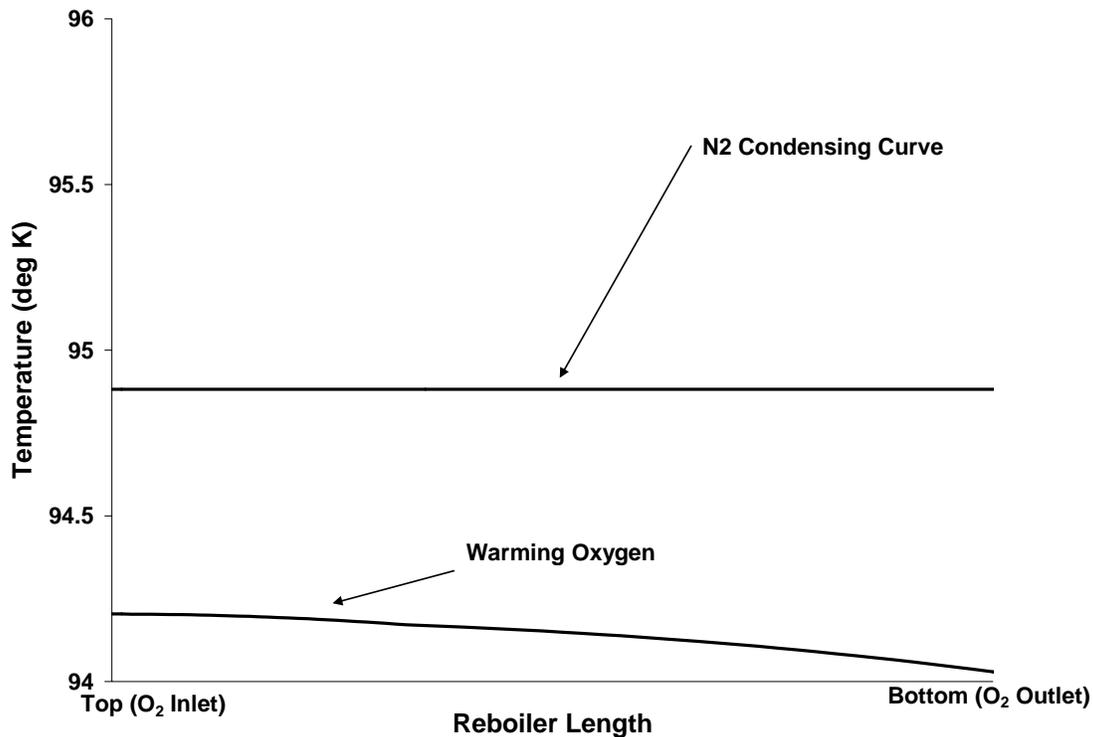


Figure 9
Downflow Reboiler Cooling Curves

7. REBOILER/CONDENSER SAFETY

The basic safety methodology is applied to the reboilers: identify the hazards, abate the hazards, and verify the abatement.

There are two general hazards which have been identified: (a) reaction between hydrocarbons and O_2 , and (b) reaction between aluminum and oxygen. The general hazards will be discussed first, along with the general abatement methods. The specific cases where the general hazards can occur within an ASU follow, along with their abatements and verifications.

7.1 General Hazard No. 1 – Reactions Between Hydrocarbons and O_2

This may occur if the hydrocarbons accumulate in O_2 above the LFL. The hydrocarbons can be dissolved in the O_2 , or they can be present as a hydrocarbon enriched phase (such as solid acetylene or liquid propane droplets). In principle, no

reaction can occur without an ignition source. However, hydrocarbons and O₂ are so reactive that reactions have been observed in industrial settings without any obvious ignition source.

Because the hydrocarbons and O₂ are so reactive, industrial experience is that only a small amount of hydrocarbons tend to accumulate before the reaction occurs. This helps to limit the extent of any damage. Still, every effort should be made to avoid accumulating hydrocarbons above the safe operating limits, which is the general abatement method.

7.2 General Hazard No. 2 – Reactions Between Aluminum and O₂

Aluminum has a long history of safe use within cryogenic air separation systems. It has been used in thousands of plants for over 60 years, because of its good properties at cryogenic temperatures. Piping, columns, heat exchangers, and equipment internals have been made of aluminum.

However, aluminum can react violently with O₂. Aluminum releases about 7 times more heat per unit mass than TNT. Aluminum and O₂ reactivity is not completely understood. Good summaries of the literature and industry experience are available in references 1, 12, and 13. Some features of the aluminum O₂ reaction:

- Aluminum is very hard to ignite. It takes a great deal of energy to initiate the O₂/aluminum reaction.
- The ignition and propagation is very dependent on purity. A very small amount of inert component makes a very dramatic difference in the ignitability and propagation characteristics of aluminum. 99.99% oxygen ignites very differently from 99.9% which is different from 99.6%. Virtually all industrial incidents have had O₂ purities over 99.5% purity.
- Argon is a more effective diluent than N₂.
- As with many materials, the specific geometry has a large effect on the ignition and propagation. Higher surface/volume ratios ignite more easily.
- As with most systems, higher pressure lowers the ignition threshold and increases the reactivity.
- If liquid oxygen is present, a Violent Energy Release (VER) can result. A VER is an aluminum combustion which is characterized by a loud report, bright light, and physical deformation or destruction of the specimen. Experiments (ref 14) demonstrated that a two-phase stream is required to give a VER. Gaseous O₂ will support combustion of aluminum, but it will not lead to a VER.

Aluminum is very hard to ignite, as demonstrated by its long history of overall safe use. The primary abatement methods are to

- prevent ignition sources from being present, and
- use aluminum in regions where ignition and/or propagation do not occur. When the pressure or purities become high, consideration is given to using other materials, whenever practical.

7.3 Specific Hazard No. 1 – Bulk Liquid Enrichment

The first specific hazard within an ASU reboiler is where the bulk liquid oxygen bath becomes enriched in hydrocarbons. Because the trace contaminants boil at a higher temperature than O₂, they will concentrate in the liquid oxygen in the reboiler. This is particularly true in the GOX process, where the vast majority of the liquid oxygen is removed as a vapor, so that the concentration factor, γ , can be very high up to 500 (see Table 2). Two methods abate this hazard:

- Limit the type and amount of trace contaminants that enter the reboiler, by operating the PPU properly. If a REVEX plant is used, the main exchangers and liquid phase adsorbers must be operated according to the design specifications.
- Maintain the proper liquid purge on the reboiler sump liquid. The generally accepted value is 0.2% of the air (which is typically 1% of the oxygen production) (ref 2), although it can be as low as 0.1% of the air with proper operating procedures.

Note that the Pumped LOX process has a safety advantage, because the LOX product provides the LOX purge on the reboiler sump. As long as the plant is making O₂ product, the reboiler sump will be purged. However, there are other specific hazards associated with boiling LOX in the main exchanger. These are discussed in ref 1.

The verification methods are:

- Monitor CO₂ on the PPU exit. This will verify that the PPU is operating properly, and because CO₂ is the least strongly held contaminant, if it is removed, then other components of concern (H₂O, C₄⁺, C₂H₂) are known to be removed.
- The hydrocarbons in the bulk liquid should be measured. The type and frequency of the measurement depends on factors, such as process cycle (GOX, Pumped LOX, or N₂ Generator), and ambient air quality. The measurement may be continuous, with a total hydrocarbon analyzer or a gas chromatograph, or in some cases, periodic batch samples may be sufficient. The ASU manufacturer should provide the specific method for each plant. Hydrocarbon analysis can also provide a useful check to ensure that the ambient air quality has not changed, either due to the general environment changing, or a process upset in a neighboring facility. Any unexplained change in hydrocarbon levels should be investigated to determine the cause.
- Take periodic C₂H₂ measurements on REVEX plants. These measurements should be taken frequently (several times per week), as per the manufacturer's specifications. There have been several serious accidents caused by acetylene accumulation.
- Measure the LOX purge rate. It is critical that a LOX purge be maintained above 0.1 to 0.2% of the air, in both REVEX and PPU plants. This LOX purge can be measured directly with a flowmeter, or it can be inferred by level measurement (such as level rise in a tank).

All of these verifications should have alarms and shutdowns. The alarm is typically set lower, to allow time to correct the situation.

7.4 Specific Hazard No. 2 – HC Accumulation within Thermosyphon Passages

The thermosyphon reboiler has the boiling oxygen flowing upwards – opposite to gravity. Therefore, without an adequate circulation rate, there will not be sufficient vapor to lift the liquid upwards, and the oxygen will pool boil. This hazard is particularly insidious, because it occurs within the passages of the thermosyphon reboiler, where there is no direct composition measurement. That is, the bulk liquid surrounding the reboiler can be within safe limits, with limited hydrocarbon concentration, while the internal passages are slowly accumulating hydrocarbons. Note that all of the passages can be operating in this state, just one, or a few.

The reduced circulation can be caused by:

- A reboiler passage can be blocked with physical debris, such as perlite or small fines left over from the manufacturing or construction process. This debris will restrict flow in the passage or passages which contain it. The gaps between the fins are 1 to 2 mm wide.
- If the bulk liquid level is too low, there will be inadequate static head to maintain an adequate circulation rate.
- If the CO₂ or N₂O concentrations are too high in the liquid phase, they will further concentrate within the reboiler passages. If they then exceed their solubility limits, they will precipitate. The solids can then block the passages.
- Any liquid water present from initial construction or plant maintenance must be removed during the initial defrost, prior to cooldown.

It is worth noting that N₂O in thermosyphon reboiler system is rarely a problem. The typical atmospheric concentration is approximately 300 to 350 ppb (0.3 to 0.35 ppm). With a concentration factor of 500 (corresponding to a purge rate of 0.2% of the air), the concentration in the reboiler sump will be 175 ppm, even if none is removed by the PPU. To reach the desired value of 125 ppm (50% of the solubility limit), the PPU must remove only approximately 30% of the N₂O, which is well within the limits of conventional technology. Note that N₂O removal is required for downflow reboilers, as discussed below.

The abatement methods are again relatively simple:

- The reboiler must be maintained at 100% submergence, to maintain adequate circulation through the reboiler.
- The plugging components (CO₂ and N₂O) must be limited to less than 50% of their solubility.
- The plant must be free of debris. Special care must be taken during startup to ensure that any small amounts of debris are flushed from the system before commissioning the reboiler.
- The plant must be designed with features that minimize the collection of water during construction, and these features must ensure proper flow

through the reboiler to heat the exchanger and then remove any water prior to cooldown.

Note that there have been several reboiler incidents caused by the presence of perlite insulation in the reboiler sump. Perlite in the reboiler sump liquid is a potentially unsafe situation. The reboiler must be immediately stopped, and liquids drained. The manufacturer should be consulted immediately for assistance to determine the source and extent of perlite contamination.

These abatements are verified by

- The reboiler level measurement must be within design limits. There is a low level alarm on the reboiler sump, and if the reboiler level is below safe limits for too long (typically 45 minutes), the plant must be shutdown.
- The reboiler level transmitter must be periodically maintained, including calibration. In recent plants, Air Products has added a full level trycock, to verify the reboiler level transmitter.
- The CO₂ concentration in the reboiler sump is periodically monitored. As well as a backup on the PPU exit, this check also ensures that there is not a trace amount of CO₂ getting past the PPU which is concentrating to unsafe levels in the reboiler sump. The frequency is based on the liquid purge rate, and varies between daily and weekly. Alarms and shutdowns should be provided.
- There are special construction and startup procedures to verify that the system is properly defrosted and free of debris, prior to starting the reboiler.

Note that a hydrocarbon analysis of the sump liquid is likely ineffective to detect this hazard. The hydrocarbon analysis is on the bulk liquid, which would not show a problem within an individual reboiler passage or passages.

7.5 Specific Hazard No. 3 – HC Accumulation in Downflow Reboiler Passages

Downflow reboilers are different from thermosyphon reboilers, and have different safety concerns. There are some features which favor each type of reboiler, so neither can be conclusively stated to be superior or inferior to the other.

Downflow reboilers have the safety advantage over thermosyphon reboilers in that the boiling O₂ flow is downwards, so that the probability of pool boiling is greatly reduced. Liquids which might contain higher amounts of hydrocarbons or plugging components will tend to drain into the liquid sump, where they can be removed.

However, downflow reboilers have been shown to accumulate the plugging components (CO₂ and N₂O), even when the concentrations are significantly below their solubility limits (ref 15 and 16). The exact mechanism is unknown, but is believed to be caused by the liquid not completely wetting the reboiler surface. Increasing the reboiler liquid rate has not been successful in eliminating the accumulation of these components. If the accumulation is extreme, it is possible that pool or dry boiling locations could be created.

The experimental work showed that the primary factor in the accumulation rate is the concentration of the plugging contaminant, and that the accumulation rate is approximately proportional to this concentration. Therefore, the key to reducing the accumulation rate is to reduce the concentration of CO₂ and N₂O fed to the downflow reboiler.

In addition, solid CO₂ and N₂O have been shown to act similarly to a weak adsorbent for hydrocarbons (ref 17). The amount of hydrocarbon “adsorption” is relatively low. The experimental work compared the ignitability to that of acetylene adsorbed on silica gel, which is not a hazard. This adsorption and ignitability were determined to be low, and not a hazard.

These hazards are abated by

- Limit the amount of undesirable hydrocarbons into the plant. The most hazardous hydrocarbons, specifically acetylene, are removed by the PPU.
- Limit the amount of CO₂ and N₂O fed to the downflow reboiler. There are several methods for this:
 - Run the PPU to limit the amount of CO₂ and N₂O into the coldbox
 - Use liquid phase adsorbents to remove CO₂ and N₂O
 - Operate to minimize the concentration factor in the reboiler sump
 - There are adsorbents which can increase the N₂O removal by the PPU, and these may be used (ref 18).
- It is recognized that even with the best abatement methods, there will be at least trace CO₂ and N₂O accumulation within the downflow reboilers. Periodic defrost is therefore necessary to remove these components.
- As mentioned above, the downflow reboiler is intrinsically free draining, so this greatly reduces the probability of pool boiling and accumulating hydrocarbons.

The verification methods are

- Monitor the CO₂ leaving the PPU, to ensure that the PPU is operating properly. Alarm and shutdowns are needed.
- The CO₂ concentration in the reboiler sump is periodically monitored. As well as a backup on the PPU exit, this check also ensures that there is not a trace amount of CO₂ getting past the PPU which is concentrating to unsafe levels in the reboiler sump. The frequency is based on the liquid purge rate, and varies between daily and weekly. Alarms and shutdowns should be provided.
- In some cases, when the downflow reboiler is defrosted, the gas leaving the reboiler area is measured for flow and/or composition, allowing the amount of N₂O, CO₂ and hydrocarbons to be monitored. This feedback is useful to establish defrost intervals for ASU's.

7.6 Specific Hazard No. 4 – Operating in Severe Haze

Occasionally, there can be massive forest fires or agricultural burning which creates a widespread smoke and/or haze. This is widespread, covering hundreds or thousands of square km's. While this is relatively infrequent, it was a significant contributing factor to a major ASU reboiler explosion (ref 4). The hazard is that the atmosphere contains significantly higher quantities of airborne aerosols. These are typically very small liquid droplets, 0.1 to 10 μ in diameter. The 0.1 to 1.0 μ particles are difficult to remove with standard filtration, and they can enter the coldbox. Experimental work has shown that these components, once they enter the coldbox, are not removed with standard defrost techniques (ref 3 and 19).

The long history of safe ASU operation shows that small amounts of aerosols are not a significant safety issue. That is, the haze found in urban areas, even those that are relatively polluted, do not need special countermeasures. However, there is a hazard if plants are operated in a long-term severe haze.

The primary abatement method for this hazard is primarily that one must recognize that this condition is a hazard. When operating in this environment, the operator must be aware of the situation. If the situation is short term, lasting for a few days, the industry experience shows that this is not a significant risk. However, if the haze situation persists, the manufacturer should be consulted, or operating headquarters notified of the situation. If the situation is severe, or if it persists for an extended period, the plant should be shutdown until the atmosphere returns to more normal condition. If the condition persists, or if during the design phase it is anticipated that this may occur, it is possible to add special filtration to reduce the amount of haze particles which enter the ASU.

It should be noted that severe atmospheric haze and its affect on ASU's has only relatively recently become an area of significant research in the industry. It is expected that the general knowledge of this potential hazard and its abatement will grow over the coming years.

7.7 Special Case - N₂ Generators

Many small ASU's are optimized to produce nitrogen, rather than oxygen, typically in quantities of 20 to 300 T/D. These plants are somewhat simpler than oxygen plants, with fewer sections and stages in the distillation column. Often they have only a single distillation column. The plants produce a nitrogen product and a waste product. Because of the different design of the distillation column(s), this waste product is less than 70% oxygen for two column N₂ generators, and is less than 50% oxygen for single column generators. The purities are limited not just by operating practice, but by the physical design of the coldbox.

When the EIGA safe practices guide for reboiler operation was developed (ref 2), a survey of industrial reboiler incidents was conducted. In reviewing this survey, one observation can be made which has not previously been discussed in the literature. Of the 47 incidents reported, none were in N₂ generators; all were in O₂ plants. There are many more nitrogen generators than O₂ plants, and it is very unlikely that the operating practices are different with regard to reboiler safety. Therefore, there must be some features of the N₂ generators that make them inherently less likely to have a reboiler incident.

The reason proposed here is that the most common cause of reboiler incidents is accumulating hydrocarbons by pool boiling within a few passages of the reboiler. The specific cause of the pool boiling varies, most often either

- Blocking a few passages with physical debris or construction defect
- Low reboiler submergence
- Blocking a few passages with a plugging component (usually CO₂)

In an oxygen plant, the boiling fluid is pure O₂, and the bubble and dew point temperature are the same. During pool boiling, the following mechanism occurs:

1. Liquid O₂ enters the passage
2. O₂ boils away, leaving behind the higher boiling trace hydrocarbons
3. This continues, until the hydrocarbons enrich enough to form a flammable mixture with the remaining O₂.

However, in a N₂ generator, the boiling fluid is impure, and it is 3 to 6°C colder than the boiling point of pure oxygen. If pool boiling leads to the following situation:

1. O₂ enriched liquid (50 to 70% O₂) enters the passage
2. During pool boiling, the evaporated vapor contains more of the volatile N₂, leaving behind a fluid enriched in O₂ and hydrocarbons.
3. As the fluid enriches in O₂, its boiling point temperature increases
4. When the temperature of the boiling O₂ equals the condensing N₂ temperature, heat transfer stops, which in turn, stops the enrichment of hydrocarbons.

This can be generalized to that if the temperature difference between the fluid dewpoint and the pure oxygen dewpoint is greater than the operating reboiler temperature difference, the reboiler can only concentrate for a relatively short period of time before the concentration will stop. That is, the ability of the reboiler to concentrate is limited if

$$T_{O_2} - T_{\text{dewpoint}} > \Delta T_{\text{reboiler}}$$

Where

T_{O_2}	= Dewpoint of O ₂ at the reboiler operating conditions
T_{dewpoint}	= Dewpoint of the bulk liquid at the reboiler operating conditions
$\Delta T_{\text{reboiler}}$	= Operating reboiler temperature difference (i.e., the ΔT between the boiling O ₂ and condensing N ₂)

This self-limiting feature of enrichment within N₂ generator reboilers has not previously been recognized, and adds a significant layer of protection for these plants. It is particularly important, because limiting the purity of the O₂ essentially eliminates the possibility of an Al/O₂ reaction.

Flammability tests have been performed on 200 to 400 gm samples of BAHX's (ref 20). These were ignited in a variety of oxygen purities and pressures. Three types of results were seen:

- No combustion – where no aluminum reacted with O_2
- Combustion
- VER

Figure 10 shows the tests, along with their reported threshold of VER's, as a function of pressure and purity.

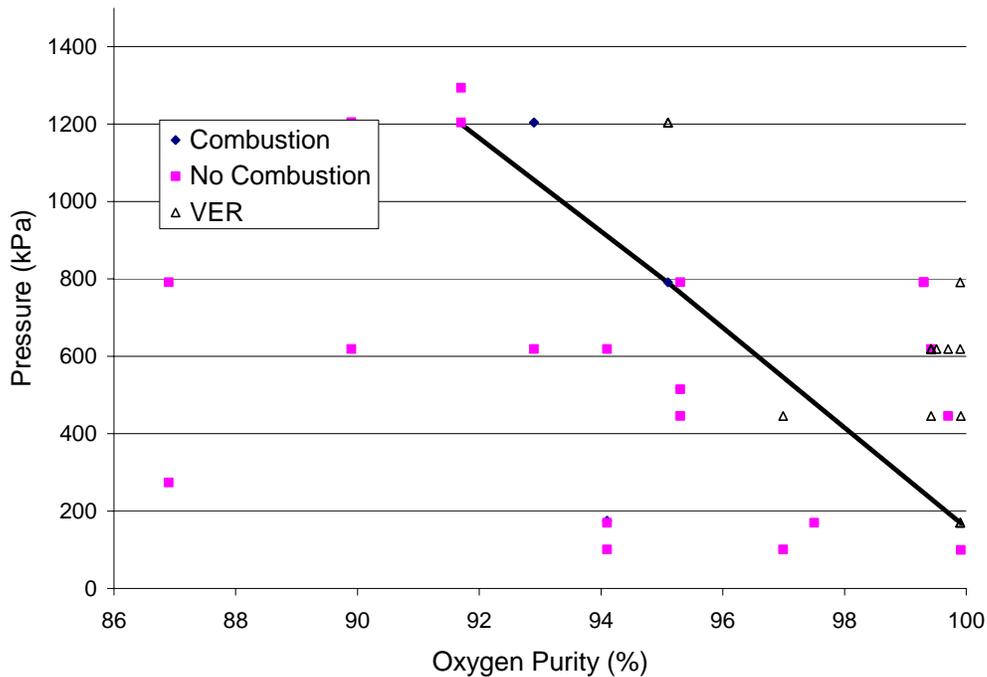


Figure 10
BAHX Sample Flammability

This data is shown again in Figure 11, with the purity axis rescaled. The operating conditions for single and double column N_2 generators are also shown, along with the maximum achievable purity. The maximum achievable purity is the purity at which the dew point of the liquid O_2 is equal to the condensing N_2 temperature. This calculation assumed a $2.8^\circ C$ reboiler ΔT for the single column, and a $1.9^\circ C$ ΔT for the double column N_2 generator. This plot shows that there is considerable margin between the maximum O_2 purity and the threshold for an Al/O_2 reaction. Note also that the purity shown is the LOX purity. The vapor-phase waste purity is lower, due to the relative volatilities of N_2 and O_2 .

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.
- The boiling oxygen passage fins have perforations every 5 to 15 mm. This reduces any area of potential pool boiling, should a blockage occur.
- 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.

8. INDUSTRY SURVEY OF REBOILER/CONDENSER INCIDENTS

BAHX have been used for over 40 years in ASU reboiler service. The overall safety experience has been very good. However, there have been cases of reboiler incidents, which have been traced back to reactions within the reboiler area. In 1998, a survey of industrial gas companies showed that there had been 47 incidents involving BAHX reboilers (ref 2). These were put into three categories:

Internal Event – Incidents that relate to minor energy releases within the reboiler heat exchanger and are not seen on the outside of the coldbox. They are generally noticed only by poor subsequent performance of the distillation and require repair of the reboiler to eliminate the problem. Equipment outside of the distillation column is seldom involved or affected.

The damage to the reboiler is in a single or few passages. In the damaged passages, the fins are typically torn, and an egg-shaped deformation less than 200 to 400 mm in diameter is seen. Figure 12 shows a cross section of a reboiler which has had such an energy release. The cause of this energy is usually that hydrocarbons accumulate within the passages until the LFL is reached. An unknown event ignites the hydrocarbon, and all of the energy comes from the hydrocarbon/O₂ reaction. The event causes leaks in the exchange between the condensing and boiling streams.

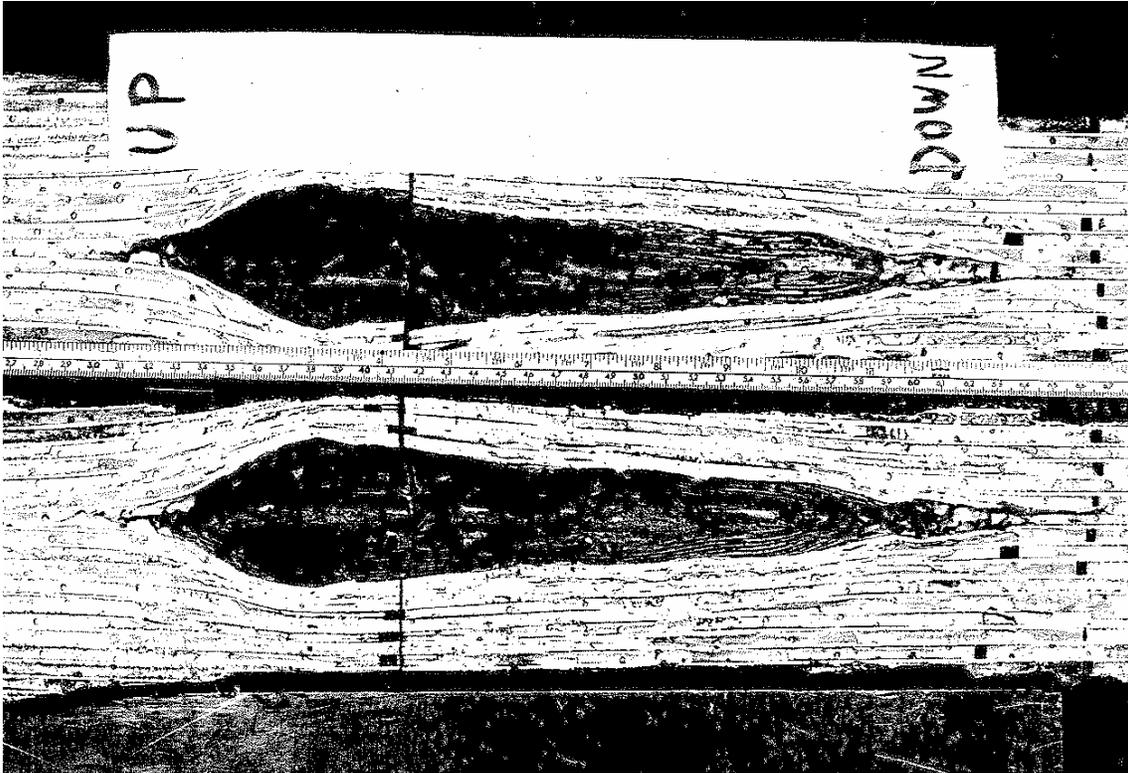


Figure 12
Cross Section of a Reboiler After an Internal Energy Release

The industry survey showed that there have been 36 such incidents. These incidents are clearly undesirable, because they cause significant operating problems, requiring immediate shutdown and repair of the ASU. However, because the damage is limited within the column system, personnel are not at risk.

Limited Event – There is damage within the coldbox, but the coldbox is not breached. Piping and equipment may be damaged, but is repairable during an extended plant outage.

Again, the damage is confined to a few passages. The damage to the coldbox can be due to the reboiler being external to the column, or that the damage causes piping breaks or that the reaction was severe enough to breach the reboiler sump. These leaks are relatively small. In a few cases, a small amount (a few grams) of aluminum may have combusted.

The industry survey lists 8 such incidents. These incidents are somewhat more significant, because there is more damage, and they may include cryogenic liquid leaks within the coldbox. While the personnel risks are slightly higher, none of these incidents resulted in personnel injury.

Major Explosions – These are explosions that breach the coldbox and cause major damage to the ASU, rendering it inoperable. There is also the possibility of off-site effects of the blast.

These events have the following sequence:

- Significant quantities of hydrocarbons accumulate in multiple passages within the reboiler
- Ignition of these hydrocarbons by an unknown mechanism. The shock wave causes all of the passages to ignite nearly simultaneously
- The high energy is sufficient to ignite the aluminum/O₂ reaction
- A significant quantity of LOX is flash vaporized
- The column and coldbox explosively rupture.

The industry survey showed that there have been three such incidents (ref 2, 4, 21). Clearly every reasonable countermeasure must be taken to prevent these incidents from occurring. From the industry experience, the key operating practice is to avoid the *widespread* accumulation of hydrocarbons. This prevents sufficient energy from being released, which could then lead to aluminum combustion.

9. SUMMARY

Each hazard has been discussed, with its corresponding abatements and abatement verification. It is more useful to an operator to summarize the key steps which must be taken and why. Table 4 below gives the seven key actions for safely operating an ASU reboiler. Following these seven steps will prevent reboiler safety problems in ASU's.

Table 4
Seven Key Steps for Safe Reboiler Operation

ACTION	REASON
Analyze CO ₂ at PPU Exit ^(1,3)	Verify Proper PPU Operation
LOX Purge $\geq 0.2\%$ of the air, and it must be measured	Ensure no contaminant buildup in the reboiler sump
HC Analyzer < 450 ppm as C ₁ equivalent ^(1,2)	Ensure no hydrocarbon buildup in the reboiler sump
Limit CO ₂ and N ₂ O in D/F Reboiler	Prevent excessive accumulation
Periodic Defrost	Remove trace components from low flow areas
Full Submergence of Thermosyphon reboiler ⁽¹⁾	Ensure adequate circulation to prevent locally high concentrations
For REVEX plants, operate liquid phase adsorbers in accordance with the manufacturer's instructions	Removes acetylene, CO ₂ and other trace contaminants

⁽¹⁾ Plant shutdown required after time delay

⁽²⁾ Not required with good air quality, and either high LOX purge or $<90\%$ O₂ in LOX

⁽³⁾ Periodically measure the reboiler sump liquid

By following these simple rules, ASU's can safely use both downflow and thermosyphon BAHX reboilers.

10. REFERENCES

- (1) "Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen", CGA Publication G-4.9, Compressed Gas Association, Chantilly, VA.
- (2) *Safe Operation of Reboilers/Condensers in Air Separation Units*, European Industrial Gases Association, IGC Document Doc 65/99/EFD.
- (3) Pawulski, R. "Aerosol Injection Testing", EIGA Production Safety Symposium, Dusseldorf, Germany, 1-2 February 2006.
- (4) Hardeveld, R.M., M.J. Groeneveld, J.Y. Lehman, and D.C. Bull, "Investigation of an Air Separation Unit Explosion", *Journal of Loss Prevention in the Process Industries*, 14 (2001), pp. 167-180.
- (5) Rotzler, R.W., J. A. Glass, W.E. Gordon, and W.R. Heslop, "Oxygen Plant Reboiler Explosion", *Chemical Engineer Progress*, June 1960 (vol 56, No. 6), pp. 68-73.
- (6) Miller, Edwin, S. Auvil, N. Giles, and G. Wilson, "The Solubility of Nitrous Oxide As a Pure Solute and in Mixtures with Carbon Dioxide in Air Separation Liquids", AIChE Meeting, Atlanta, GA, Paper Session T8001c, March 5-9, 2000.
- (7) Menses, D., J.Y. Thonneller, C. Szulman, E. Werlen, "Trace Contaminant Behavior in Air Separation Units", Cryogenics 2000 Conference, Prague.
- (8) Schmidt, W.P., K.W. Kovak, W.R. Licht, and S.L. Feldman, "Managing Trace Contaminants in Cryogenic Air Separation", AIChE Meeting, Atlanta, GA, Paper T8001b, March 5-9, 2000.
- (9) Schmidt, W.P. K.S. Winegardner, M. Dennehy, and H. Castle-Smith, "Safe Design and Operation of a Cryogenic Air Separation Unit", *Process Safety Progress*, December 2001 (Vol. 20, No. 4), pp. 269-279.
- (10) McKinley, C., F. Himmelberger, "Oxygen Plant Safety Principals", *Chemical Engineering Progress*, March 1957 (Vol. 53, No. 3), pp 112-121.
- (11) Lunsford, K.M. "Advantages of Brazed Aluminum Heat Exchangers", *Hydrocarbon Processing*, July 1996, pp. 55-64.
- (12) "Safe Use of Aluminum-Structured Packing for Oxygen Distillation", CGA Publication G-4.8, Compressed Gas Association, Chantilly, VA.
- (13) Werley, B. L., H. Barthelemy, R. Gates, J.W. Slusser, K.B. Wilson, R. Zawierucha, "A Critical Review of Flammability Data for Aluminum", *Flammability and Sensitivity of Materials in Oxygen Enriched Atmospheres: Sixth Volume, ASTM STP 1197*, D.D. Janoff and J.M. Stoltzfus, Eds., American Society for Testing and Materials, West Conshohocken, PA, 1993.
- (14) Mensch, M.M., J.P. Hass, K.K. Kuo, "Combustion and Flame Spreading of Aluminum Tubing in High Pressure Oxygen",
- (15) Houghton, P.A., S. Sunder, A.O. Weist, and T.P. Trexler, "Trace Component Accumulation in Downflow Reboilers", AIChE Meeting, Atlanta, GA, Paper T8001d, March 5-9, 2000.
- (16) Hashimoto, H. and S. Sakaue, "Behaviour of N₂O in Downflow Reboilers", Nippon Sanso Engineering Reports, No. 22 (2003), pp.22-23.
- (17) Lassman, E., M. Meilinger, "Determination of Hydrocarbon Adsorption on Solid CO₂ and N₂O in LOX at Ambient Pressure", *Flammability and Sensitivity of Materials*, ASTM STP 1395, 2000.

- (18) Golden, T. C., Taylor, F. W., Johnson, L. M., Malik, N. H. and Raiswell, C. J., "Purification of Air", U. S. Patent 6,106,593 (22 August 2000).
- (19) Meilinger, M. "Promoted Ignition-Combustion Tests with Structured Packing in Gaseous Oxygen with Argon or Nitrogen Dilution at 0.1 and 0.6 MPa", *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Tenth Volume, ASTM STP 1454*, T.A. Steinberg, H.D. Beeson, and B.E. Newton, eds., ASTM International, West Conshohocken, PA, 2003.
- (20) Zawierucha, R. and J.F. Million, "Promoted Ignition-Combustion Tests of Brazed Aluminum Heat Exchanger Samples in Gaseous and Liquid-Oxygen Environments", *Flammability and Sensitivity of Materials in Oxygen Enriched Atmospheres: Ninth Volume, ASTM STP 1395*, T.A. Steinberg, B. E. Newton, H.D. Beeson, Ed., American Society for Testing and Materials, West Conshohocken, PA, 2000.
- (21) Lehman, J.Y. X.C. Wei, Z.X. Hua, G. Delannoy, "Investigation of the Fushun ASU Explosion in 1997", *Journal of Loss Prevention in the Process Industries*, 16 (2003), pp. 209-221.

Table 2 - Trace Contaminants in Air

Species	Class C=Corrosive R=Reactive P=Plugging	Typical Design Basis for concentration air ^[1] (ppm)	Typical % removal in PPU ^[2]	Concentration factor, γ (purge flow = 0.2% of air flow)	Concentration in LOX sump, with conventional PPU and 0.2% purge (ppm)	Pure Component Solubility in LOX at 1.4 bar ^[3] (ppm)
CO ₂	P	400	>99%	430	3 ^[4]	7 ^[5]
SO ₂	C, P	0.1	100%	500	0	N/A
HCl	C	0.05	100%	490	0	N/A
H ₂ O	P	10,000 (approx.)	100%	500	0	N/A
N ₂ O	P	0.3	30-70%	470	40-100 ^[4]	250 ^[5]
NO _x (NO+NO ₂)	P, R	0.05	100%	500	0	N/A
O ₃	R	0.2	100%	480	0	N/A
CH ₄	R	10	0%	16	160	soluble
C ₂ H ₆	R	0.1	0%	490	49	3 x 10 ⁵ ^[6]
C ₂ H ₄	R	0.3	50%	350	53	4 x 10 ⁴ ^[7]
C ₂ H ₂	R	1.0	100%	140	0	8 ^[7]
C ₃ H ₈	R	0.05	67%	500	8	7 x 10 ⁴ ^[8]
C ₃ H ₆	R	0.2	100%	500	0	1 x 10 ⁴ ^[8]
C ₄ ⁺	R	1.0	100%	500	0	2 x 10 ² ^[9]

- Notes:
- [1] This is a typical design basis. For most components, the actual value will be lower.
 - [2] Approximate breakthrough order for conventional PPU's (first to last):
CH₄ > C₂H₆ > NO > C₃H₈ > N₂O > C₂H₄ > CO₂ >> C₃H₆, NO₂, HCl, SO₂, C₂H₂, C₄⁺ > H₂O
 - [3] 1.4 bara is a typical low pressure column sump pressure
 - [4] If both CO₂ and N₂O are present, their co-solubility in the solid precipitate must be considered.
 - [5] Solid phase solubility from APCI's proprietary thermodynamic computer program.
 - [6] Second liquid phase solubility. Solid phase does not form.
 - [7] Solid phase solubility
 - [8] Second liquid phase forms. The C₃H₈ and that C₃H₆ solubilities are not precisely known.
 - [9] Solid phase solubility for butane.

APPENDIX 1 REVEX PLANTS

Reversing Heat Exchanger (REVEX) plants were developed in the 1940's. In this configuration of an ASU, air is compressed, cooled to ambient temperature, and then sent to the main heat exchanger. The trace contaminants are not removed from the air, and enter the main heat exchanger. As the air is cooled, H₂O, CO₂, and high boiling hydrocarbons freeze out in the main exchanger, and are retained there. After 4 to 10 minutes, the air passage is depressurized, and dry, cold waste gas from the LP column is sent countercurrently through the passage. As this stream passes through the heat exchanger, the almost all of the trace impurities evaporate and leave with the warm waste gas.

There are two parallel sets of essentially identical passages for the waste and air. These switch back and forth, so that there is always one set of passages feeding the distillation column with air, and the other is removing the waste gas.

The cold air leaving the main exchanger still contains several trace contaminants. CO₂ is present at 0.2 to 2 ppm, and none of the acetylene in the air is removed. All of the methane, ethane, ethylene, propylene, propane leave the main exchanger, along with all of the N₂O. Trace amounts of the higher boiling hydrocarbons also enter the distillation system.

To deal with many of these components, particularly acetylene, liquid phase adsorbers are used. (These are also called "filters".) The adsorbers use silica gel to remove acetylene, CO₂, propylene, and N₂O. Acetylene is the most important, because it will concentrate to unsafe levels if not removed.

Typically plants have two sets of adsorbers:

- "Hydrocarbon Adsorbers" on the oxygen rich liquid leaving the bottom of the high pressure column. There are two adsorbers in parallel, with one always online, and the other is regenerated. Typical online times are 1 to 7 days.
- A "Guard Adsorber", which takes liquid from the LP column sump, adsorbs any remaining trace contaminants, returns it to the LP column. This adsorber should theoretically not see any significant amounts of contaminants. However, it is installed in the event that the hydrocarbon adsorbers have a process upset.

There are several operating problems with REVEX plants:

- A PPU plant removes the acetylene before it enters the plant. Acetylene is much more strongly adsorbed than CO₂, so it is virtually impossible for it to enter the plant. However, in a REVEX, the acetylene enters the coldbox, and is dealt with there. While this can be done safely, it removes a layer of inherently safe protection.
- The heat exchangers have pressure and temperature cycles every 4 to 10 minutes. This mechanically fatigues the exchangers. After 10 to 20 years,

the heat exchangers leak between passages, and must be replaced. In addition, any air within the main exchanger is lost when the passages are switched. This air loss increases the plant operating power by approximately 2%.

- The temperatures within the heat exchanger must be kept within a narrow operating range for the components to freeze out and evaporate. Upsets can happen, which then can lead to safety problems or require a defrost to remove plugging components.
- The liquid phase adsorbers must be operated properly. The operation reduces plant efficiency. The silica gel can turn to dust, or if the adsorbers have mechanical problems, the silica gel can get into the general process and end up in the reboiler sump, where it can plug passages within the reboiler.
- There are trace contaminants which are not completely removed by the switching cycle. The plant must be defrosted periodically to remove these contaminants.

For the reasons above, REVEX plants are no longer constructed. However, due to the long operating life of most ASU's, many REVEX plants are still running. One operating consideration is that as the REVEX main exchangers near the end of their life, it is possible to avoid replacing them by installing a PPU before the coldbox. This needs to be evaluated on a case-by-case basis. Often the evaluation shows operating and safety benefits.