There have been a number of serious mishaps in large air separation plants which have caused considerable concern among users of this process. Prevention of such mishaps is not as yet satisfactorily assured. It frequently happens that an air separation plant will operate for years with no untoward happenings and then, for no apparent reason, a vaporizer section of the column will blow up. If this section of all air separation plants were to blow up regularly, let us say weekly, the answer to the problem would be much easier to find. Each design group and user has, however, developed certain criteria of design and operation which have helped to reduce, if not to eliminate, such mishaps completely. Mr. Kerry has, we are advised, presented the thinking of many in the industry on the possible causes of column explosions and the means to circumvent them.

—Editor

safe design and operation of
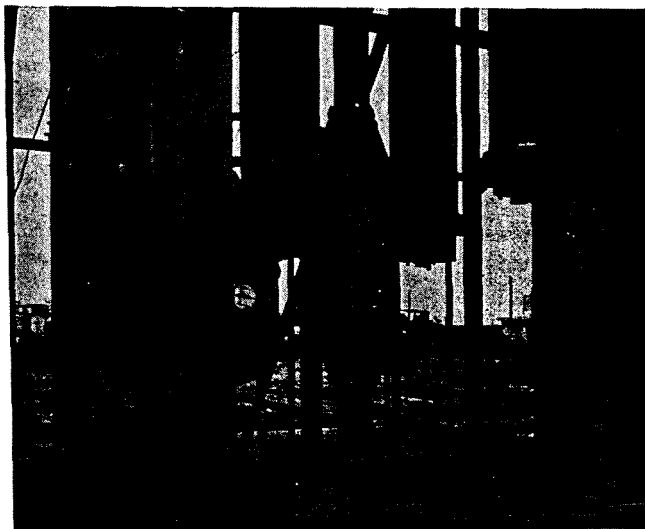
Auxiliary vaporizer and separator in position prior to piping connections and enclosure.

LOW TEMPERATURE AIR SEPARATION PLANTS

F. G. Kerry | American Air Liquide, Inc.
New York City, N. Y.

The past history of the low temperature industry, in existence now for almost sixty years, shows a fairly creditable record of safety which may be attributed primarily to the extreme caution and respect design engineers and operators have shown for low temperature fractionation equipment. There are no detailed statistics on air separation plant explosions or mishaps. This does not imply that the industry has concealed mishaps or that its members did not cooperate to reduce mishaps to a minimum. The industry could not have reached its present remarkable growth unless it had accepted safety as its number one consideration. The main purpose of this paper is to present in as orderly form as possible general data and information which could be of service to all users of production low temperature fractionation equipment.

In the early days of the oxygen industry, air plant mishaps were, as a general rule, comparatively rare, confined and not very damaging. This can be explained by the caution and respect operators showed for the oxygen unit and to the existence of many areas with uncontaminated air. The reason for the mishaps was not always known. However, the oxygen industry was, and still is, so closely allied with the production and distribution of acetylene, whose explosive properties are only too well known, that it was a simple matter to write off an explosion as acetylene entrainment. Furthermore, oxygen units of the time were small, the biggest producing only a few tons of oxygen per day; even more important was the fact that few, if any, operated continuously. Weekly or monthly shutdowns were the rule, not the exception. Impurity accumulation, therefore, never reached serious proportions.

Acetylene the Culprit?

It was not until the late thirties and during the early part of World War II, when oxygen plants were being built on a larger scale and operated on a longer continuous basis, that mishaps began to occur with greater frequency and with greater intensity. The industry believed generally that acetylene was still the main culprit, although it did rule out possible entrainment of other hydrocarbons. Atmospheric pollution due to industry and automobiles was being studied seriously, but the main blame was

still pinned on the general proximity of acetylene-producing plants or acetylene cylinders. To overcome mishaps, design engineers paid greater attention to proper location of intake stacks. Studies were made of neighboring industries, direction of prevailing winds, etc. In some cases, dual stacks were placed at 180 degrees. In the latter case, the use of one or the other stack depended on the direction of the wind.

In the early 1940's, Air Liquide in Canada found that the liquid oxygen in the main vaporizer contained not only acetylene but other hydrocarbons whose exact composition could not then be determined. A series of tests was planned to determine entrainment of acetylene and other hydrocarbons. The oxygen plant in Montreal was parallel to the acetylene plant and separated by a wide roadway. It was thought, therefore, that the study would reveal the influence of wind direction on acetylene entrainment as well as the cumulative effect of acetylene in the oxygen vaporizer.

Since the oxygen plant had two separate units, it was decided to run one with its standard oil-lubricated compressor, the other and smaller oxygen unit by means of a water-lubricated compressor. This test was to determine the influence of lubricating oil on hydrocarbon accumulation. Both units, one producing 200 meters per hour of oxygen, the other 100 meters per hour, had the same type of vertical multitube reboiler with flat tube sheets (Figure 1). The tests, run over a long period of time and only partially shown in Figure 2, showed quite conclusively that, if maintained below their solubility limit, acetylene and hydrocarbons did not accumulate,
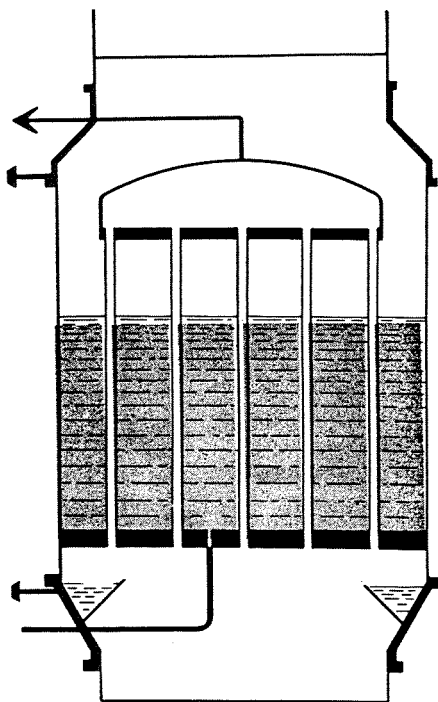
Fig. 1. Typical vertical multitube vaporizer.

but varied quantitatively and rapidly with the direction of the wind. The plant supplied by an oil-lubricated compressor showed a higher acetylene content than the one supplied with a water-lubricated compressor. This production of acetylene and hydrocarbons from thermal cracking of oil vapor had been suspected but never actually pinpointed as in this test. Obviously, greater care was needed in selection and operation of oil-lubricated compressors so that interstage and discharge temperatures would not become excessive.

Silica Gel Filters

A real contribution was the development and use of silica gel filters for the removal of acetylene from liquid oxygen. Developed in Germany and quickly put into use by all important oxygen manufacturers, these filters immediately reduced to a minimum the danger from acetylene explosions. The amount of silica gel then recommended was 10 kg./1,000 meters/hr. of air or 37 lbs./1,000 cu.ft./min. The filters were designed to remove 1 ppm of acetylene in the incoming air or 2 ppm entrained in the rich liquid at the bottom of the high pressure column. This liquid, containing 39 per cent oxygen, passes through the filters on its way to the low pressure column. With the use of silica gel filters and the sharp reduction in the number of mishaps, a few design engineers and some oxygen plant owners and operators were lulled into a false sense of security.

Fortunately, the majority of the oxygen industry did not relax its research work

since the effect of a number of unknown factors remained unresolved. Attention had to be paid to the actual design of the filters themselves from the standpoint of: contamination from other impurities; permissible adsorptive capacity; regeneration temperatures and procedures; deterioration and life expectancy of the adsorbing material; and finally, design of the recipients themselves for easy inspection and replacement of adsorbing matter. Another important problem was the design of the vaporizer itself. The standard vertical multitube type was satisfactory in small sizes but, as plants and consequently vaporizers grew in size, even vaporization of liquid oxygen became a problem which manifested itself in serious accumulation of excess acetylene and hydrocarbons in the vaporizer itself.

The most important problem was contamination of air entering the oxygen plant either from thermal cracking of oil vapor from the compressor or from outside sources. The proximity of oxygen plants to metallurgical, chemical, and petrochemical processes made long pipelines for air intake almost imperative. But, with the tremendous expansion of industry, it was getting harder and harder to find an uncontaminated source of atmospheric air. Present-day atmospheric pollution around heavily industrialized areas is such that complete reliance cannot be put on normally designed rich liquid filters. Furthermore, it is not sound economic practice to overdesign these filters and switch them more frequently, since this results in a tremendous loss of refrigeration. Every time a filter is taken out of operation, the entire rich liquid in the filter is drained and wasted before deriming.

The industry had to know what contaminants were responsible for the mishaps, what physical and chemical reactions took place to produce explosive compounds and finally, what triggered off explosions. These questions are still not answered conclusively, but there is enough circumstantial evidence to narrow down the number of conditions responsible for explosions.

Chemistry of Contaminants

As mentioned previously, there are no detailed statistics on oxygen plant mishaps. Very few post-mortems have produced tangible results; this is primarily due to the complexity of the factors involved. Most mishaps were more in the nature of detonations, however small the order of magnitude, rather than combustible explosions. Under normal conditions, conclusions on the explosive combustion of hydrocarbons can be derived from:

1. Flame velocities
2. Spectroscopic analysis
3. Analysis of end products

In the case of detonations rather than explosive combustions, measurement of flame velocities or spectroscopic analysis is of no assistance. Furthermore, in the presence of excess oxygen, the chemical reaction may be complete, without any carbon deposit:

$$C_2H_2 + O_2 \rightarrow 2CO + H_2$$
$$2CO + O_2 \rightarrow 2CO_2$$
$$2H_2 + O_2 \rightarrow H_2O$$
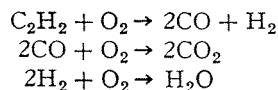
Intensity of the explosion could be measured by studying the form of the wrecked apparatus or fragments, but this would reveal only the energy release in the chemical reaction and not necessarily the nature of the detonating compounds. Only one avenue of approach remains; namely, analysis of the end products, if any, found on the surfaces of the tubes or vessels. A wiser plan is to study the physical and chemical reactions of troublesome contaminants which could enter an oxygen plant and to design for their elimination.

For two specific reasons any straightforward hypotheses on possible chemical reactions of the contaminants would be foolhardy. In the first place, the constituents are in amounts which would normally be below their explosive limits in oxygen. Secondly, at such temperature levels no chemical reactions should take place. But, since chemical reactions and explosions do take place, the chemical field involving polymerization and partial oxidation in the presence of sensitizers should be explored carefully rather than limiting investigations to straightforward explosions with known hydrocarbons.

ACETYLENE

Acetylene has always been treated with caution and respect. All chemical engineers are familiar with its wide explosive limits, its low ignition temperature, its instability when compressed and its ability to form explosive acetylides:

	Acetylene	Methane
Explosive limits in air	2.4-81%	6-14%
Ignition temperature	330° C.	600° C.

The general atmosphere contains around 0.001 ppm of acetylene. In average industrial areas, this quantity may reach 1 ppm; in the proximity of petrochemical industries involving thermal cracking, acetylene content may well reach 15 to 30 ppm for short periods. For a long time, it was believed that detonations in oxygen plants were due to copper acetylides, Cu_2C_2. Obviously, considering the amount of copper used in the construction of oxygen plants, this was a possibility. However, mishaps have occurred in plants fabricated largely of stainless steel and aluminum and very little copper. Of course, the main vaporizer still contains a high percentage of copper. Also it is unlikely that acetylides would be formed at very low temperature levels ($-180°$ C.) in the complete absence of moisture. Conditions for the formation of Cu_2C_2 do not exist in the vaporizer during normal operation. Cu_2C_2 could possibly be formed during deriming periods if hot moist contaminated air were blown into

the plant. However, a deriming operation is usually so brief that, if any copper acetylide were formed, it would be in trace form and its consequences could be ignored. Copper acetylides have been formed in the warm exchanger system of low temperature separation plants involving raw moist hydrocarbon feeds with very high acetylene content (1,000 ppm to 1,500 ppm) and the acetylides so formed have been entrained in the cold end. These conditions, however, are not duplicated in air separation units.

There is no doubt that acetylene gets into air plants and that the amount in excess of its solubility limit (5 ppm) is precipitated as a solid which either floats in the liquid oxygen or attaches itself to a vaporizer tube. If this were maintained for as long as three months, a serious amount of solid acetylene could accumulate. For instance, if 1 ppm of C_2H_2 be permitted to accumulate as a precipitant in the main vaporizer of a plant producing 100 tons per day of oxygen, the total weight of the precipitant would be around 1 pound. So long as the acetylene remains frozen solid, there is no danger since acetylene has remarkable stability in the solid state. But, if this solid acetylene has a considerable cross section, sublimation or liquefaction will not take place when it is heated up. Instead, there is great danger that it will polymerize or that it will break down into unstable and extremely explosive complex components. This can take place during deriming operations. It is interesting that a remarkably high percentage of explosions have taken place during restarts following plant stoppages.

OTHER HYDROCARBONS

1. Methane, because of its higher solubility limit, has little, if any, effect on the operation of oxygen plants. In 1955, Air Liquide in Canada ran a series of tests on a gaseous nitrogen plant located near several refineries. Methane content in the main vaporizer varied from a few ppm to 150 ppm and back almost as quickly as the wind changed direction. There was no cumulative effect from methane. Tests were run with new silica gel filters, with filters freshly reactivated, and with filters just about to be reactivated. These tests proved that filters have no effect on methane; fortunately, methane is very soluble in liquid oxygen and reevaporates with oxygen in the same amount as it enters the plant.

2. Hydrocarbons heavier than methane have been found in air plants but, with the exception of acetylene, they have never been analyzed quantitatively with any degree of accuracy. It also appears probable, although confirmation does not exist, that heavy hydrocarbons (particularly the unsaturates) may well undergo polymerization or partial oxidation in their passage through the compressor, especially in the presence of nitric oxide and/or nitrogen dioxide (1):

$$C_2H_4 + O_2 \rightarrow 2HC\text{-}HO \text{ at } 295° \text{ C.}$$
$$+ 80 \text{ secs}$$
$$C_2H_2 + O_2 \rightarrow CHO \cdot CHO$$
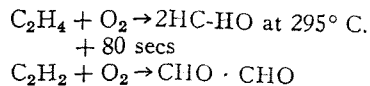
Oil-lubricated reciprocating compressors with high compression ratios do introduce oil vapor into the air stream. It is likely that some cracking takes place. This has manifested itself in unusually quick filter contamination, in flash fires at compressor valves, and in higher than expected acetylene contents in the main vaporizer.

OXIDES OF NITROGEN

With increasing use of oxygen plants in ammonia production and their proximity to nitric acid plants, the presence of nitrogen oxides and their influence on hydrocarbons should not be disregarded. In the low temperature separation of coke oven gas, it has always been known that NO helps to bring about the polymerization of unsaturated hydrocarbons, especially butadiene and cyclopentadiene. The resultant product is a gummy matter which can foul up exchangers; what is worse, this complex compound has explosive properties. The analysis of this product is approximately (2):

C	26—60%
H_2	4— 6%
N	4— 8%
O_2	20—40%
Ash	0—50%

Although NO has been known to have a chain-breaking influence, it is likely that NO_2 has a strong catalytic effect. All experiences with oxidation of hydrocarbons indicate that such chain reactions may be retarded or speeded up by addition of small quantities of various substances. It has also been adequately established that NO and NO_2 have a catalytic or sensitizing effect on hydrocarbon oxidation and polymerization. Whether NO and NO_2 have an independent influence or whether they are involved in the same reaction has not been proved; however, the latter is more likely. Nitrogen dioxide has a favorable effect on an H_2-O_2 explosion. At 400° C. below the explosion limits of $2H_2$ and O_2 (440° C., 200 mm of H_2 and 100 mm of O_2 exploded with the addition of 0.083 mm of NO_2 (3). In the presence of nitrogen oxides, acetylene reacts at very low temperatures, between 170° C. and 250° C. The result is trimerous glyoxal up to 50 per cent of the combined acetylene. In this reaction, NO_2 is effective as a homogeneous catalyst; it is reduced to NO (4):

$$NO_2 \rightarrow NO + O$$
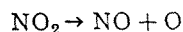
NO_2 also has an accelerating effect on methane oxidation. Oxygen atoms induce a reaction chain which could be produced as follows (5, 6):

$$NO + O_2 = NO_2 + O \rightarrow 47 \text{ K cal.}$$
$$NO_2 = NO + O \rightarrow 67 \text{ K cal.}$$
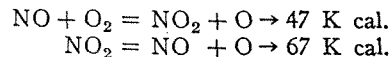
At 316° C. and 720 mm of mercury oxidation of ethane takes place as follows (7):

| Mixture & Addition	Induction Time min.	Reaction Time min.
$C_2H_6 + O_2$ (dry)	30	70
+ 1% H_2O vapor	10	25
+ 1% NO_2	0	20

NO_2 is also a strong sensitizer for $C_5H_{12} + 2O_2$. By the addition of 0.004% of NO_2, the reaction time can be reduced from 75 seconds to 22 seconds (8). A few ppm of NO_2 could react with a few ppm of hydrocarbons in the atmosphere in the presence of sunlight to produce a complex hydrocarbon; the by-product would be ozone (9). The actual reaction is by photolysis:

$$NO_2 \rightarrow NO + O$$
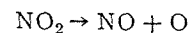
The oxygen atom so produced reacts with an oxygen molecule:

$$O + O_2 \rightarrow O_3$$
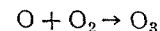
In the absence of organic material, the nitric oxide reacts with ozone:

$$NO + O_3 \rightarrow NO_2 + O_2$$
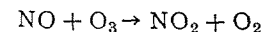
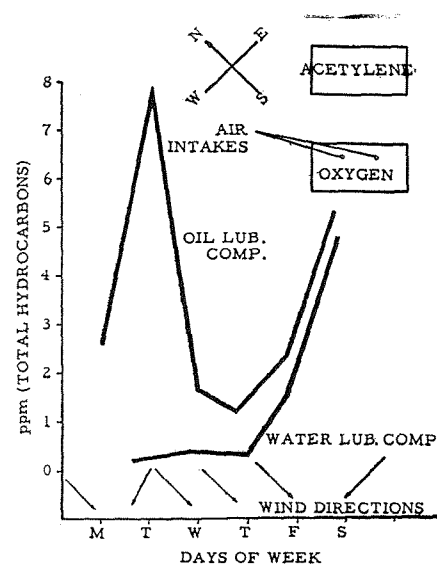This prevents any accumulation of ozone.

Fig. 2. Acetylene and hydrocarbon content vs. wind direction.

However, in the presence of organic substances, free radicals arising from the oxidation of organic material are believed to combine with nitric oxide to form a complex compound which could be called peroxyacyl nitrite. In this case, ozone would accumulate. Laboratory experiments carried out by the aforementioned authors have confirmed these results. It has also been determined that, in heavy petrochemical and refinery areas, the ozone concentration in the atmosphere can reach 1 ppm for short periods.

Ozone

Ozone has great affinity for silica gel and may well contaminate the filters and lower their efficiency for hydrocarbon removal. Liquid ozone is also readily soluble in liquid oxygen. But, since it has a higher boiling point than liquid oxygen, liquid ozone may well reach a dangerous concentration if the air plant is stopped and the main vaporizer is permitted to boil off indefinitely. Ozone is the most unstable of the contaminants that can enter an oxygen plant, and may well supply the key to the most important unsolved problem, namely what actually triggers off a detonation.

Safe Design Practices

The next step is to review what the industry has done and is doing to design air separation units with a maximum of safety. In plants with standard heat exchangers, contaminants go right through and end up in the vaporizer which carries the entire production of oxygen in liquid form (Figure 3). In the vapor-

izer, the liquid oxygen product is in heat exchange with the slightly warmer gaseous nitrogen product which rises to the top of the high pressure column. This heat exchange results in the liquefaction of the nitrogen which is then sent to the top of the low pressure tower as a reflux; this results in the enrichment of the oxygen product by the evaporation and recondensation of the liquid in the vaporizer. By the ultimate evaporation of the liquid oxygen at very low pressure and its reentry in the front exchanger system, this design permits a very high recovery of the energy expended in air compression.

Air separation units producing gaseous products are very efficient units and can operate at low air-compressor requirements compared to units in which the oxygen product is removed as a liquid from the vaporizer. Since contaminants end up in the vaporizer, the obvious conclusion is that gaseous oxygen producing units are not as safe to operate as liquid oxygen producing units which discharged the liquid oxygen product and the entrained contaminants outside the plant. From a design standpoint this statement is correct for two reasons: (1) the vaporizer is drained continuously; (2) the oxygen vaporizes at a higher temperature level, which means that the hydrocarbons are eliminated completely. However, the same rules of safe operation must be applied in both cases.

To design a safer gaseous oxygen producing unit, Air Liquide engineers incorporated an auxiliary vaporizer which received and vaporized the liquid oxygen from the bottom of the main

vaporizer. This portion of liquid contained the highest percentage of contaminants. This auxiliary vaporizer, which can handle anywhere from 30% to 100% of the total liquid oxygen product, is so designed (Figure 4) that vaporization takes place in the tubes and not in the shell as in the case of the main vaporizer. Vaporization of liquid in the tubes is more turbulent and hence slightly less efficient, but the liquid continually purges the tubes and there is, therefore, less likelihood of any accumulation of contaminants not in solution. In this manner, a higher percentage of contaminants are reevaporated with the liquid. Finally, a small amount of liquid from the auxiliary vaporizer is drained into a small vessel generally called an oxygen separator. This separator contains a liquid product with the highest concentration of contaminants.

As expected, explosions have occurred only in the auxiliary vaporizer and separator. Fortunately, the separator is nothing more than a glorified bursting disc and is expendable; the auxiliary vaporizer confines the order of magnitude of the explosion reaction because this reaction takes place in narrow tubes which offer strong resistance to a relatively small contaminant concentration per tube. As a general rule, this auxiliary vaporizer and separator are apart from the main vaporizer and fractionation equipment and are placed near the floor level close to the outer casing wall. Sometimes they are even separated from the main apparatus by a protective shield. Of course, a continuous analysis of the liquid in the separator should be made and, if contamination exceeds a safe limit, the liquid should be purged outside. In heavily contaminated areas, a continuous purge from the separator may be advisable. For a gaseous oxygen producing unit in an area of normal contamination, an auxiliary vaporizer and separator need not be considered for a productive capacity under 25 tons of oxygen/day if the main vaporizer is properly designed and if a slight continuous purge from the bottom of the main vaporizer is maintained. Nevertheless, continual analysis of the liquid product should be maintained. Above a capacity of 25 tons per day, all oxygen plants should have an auxiliary vaporizer and oxygen separator.

VAPORIZER DESIGN

In an ideal vaporizer the liquid should flow continually and smoothly as a very thin film over a very large surface. This condition would satisfy all requirements for efficient design and safety. Such lamellar flow would give:

1. Efficient heat transfer resulting in less temperature difference between liquid oxygen and gaseous nitrogen.
2. A wide distribution of contaminants either in or out of solution.

Fig. 5. Forced-feed, film-type vaporizer.
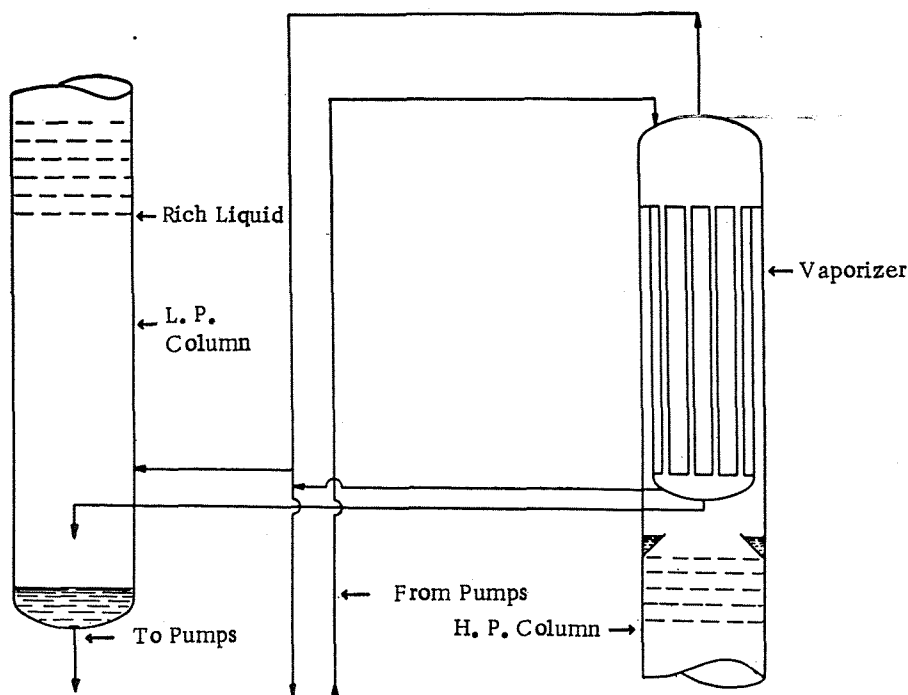
3. No dry spots at which contaminants could attach themselves.

4. A continuous purging or flushing action to prevent any concentration of contaminants.

Such an ideal vaporizer has been closely approached by Air Liquide engineers in their design of a forced-feed, film-type vaporizer. This vaporizer (Figure 5) consists of a bundle of long vertical tubes through which liquid oxygen is passed from top to bottom as a thin film spread out over the entire inner wall of the tubes. The liquid coming out from the bottom is then passed to a low pressure recirculating pump and returned to the top of the vaporizer. In this manner more liquid is passed over the inner surface of the vertical tubes than is evaporated.

This type of vaporizer has proven efficient from several design standpoints:

1. Very low temperature differential.

2. No large storage of liquid oxygen with the consequent contaminant concentration.

3. The liquid is in constant motion, providing a continuous flushing action.

4. Wide distribution of liquid helps reevaporate small concentrations of contaminants.

5. If any mishap does occur, it will be confined in a tube of fairly high strength.

Almost fourteen large-scale oxygen producing units having a capacity of 90 to 350 tons/day and using the film-type vaporizer have already gone into operation since 1949. No mishaps have occurred in any of them. This statement does not imply that this type of vaporizer is foolproof and that all other safety considerations may be disregarded. In some instances, an auxiliary vaporizer and separator have been installed as a precautionary safety measure. As indicated above, these film-type
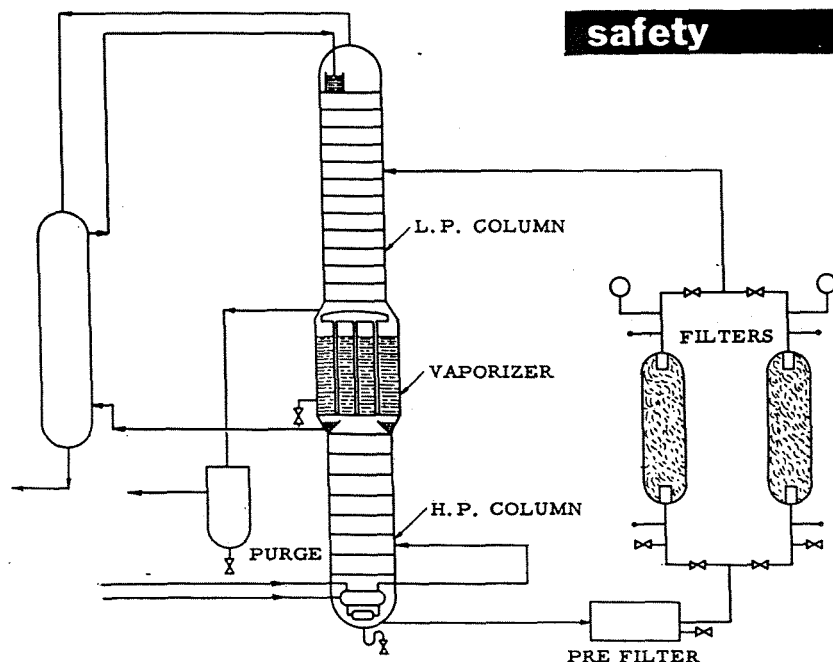
Fig. 3. Standard plant—no auxiliary vaporizer.

vaporizers have been installed in fairly large oxygen producing units. At present, however, an attempt is being made to redesign them in order to install them in plants having a productive capacity as low as 50 tons/day. It is felt that this would be an absolute economic and operative size limit.

SILICA GEL FILTERS

To date, the most positive safety measure on hand is the silica gel filter system (Figure 3). The liquid at the bottom of the high pressure column contains all the oxygen product and about 50 mols of total oxygen plus nitrogen out of every 100 mols of incoming air. This is known as rich liquid, that is, liquid rich in oxygen. On its way to the middle of the low pressure column, the rich liquid is passed through a silica gel filter. A filter with the necessary adsorptive capacity can remove more than 96.5% of the entrained acetylene. Basically, the system is quite simple; however, close attention must be paid to the filter design details:

DESIGN DETAILS OF SILICA GEL FILTERS

1. A suitable reflux arrangement must be set up in the high pressure column to concentrate all entrained impurities in the rich liquid.

2. A mechanical prefilter may be necessary to trap out solid carbon dioxide which otherwise would be adsorbed by the main filter and would thus cut down the filter's effectiveness.

3. The main filter must be designed generously, for several reasons:

   a) It should have adequate cross section to ensure free passage with minimum pressure drop and longer residual time.

   b) The filter should be long enough so that the top of the filter always remains uncontaminated. This assures high removal efficiency.

   c) The total amount of silica gel should exceed by a wide margin that necessary to remove the minimum amount of permissible acetylene. This assures complete removal of the dangerous hydrocarbons, such as acetylene, even though other hydrocarbons, particularly ozone, may contaminate the filter.

   d) As stated previously, every time silica gel filters are switched there is a

complete loss of the contained liquid. The filters should not be switched any more frequently than every four to seven days, otherwise the refrigeration efficiency of the plant will be impaired seriously.

   e) As a rule, design engineers use 80 to 100 pounds of silica gel per filter per 1,000 std.cu.ft./min. of air entering the air separation unit. In industrial areas 80 lbs. per 1,000 std.cu.ft./min. is a much safer design figure than the original 37 pounds used fifteen years ago. In other words, for a 100 ton/day oxygen producing unit which requires about 9,000 std.cu.ft./min. of air, each filter is filled with about 720 to 1,000 pounds of silica gel for a four- to seven-day run.

4. The mechanical design of the filter assembly should permit easy inspection and replacement of the silica gel. When filters become heavily contaminated from heavy hydrocarbons and oil vapor they should be replaced, since no amount of regeneration will restore their effectiveness. Filter contamination is indicated by a permanent black tinge. Filters should also be inspected for deterioration since powdered silica gel may get into the low pressure column and

foul up the trays. What is worse, the powder may develop a high static electric charge during its high-speed passage through the piping. These difficulties may be overcome by the use of an afterfilter and use of stainless steel for all process piping.

5. The regeneration system should be designed for a regeneration temperature of 180° F. minimum. Recent tests indicate that better and safer results are obtained with a regeneration temperature of 280° F. to 350° F. Above that temperature, the silica gel may be impaired.

The importance of maintaining a high adsorption efficiency in the filter cannot be overstressed. For example, let it be assumed that (see Figure 3):

   a) 1 ppm of acetylene enters the plant;

   b) filter efficiency is 96.5%;

   c) the K factor for acetylene is 1/15.

Under these conditions, $(1 - 96.5/100) \times 100/20$ or 0.175 ppm of acetylene leaves the vaporizer with every 20 mols of oxygen. This means that 0.175×15 or 2.6 ppm of C_2H_2 remain in solution with the liquid oxygen in the vaporizer. In other words, with a high filter efficiency of 96.5%, it is
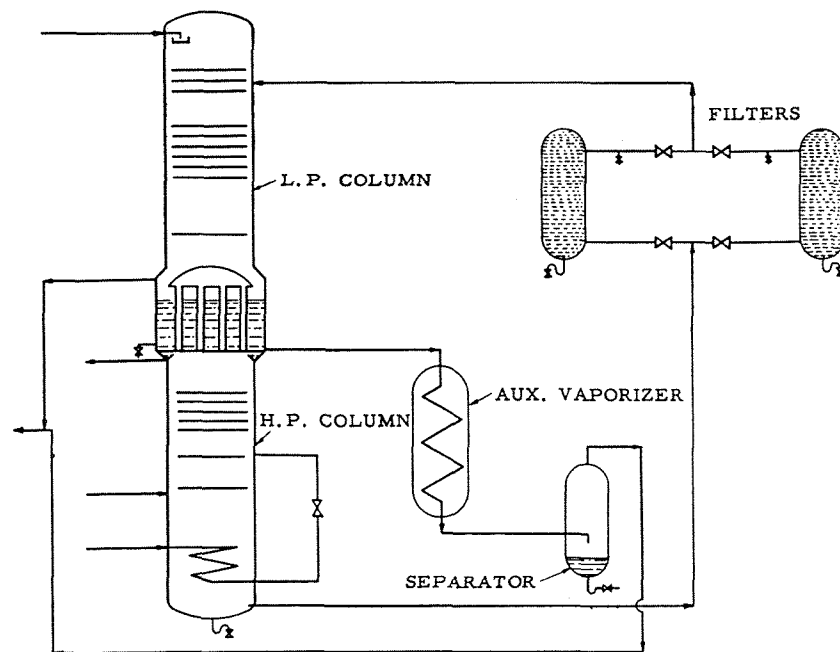
Fig. 4. Standard plant with auxiliary vaporizer.

the main vaporizer and that $0.33 \times 1/15$ or 0.02 ppm or 0.2×10^{-6} mols leave the main vaporizer with the 10 mols of oxygen that are evaporated in the normal manner. In other words, $0.33 + 0.02$ or 0.35×10^{-6} mols of C_2H_2 remain with every 20 mols of oxygen product. Since this amount was carried in by 50 mols of rich liquid, then $0.35 \times 1/50$ or 0.07×10^{-6} mols of C_2H_2 remained after the filters. This means that the filter efficiency was 96.5% if 1 ppm of C_2H_2 existed in 100 mols of air. An auxiliary vaporizer can cut down the acetylene in solution in the main vaporizer to 0.33 ppm, which means a much safer operation. Then, if the acetylene content in the air goes up from 1 to 2 ppm, or if the filter efficiency drops to say 90%, the amount of acetylene in the main vaporizer will still be well below 1 ppm. Of course, the small amount of liquid in the oxygen separator becomes supersaturated with acetylene and precipitation will occur. However, in this case, the liquid in the oxygen separator is purged out.

In both of these examples, 5 ppm has been assumed as the solubility limit of acetylene in liquid oxygen. This is an experimental value and holds true under normal conditions. However, in large oxygen plants with common vertical multi-tube vaporizers, or in any type of vaporizer which has a large amount of stationary liquid oxygen present, it would be extremely dangerous to assume a design solubility limit of 5 ppm, especially if there is no auxiliary vaporizer. Wherever there is a large amount of liquid, the acetylene may not dissolve evenly and precipitation of solid acetylene may occur in any one section of the vaporizer even though the overall ratio of acetylene to oxygen does not exceed 5 ppm. For this specific reason, whenever standard, large bath-type main vaporizers are used, most design engineers recommend that the acetylene content in the main vaporizer be kept down to less than 2 ppm.

possible to treat air with slightly less than 2 ppm of acetylene. However, if the filter efficiency drops to 93%, we obtain $(1 - 93/100) \times 100/20$ or 0.35 ppm of C_2H_2 in the gaseous oxygen product or 5.2 ppm with the liquid oxygen in the vaporizer. Since 5 ppm is the solubility limit, disregarding other considerations, we are then limited to 1 ppm of C_2H_2 in the air. It is safe practice to assume a filter efficiency of 93% and to permit only 1 ppm of C_2H_2 in the incoming air.

For an oxygen plant with an auxiliary vaporizer and separator, (Figure 4), the following calculations apply. Let it be assumed that:

a) there is 5 ppm of C_2H_2 in solution with the liquid in the separator;

b) the K factor for acetylene is 1/15;

c) 10 mols of oxygen enter the auxiliary vaporizer and 10 mols go out from the main vaporizer.

Under these conditions, 5/15 or 0.33 ppm or 3.3×10^{-6} mols of acetylene would enter and leave the separator with the 10 mols of oxygen. This also means that 0.33 ppm are in solution with the liquid oxygen in

---

AIR COMPRESSORS

Selection of the right air compressor is of the utmost importance. Whenever oil-lubricated reciprocating compressors are used, there is always danger of oil mist and oil vapor entrainment. Any financial economy realized from the choice of a compressor with a high compression ratio per stage must be weighed against the dangers due to high discharge temperature: cracking of oil; carbon deposit on valves; flash fires at the discharge end; oil vapor entering the system; and what is worse, the possibility that oil vapor may be cracked and produce dangerous hydrocarbons such as acetylene. It is always advisable to keep the compression ratio per stage sufficiently low that the discharge temperature never exceeds 300° F. In fact, it is good practice to keep it around 280° F. This will keep oil and vapor entrainment to a minimum.

A mechanical filter will not remove oil vapor. It is necessary to use adsorbent-type filters. The best solution is to use an external refrigerant to drop the air temperature down to +40° F. just before the filters. Actual practice

has proved that this is the best system for the protection of any low temperature unit against oil vapor entrainment arising from compression. The obvious solution is to use turboblowers wherever possible. One of the main advantages of low-pressure or medium-pressure oxygen plants is that they can be used with turboblowers which avoid the oil problem and are also economical to install. However, even with turboblowers, the question of proper cooling should not be minimized.

As pointed out previously, air contaminants such as hydrocarbons may well undergo partial oxidation or polymerization in the presence of NO, NO_2 or ozone during their passage through the compressor. This condition may well exist during the hot summer months, especially if the intercoolers are permitted to foul up.

EXPANSION MACHINES

Expansion machines should be so designed that there is no possibility of oil seepage into the expanded air. If oil does leak, the rich liquid filters will be contaminated and rendered useless for removal of entrained hydrocarbon.

CATALYTIC OXIDATION AND PREFILTERS

There are industrial areas whose atmosphere is so heavily contaminated that it would be impossible either to put in a long air intake or to rely only on the rich liquid filters. Under these conditions, there are two possible solutions; both are now being tried out for the first time.

A small Air Liquide oxygen plant in France has been in operation for well over a year in an area heavily contaminated with acetylene (10 to 30 ppm). After the compressor and before the aftercooler, the hot air passes through a tower packed with a special catalyst which oxidizes the acetylene and reduces it to less than 1 ppm. While this catalyst shows promise, it still requires study from the standpoint of manufacture, mechanical strength, and regeneration before it can be used on a large scale.

General commercial grades of a similar catalyst are being studied now in Air Liquide's research laboratory in Montreal, but it will take some time to develop a catalyst which will operate with a minimum of preheat, which will resist

oil contamination from the compressor and which will be regenerated easily. It is felt that catalytic oxidation may well prove to be the final avenue of approach to contamination removal problems.

In the meantime, several oxygen plants are now being built with large prefilters. These prefilters are large vessels filled with silica gel and are placed between the warm exchanger system and the liquefier. At this temperature level, silica gel will remove the bulk of all hydrocarbons below methane. In other words, the rich liquid filters will have only the function for which they were designed; namely, the removal of hydrocarbons in trace form. These prefilters will operate alternately; one will be in operation while the other is being regenerated.

Chemical Analysis

Prior to its entry into the low temperature unit, air should be analyzed for:

1. Carbon dioxide
2. Nitric oxide
3. Nitrogen dioxide
4. Ozone
5. Acetylene
6. Hydrocarbons (unsaturates)

Methods and procedures for chemical analysis are available from oxygen plant designers. Analyses should also be made on the liquid oxygen in the main vaporizer and in the separator (if used).

For safe limits, air should have the following maximum contaminants:

Acetylene ....less than 1 ppm
NO + NO₂ ....less than 1 ppm
Ozone ....less than 0.1 ppm
CO₂ ....less than 5 ppm
Oil vapor ....zero

The liquid oxygen should have:

Acetylene ....less than 2 ppm *
Hydrocarbons
   (other than methane) ..zero

*In the main vaporizer. Less than 5 ppm in the separator.

Once a year the entire plant should be shut down and derimed completely. During this period, mechanical maintenance can be carried out. Deriming operations should be carried out according to the plant designer's instructions. Finally, the plant should be flushed with a dry gas before restarting. A dew point test should be made of the air leaving every single outlet or purge.

Conclusions

An air separation unit is no more complicated, involved, or dangerous than any chemical plant involving fractionation. With constant analysis of air, the operation of an oxygen plant should be extremely stable and easy. Unfortunately, some plant operators have consistently ignored basic operating rules, and plant designers, in their eagerness to promote the use of oxygen, have minimized the general rules to be followed for safe operation.

Plant designers contend, and rightfully so, that a plant is much safer if it operates at high air pressure and produces liquid oxygen which is then withdrawn either as a liquid or is passed through liquid oxygen pumps and converted into high pressure gas. From a design standpoint, the previous statement is true; however, since no design is foolproof, one should remember that the basic rules for safe operation still apply:

1. In a high pressure plant great care must be exercised to keep air discharge temperatures at the compressor down to eliminate oil vapor entrainment and oil vapor cracking. Therefore, low compression ratios and suitable and adequate oil filtering equipment are a must.

2. While the liquid oxygen may be withdrawn from the vaporizer, this does not mean that no contaminants exist in the vaporizer. Consequently, every rule of safe operation applicable to a gas producing unit must be followed for a liquid producing unit.

3. Every rule for checking rich liquid filters, performing constant analyses, and keeping the vaporizer at top level should be followed strictly.

SAFE OPERATING PRACTICES

• Once an oxygen plant of specific design has been installed it must be operated strictly according to the designer's recommendations.

• Compressors should be properly maintained; interstage coolers and aftercoolers should be free of fouling matter. In this manner, discharge temperatures will be kept low, around 280° F., and very little oil will be cracked or vaporized.

• If bauxite or other adsorbent-type filters are used to curtail oil vapor entrainment, they should be examined periodically. Once contaminated, they should be replaced with fresh adsorbing material since regeneration would be useless.

• Precooling the air temperature to, say, +75° F. or even +40° F. is a good operating recommendation. Such precooling not only helps to cut down oil vapor entrainment and to reduce considerably the water carried by air, but it also leads to better control by helping to stabilize the operation of the low temperature unit.

• The rich liquid filters should be switched and regenerated according to the designer's recommendations. At no time, however, should the switching exceed seven days or the regeneration temperature drop below 180° F. The entire volume of liquid in the filter should be drained completely before regeneration. The regenerating air or nitrogen should be dry and oil-free. If the silica gel begins to look brownish in

Literature Cited

1. Lenher, S., J.A.C.S., **53**, 2962 (1931).
2. Pierrain, Jean, Chimie et Industrie, 189, **70**, No. 2 (August, 1953).
3. Gibson, C. H., and C. N. Hinshelwood, Proc. Roy. Soc. London, A, 130, 640 (1931).
4. Lenher, S., J.A.C.S., **53**, 2962 (1931).
5. Norrish, R. G. W., and J. Wallace, Proc. Roy. Soc. London, 150, 36 (1935).
6. Norrish, R. G. W., and J. G. A. Griffiths, Proc. Roy. Soc. London, A, 139, 147 (1933).
7. Bone, W. A., and S. G. Hill, Proc. Roy. Soc. London, A, 129, 434 (1930).
8. Jost, W., "Explosion and Combustion Processes in Gases," McGraw-Hill Publishing Company, New York (1946).
9. Stephens, E. R., W. E. Scott, P. L. Haust, and R. C. Doerr, preprint lecture to A.P.I., Montreal (May 16, 1956).

appearance, it should be replaced with a fresh charge.

• The liquid in the main vaporizer should always be maintained at top level. If the plant has to be stopped for any period of time, the vaporizer may have to be drained completely. Available statistics indicate that the great majority of mishaps have taken place when the vaporizer was operating at below normal level. This implies that the explosive contaminants were given a chance to conglomerate on dry surfaces. In other words, one must consider the relationship of the total amount of contaminants to the amount of gaseous oxygen present and not the total amount of oxygen whether gas or liquid.

• In heavily contaminated areas, where there is a risk of running over the solubility limit of acetylene, 5 ppm, the liquid in the lower portion of the vaporizer should be purged continually (up to 3% of the total production). Under similar conditions, but where an auxiliary vaporizer and separator are used, the liquid in the separator (up to 3% of total production) should be purged. In the latter case, the controlling factor would be the acetylene or hydrocarbon analysis of the liquid in the separator. In both cases the purging operation must not be abrupt as it may affect the operating level of the main vaporizer.