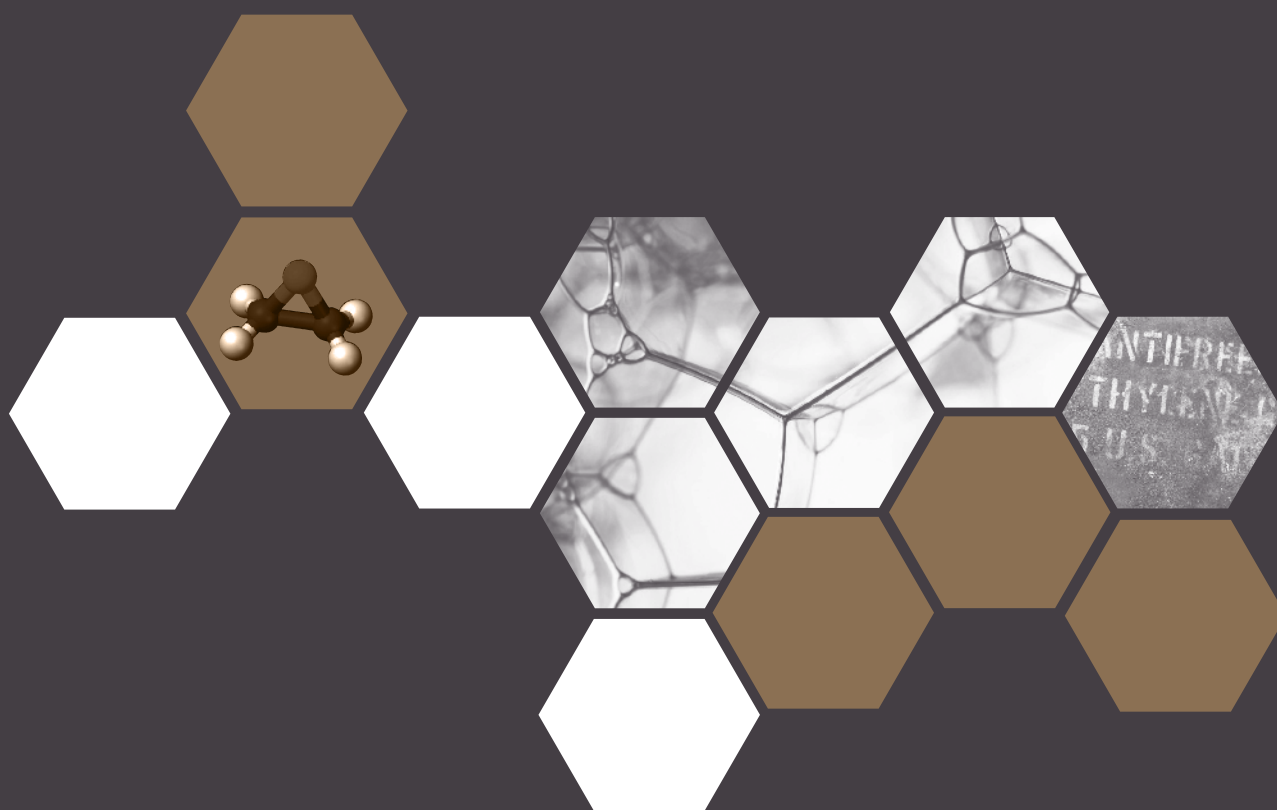


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To the Reader

Manual Preparation

As members and affiliated companies of the American Chemistry Council, we support efforts to improve the industry's responsible management of chemicals. To assist in this effort, the American Chemistry Council's Ethylene Oxide/Ethylene Glycols Panel supported the creation and publication of this manual. The Panel is comprised of the following companies:

Balchem Corporation/ARC Specialty Products

BASF Corporation

Bayer Material Science LLC

Celanese Ltd.

Champion Technologies

Croda, Inc.

The Dow Chemical Company

Eastman Chemical Company

Honeywell

Shell Chemical LP

The development of this manual was led by the Panel's Ethylene Oxide Safety Task Group (EOSTG), a group comprised of producers and users of ethylene oxide. The EOSTG functions to generate, collect, evaluate and share information to support product stewardship with regard to ethylene oxide. The EOSTG formed a manual work group, chaired by Keith Vogel of Lyondell Chemical Company, to lead the development of this document. The following work group members provided significant contributions:

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6.0 Design of Facilities

6.1 Introduction

The characteristics of EO – including flammability, toxicity and reactivity – are crucial considerations in the design of facilities for the storage, transport, and processing of this material. This Chapter, which summarizes some important issues relevant to EO facility design, addresses not just the chemical and physical characteristics of EO, but also includes discussion of the practical experience of industry. It is particularly helpful to review Chapter 2, Properties of EO, and Chapter 5, Hazards of EO, before reading this Chapter.

Note that risk assessment and hazard analysis, mandated by OSHA Regulations at 29 CFR 1910.119, are an integral part of the initial design of the facility and must also be conducted before making modifications to equipment and procedures.

6.2 Plant Layout and Siting

This section addresses general considerations for siting of EO storage vessels, pumps and piping. Some important considerations in selecting the location of EO storage vessels include:

- Criteria developed for LPG in NFPA [1], [2], [3] and API [4] standards to establish separation distances;
- Distance from operating plants, offices and perimeter fences;
- Distance (and adequate isolation) from fire hazards and potential ignition sources;
- Whether the location is a low fire risk area;
- Accessibility of the vessel to emergency responders (e.g., is it in an “open” area);
- Intended use of the storage vessel for inventory control (e.g., for EO in process feed vessels in the immediate vicinity of the plant, consider the minimum quantity of inventory compatible with the effective control and safe operation of the process concerned);
- Potential impacts of a release on the community; and
- Site security.

EO pumps are potential sources of fire hazard; for example, a mechanical seal failure and EO release, followed by fire. When locating a pump, consider the possible effects of a pump seal fire on surrounding equipment or railcars. Two techniques available to help mitigate potential hazards include pump installation within a diked or curbed area with leaks/spills routed to a secondary containment area and pump installation in a separate containment area from storage vessels.

EO piping is also a potential source of fire hazard. For routing EO piping, some key considerations include:

- Proximity to utility piping and systems essential to plant safety in the event of an EO fire;
- Minimizing EO piping through hazardous plant areas;
- Minimizing EO piping adjacent to higher temperature lines (>400°F/204°C) where there is a possibility of heating the EO in the piping;
- Minimizing EO piping close to lines containing corrosive chemicals that could damage the pipe; and
- Protecting grade-level pipe runs from impact damage, especially if piping is adjacent to road and railways.

Routing EO piping underground increases the possibility of corrosion and makes inspection more difficult. It may, however, reduce or eliminate the need for insulation, and it may significantly reduce or eliminate potential exposure to fire. For EO piping routed underground, installation of a cathodic protection system which is regularly maintained will help protect the EO piping from corrosion.

Electrical equipment in areas that produce, store, use, load or unload EO must conform to National Electrical Code, Class I, Division 1 or 2, Group B (or Group C if conduit seals comply with NEC paragraph 501-5(a)).

6.3 Materials of Construction

Because of the reactivity of EO, materials in contact with EO must be chosen with care.

Metallic Materials (Metals and Alloys)

Equipment for storage and handling of EO is generally fabricated from 300 series austenitic stainless steels or mild carbon steel. Stainless steels have the advantage of minimizing the potential for rust, which can catalyze EO polymerization. Cast iron is not considered suitable for EO use due to the low ductility of the material.

Austenitic stainless steels such as Type 304 and Type 316 are typically used for tubing, small piping, instrumentation and other equipment that cannot be readily cleaned of rust. Use of austenitic stainless steels is also appropriate in areas where EO liquid or vapor is likely to remain stagnant for periods of time.

Note that, depending on location and process conditions, stainless steels can be subject to stress corrosion cracking from naturally occurring atmospheric chlorides. External coating in such circumstances is an appropriate measure to address corrosion potential.

When carbon steels are chosen, it is important that they retain integrity under the full range of temperatures encountered in the specific application. Also note that the presence of rust (iron oxide, in the form of red hematite or black magnetite) on internal surfaces of carbon steel equipment leads to polymerization of EO.

Carbon steels are also susceptible to external corrosion from wet external insulation and wet metal surfaces. These conditions can occur from ingress of rainwater and also by condensation of atmospheric moisture on cold metal surfaces (for example, equipment containing refrigerated EO). Use of a suitable coating on the carbon steel equipment and periodic monitoring of the physical integrity of the coating and equipment, can help minimize the risk of corrosion. Monitoring is conducted in accordance with the plant's mechanical integrity program (required under OSHA Regulations at 29 CFR 1910.119). External corrosion is a concern when the operating temperature of the equipment is below approximately 200°F (93°C) because this temperature range is too low to evaporate water

that penetrates under insulation. For example, the typical operating temperatures of EO purification columns make them particularly vulnerable to external corrosion. There have been several cases where carbon steel EO purification columns experienced serious external corrosion above insulation support rings where water was trapped. External corrosion has also been observed in carbon steel EO storage vessels and piping.

Historically, metals such as copper and silver and their alloys have not been used in EO service. This was based on the potential for the formation of metal acetylides, which are explosive. The current EO production technologies in use in North America do not result in the formation of acetylene.

Published literature describing the compatibility of mercury with EO presents an inconsistent view concerning hazards that may result from the contact of these two substances. Some papers suggest that elemental mercury can promote and accelerate the decomposition of EO. Others suggest that the presence of small, trace quantities of acetylenes contained in the EO is the source of the hazard (acetylenes react with the mercury to form explosive mercury acetylides). While the literature does not present a consensus view as to whether elemental mercury may present a potential safety hazard if it comes into contact with EO, limiting the use of mercury in EO service, where appropriate or practicable, may reduce the risk of a reactive hazard.

Non-Metallic Materials

EO rapidly attacks and degrades many of the organic polymers and elastomers that are used to make O-rings, packing material and gaskets. When selecting non-metallic materials of construction in contact with EO, it is important to understand the rate of degradation of the material. A good starting point is to review available test data specific to the EO service being considered. However, because material degradation may be affected by multiple complex factors, industry field testing or field experience with the material may also be extremely useful in helping to inform the selection.

If neither test data nor field experience data is available to help select a material of construction, consider conducting a field test that includes an analysis of consequence of material failure. If a field test is used, additional measures to monitor

and evaluate the performance of the material are generally implemented, which may include:

- Testing the material in a limited number of applications;
- Testing the material in a type of application where the consequence of a material failure is minimized (for example, testing only the inboard seal on a double mechanical seal);
- Increasing the frequency of monitoring for EO leaks; and
- Increasing the frequency of inspection of the material being tested.

Gaskets

Design criteria for gaskets include materials of construction, gasket thickness and torque. There may be other gasket design criteria relevant to the specific joint. Once a facility specifies the gasket(s) to be used in EO service, it is useful to adopt a process or system to check that the specified gasket(s) are actually in use. There have been cases in the industry where one gasket was specified but a different gasket was inadvertently installed, resulting in an EO leak.

Asbestos and asbestos-filled materials are not durable in EO service. Industry experience has shown that asbestos gaskets are attacked by EO and have failed catastrophically without any prior warning. (Figure 6.1)

Polytetrafluoroethylene (PTFE) is chemically resistant to EO at temperatures as high as 400 - 500°F (204 - 260°C). Virgin (non-filled) PTFE, exhibits cold flow behavior at all temperatures and does not work well as a gasket material in most conventional applications. Several EO operations have experienced cold flow incidents with virgin PTFE (non-filled) gaskets resulting in EO releases. (Figure 6.2) At least one of these incidents was followed by ignition and significant damage to the facility. In well-confined applications (such as valve packing and tongue and groove joints), virgin PTFE can be used successfully.

Because of its tendency to cold flow, PTFE for gasket applications is typically filled with glass fibers or ceramic particles to increase its dimensional stability. Glass and ceramic filled PTFE may absorb EO. If this occurs, the EO polymerizes within the PTFE-filler matrix and the resulting EO

Figure 6.1 Degradation of Compressed Asbestos Valve Bonnet Gaskets by Ethylene Oxide

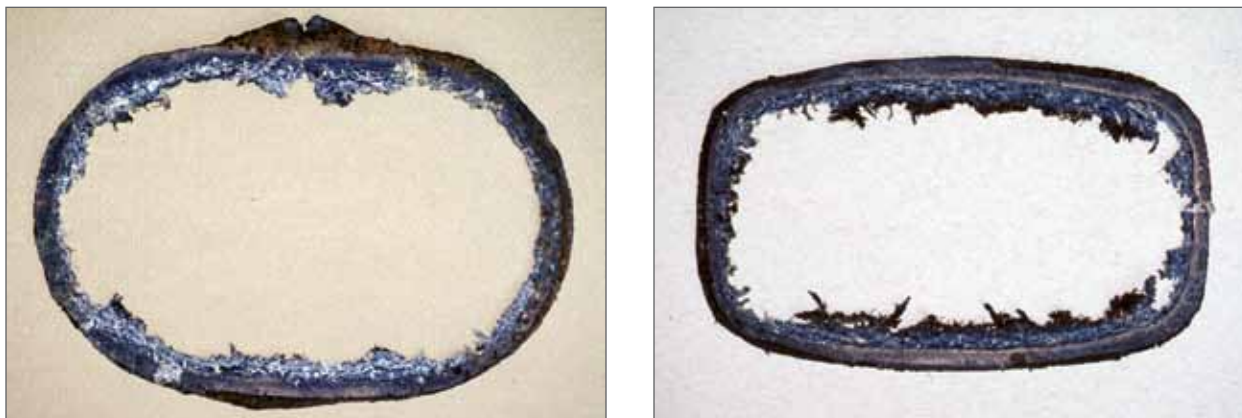


Figure 6.2 PTFE Gasket Failures in EO Service Due to Cold Flow



polymer causes swelling and failure of the gasket. Glass and ceramic filled PTFE gaskets have failed in many applications in EO service, especially at higher temperatures (Figure 6.3)

Spiral wound gaskets with stainless steel windings and virgin PTFE or graphite filler have been successfully used to seal raised face flanges and valve bonnets in EO service. However, there have also been many incidents where EO permeated between the windings and the filler material and polymerized. If EO permeates this space, EO polymer can swell and generate enough force to cause deformation or unwinding of the gasket (Figure 6.4). Inner and outer retaining rings will help avoid unwinding of the spiral wound gasket in the event that EO polymer forms within the windings. In isolated instances, polymer formation may deform the gasket windings even with inner and outer retaining rings (Figure 6.4, 6.4a) When installing spiral wound gaskets, compressing the gasket evenly will help reduce the possibility of gasket failure due to EO permeating between the windings and filler. Proper gasket placement, flange alignment and torquing procedures have been used effectively to achieve even compression.

High purity (98% or higher), flexible compressed graphite is a commonly used gasket and packing material in EO service. This material has no fillers or binders and is chemically compatible for use with EO. High purity, flexible compressed graphite is available in flat sheet form as well as crinkled tape for valve packing. The sheet form of flexible graphite is somewhat fragile, so for gasket applications the sheet is typically used as filler for stainless steel spiral wound gaskets. (Figure 6.5)

In EO service applications where spiral wound gaskets cannot be used, laminated flexible compressed graphite gaskets are often used. Several manufacturers produce gaskets from two layers of flexible compressed graphite laminated to a 0.004" tang (perforated) stainless steel sheet. Because the graphite is laminated to tang stainless steel sheet, there are no adhesives used in the lamination process. (Figures 6.7 and 6.8) If a laminated gasket is used, it is important to specify a tang stainless steel sheet rather than flat stainless steel sheet. Tests have shown that EO will attack some adhesives that are used to bond flexible graphite to flat stainless steel sheet (Figure 6.8).

Figure 6.3 Glass Filled PTFE Gasket Failure Due to EO Polymerization in PTFE-Glass Matrix



Figure 6.4a Deformation of a Spiral Wound Stainless Steel-PTFE Gasket Due to EO Permeation and Polymerization



Figure 6.4b Deformation of a Spiral Wound Stainless Steel-PTFE Gasket



Figure 6.5 Spiral Wound Gasket with Stainless Steel Windings, Flexible Compressed Graphite Filler, and Inner and Outer Retaining Rings



Figure 6.6 Laminated Gasket Made of Polycarbon Sigraflex™ BTCSS Flexible Compressed Graphite – Laminated on Stainless Steel Tang Sheet

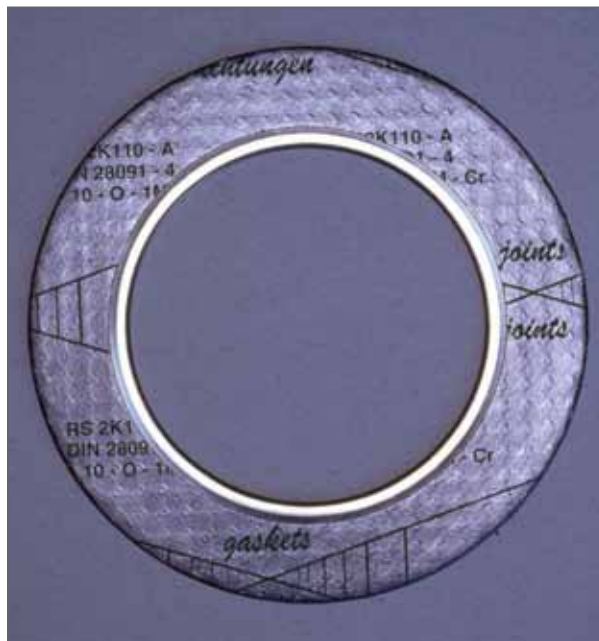


Figure 6.7 Laminated Gasket Made of UCAR Grafoil GH™ E Flexible Compressed Graphite – Laminated on Stainless Steel Tang Sheet

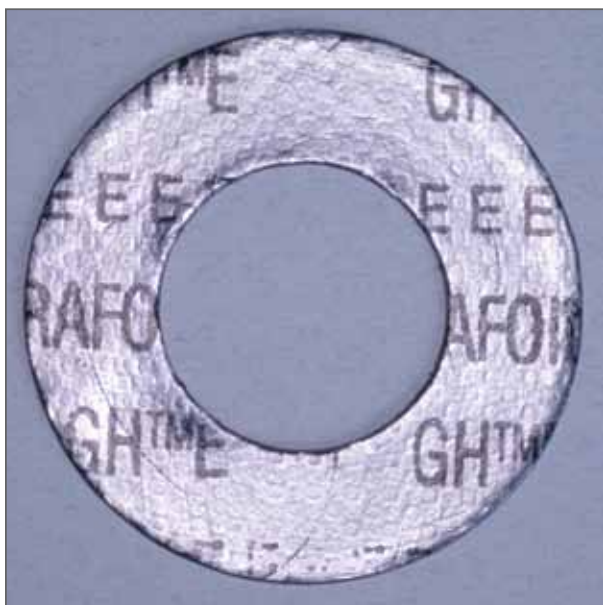
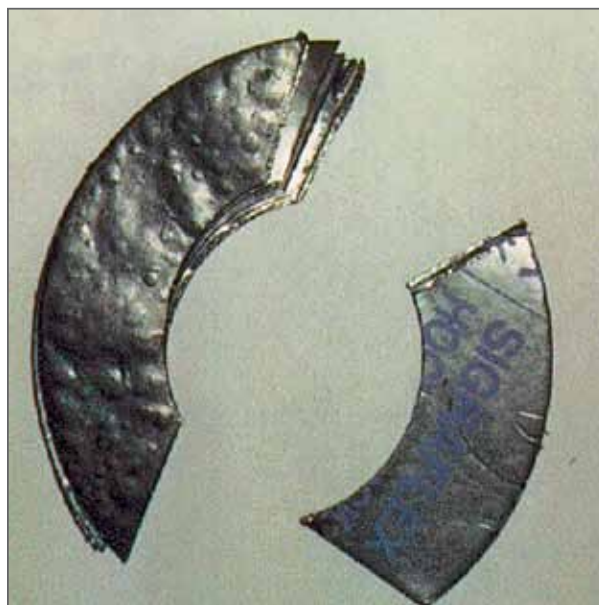


Figure 6.8 Gasket Test Showing Failure of Compressed Graphite Gasket, Laminated on Flat Stainless Steel Sheet with an Adhesive



O-Rings

Elastomers, which are most commonly used to make O-rings, often will degrade in EO service. Experience within the EO industry has shown only a few elastomers to perform well in EO service. Note that elastomers that have performed well in EO service may not perform well in applications that involve with mixtures of EO and other chemicals. For example, industry experience has shown that even though some elastomers perform well in applications in pure EO service, they will degrade in high temperature EO/water mixtures. (Figures 6.9, 6.10, 6.11)

The following is a list of elastomeric O-ring materials that laboratory tests have shown to be compatible with EO (refer to Appendix B for test methods and results):

- Chemraz® 505
- Kalrez® 2035
- Kalrez® 6375
- Parker EPDM-740-75
- Parker EPDM-962-90
- Parker E-515-8-EPM

The following elastomers are commonly used O-ring materials in many non-EO applications in the chemical industry. Laboratory test results show that these materials are not compatible with EO.

- Kalrez® 1050 LF
- Viton® 2F (V1163-75 FKM75A)
- Nitrile (N304-75 LT Nitrile 75)
- Butyl Rubber (Bu-70)

Figure 6.9 Butyl Rubber O-Ring Before and After Exposure to EO for 30 days



Figure 6.10 Example of Degraded O-ring Attacked by EO

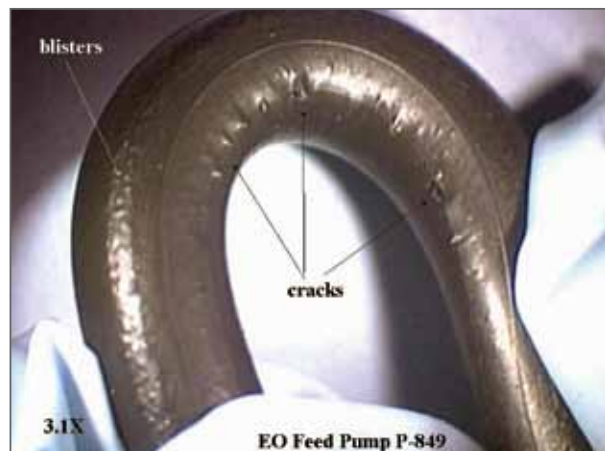
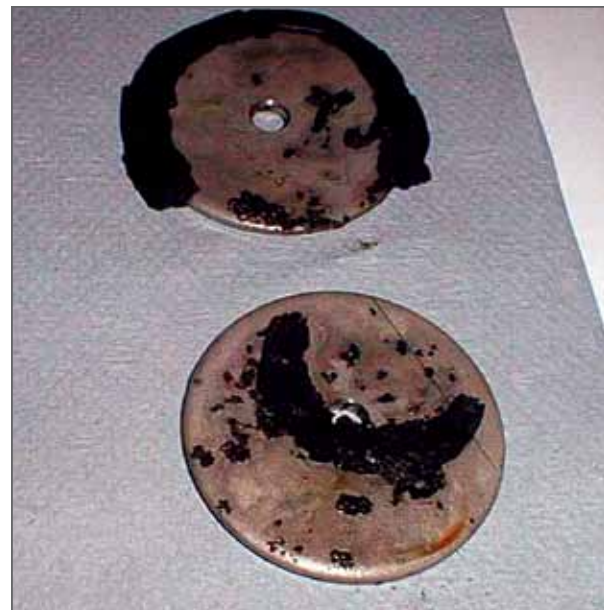


Figure 6.11 Example of Severely Degraded O-ring in High Temperature EO-water Service



Packing (Valves)

Both flexible graphite and PTFE have been successfully used as packing materials in EO service. Corrugated, flexible, compressed, high purity (98%) graphite ribbon and virgin PTFE rings or chevrons, are examples of typically used packing materials.

Durability of non-metallic materials in EO service varies with the material used and with the process conditions. An inspection program can help determine the durability and required change-out frequency for the materials selected for a given application.

Insulation

Insulation provides a degree of protection for metal walls of vessels, piping and other equipment from being heated to EO decomposition temperature by external flames. Selection of insulating materials for EO service takes into consideration many factors.

Use of closed cell non-combustible insulation materials, such as cellular glass, reduces the potential for water absorption and for exothermic reactions in the event of an EO leak under insulation. Porous insulating materials such as magnesium silicate, calcium silicate, fiberglass, mineral wool, or asbestos can absorb moisture from the environment and retain EO, which may have leaked from gaskets, pinhole leaks, or elsewhere. If water is also contained in the insulation, the EO will react with the water to form polyglycols in a highly exothermic process, creating heat in and under the insulation. The heat of reaction is trapped by the insulation, resulting in high surface temperatures. In addition to the heat generated by the exothermic polyglycol formation, the polyglycols act as a fuel reserve. With air ingress into the insulation, polyglycols can spontaneously combust at temperatures of less than 212°F (100°C), depending on the liquid loading, insulation type, thickness, and rate of air ingress. EO leaks under porous insulation resulting in hot spots and internal ignition have been implicated in major industrial incidents. Two such incidents are discussed in Chapter 5.

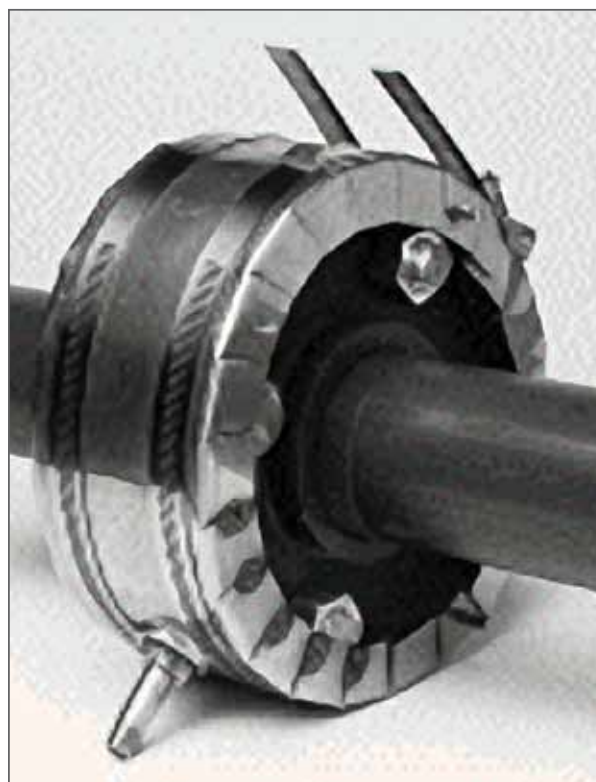
Note that although polyurethane foam is a non-porous insulation material, it is combustible and will not provide insulation protection in a fire scenario. Loss of insulation in a fire scenario can result in an

EO decomposition.

Aluminum insulation jacketing (sometimes called sheathing) and banding have a relatively low melting point. In a fire scenario, insulation can be lost when aluminum sheathing and bands melt or burn. Stainless steel or galvanized carbon steel jacketing and banding has superior fire resistance to aluminum.

For insulated flanges, it is helpful to install leak detection tubes at the flanges. Sealed stainless steel bands installed around the flange can help prevent transport of liquid along the piping. (Figure 6.12) In horizontal lines, pre-formed snap-on insulation boxes can be adapted so that in the event of leakage the liquid will be drained.

Figure 6.12 Example of Flange Seal Band with Leak Detection Drip Tube



6.4 Unloading Facilities – Bulk Receipt of EO

Design consideration for EO unloading facilities seeks, among other things, to minimize the potential for contamination of EO. One mechanism to achieve this is to design a system dedicated exclusively to EO.

Backflow of process contaminants into an unloading EO railcar can contaminate the EO, so facility design will seek to avoid the potential for backflow. Intermediate storage vessels downstream from the offloading facility are commonly used to avoid backflow, but other engineering controls have been successfully used.

Locate the EO unloading area with sufficient separation from inventories of flammable materials and with sufficient space to allow movement of railcars. Provide sufficient space in the unloading area for vehicle access.

Acceptable means of transfer from a railcar or intermodal (IM) portable tank into the storage facility include pressurization with nitrogen gas and pumping. If pressurization is used, design considerations include controlling the pressure applied to the railcar and adopting an appropriate means for venting off excess pressure. If EO railcars are pressure off-loaded with excessive nitrogen pressure, the relief valve O-rings may be damaged by premature weeping of the relief valve (75 psig safety valve setting per DOT requirements). Off-loading at pressures no greater than 50-55 psig greatly reduces this potential.

Because of the flammability and reactivity hazards of EO, pressurized transfer by heating is not an acceptable practice.

Typical layouts for a pressure transfer facility and a pump transfer facility are shown in Figures 6.13, 6.14, and 6.15.

Design of unloading facilities also takes into consideration adequate electrical grounding, which prevents dangerous differences in electrical potential developing between the carrying vessel, body of the vehicle, piping, and ground or earth

while unloading the shipping vessel. If a manual grounding system is used, consider including a ground indication light and/or interlocks.

Installation of a water deluge system and fire monitors at the unloading site can help support on-site fire fighting, enhance the ability to “knock down” EO vapors, and provide water for the dilution of EO that might pool in the unloading area in the event of a release. Water deluge systems that can be activated manually (either at the unloading site or at a remote location); by combustible gas detectors; or by high temperature sensors are available for use in EO service.

Facility design considerations also include mechanisms to access the railcar dome while unloading. DOT regulations require protection against inadvertent movement of the railcar during connection of the loading/unloading hoses. Use of an elevated rack for railcar dome access is an appropriate approach.

Figure 6.13 EO Unloading Facilities



Figure 6.14 Representative layout of Ethylene Oxide unloading facilities – Pressurized transfer

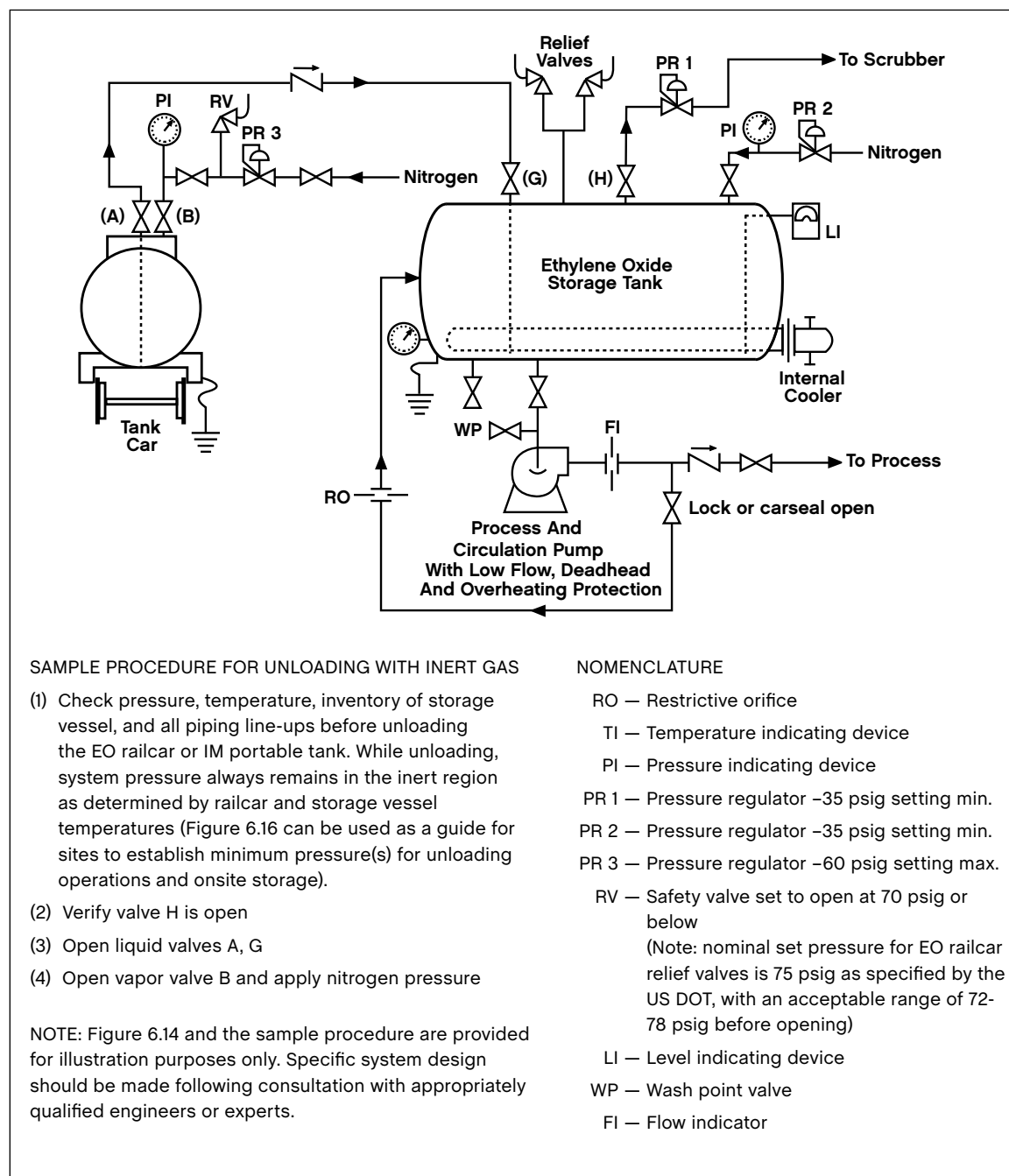
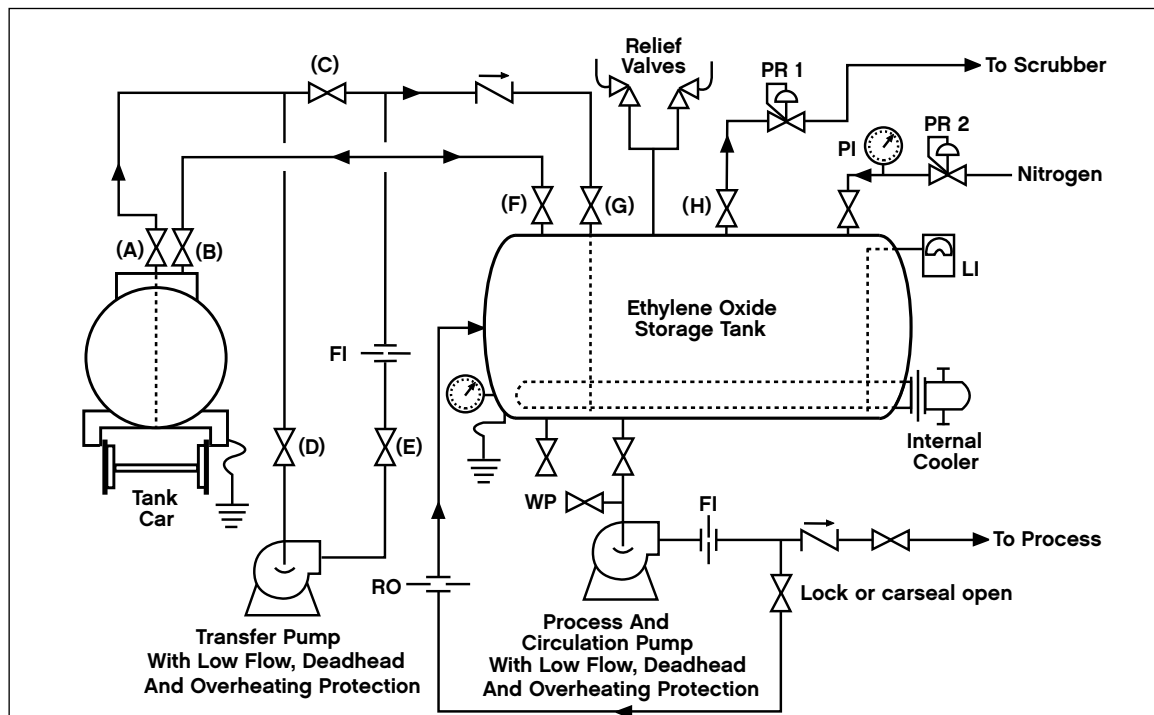


Figure 6.15 Representative layout of Ethylene Oxide unloading facilities – Pump transfer



SAMPLE PROCEDURE FOR UNLOADING WITH TRANSFER PUMP –

- (1) Check pressure, temperature, inventory of storage vessel, and all pipe line-ups before unloading the EO railcar. While unloading, system pressure always remains in the inert region as determined by railcar and storage vessel temperatures (Figure 6.16 can be used as a guide for sites to establish minimum pressure(s) for unloading operations and onsite storage).
- (2) Open liquid valves A, D, E, G
- (3) Close liquid valve C
- (4) Open vapor valves B, F
- (5) Check that the transfer pump is properly primed and not vapor bound

NOTE: Figure 6.15 and the sample procedure are provided for illustration purposes only. Specific system design should be made following consultation with appropriately qualified engineers or experts.

NOMENCLATURE

- RO – Restrictive orifice
- LI – Level indicating device
- TI – Temperature indicating device
- WP – Wash point valve
- PI – Pressure indicating device
- FI – Flow indicator
- PR 1 – Pressure regulator -35 psig setting min.
- PR 2 – Pressure regulator -35 psig setting min.
- PR 3 – Pressure regulator -60 psig setting max.
- RV – Safety valve set to open at 70 psig or below
(Note: nominal set pressure for EO railcar relief valves is 75 psig as specified by the U.S. DOT, with an acceptable range of 72-78 psig before opening)

6.5 EO Storage

EO Storage Vessels – Types

A variety of EO bulk storage vessels have been successfully used by industry. Considerations for vessel type selection include site location, size of space available, and regulatory requirements, as well as the features of the types of vessels noted as follows:

- Aboveground and free standing vessels (three types):
 - **Cylindrical (vertical)**. Advantages: minimum flame impingement; ease of monitoring inventory; less potential for accumulation of polymer.
 - **Cylindrical (horizontal)**. Advantages: less exposure to flying debris in the event of an incident.
 - **Spheres**. Advantages: less potential for accumulation of polymer.
- Mounded (vessels at grade level covered with sand or soil) and buried vessels.
 - **Advantages**: passive fire protection and protection against impact.
 - **Disadvantages**: unable to readily detect leaks if not double walled; top take off eliminates the need for underground flange connections but increases potential for polymer accumulation in the sump; it can be difficult to inspect external shell condition, sometimes necessitating internal entry to verify shell integrity.

Selection of storage vessel type will be dependent on company philosophy, plot space, and regulatory requirements. Long-term and extended storage of EO should be made in storage vessels designed or appropriately managed for this purpose.

Design Considerations – EO Storage Vessels

Vessel capacity is a relevant design consideration for storage vessels. Providing sufficient vessel capacity to allow unloading of an entire railcar in one continuous operation will minimize railcar connection/disconnection operations and the potential for EO release and personnel exposure.

NOTE: EO in railcars is not as readily monitored for temperature or pressure increases as in specially designed storage vessels. Railcars have no capability for external heat removal in case of EO polymerization or reaction with a contaminant. EO railcar relief valves are generally sized for fire conditions and not for reaction scenarios.

Diking and containment are other important considerations when designing an EO storage area. Locating above-grade EO storage vessels within a diked area, or an area otherwise designed to contain vessel leaks or spills, can help prevent other product spills from entering the EO storage area. Protection of an EO storage vessel from possible exposure to a pool fire should be a major consideration when designing an EO storage area. A pool fire under an EO storage vessel is a very hazardous situation that can lead to an EO decomposition. If diking is used, it is very important to design the EO storage area with an adequate grade under the storage vessel and in the storage vessel dike area so that any liquid release will drain away from the vessel and cannot form a pool beneath or adjacent to the vessel. Another containment option is the use of a drainage system under EO storage vessels that routes liquid to a secondary containment area located well away from the EO storage vessel. This approach can be used to contain both EO spills and firewater or dilution water.

Fire Protection Systems

Fire protection measures are also considered in the design process. Passive fire protection, such as insulation, can provide additional fire protection for those vessels located above grade and not mounded or buried. Remotely operated, fire-resistant valves allow isolation of the storage vessel in the event of an emergency. Additionally, excess flow check valves can be used at the vessel inlet and outlet lines to minimize releases in the event of downstream piping and equipment failure.

NFPA 58 and API 2510 and 2510A may apply to the design of fire protection systems for EO storage and processing areas. These codes describe fire protection systems with passive (insulation) and active (deluge/sprinkler) systems. Areas appropriate for deluge protection can be identified

using process hazards analysis methods that examine the severity of the consequences of a fire scenario.

A fire protection system takes into consideration whether fire water supplies are located so as to be readily available and sufficient in volume so as to adequately dilute a spill. Drainage design for the system includes the capacity to retain emergency water whether used for cooling, fire fighting, or dilution purposes.

Storage vessel design pressure and inerting of storage vessels

A primary consideration in vessel design is vessel pressure. Consult the current ASME Code for Unified Pressure Tanks for the minimum design working pressure consistent with process requirements, including consideration of the blanket inert gas pressure needed to maintain a non-decomposable vapor space.

Understanding pressure is extremely important due to the potential for pure EO vapor to decompose explosively. Refer to Section 2.3 for more information. EO vapor spaces can be rendered non-decomposable by dilution with the appropriate concentration of an inert gas. In practice, vessels are most often inerted with nitrogen and are maintained in the non-decomposable region by controlling pressure and temperature.

CAUTION: Carbon dioxide is generally not used as an inerting gas. CO₂ exhibits very high solubility in liquid EO (approximately ten times that of nitrogen).

Based on existing published data, Figure 6.16 illustrates the storage pressure needed in fixed storage vessels to achieve a non-decomposable EO vapor space, as a function of liquid storage temperature. (Refer to Chapter 9 and Appendix C for pressurization of railcars.) The figure assumes use of nitrogen as the inerting gas. The graph is a useful tool for calculating an appropriate storage temperature for EO facilities and operations. In selecting an inerting pressure, a key consideration is to maintain the vapor space in the non-decomposable or inert range over the full range of EO storage temperatures. Calculating the inerting pressure required in the event of loss of cooling can be factored into the storage vessel design process.

Storage vessel contamination, backflow and inerting

Contamination of EO in storage vessels can lead to an uncontrolled runaway reaction with serious consequences if facility design does not include measures to prevent or mitigate such incidents. Possible sources of storage vessel contamination include:

- Backflow from other process areas
- Incorrect vessel line-ups, allowing other materials to enter the storage vessel
- Contaminants in the inerting gas
- Contaminants such as water, cleaning solutions and other materials inadvertently remaining after maintenance

Backflow of process fluids into EO storage vessels from other process areas, such as reactors, can result in an extremely rapid, exothermic reaction. Be aware that storage vessel emergency relief valve /device sizing and cooling system capacity (if so equipped) may not consider runaway reactions as a design case. Consequently, system engineering is critical to prevent or minimize backflow from occurring.

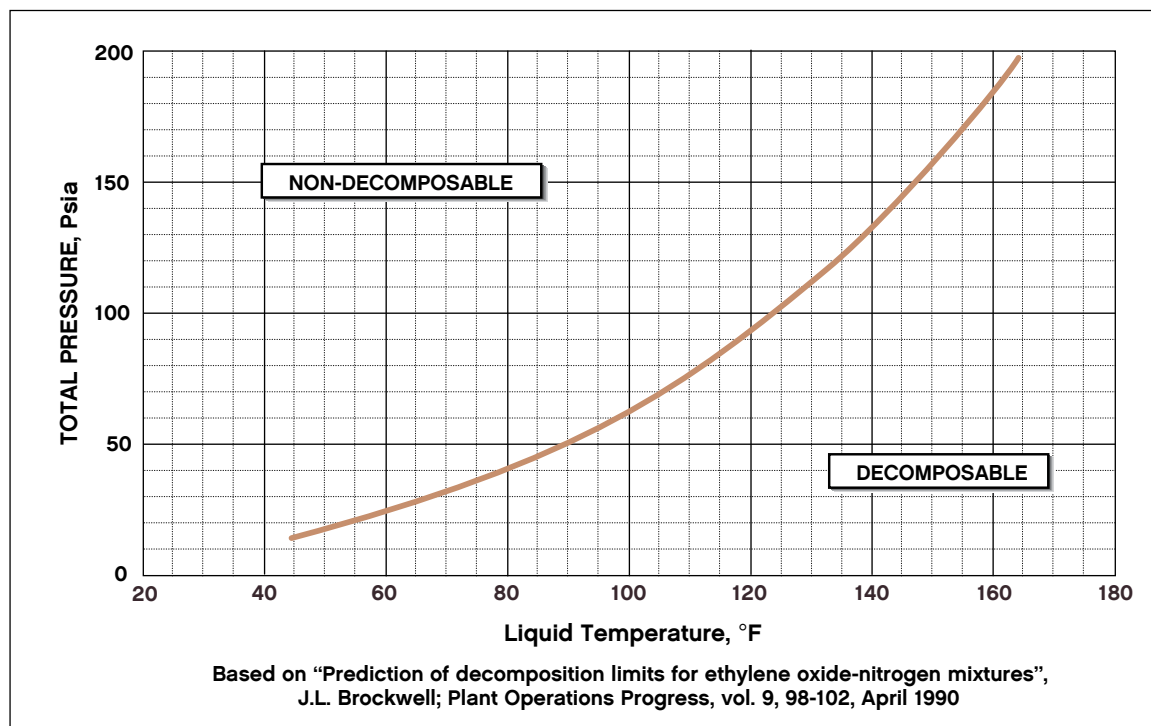
Engineered backflow prevention systems can provide a reliable and robust system to prevent backflow of process fluids into EO pipeline and storage facilities. See discussion on *Prevention of Backflow in Reactors* in Section 6.6, Reaction Systems, for more information.

Historically, check valves have been used as part of an overall system to prevent backflow of process fluids into EO supply pipeline and storage systems. Industrial experience has shown that a single check valve alone may not be an adequate backflow prevention device. Multiple check valves of the same type may experience common mode failures. Consider multiple check valves of different types and/or automatic isolation valves to protect against backflow.

EO users should be aware that inerting systems are themselves potential sources of contamination. Systems used to prevent inert gas contamination include:

- Dedicated sources of inert gas, such as high-pressure cylinders, or liquid nitrogen storage and vaporizers.

Figure 6.16 Total pressure required to inert vapor above Ethylene Oxide with nitrogen diluent



- Area knockout pots with high liquid level alarms or interlocks on nitrogen supply lines. This design can prevent contamination of EO with other chemicals while also preventing the contamination of other plant systems with EO.
- Continuous analyzers (for contaminants) on inerting systems.
- On a high pressure nitrogen supply pipeline – (1) the EO user uses nitrogen first, ahead and upstream of all other users and/or (2) there are backflow prevention systems at each point of nitrogen withdrawal, for each user (a single check valve is not relied on as the sole means of preventing inert gas contamination).

Incorrect vessel and pipeline manifolding can also lead to contamination of the EO storage vessel, resulting in the potential for violent reaction. Dedicated EO storage and piping systems are used from off-loading to storage to reduce the potential for contamination. Clearly marked and identified EO pipelines, especially in the receiving area, have been used to prevent unloading an incompatible fluid into an EO vessel.

Storage vessel pressure relief systems

Pressure relief devices are sized to relieve pressure developed by the controlling contingency identified for that process. A safety analysis of the process is conducted to define the characteristics of the controlling contingencies. Pressure relief devices, however, are not designed to provide relief in cases such as explosive decomposition of EO. Additional information about proper sizing of relief systems can be found at:

- API Recommended Practices #520-521 (addresses sizing of pressure relief valves; these practices do not cover reaction scenarios)
- NFPA 58: Liquefied Petroleum Gas Code (pressure relief guidelines)
- ASME Code for Unfired Pressure Vessels (design standards for relief protection).

Uncontrolled releases can be minimized by setting an adequate margin between ordinary operating pressure and the design pressure of the storage vessel to minimize such uncontrolled releases.

With regard to the routing of relief valve discharges, some systems are designed to vent to the atmosphere, while other systems are designed to feed into a flare or scrubber. If routing to a scrubber, consider the pressure drop across the scrubber and the possibility of plugging or damage in the scrubber in the design. If vented to atmosphere, discharges from pressure relief devices are designed with adequate height and discharge velocity to prevent contact of flammable vapor clouds with potential ignition sources. Addition of steam to the relief valve outlet piping, manually or automatically, can improve dispersion and reduce flammability of the EO plume. Relief valve discharge piping routed to the atmosphere is also designed to minimize potential for human exposure. See Section 6.8 for additional information on design considerations for controlling vent emissions.

Atmospheric discharge from safety valves and vents can result in a fire or an explosion. In some incidents, flames from ignited vent streams were found to have impinged on vessel walls or piping. Directing vents and safety valve discharges of EO and other flammables well away from equipment or piping containing EO is therefore an important design step.

Rupture disks on EO storage vessels should not be used for pressure relief because they will not reseal. Use of a rupture disk in conjunction with a pressure relief valve for control of fugitive emissions may, however, be appropriate.

In EO pressure relief system nozzles, blockage by polymerization has been observed in both EO liquid and vapor service (in EO vapor service, the EO condenses and polymerizes). This condition can be minimized or avoided by a number of different approaches, including, but not limited to:

- Locating pressure relief devices as close to the vessel shell as possible. Stagnant vapor in long lengths of dead-ended pipe may promote polymer formation.
- Bursting/rupture disks can be placed on the upstream side of the pressure relief valves to help prevent accumulation of polymer in the pressure relief valve. (Non-reclosing bursting/rupture disks are generally not used as a

method of emergency relief; such devices would allow the continued escape of EO from the storage vessel.) If equipped with a bursting/rupture disk upstream of the pressure relief valve, a method of indicating failure of the disk, such as a pressure gauge between the disk and pressure relief valve, might be considered.

- Introducing a small nitrogen stream into the nozzle upstream of either the bursting disk or relief valve to sweep away EO and prevent polymer formation in the nozzles. If the discharge is in to a header system, a nitrogen sweep downstream of the relief valve may be warranted.
- Using stainless steel as a material of construction for piping, isolation valves, and relief valves.

Note that the lifting of a storage vessel relief valve or similar action by other pressure relief devices is not considered to be a routine pressure management event for EO service. These devices are intended to function as emergency venting devices and not as a part of routine pressure control practices.

Instrumentation

EO storage instrumentation is designed to provide accurate level measurement, accurate temperature measurement and sufficient data to determine that the storage vessel is inerted at an adequate pressure to stay out of the decomposable region. Consider the following when designing instrument systems for EO storage:

- Remote monitoring and trending of EO storage instrumentation.
- Installation of multiple, independent level measurements (a level measurement with an independent high level alarm).
- Installation of multiple, independent temperature measurements and alarming on high temperatures.
 - Multiple temperature measurements might include, especially for larger storage vessels, temperature monitors at different liquid levels to differentiate between potentially stratified EO layers that could represent isolated areas of reaction.

- Monitoring and alarming on rate of rise of storage temperature. Changes in the rate could indicate intensification of a contamination reaction and help signal the need for corrective actions or emergency response.
- Monitoring of pressure, with alarms for both high and low pressure (low pressures indicate loss of inerting gas).

The use of stainless steel tubing for instrument impulse lines in EO service will reduce the likelihood of polymer formation and plugging. Also note that the use of remote diaphragm, sealed differential pressure transmitters, “bubbler” dip tubes, ultrasonic level devices, vessel radar or nuclear level indicators can reduce the potential for erroneous level indication caused by polymer formation. Gauge glasses are typically not used because they have the potential to be damaged and/or leak. As mentioned above, plugging from polymer formation can result in false gauge level indications.

Although the use of mercury in instrument systems has declined considerably in the past few decades, instances do occur where elemental mercury may be present within an instrument system or device. See the *Metallic Materials* discussion in Section 6.3 for more information about the use of mercury in EO service.

Refrigeration

EO can be stored in refrigerated or non-refrigerated storage vessels. Refrigerated storage has the following benefits:

- Lower temperatures decrease the rate of EO polymerization, reducing the potential for polymerization-related difficulties such as vessel nozzle plugging.
- If the EO is contaminated, refrigeration systems can remove all or part of the heat of reaction. In some cases, this substantially assists in control of the reaction; in others, it slows the reaction, providing more time to implement control or disposal measures.
- Lower EO storage temperature allows a lower inert gas pressure to maintain the vapor space in the non-decomposable region.
- Lower temperatures will result in a smaller fraction of EO being vaporized in the event of a leak. The hazard of a pool of EO liquid may be mitigated more successfully than that of a vapor cloud.

One possible drawback of refrigeration, especially at low temperatures, is a reduction of the solubility of EO polymer, which may cause the precipitation of polymer that has already formed. This can cause plugging of instrument tubing and plugging of transfer lines.

Another issue that must be considered with refrigerated EO storage is detection of a reaction in the storage vessel. If a reaction occurs in an EO storage vessel and the refrigeration system is controlling the EO temperature, the refrigeration system will remove the heat of reaction until the refrigeration system capacity is exceeded. In this scenario, the operator may not be aware a reaction is occurring until the reaction has been going on for quite a while. If refrigeration is used for EO storage, consider installing instrumentation to calculate the heat load on the refrigeration system and include an alarm on high heat load and increasing heat load.

Reference [5] is a useful study of the relative risks of storing EO at moderate temperature and pressure versus low temperature and pressure.

EO storage refrigeration designs can incorporate refrigerated coils within the storage vessel, an external vessel cooling jacket, or an external heat exchanger and circulation pump. Internal coils can offer better heat removal in the event of an exothermic reaction within the storage vessel. Internal coils, however, can potentially contaminate the storage vessel if a leak occurs. Depending on the coil configuration, heat transfer area for internal and external coils may be less at lower levels in the vessel as the coils are not in contact with the liquid. Heat transfer fluids such as water or glycols could react with the EO in the vessel. External heat exchangers may also contaminate the vessel contents due to leakage, but the leak can be readily isolated for a more timely and expeditious repair. External vessel cooling jackets minimize the potential for contamination but may be less effective at heat removal.

Maintaining the refrigeration system coolant pressure below that of the storage vessel reduces the potential for contamination of the vessel contents in the event of an exchanger leak. In such a case, a leak can be identified by routinely monitoring the coolant for EO.

In practice, storage temperatures range from 20°F to 80°F (-6°C to 26°C), with a typical range of 40°F to 60°F (4°C to 15°C). Operating with temperatures in the lower end of the range can result in precipitation of EO polymer. The consequence of this can be reduced by operating at EO storage temperatures comparable to those of the EO supplier.

Consider incorporating alarms in the refrigeration system design to alert individuals in the event the system shuts down or begins to lose cooling capacity.

Emergency Disposal of Vessel Contents

Design of an EO storage system includes provisions for the disposal of EO inventory in the event of a contamination reaction. The objective is to safely dispose of storage system contents before the rate of temperature increase becomes too rapid and/or the concentration of EO in the vapor phase approaches or enters the non-inert region. Options in current practice include:

- Reacting the EO to glycols or other derivatives by feeding to downstream users (under emergency disposal conditions, a rapid rate of consumption is the goal of the reaction)
- Depressuring the storage vessel. Examples include discharge into a scrubber, flare system, or to an elevated discharge point. Depressuring can be a highly effective response because evaporation of the EO during this procedure provides an auto-refrigeration effect, which cools the vessel contents. See section 6.8 for the EO-specific design considerations for a flare system.
- Transferring to a holding system and diluting with water. If the transfer is to a body of water such as a pond, the volume of the pond must be sufficiently high to allow a dilution ratio of at least 22:1 volume/volume water to EO to limit the flammability of the vapor above the

resultant mixture. In fresh water, EO hydrolyzes to ethylene glycol very slowly, with a measured half-life of 14 days. Acids or bases can be directed to the pond to catalyze the water – EO reaction and speed the conversion of EO into glycol. During conversion EO vapor will continue to be evolved.

EO users must carefully consider the effects of any of these actions on the health and safety of their workers and communities and on the environment. These actions should only be taken as part of a well-defined, site-specific emergency response plan that has addressed environmental and worker safety regulatory requirements. See also the discussion in Chapter 10 regarding emergency response and the discussion of personal protective equipment selection in Chapter 7.

6.6 Reaction Systems

Consider the following elements in the design of EO reaction systems:

- Prevention/minimization of backflow from reactors into EO storage vessels.
- Prevention/minimization of build up of unreacted EO.
- Prevention/minimization of explosive mixtures in reactor vapor space.
- Heat duty requirements.
- Catastrophic failure modes.
- Materials of construction.

More details about these elements are discussed below.

Prevention of Backflow from Reactors

Catalysts in widespread use in EO reaction systems, such as KOH, have the capability to initiate EO polymerization and accelerate other reactions if they backflow into EO storage vessels. These reactions are exothermic and can result in uncontrolled heat release and vessel rupture. Note that storage vessel emergency relief sizing does not normally consider runaway reaction as a design case. Likewise, storage vessel cooling systems are ordinarily designed to remove heat gain from ambient sources or to remove temperature after unloading a railcar. Storage vessel cooling systems are generally not designed to address

the extremely rapid reaction rate of EO and its highly exothermic nature, so it is important that engineered systems be employed that prevent backflow from occurring. Examples of engineered systems for backflow prevention include:

- Triple block and double bleed automatic valves activated by three independent inputs;
- Double block and single bleed automatic valves activated by two independent inputs;
- Double block and single bleed automatic valves activated by one independent input; and
- Multiple high performance check valves (single check valves are generally not considered a reliable means, by themselves, to prevent EO backflow).
- Combinations of automatic block valves and check valves

Historically, check valves have been used as part of an overall system to prevent backflow of process fluids into EO supply pipeline and storage systems. Industrial experience has shown that a single check valve alone may not be an adequate backflow prevention device. Multiple check valves of the same type may experience common mode failures. Consider multiple check valves of different types and/or automatic isolation valves to protect against backflow.

The operation of an engineered backflow prevention system should be checked on a regular basis. For instrumented systems, consider the need for redundancy of the sensing element, logic solver and final control element to provide a robust protection system. Diversity in sensing elements is often used in engineering design, such as pairing a low flow sensor with a differential pressure meter across the EO feed valves. Setting the EO feed pump discharge pressure higher than the reactor safety valve set pressure is a common practice to minimize the potential for backflow.

Prevention of Buildup of Unreacted EO

Accumulation of unreacted EO in a reaction system can result in a runaway reaction exceeding the designed heat removal and relief capacity of the system. The rate of reaction is almost always dependent upon the concentration of EO present; thus, by controlling the EO feed rate and the reaction temperature, the reaction rate is also

controlled. Establishing automatic EO feed shut down points based on maximum allowable feed rates at a minimum reaction temperature or on analyzed unreacted EO concentration present in a reactor are common protection methods. On-line analyzers are another means of continually monitoring unreacted EO levels.

Some conditions that can lead to an accumulation of unreacted EO include:

- EO addition rate higher than design limits
- Poor mixing of reactants and catalysts
- Low concentration or lack of catalyst
- Low reaction temperature

If the control parameters are outside the design limits, automatic shutdown of EO feed is typical.

Possible indications of unreacted EO include:

- High reactor pressure
- High EO concentration in EO vapor space
- Lack of heat of reaction

An additional hazard occurs if reactor product contains significant quantities of unreacted EO. This can result in release of EO vapor from product storage vessels. Not providing sufficient reaction time can contribute to such a condition. See Section 5.3 for a discussion on a release of unreacted EO.

Prevention of Explosive Decomposition of EO in Reactor Vapor Space

The amount of diluent required to provide a non-decomposable mixture in the reactor vapor space varies with temperature and EO concentration. The reactor pressure control system should be designed to provide adequate diluent pressure to prevent decomposable mixtures over the expected range of reactor operation. Parameters to be considered when determining decomposability limits include:

- Temperature operating range
- Pressure operating range
- Reactor mechanical design (for example, batch, semi-batch, CSTR, plug flow, or circulating loop reactor)
- Solubility of nitrogen or other diluent employed in the reaction mixture

Some reaction system designs allow decomposable EO concentrations in the vapor space. These designs have typically eliminated sources of ignition such as mechanical agitators. In such designs, it is important to eliminate external sources of heat such as hotspots in the insulation.

Figure 6.17 illustrates the molar nitrogen concentration at the EO decomposable limit versus temperature for several total system pressures as measured by June and Dye. [6]. All data is for the nitrogen-EO binary system. The presence of other materials may invalidate these predictions. This graph differs from Figure 6.16 in that it addresses EO concentrations at saturation and below. Figure 6.16 is applicable only to systems containing both liquid and vapor EO in equilibrium. For systems such as vessels and reactors where no liquid EO is present, Figure 6.17 may be used as a tool to assist in the determination of the nitrogen pressure required to have a non-decomposable composition. An alternate way of representing the data that may be more useful if the vapor oxide concentration is being measured is to plot mole%

EO versus total system pressure as is presented in Figure 6.18.

Unless a process specifically requires oxygen for the process chemistry, all air or oxygen should be excluded from the reactor space. The presence of oxygen reduces the lower decomposable concentration of EO and reduces the minimum ignition energy for EO. See Section 2.3 for further discussions on the combustion properties of EO.

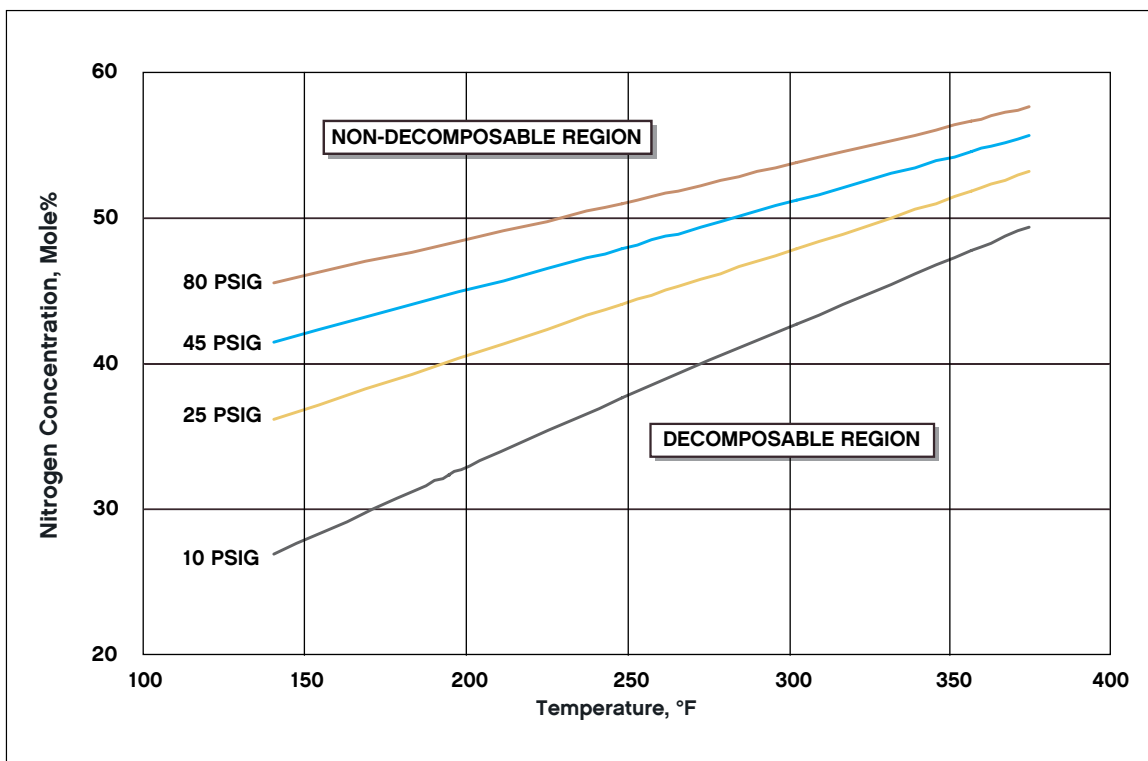
Reactor Design and Instrumentation

Consider designing reactor cooling systems with excess capacity to remove the heat generated by the onset of a runaway reaction. Since designing to remove 100% of the heat generated in a runaway reaction scenario may not be practical, automatic EO feed shutdowns are often utilized to restrict the magnitude of incidents.

Consider designing reactor control systems to stop EO addition in the event of the following:

- Excess rate of EO feed
- Failure to add other reactants

Figure 6.17 EO Decomposable Limits versus Molar Nitrogen Concentration
Ethylene Oxide Decomposition Limits
(Required Diluent Concentration as a Function of Total System Pressure)



- Failure to add catalyst
- Loss of mixing or agitation
- High reactor temperature
- Low reactor temperature
- Loss of cooling
- High reactor pressure
- Low reactor pressure
- Loss of utilities such as electricity
- High EO concentration in vapor or liquid

If practicable, reactor vent and/or safety valve capacity can be sized to help mitigate upset conditions.

Process analyzers can be used to monitor EO concentration in the reactor vapor space to maintain operation below the decomposable limit. When process analyzers are used as part of a safety system, continuing maintenance is important to maintaining high reliability. Analyzer cycle time

is a consideration in the design of safety systems. Redundancy and on-line error detection are common features when analyzers are used as part of reaction shut down systems.

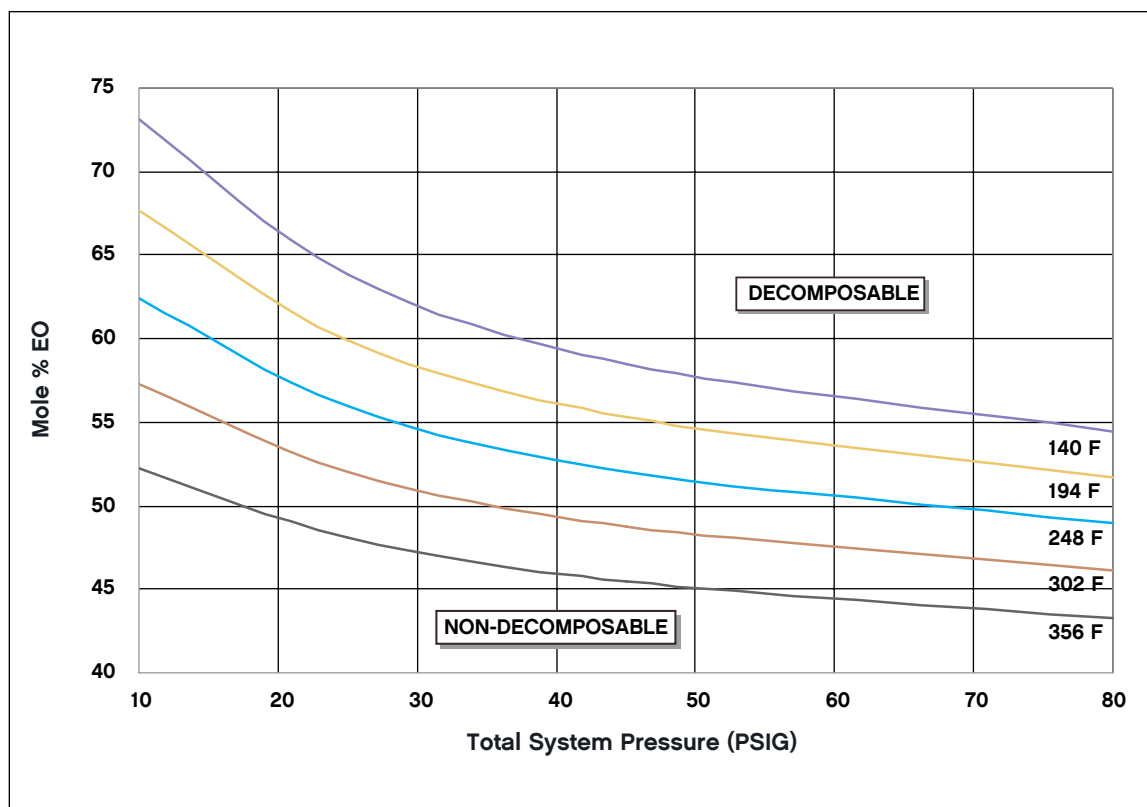
6.7 Piping and Pumps

Piping Systems

Carbon and stainless steel are suitable materials for EO service piping. Piping constructed of non-metallic materials has limited fire resistance, can be subject to chemical attack, and is not considered suitable for EO service. Stainless steel piping systems retard the development of rust, so these systems may eliminate the need to remove rust from the interior of the piping prior to initial service and after outages where the interior of the pipe is exposed to the atmosphere. Carbon steel systems, on the other hand, may require significantly more service over their lifetimes to remove rust.

Figure 6.18 Decomposition Limit of Mole % EO versus Total System Pressure

EO Decomposition Limits
(Mole % EO versus Total Pressure for EO-N₂ Binary System)



Proper installation and maintenance of insulated piping is especially important because moisture can infiltrate under the insulation, damaging the pipe's protective coating and reducing metal thickness and strength. Carbon steel systems are more susceptible to water-initiated external corrosion than stainless steel systems, but regardless of the type of steel used, it is important to periodically remove insulation and verify the integrity of piping systems.

EO polymerization is a design consideration for EO piping systems due to the relatively high amount of surface area of the piping system. Polymerization, once begun, can continue over extended periods of time in a piping system. Construction of piping systems to minimize the number of low points and dead spots ("stagnant areas") helps avoid or slow polymerization. Designing piping lines to be as short as possible with gravity drainage to points at which contents can be purged from the system with nitrogen is another useful technique. In areas where emptying stagnant EO lines is not feasible — for example, a long EO charging line to a batch reactor — a pipe loop that circulates back to the storage vessel may be considered as a design option. Chilled tracing of lines that may sit idle can also reduce the polymerization potential.

Welded and/or flanged construction is generally used in EO piping systems because it is considered to have less leak potential than threaded joints. For instrumentation connections, consider using welded or flanged construction up to the instrument/instrument tubing isolation valve. The design process should seek to minimize the number of flanges because each flange represents a potential leak source (including fugitive emissions). Where flanges are necessary, they should utilize gasket materials suitable for EO service.

Preventing or minimizing introduction of contaminants into the system is a critical design element for an EO piping system. Some key considerations are:

- Operating EO piping as dedicated piping for EO product only;

- Minimizing valves in EO piping that can be used to connect/introduce foreign products into the piping system;
- Providing clearly visible, permanent labels on EO piping; and
- Minimizing permanent connections to water, steam, or other substances that are reactive with EO.

Use of Hoses in EO Service

Hoses are generally not used for process line applications in EO service because they cannot be effectively insulated for fire protection. In an external fire situation, a hose containing EO is very vulnerable to EO decomposition.

There are four applications where hoses are commonly used in EO service. The first three are 1) EO sample systems; 2) EO loading or off-loading connection to railcars; and 3) hoses for blowing EO equipment clear of EO with nitrogen. For these three applications, the hoses are used for a limited time period and then blown clear of EO with nitrogen. The fourth application where hoses are commonly used in EO service is in filling and unloading small EO containers such as EO drums or cylinders. In this type of application, hoses are often in continuous use, but they are also well protected with deluge systems and blown clear of EO with nitrogen after use. When hoses are used in EO service, larger hoses are typically corrugated stainless steel with a stainless steel braid outer jacket with welded fittings. For small sampling hoses, PTFE hoses with stainless steel outer braid are sometimes used. Note that the crimped or banded-type end fittings often used in conjunction with PTFE hoses may be more susceptible to end connector separation than welded-type end connections.

It is extremely important to note that loading arms or hoses used for loading and off-loading EO railcars cannot be insulated for fire protection. For this reason, consider the use of deluge systems and/or fire monitors to protect the hoses and arms.

Thermal expansion protection in liquid piping systems

EO has a high coefficient of thermal expansion. Heating (ambient heating or otherwise) of a closed or isolated system containing EO can result in high pressures in a short time period, leading to gasket failures, or in more severe cases, line or equipment rupture. For this reason, liquid EO is not confined in lines closed at both ends unless this is otherwise unavoidable. Where the confining of liquid EO is unavoidable, lines are equipped with adequate relief valves to address potential high pressures. EO discharged from the relief valves is then captured and either returned to an appropriate location in the process or disposed of in accordance with applicable plant requirements and regulatory provisions.

Diaphragm-type surge suppressors providing a vapor space that can be displaced by expanding liquid have been utilized for EO systems on a limited basis with varying levels of success. A key issue with this type of device is proper material selection for the diaphragm. Suppressor protection devices of this type are routinely inspected and maintained so that the device will perform as needed. Consult the manufacturer for more information to select a design appropriate to facility needs.

Surge suppressors without diaphragms that provide an inert compressible vapor space in direct contact with EO (commonly known as nitrogen snubbers) have also been used in EO service to accommodate thermal expansion. Because nitrogen is soluble in EO, it is important to periodically verify the inert gas volume needed to maintain the effectiveness of the nitrogen snubber. Some nitrogen snubbers have a small, continuous nitrogen make-up flow.

Two alternate means of addressing thermal expansion are to install chilled water tracing, or install a continuous circulation loop on piping that may be susceptible to thermal expansion.

In piping systems without the surge suppressors described above or without pressure relief systems, consideration can be given to displacing a portion of the liquid EO in a piping system with an inert compressible gas prior to isolating the liquid

system. A high purity nitrogen supply is generally appropriate for this type application. System and atmospheric conditions are monitored by qualified personnel in order to determine the proper volume of inert gas required.

Valves

The potential for trapped EO in valve cavities is an important consideration in valve design, as well as in facility design. EO trapped in valve cavities can polymerize and render the valve inoperative, or create an undesirable pressure buildup due to thermal expansion. To address this issue, valve designs can be selected that minimize trapping of EO. Gate valves, globe valves, and high-performance butterfly valves have all performed well in EO service. Ball valves and plug valve designs have also been successfully used in EO service, although some have the potential to trap EO liquid when the valve is in the closed position.

Controlling fugitive emissions is also an important consideration in valve design and selection.

Decomposition Flame Arrestors

Control and avoidance of ignition sources and the use of an inert gas diluent are available mechanisms used to help avoid decomposition events. Where process conditions prevent the use of these mechanisms, consider the use of decomposition flame arrestors. Flame arrestors function by preventing the passage of a decomposition “flame” in one part of the process from propagating to an area with a large inventory of material. The use of flame arrestors may be considered in EO lines entering or leaving an EO storage or processing area where large inventories may be present. “In-process” flame arrestors can also complement the use of vapor (EO) compressors or air-cooled heat exchangers. “Off the shelf,” conventional flame arrestors are not likely to be designed for the high propagation speed of EO decomposition flame fronts. A general disadvantage of flame arrestors is their high surface area and small passages, which makes them susceptible to plugging if EO polymerization occurs.

One example of a simple flame arrestor design that has been used packs a bundle of half-inch diameter tubes into a pipe shell. Limited testing suggested that this design might be effective in EO service. Research has indicated that the diameter and length of the tubes are critical to an effective design. However, there are to date no published data on the effectiveness of flame arrestors for EO service to help guide design considerations.

Pumps

Carbon steel, stainless steel or ductile iron are appropriate materials for pump bodies in EO service. The brittle nature of cast iron makes its use inappropriate for EO systems.

Pump Designs

Centrifugal-type pumps are commonly used in a wide range of EO service conditions. Diaphragm-type pumps are also used but their use is generally limited to situations where process conditions favor this type of pump (e.g., high pressure, low flow) over centrifugal designs. Other types of pump designs are not widely used in EO service; before using another design type, consult with qualified engineering personnel.

Pumps with double or tandem mechanical seals and sealless pumps are commonly used for purposes of reducing fugitive emissions in compliance with applicable regulatory requirements. In the event of seal or pump failure, these pumps may result in a lower volume of EO being released (reducing potential personnel exposure and fire and explosion hazards) than single seal designs.

Pumps with Double or Tandem Seals

Pumps with double or tandem mechanical seals are widely used in EO service. Double seal systems using a pressurized seal fluid introduce small volumes of seal fluid into the process across the inboard seal; an important criterion, therefore, in the selection of a seal fluid is its relative non-reactivity while in contact with EO. Tandem seals with an unpressurized seal fluid system greatly reduce the potential for introducing seal fluid into the process, but require a suitable disposal system for collecting and disposing of EO vented from the seal system. Consider including the following components in a seal fluid system:

- Local or remote monitoring of seal pot level with low and high level alarms;
- Instruments/remote alarms capable of warning of excessive seal pot pressure resulting from a seal failure; and
- Safety relief device(s) on pressure seal pots.

A bypass flush of EO from the pump discharge to the inner seals removes frictional heat.

Seal fluids successfully used on double and tandem mechanical seal systems include 50% aqueous solutions of ethylene glycol, pure ethylene glycol, and/or pure diethylene glycol. Note that a properly functioning double mechanical seal/pressurized seal fluid system continuously adds small volumes of seal fluid into the EO product being pumped. This generally does not have product quality implications and is considered acceptable for pumping applications where the pumped EO is continuously consumed or converted to other products; it may therefore be less acceptable for pumps loading transportation containers or feeding EO into storage vessels with long product turnover time intervals.

Dry gas (nitrogen) seal systems use nitrogen as the seal purge material. These seals allow a very small, continuous flow of nitrogen into the process. Dry gas seals have been successfully used in EO service. When dry gas seals are used, it is important to monitor the nitrogen pressure and the flow and alarm on low pressure and high flow. A low nitrogen pressure or a high nitrogen flow indicates a seal failure.

Sealless pumps

Sealless pump designs such as magnetic drive pumps and canned motor pumps have also been successfully used in EO service. An advantage of these types of pumps is the elimination of fugitive emissions because of the elimination of an external seal system on the pump shaft between the impellor and driver.

Design considerations for these types of pumps include:

- EO without foreign particles or polymer is used to lubricate pump bearings. Evaluate the need for a filtering system (magnetic or element type) to remove particles and polymer from the EO in

the suction line feeding these types of pumps. Magnetic filters are commonly used on pumps with magnetic couplings.

- Sealless pumps are more susceptible to damage caused by low suction pressure than some other pump designs. Consult the pump manufacturer's net positive suction head (NPSH) requirements with regard to the suction line.
- Entrained gases in EO such as nitrogen can impede pump operation; two such examples are reduced or lost suction or reduced pump bearing lubrication. Removal of entrained gases from EO used to lubricate bearings will help maintain effective pump operation. If necessary, equipment can be installed to remove entrained gases from liquid before it enters the pump.
- Damage to the containment shell can result in a flammable toxic release. A double containment shell design can reduce the likelihood of a release .

If a rotor on a magnetic drive pump locks up, the magnets decouple and the driver continues to run, then the pump contents will experience a rapid temperature rise due to the magnetic flux. Consequently, the response time available to prevent pump failure and decomposition of pump contents may be significantly less than the response time likely to be available in a similar incident with a conventional centrifugal pump. Consider the use of high and low power meter monitoring and shutdown to address this issue.

Pump Hazard Mitigation

Physical Facilities

Locating pumps within an impervious containment area provides protection against spills or leaks leaving the plant site or spreading to other process areas inside the plant. This type of protection is commonly provided by locating pumps inside curbed areas constructed of concrete or other materials suitable for containing EO liquid.

Because EO spills may ignite, creating the potential for flame impingement on nearby equipment, locate pumps and any associated containment areas an appropriate distance from process equipment, transportation container loading/

unloading areas, and storage vessels. Equipping pump areas with fixed firewater spray systems and/or remote firewater monitors provides additional spill ignition protection. If water spray systems are used, many are available that are capable of remote activation, such as by heat-sensitive devices, combustible gas detectors, and/or personnel.

Combustible gas detectors (CGD) or EO-specific sensors/alarms can be installed in the immediate vicinity of the pump. Consider using CGDs/EO-specific sensors to activate pump area water spray systems.

Pumps can be located an adequate distance from a road to address possible damage from a vehicle collision. If a pump is located in close proximity to a road, consider additional facility designs to protect the pump, such as placing a physical barrier at the edge of the roadway or adding additional physical protection around or to the pump.

Pump Instrumentation

EO overheating — which can lead to a violent decomposition — is a primary safety focus in the design of EO pumping systems. There are many possible sources of additional heat to pumped EO, including: operation of EO pumps in a dead-headed or non-flow condition; improper pump operation; undetected pump mechanical damage; or inadequate cooling of recycle streams. For examples of specific protective measures to address EO overheating in pumps, refer to Figure 6.19

Redundant sensors and multiple shutdown initiators are valuable tools in EO pump safety systems for identifying and responding to overheating scenarios, but before selecting a sensor/shutdown system, it is helpful to conduct a thorough process hazard analysis of the system with the support of appropriately qualified engineers. The decision regarding the number of alarms and shutdown initiators to install in a specific system considers the potential severity of and opportunity for an EO incident with regard to the pumping system under consideration. EO pumping systems have been successfully protected by alarms and shutdowns with systems using two sensors where one sensor is triggered (1 out of 2 initiation). Additional sensors can be

added with alarms/shutdowns triggered by a group of sensors (2 out of 3 initiation). In certain circumstances, it may also be appropriate to set alarms/shutdowns to trigger when all sensors reach their initiation point (2 out of 2 or 3 out of 3 initiation), but this approach is generally not used without complete review and approval in advance from qualified personnel.

Maintaining minimum flow through a recycle line can be used to prevent pump deadheading when forward flow is shut off. Minimum flow can either be constant (through a fixed orifice) or automated (through a control valve when forward flow is lost). Two mechanisms to control the heat of the EO in the recycle line are to equip the recycle line with a cooler or to return the recycle line to a large heat sink, such as a large storage vessel or process vessel.

Additional protective measures may be necessary for pumps operating above 3600 rpm. Consult with the pump manufacturer regarding these types of operations.

Where EO pumping systems are connected to large inventories of material such as in storage vessels or rail cars, failed pumping systems are isolated as quickly as possible. Design considerations include

measures to rapidly isolate the pump, such as use of remotely activated isolation valves on pump suction piping and discharge piping.

Filter Systems

Filter systems are designed to trap and remove solid particles from EO. EO can be filtered before it is delivered to the customer; before it is delivered to storage; before it is loaded into transportation containers; before delivery to a pump; or at other points in the process. Both magnetic-type filters and removable element-type filters have been successfully used by industry.

Magnetic-type filters are designed to attract and remove iron and iron oxide particles from the EO. These materials are not present in the EO product initially, but can enter the EO as it comes into contact with carbon steel, such as that in piping or equipment.

Removable filter elements are designed to remove iron and iron oxide as well as polymer that may have formed and precipitated from the product as it moves through the process.

A large variety of removable filter elements and filter designs may be applicable for EO service operation. Cotton and polypropylene are two materials that

Table 6.1 EO Pump Shutdown and Alarm Considerations

Pump Type	Potential Hazard	Typical Protection Systems
Centrifugal, magnetic drive, or canned	EO decomposition resulting from high temperature	Minimum flow recycle (automated or always open)
		Low flow shutdown
		High discharge temperature shutdown
		Delta temperature across pump shutdown
		Pump motor low power shutdown
		Pump motor high power shutdown
		Low Level in pump suction vessel
Canned	EO release/ EO decomposition	Rotor thrust displacement shutdown
Centrifugal - double seal	EO seal failure release	Seal pot low pressure alarm
		Seal pot low level alarm
Centrifugal - tandem seal	EO seal failure release	Seal pot high level alarm
		Seal pot high pressure

have been successfully used in EO service.

Bear in mind the possibility of thermal expansion occurring when filters are not operated with continuous flow. Iron oxide particles inside filter vessels and filter elements have the ability to catalyze EO polymerization reactions if stagnant EO is present for extended periods of time. Periodic removal of these particles and periodic changing or cleaning of filters elements (not leaving filters in place with stagnant EO for extended periods of time) will minimize the potential for the initiation of a polymerization reaction. There have been multiple incidents of runaway reactions in EO filters due to rust catalyzed EO polymerization. See Section 5.6 for a discussion of EO filter incidents.

6.8 Handling of Vents and Effluent

Vent Scrubbers

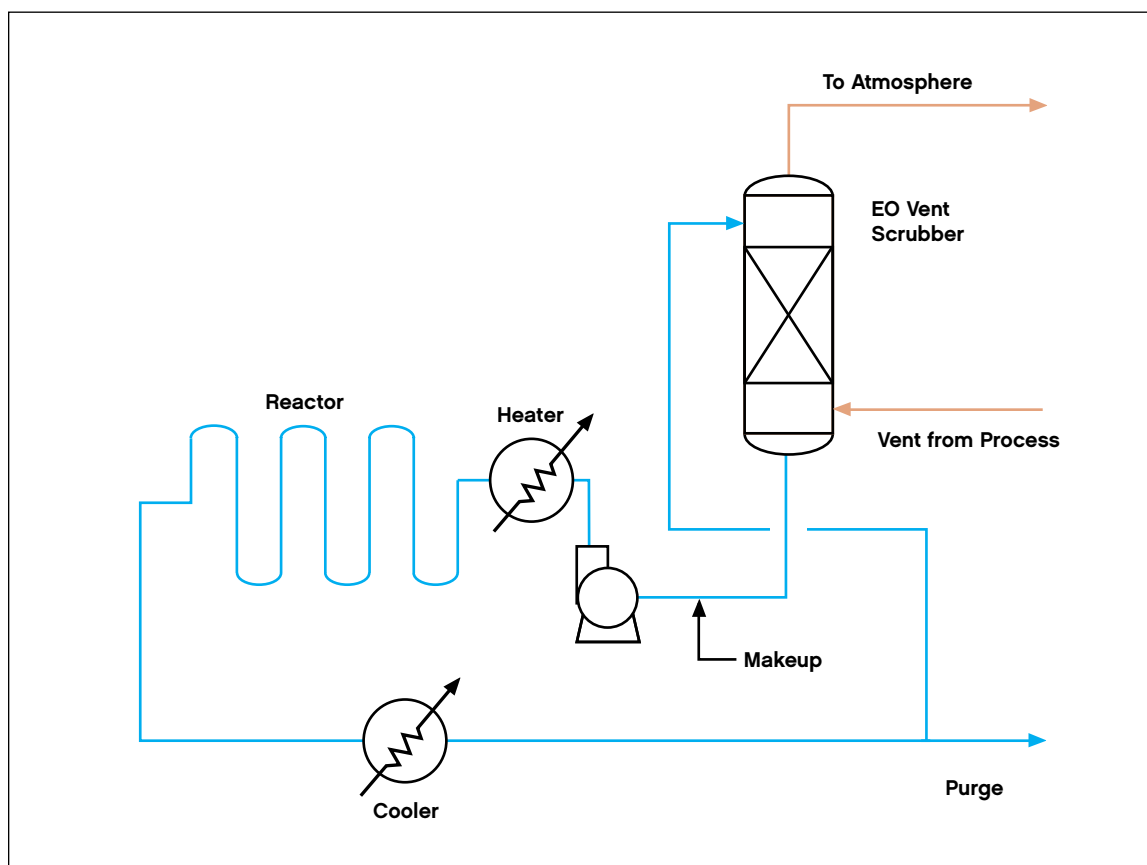
Aqueous systems for absorbing EO in process vents are in widespread use in industry. These systems can be designed for very high efficiency of EO removal. Vent gas is typically fed to a

scrubber column filled with random packing such as Pall rings. EO is absorbed by an aqueous stream running countercurrent to the vent gas. EO absorption efficiency improves with lower temperature and/or higher absorbent flow rate. EO/water mixtures are highly non-ideal, so in scrubber design, Raoult's Law deviation factors are applied. Scrubbed gas can usually be discharged to the atmosphere in accordance with applicable environmental regulatory requirements.

A recirculation system using pumps, solution heat exchangers/reactors, and storage vessel(s) are required in some but not all applications.

The absorbed EO in the aqueous effluent can be recovered in the manufacturing process or can be converted to glycol in a separate reaction system. Design of the system for recovering EO through the manufacturing process is specific to the user and is not discussed here. For many EO users, the EO is reacted to glycol. Although thermal hydrolysis has been used to react EO to glycol (Figure 6.19), acid and base reactions are more commonly used. Either strong base or acid is added to the

Figure 6.19 Ethylene Oxide Vent Scrubber System



absorbent stream as a hydrolysis reaction catalyst (acids are more effective EO hydrolysis catalysts than bases). Phosphoric acid, sulfuric acid, and caustic soda are commonly used for this purpose. Hydrochloric acid is typically not used for glycol reaction systems due to the potential to form chlorohydrins. Hydrochloric acid has, however, been used in scrubber systems where the EO and dilute acid solution are consumed in the manufacturing process.

It is important to take appropriate steps to avoid contamination of the process due to backflow from the scrubber systems, especially if acid or base solutions are used. Likewise, liquid EO entering the scrubber system can result in large exothermic reactions, especially in the presence of catalysts such as acids or bases. There have been multiple incidents where fiberglass EO scrubbers and polypropylene scrubber packing were melted due to overload of an acid catalyzed EO scrubber with liquid EO.

Design considerations and equipment configuration are specific to the relevant process. Scrubber design may be different for intermittent processes (for example, filling a storage vessel from a railcar) and continuous processes. Reactor venting accommodates the vessel pressure let down during normal operation and also allows for overpressure releases during a process upset. A process hazard analysis covering both the process and the scrubber (including interlocks) can be a valuable tool in support of safe operation.

An EO scrubber system may shut down due to hardware failure or conditions outside the normal operating range. Plant design and operating procedures anticipating shut down scenarios can include instrumentation or response practices to minimize EO emissions.

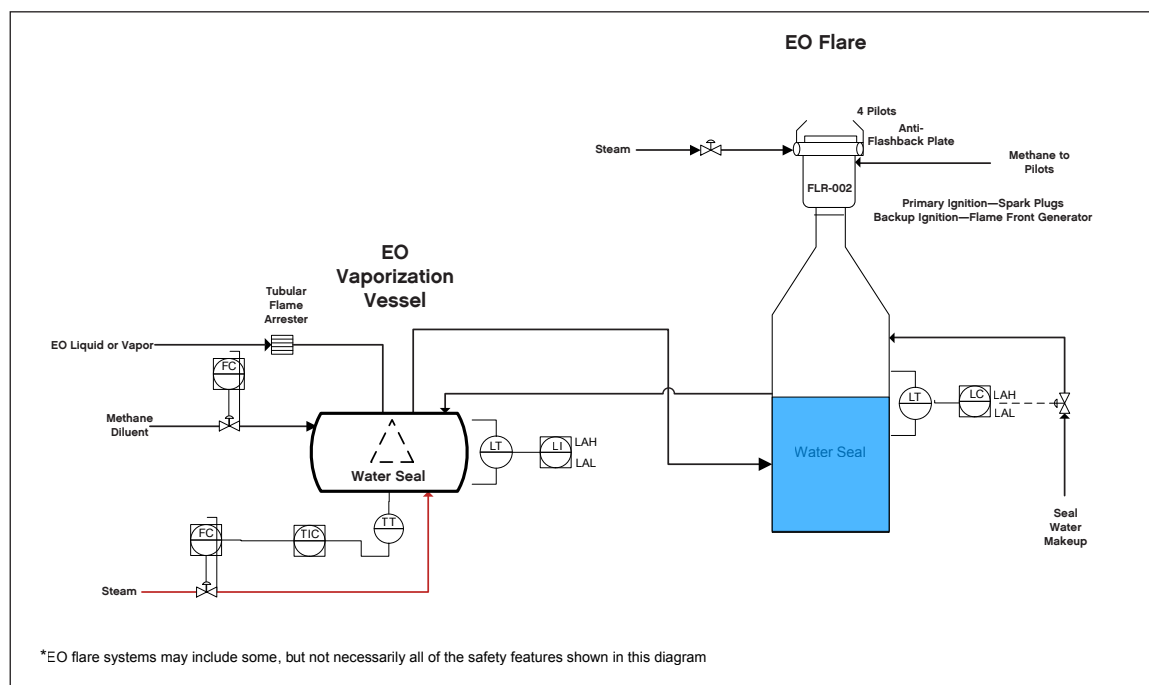
Flares

Several EO producers and users successfully use flares to handle EO containing vents. A critical design consideration for such flares is the prevention of decomposition flame propagation backward from the flare tip into the flare header system (flashback). The flame velocity of an EO decomposition flame can be very high. The decomposition flashback velocity is, among other things, dependent on the system geometry as

well as the temperature and composition of the gas mixture. Because an EO decomposition flame can transition from a deflagration to a detonation, the decomposition flame velocity greatly exceeds the normal EO combustion flame velocity, and can be much greater than sonic velocity. Because of the high velocity of the decomposition flame, the typical forward velocity in a flare header will not protect against reverse propagation of a decomposition flame. To address this, consider installing additional layers of protection in waste gas systems connected to down stream combustion equipment. Such additional design options for flare systems can include primary safeguards, such as the velocity section at the flare tip, flame arrestors and redundant safeguards, such as IR instrumentation and liquid seals, as described below:

- **Dilution:** EO to a flare can be diluted with methane into a non-decomposable mixture. By using methane instead of an inert gas like nitrogen, the heating value of the stream can be maintained to meet regulatory requirements. Dilution reduces the likelihood of a decomposition flame in the header, and is typically a “primary” level of protection for an EO flare system.
- **Velocity section:** The velocity section is a device used to prevent flashback initiated at the flare tip or in the combustion chamber of a thermal oxidizer. This device is located directly at the ignition source or at the inlet of the waste gas to the flare or thermal oxidizer. The distance between the velocity section and the flare or the thermal oxidizer is minimized. In case there is flashback, the outgoing speed required to exceed the flashback velocity is maintained by addition of a monitored flow of an inert gas or methane into the waste gas pipe. When this flow falls below a set operational minimum, a gas stream (at a flow greater than the operational minimum flow) is introduced into the waste gas pipe. The performance of a velocity section depends on the forward speed of the waste gases exceeding the flashback velocity of the flammable gases.
- **Flame arrestor:** A flame arrestor prevents propagation of the flame for a limited period of time. Rapid cooling of the flare header can result in the backflow of air from the

Figure 6.20 Schematic of Typical Flaring System



atmosphere into the flare system and possible formation of a flammable mixture capable of ignition by the flare pilot. Properly designed flare tips and flame arrestors are designed to prevent this hazard scenario from occurring. If an ignition occurs, however, the flame arrestor can only prevent propagation of the flame for a limited period of time (the gap width of the flame arrestor is smaller than the limiting gap width of the flammable gas). If continuous combustion heats a flame arrestor, it may lose its effectiveness with regard to flashback; therefore, the temperature at the flame arrestor is monitored. When the permissible temperature is exceeded, an inert gas is introduced into the waste gas pipe. The design basis for the inert gas flow rate is set so the flame at the flame arrestor will be extinguished.

Ignition of a non-inerted EO vapor mixture inside a flare system can result in an EO decomposition. The flame front generated by a decomposition travels at a very high velocity and may not be quenched by a flame arrestor designed for a combustion flame (conventional flame arrestor). In such cases, consider testing the specific device with regard to EO decomposition flame propagation.

- IR instrumentation:** IR instrumentation is placed in the waste gas pipe upstream of the flare or thermal oxidizer. When the IR instrumentation senses a flashback, it activates the feed of inert gas into the waste gas pipe to extinguish the flame. The length of the waste gas pipe between the IR-instrumentation and the inert gas inlet is set at a distance sufficient to extinguish a flashback. IR instrumentation is generally implemented as a redundant safeguard together with a velocity section or a flame arrestor.
- Liquid seal:** When the waste gas is introduced into the liquid seal, it is distributed into individual bubbles to prevent a continuous pathway between the inlet and the outlet streams (hence avoiding a flow path for a flashback). Water or water mixtures are typically used as a sealing medium. Continuous makeup or level control is often used to maintain design liquid level. Because of the potential for losing a liquid seal (for example, blowing the seal out or loss of liquid level), this option provides less robust protection against flashback than the other options discussed in this section. Liquid seals are therefore generally used as redundant safeguards in conjunction with the use of a velocity section or a flame arrestor.

Thermal and Catalytic Oxidizers

Thermal and catalytic oxidizers have been used to control EO emissions from some processes. There have, however, been serious incidents involving several thermal and catalytic oxidizers used at sterilization facilities for control of EO emissions. During 1997, there were explosions at three plants that use catalytic oxidizers for destruction of EO in process vents. Each of the explosions either damaged or destroyed the catalytic oxidizer. One of the three incidents occurred during startup testing of the oxidizer. In another of the three incidents, there was an explosion with a fireball, and the oxidizer system and the building were destroyed. Subsequent government investigations concluded that in all three cases, overfeeding of the oxidizer emission control devices resulted when a high concentration of EO was inadvertently sent to the devices. [7]

Sewer Systems and Waste Disposal Facilities

If EO is drained (or could inadvertently be drained) to a sewer system, the potential exists for EO emissions to occur in the sewer system and treatment facility, and for accumulation of flammable vapors in the sewers, lift stations, and waste water storage vessels. Installation of online analyzers, nitrogen purges, and emission control devices may be appropriate in such cases. Because of the combustibility of EO vapors in air, there is significant potential for an explosion in a closed sewer system. Consider using a design with open flumes and/or open top wastewater vessels in order to minimize the potential for fire or explosion. (The potential for fire exists if the EO is not diluted with water with a ratio of greater than 100:1.)

Wastewater containing low concentrations (less than 1000 ppm) of EO has been successfully disposed of in biological waste treatment facilities after proper acclimation of the system. Check applicable environmental regulatory requirements before sending EO to a disposal facility. See Section 4.2 for a discussion of biodegradation of EO.

6.9 Miscellaneous

Electrical Equipment

Electrical area classification Class I, Division 1, Group B or Class I, Division 2, Group B (National Electrical Code [3]) are used where atmospheres contain or may contain EO under normal or abnormal conditions. Group C may be used if conduit seals comply with National Electrical Code paragraph 501-5(a). Chapter 5 of the National Electrical Code [3] deals with hazardous atmospheres, classifications, and equipment requirements. Additional references for area classification can be found in API RP500 [4] and NFPA 497A [2].

The National Electrical Code requires other equipment, such as lighting fixtures, resistors, and solenoid coils to have normal operating surface temperatures that do not exceed the ignition temperature of EO. See Section 501 of the National Electrical Code [3] for further details.

Leak Detection Systems

Fixed-point combustible gas detectors are often used in petrochemical processing plants. These can be calibrated specifically for EO and are often used to trip deluge systems in plants. Note, however, that these detectors are generally not designed for monitoring for industrial hygiene purposes. The low concentrations of allowable exposure and the low Reportable Quantity for environmental releases make more sensitive leak detection equipment desirable for EO processes. Gas Chromatograph-based leak detection systems sensitive to 1 ppm EO are in use both in process plants and laboratories where EO may be present. These systems generally have multiple fixed sample locations connected to a single analyzer. Electrochemical sensors have also been used, but are not EO specific and are subject to interference from other chemicals.

Sampling Systems

There are a number of design considerations for EO sampling systems. Minimizing EO leaks or personnel exposure is an important starting point. An effective system design allows capture of a representative sample of EO without releasing EO to the environment or exposing the sample collector. Potential for personnel exposure to EO during sample preparation and analysis can be minimized by use of a laboratory hood. Dry-disconnect tubing fittings can also be used for the connection from the sample tubing to the cylinder.

Residual EO in the sample cylinder can be managed by purging the sample connection with nitrogen and depressuring the sample system to a vent collection system. Using a vacuum water jet system to evacuate the sample cylinder prior to disconnecting is another effective technique.

A well-designed system seeks to avoid overfilling the sample cylinder with liquid. Overfilling results in the potential for cylinder overpressure from liquid expansion. For this reason, typical EO sample cylinders are stainless steel with an internal dip tube to prevent overfilling with liquid. The cylinder is filled while positioned vertically with the dip tube at the top, and only the valve with the dip tube connects to the sample system.

To reduce the temperature of the EO in the sample cylinder, store cylinders under refrigeration (before and during sample analysis) until the remaining EO is returned to process use or disposed of in accordance with applicable environmental regulatory requirements.

Figure 6.21 EO Sampling System

