

CGA G-4.14 — 2024

3RD EDITION

**DESIGN,
MANUFACTURE,
INSTALLATION,
OPERATION, AND
MAINTENANCE OF
VALVES USED IN
LIQUID OXYGEN AND
COLD GASEOUS
OXYGEN SYSTEMS**



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PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has issued CGA G-4.14, *Design, Manufacture, Installation, Operation, and Maintenance of Valves Used in Liquid Oxygen and Cold Gaseous Oxygen Systems* jointly produced by members of the International Harmonization Council and originally published by the European Industrial Gases Association (EIGA) as EIGA Doc 200, *Design, Manufacture, Installation, Operation, and Maintenance of Valves Used in Liquid Oxygen and Cold Gaseous Oxygen Systems*.

This publication is intended as an international harmonized standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

This publication has been prepared by a group of experts in industrial gases technology or oxygen equipment representing oxygen manufacturers and is based on technical information and experience currently available.

The use of incompatible materials, unsuitable lubricants, improper cleaning and/or ingress of impurities, and procedural failures have been identified as root causes of a number of severe incidents that occurred over the past few years involving liquid oxygen valves with concentrations greater than 90 mol% of oxygen. This indicates the need for continual improvement in the fundamental knowledge of design, material selection, manufacturing, cleaning, installation, operation, maintenance processes, and storage related to valves in liquid oxygen service. This is necessary for liquid oxygen valve specifiers, suppliers, and manufacturers as well as those who clean, assemble, install, operate, and maintain these valves.

In order to avoid similar incidents with potentially fatal consequences, requirements for cold oxygen systems are outlined in this publication.

The industrial gases industry has demonstrated that personnel who are involved in the design, selection, manufacturing, handling, cleaning, installation, and maintenance of valves in cold oxygen service require training in these respective areas.

2 Scope

This publication covers isolation valves, control valves, check valves, pressure relief valves, drain, and vent valves in air separation units (ASUs), their backup and storage piping system, and customer station bulk storage tank systems. It addresses the design, material selection, manufacturing, cleaning, installation, operation, and maintenance of oxygen service valves operating at temperatures less than -22°F (-30°C).

The information contained in this publication only applies to new installations designed after the publication of this document and not to existing installations. However, the information contained in this publication may benefit existing installations or those in the project phase. Furthermore, to the extent that they exist, national laws may supersede the practices included in this publication. It should be noted that all local regulations, tests, safety procedures, or methods are not included in this publication and that abnormal or unusual circumstances could warrant additional requirements.

Valves in warm service connecting instrumentation devices are excluded from the scope of this publication. Some of the principles discussed in this publication may be used for other cold oxygen applications.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 **Autoignition temperature**

Temperature at which a substance will spontaneously ignite in a specified oxidant at a given pressure.

3.2.2 **Burn resistant metals or metal alloys**

Metals or metal alloys that will not sustain burn propagation when ignited and demonstrate minimal consumption under the specific process conditions that the metal experiences at ignition.

3.2.3 **Cold oxygen**

Liquid, supercritical fluid or cold gas with a temperature less than $-22\text{ }^{\circ}\text{F}$ ($-30\text{ }^{\circ}\text{C}$) and an oxygen concentration greater than 23.5 mol%.

3.2.4 **Dry, oil-free, air or nitrogen**

Air or nitrogen with a dew point of $-40\text{ }^{\circ}\text{F}$ ($-40\text{ }^{\circ}\text{C}$) or less and an oil content of 0.5 mg/m^3 or less.

3.2.5 **Lockout/tagout**

Safety procedure used to ensure that sources of energy (e.g., electrical, chemical, pressure) are shut off, isolated, and labelled prior to the start of maintenance work.

NOTE—This condition is maintained during the work and reversed when preparing for restart.

3.2.6 **Nonmetallic material**

Any material, other than metal, or any composite material in which the metal constituent is not the most easily ignited component and for which the individual constituent cannot be evaluated independently (see ASTM G63, *Standard Guide for Evaluating Nonmetallic Materials for Oxygen Service* [1]).¹

3.2.7 **Valve manufacturer**

Organization that manufactures a valve assembly and is responsible for its design.

3.2.8 **Valve specifier**

Individual or organization that has responsibility for defining technical and/or procurement requirements for oxygen valves and their actuation systems, where applicable.

3.2.9 **Valve supplier**

Organization that supplies a complete oxygen valve. This can be a valve manufacturer or a third-party.

4 Oxygen properties, hazards, and hazard analysis and risk assessment

4.1 **Oxygen properties**

Oxygen, which is essential to life, is colorless, odorless, and tasteless. The normal concentration in air is approximately 21% by volume.

The presence of an oxygen-enriched atmosphere cannot be detected by human senses. Oxygen also does not produce any physiological effects that could alert personnel to the presence of oxygen enrichment. Increasing the oxygen concentration of the air at atmospheric pressure does not constitute a significant health hazard.

At atmospheric pressure, liquid oxygen boils at $-297\text{ }^{\circ}\text{F}$ ($-183\text{ }^{\circ}\text{C}$) and has a slight blue color.

Oxygen is heavier than air. It can accumulate in low lying areas such as pits, trenches, and underground cavities or rooms. This is particularly relevant when there is a cold oxygen release. In that case, the cold gaseous oxygen generated from a release is significantly heavier than air.

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

4.2 Oxygen hazards

Oxygen is not flammable but supports and accelerates combustion. Oxygen concentrations greater than 23.5% create fire hazards but not asphyxiation hazards. Flammable materials, including some materials that are normally relatively nonflammable in air, burn very rapidly in high oxygen concentrations. As concentrations increase greater than 23.5% oxygen, ease of ignition of clothing increases dramatically. Once ignited by even a relatively weak ignition source such as a spark or cigarette, clothing can burst into flames and burn rapidly. Greater than 40% oxygen, the fibers on clothing and body hair and oil are subject to flash fire when ignited, which spreads rapidly over the entire exposed surface.

Personnel should not be exposed to oxygen-enriched atmospheres because of the increased risk of fire. Areas where it is possible to have high oxygen content shall be well ventilated. Vents shall be piped outside of buildings or to a safe area. Where an oxygen-enriched atmosphere is possible, special precautions shall be taken such as installation of oxygen analyzers with alarms, ensuring a minimum number of air changes per hour, implementing special entry procedures, or a combination of these procedures. Warning signs shall be posted at all entrances to alert personnel to the potential hazard of an oxygen-enriched atmosphere. For additional information on oxygen hazards, see CGA P-45, *Fire Hazards of Oxygen and Oxygen-Enriched Atmospheres* [2].

4.3 Oxygen hazard analysis and risk assessment

The three elements necessary for an oxygen valve fire to occur are an ignition source, oxygen, and a flammable material (fuel). Since oxygen is assumed to be present in all liquid oxygen or cold gaseous oxygen systems, it is important to have a clear understanding of any potential ignition sources and mechanisms present in the system as well as good knowledge of the flammability properties of the materials present in the valve.

A risk assessment and oxygen hazard analysis shall be carried out by personnel with knowledge and training in the field of oxygen compatibility and familiarity with relevant CGA, EIGA, American Society for Testing and Materials (ASTM), and other applicable standards. This assessment shall be done for a defined valve model. If this model is used again for the same process applications, the assessment does not need to be repeated unless the design has changed.

The risk assessment should consider that active ignition mechanisms can occur due to inadvertent causes (for example, failure to remove or prevent contamination) and can be different between steady state operation and transient conditions or process upsets, including those in which gaseous oxygen can be present.

An oxygen hazard analysis is a method used to evaluate the risk of fire in an oxygen system. It assesses the probability of ignition or consequence of ignition (ignition versus sustained burning based on operating conditions). It can be used to select materials for new designs or to evaluate the compatibility of materials in existing valves. In general, acceptance criteria for materials in a given application depend on two key factors, ignitability and flammability. Various processes for oxygen hazard analysis have been published over the years with different steps to assess the probability of ignition and sustained combustion.

The oxygen hazard analysis process includes the following steps as shown in Figure 1.

a) Assemble required information and resources:

- Application conditions (oxygen concentration, pressure, temperature, etc.) with particular attention to transient conditions (i.e., cooldown) and worst-case scenarios (for example, valve failure) of the oxygen system in which the valves are used;
- References of valves used in similar operating conditions (see 13.1.2);
- Assembly and component drawings, materials of construction, and flammability data for materials;
- Procedures used during manufacturing, cleaning, installation, operation, and maintenance; and
- Experienced personnel/team familiar with relevant industrial guidelines (CGA, EIGA, ASTM, and other applicable standards).

- b) Evaluate the flammability of materials in application pressure and minimal cross sectional thickness.
- c) Evaluate probability of ignition based upon contributing factors present:
 - Review potential for contamination;
 - Review type and location of nonmetals;
 - Review type and location of metal trim and determine location of thin sections on trim and valve body/bonnet;
 - Assess and document location of potential ignition mechanisms (such as friction, mechanical impact) and possible kindling chain, particularly with respect to location of nonmetals and thin metal sections; and
 - Consider operational history of existing valve models under known operating conditions for example, stainless steel valves in customer station applications.
- d) Evaluate potential consequences of a fire on personnel, equipment, and operations.
- e) Identify mitigation steps to reduce probability of ignition or eliminate or mitigate risk of ignition/kindling chain and hazards to personnel, equipment, and operation. These steps include:
 - Ensure the design and manufacturing process allows for cleaning of all components to the required specifications;
 - Avoid the use of lubricants where possible. Where lubricants are used, ensure they are compatible in oxygen service (see 6.4);
 - Eliminate or minimize mass of nonmetal component(s);
 - Use nonmetals with a higher autoignition temperature (AIT), higher mechanical impact resistance, and lower heat of combustion;
 - Use burn-resistant alloys suitable for the operating conditions;
 - Design so metal components are at a thickness that is burn resistant and suitable for the operating conditions;
 - Design to protect nonmetals by avoiding contact with direct flow;
 - Design to protect exposed nonmetals by encapsulating in metal as much as possible;
 - Change operating parameters for transient/worst-case scenarios; or
 - Mitigate consequences by using barriers or isolating the component from personnel.
- f) Document results of oxygen hazard analysis, including specific design drawings, bill of materials, cleaning documents and certifications, recommendations, resulting design and/or process changes, hazards identified, and mitigation steps.

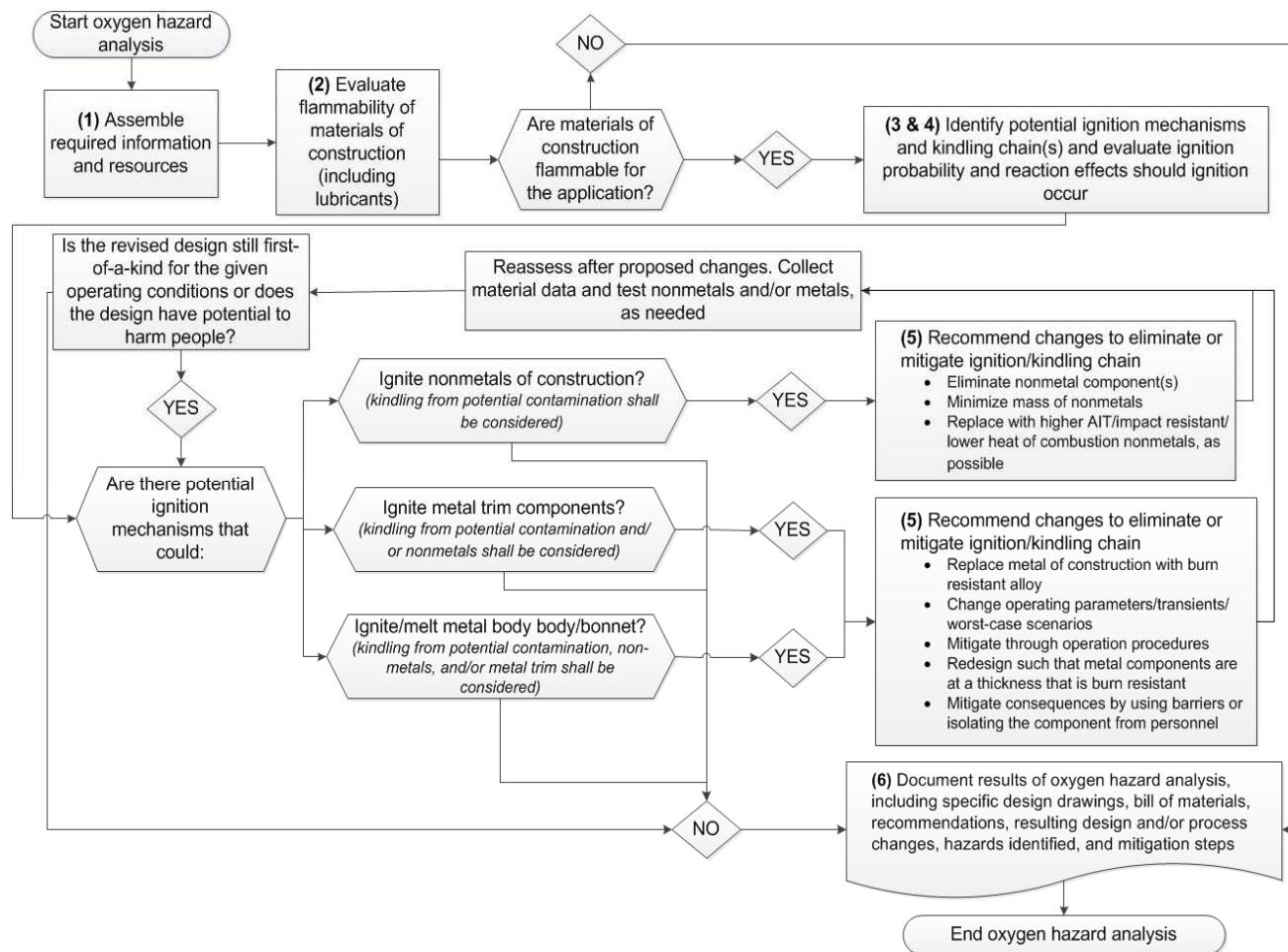


Figure 1—Flowchart showing an oxygen hazard analysis

5 Kindling chain, ignition mechanisms, and contributing factors

5.1 Kindling chain and ignition mechanisms

The most common ignition mechanisms (thermal energy sources) are the result of improper system or component cleaning, improper operation, or improper maintenance. System parameters such as oxygen concentration, pressure, gas velocity, and temperature are factors influencing ignition mechanisms and propensity for material ignition and combustion.

In a kindling chain, an easily ignitable material ignites (such as contamination in the system or a nonmetallic component) and the energy released from this combustion ignites a more ignition resistant material, which in turn ignites an even more ignition resistant material (such as a metallic component). The kindling chain process is a function of each material's inherent minimum ignition energy requirement, heat of combustion, and heat transfer (thermal conductivity) characteristics. The combustion propagation rate of a material, once ignited, becomes a factor of its chemical composition and physical and mechanical properties including thickness and surface area to mass ratio. The kindling chain is minimized by ensuring the system is cleaned for oxygen requirements and that the metals and nonmetals present have a low probability for ignition and combustion propagation, if ignited, see CGA G-4.4, *Oxygen Pipeline and Piping Systems* [3]. Design features such as heat sinks and fire stops can also help mitigate ignition and combustion propagation via efficient heat transfer mechanism.

Figure 2 is a representation of a generic kindling chain showing successive ignition and combustion from what typically are the easiest to most difficult to ignite components in a valve. The energy gap shown can be defined as the difference in the maximum baseline thermal energy generated during operation and the thermal energy required to ignite the most flammable component or contaminant, if present. Also, shown in Figure 2 are example strategies and approaches for two risk mitigation methods that can be used in conjunction with one another. These are:

- Reduce the probability of ignition by eliminating ignition mechanisms where possible; and
- Increase the burn resistance of valve components in order to disrupt successive ignition/combustion (i.e., break the kindling chain) to both decrease the probability of metal combustion and impact severity of an event in a valve.

5.1.1 Kindling chain

Contamination is a common link in the kindling chain. Contamination sources include but are not limited to:

- dirt, debris, particles, hydrocarbons (hydrocarbon lubricants, machining oils, etc.), entering a valve during assembly or maintenance;
- residues such as cleaning agents, dirt, or debris remaining in a valve due to improper cleaning;
- lubricants or thread sealants that migrate into the oxygen wetted area from threads or from accessories such as actuators and gearboxes;
- contaminated compatible lubricant (metallic particles and hydrocarbons);
- metallic flakes and particles formed during assembly;
- light hydrocarbons (e.g., methane, ethane, propane) accumulated as a result of dead-end pool boiling or dry boiling in liquid oxygen systems;
- particulates originating from breakdown of seals, valve friction, shearing metal pieces, cavitation, degradation of nonmetallic components, and migration of impurities from gaskets, packing, and seat material;
- items accidentally dropped into the system by personnel; and
- environmental contamination from improper, unprotected storage.

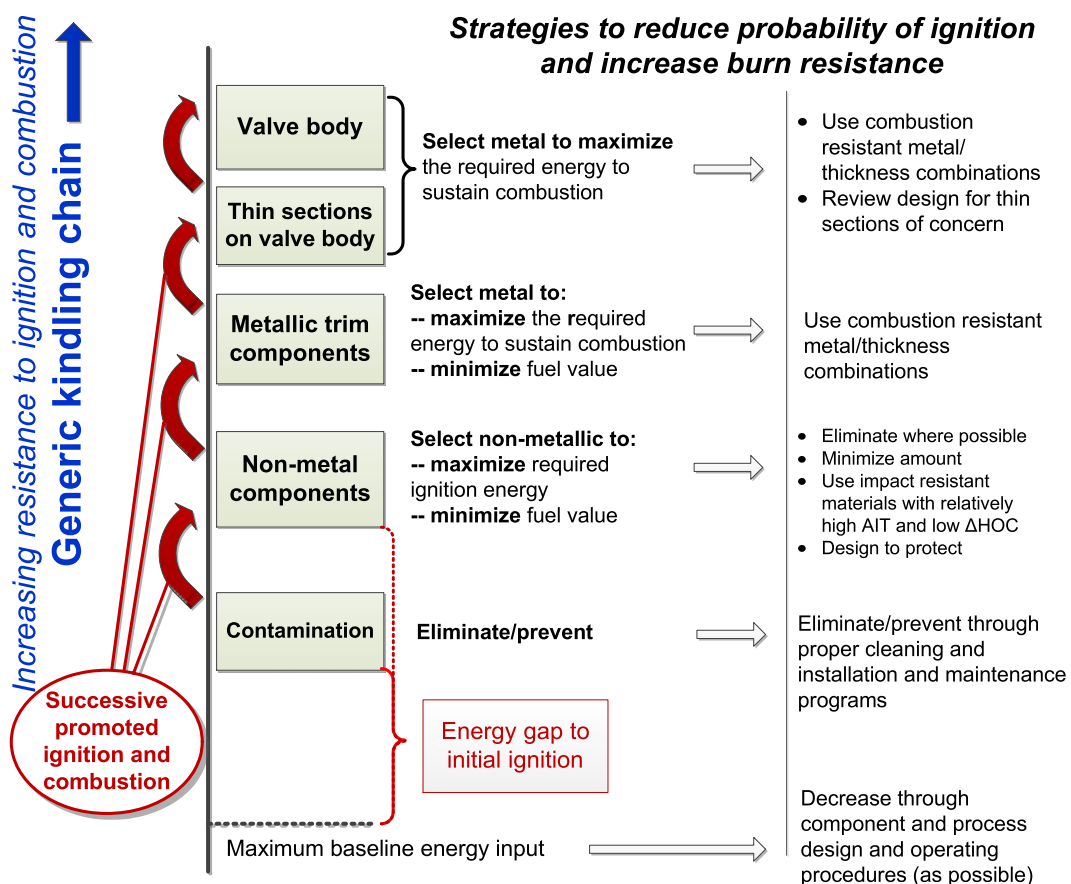


Figure 2—Generic kindling chain

5.1.2 Ignition mechanisms

The following are some common ignition mechanisms.

5.1.2.1 Frictional heating

Frictional heating can occur between stationary and moving parts, that is with relative motion, and can occur with both metallic and/or nonmetallic materials. This can be due to poor design or when gaps or clearances become reduced during operation. This can also produce particles. Frictional heating is a consequence of surface finish, shape, ability to dissipate heat, size, and valve type. Frictional heating is one of the most active ignition mechanisms in cold oxygen systems and this grows as pipe diameters or pressures increase.

5.1.2.2 Particle impact

Particle impact is considered an unlikely ignition mechanism in liquid oxygen. Although some high pressure gaseous oxygen incidents have been attributed to particle impact, there are no known liquid oxygen incidents that have been attributed to particle impact. The main barriers to ignition by particle impact are low velocities in liquid oxygen and the low operating temperature. In addition, credit may be taken in systems where any particles in the liquid oxygen are removed. For example, by pump inlet filters leaving the pressurized cold oxygen systems particle-free. Therefore, particle impact is more of a hazard for cold gaseous oxygen.

During transient conditions, such as the cooling down or warming up of a cold oxygen system or during upset conditions, vaporized oxygen is present in the system. In this case, potentially flammable particulate contamination can ignite and kindle target metals by impingement at high gaseous oxygen velocities.

5.1.2.3 Mechanical impact

Heat is generated from the transfer of kinetic energy as a result of a single or repeated impact of nonmetal or metal resulting from vibration, a quick closing valve, or a chattering check or relief valve. This mechanism was identified as the energy source for many liquid oxygen incidents including when two-phase conditions were present leading to the ignition of nonmetallic materials used for valve seats or seals. Direct mechanical impact on bulk metal alone is not considered to be credible for ignition of most metals.

5.1.2.4 Dry boiling and pool boiling

By their nature, liquid oxygen systems face the additional risk of hydrocarbon accumulation wherever boiling of liquid oxygen occurs. However, this ignition mechanism is more related to process and system design and not directly related to cold oxygen valves.

5.1.2.5 Adiabatic compression

Heat is generated when a gas is rapidly compressed from low pressure to high pressure. Ignition by adiabatic compression is usually considered as non-active in liquid oxygen. It can be active in transient conditions such as the cooldown or warm-up sequence of a cold oxygen system. This can be sufficient to reach the AIT of nonmetallic materials and organic contaminants directly exposed to the adiabatic compression and to ignite these materials. This ignition mechanism is more relevant with quick opening valves.

5.1.2.6 Electrical arcing

Electrical arcing from a power source with sufficient energy to ignite the material receiving the arc-lightning strikes and electrical surge of non-grounded system could cause ignition when it arcs to a metallic flammable material.

5.1.2.7 Static discharge

Ignition can occur when a static charge discharges with enough energy to ignite the material receiving the discharge or exposed to the discharge energy. Static discharge is more likely to occur in a dry environment, which is the case in cold oxygen systems.

5.2 Contributing factors

The following factors in combination with ignition mechanisms in 5.1 can influence the probability and/or severity of an incident:

- Personnel exposure in the immediate vicinity of a cold system when started, shut down, or in operation;
- Oxygen leak leading to upset conditions (for example, oxygen enrichment, dry boiling, and high velocity);
- Light hydrocarbon accumulation due to dry boiling and pool boiling;
- Rapid vaporization/flashing;
- Cavitation;
- Mechanical failure/rupture of a component of a valve;
- Excessive vibration resulting from incorrect internal valve clearances, improper assembly, or excessive piping loads;
- Contamination of any kind (that can be present or introduced into the system) due to inadequate cleaning, residual contamination from cleaning agents/cleaning process, contaminated soft goods and/or lubricants, post cleaning testing such as hydro testing, packaging, site assembly, and maintenance procedures;
- Mechanical stress due to sudden temperature changes;