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RECORD OF REVISIONS

Rev	Date	Description	POC	RM
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Contact the Standards POC for upkeep, interpretation, and variance issues.

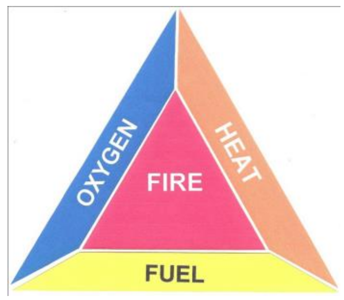
Chapter 17	**Pressure Safety POC**

This document is online at https://engstandards.lanl.gov

1.0 Oxygen Pressure System Hazards

A. Oxygen System Hazards

The fire triangle is a model for conveying the three elements required to generate a fire: fuel, oxygen (oxidizer), and heat (ignition). The three elements must be combined in the right proportions for a fire to occur. If one of the three elements is removed, the fire does not occur or is extinguished.



Oxygen is a strong oxidizer that supports combustion and is reactive at ambient conditions. The reactivity of oxygen increases as the oxygen concentration, pressure, or temperature within a pressure system increases. An increase in oxygen reactivity increases the risk of an oxygen fire.

Oxygen systems always have two of the three elements to generate a fire. The container or pressure system supplies the fuel. The oxygen is the oxidizer.

B. Control of Oxygen System Hazards

The only way to prevent an oxygen system from burning is to prevent ignition. Control of ignition is achieved by selecting and controlling the materials used in the system, and minimizing the heat generation that can lead to ignition.

The degree the materials and ignition mechanisms must be controlled is a function of the oxygen concentration, the design pressure, and design temperature. Application of requirements to oxygen system is a graded approach. As the hazard of the oxygen system increases, the rigor necessary for a safe system increases.

At low oxygen concentration, low pressures, and low temperatures, where the risk of an oxygen fire is low, cleaning may be the only control necessary. For example, the medical industry uses National Fire Protection Association (NFPA) 99 for oxygen at **less than 350 psig** regularly with nonmetallic materials. LANL defines high-pressure oxygen as 350 psig or higher because it will require an evaluation of non-metallic materials.

High-pressure oxygen systems **greater than 350 psig** must by necessity use a more rigorous approach on the design, material selection, component selection, cleaning, maintenance, and operation. Most materials, both metals and nonmetals, are flammable in high-pressure oxygen; therefore, systems must be designed to control ignition hazards.

The method to perform an Oxygen Hazards Analysis is a Failure Modes and Effects Analysis (FMEA). Below are general references on how to perform an FMEA.

https://asq.org/quality-resources/fmea#Procedure

https://www.sixsigmadaily.com/steps-in-failure-modes-and-effects-analysis/

https://www.juran.com/blog/guide-to-failure-mode-and-effect-analysis-fmea/

The LANL FMEA reference is FSD-300-3-001, *Hazard Analysis Manual*. This FSD is related to P300, *Integrated Work Management*.

2.0 Material Selection

A. There are four basic criteria when selecting a pipe or tubing material for gaseous oxygen service: concentration of oxygen, design pressure, design temperature and oxygen flow velocity. Per Fig. 1, if the system operates below 200 psig at 200°F then carbon steel or stainless steel would be suitable material at almost any velocity. However, above those markers, velocity becomes an issue and the material selection narrows.

B. In operating conditions at or below 200°F and 200 psig, carbon steel, 316 SS or, copper (Type K) is acceptable for use in 99.5 mole percent oxygen (ref. Material Selection for Gaseous Oxygen Service, William M. Huitt). Above those operating conditions, copper (Type K) would be acceptable.

C. If a system is operating in a range above the curve in Fig. 1, copper tubing should be selected. This applies also in flow-through valves, where velocity could be an issue, and where oxygen gas impinges directly on ferrous piping. Where velocity of flow through a valve may approach sonic velocity, copper-based materials will be required. Where direct impingement on ferrous piping occurs, velocity should be reduced to one half the values of Fig. 1, or the impingement surface must be a copper-based alloy. One major factor when selecting material for oxygen service is the material's Melting Point Burn Ratio (BR_{mp}). This is defined in ASTM G94 as: *Numerous metals burn essentially in the molten state. Therefore, combustion of the metal must be able to produce melting of the metal itself. The BR_{mp} is a ratio of the heat released during combustion of a metal to the heat required to both warm the metal to its melting point and provide the latent heat of fusion. It is further defined by:*

$$BR_{mp} = \Delta H_{combustion}/(\Delta H_{rt\text{-}mp} + \Delta H_{fusion})$$

Where:

ΔH = *heat of combustion*

$\Delta H_{rt\text{-}mp}$ = *heat required to warm the metal from room temperature (rt) to the melting point (mp)*

ΔH_{fusion} = *latent heat of fusion*

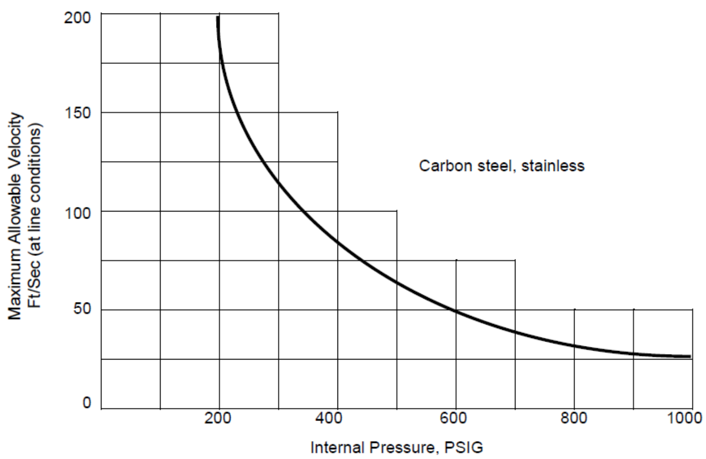


Figure 1 Maximum velocity versus internal pressure for steel pipelines (99.5 mole% or higher oxygen)
(Griffith and Wallis, Journal of Heat Transfer, August 1961)

Table 1 Calculated Melting-Point Burn Ratios[A]

Material	BR_{mp}
Silver	0.40
Copper	2.00
90-10 copper-nickel[B]	2.39
CDA 938 tin bronze[B]	2.83
CDA 314 leaded commercial bronze[B]	2.57
Monel 400[B]	3.02
Cobalt	3.50
Monel K500[B]	3.64
Nickel	3.70
CDA 828 beryllium copper[B]	4.49
AISI 4140 low alloy steel[B]	5.10
Ductile iron	5.10
Cast iron	5.10
AISI 1025 carbon steel[B]	5.10
Iron	5.10
17-4 PH[B]	5.32
410 SS[B]	5.39
CA 15 stainless steel[B] (see A296)	5.39
304 stainless steel[B]	5.39
Titanium	13.1
Lead	18.6
Zinc	19.3
Lead babbit[B]	20.6
Magnesium	22.4
Aluminum	29.0
Tin Babbit[B]	42.6
Tin	44.8

[A] From Monroe, Bates & Pears, *Flammability and Sensitivity of Materials in Oxygen*

[B] Presented for comparison only. Alloys may exhibit flammability vastly inconsistent with the BR_{mp} ranking.

D. In Table 1, you can see the hierarchy of metals as it pertains to their burn ratios. Carbon steels, stainless steels, and coppers have the lower, more acceptable burn ratios, with copper being the lowest of those three. In the event flame propagation does occur due to some ignition mechanism, those metals will tend to impede combustion of the metals themselves. The same result is indicated in ASTM G94, Table X1.1 – Promoted Combustion Test results, where combustion tests were carried out in 99.5 mole% oxygen. Copper had a non-propagation rate at 1000, 5000 & 8000 psig. 316 stainless steel had a non-propagation rate at 500 psig and various declared burn rates from 1000 to 10000 psig. Ductile iron (closest example of carbon steel) had a burn rate of 0.14 in/sec at 500 psig (the lowest pressure at which these tests were performed).

3.0 Oxygen Cleaning

A. Cleaning of oxygen piping components including pipe or tubing and fittings involves the removal of contaminants including the surface residue from manufacturing, hot work, and assembly operations, as well as the removal of all cleaning agents and the prevention of recontamination before final assembly, installation, and use. These cleaning agents and contaminants include solvents, acids, alkalis, thread lubricants, filings, dirt, scale, slag, ling, weld splatter, organic materials such as oil, grease, crayon, or paint, and other foreign materials.

B. The ASME Designer is responsible for determining the required cleaning for the oxygen pressure system, for example:

1. The ASTM G93, *Standard Practice for Cleanliness Levels and Cleaning Methods for Material and Equipment Used in Oxygen-Enriched Environments*, CGA G-4.1, *Cleaning Equipment for Oxygen Service*, and EIG/IGC 33, *Cleaning of Equipment for Oxygen Service Guideline,* provide the methods to clean for oxygen service. The required clean level for oxygen service is addressed in ASTM G93, EIGA/IGA 33, and CGA 4.3, *Commodity Specification for Oxygen*.

2. Tubes, valves, fittings, station outlets, and other piping components shall have been cleaned for oxygen service by the manufacturer prior to installation in accordance with the mandatory requirements of CGA G-4.1, *Cleaning Equipment for Oxygen Service*, or equivalent standard except that fittings shall be permitted to be cleaned by a supplier or agency other than the manufacturer.

3. High-pressure oxygen systems require cleaning per ASTM G93 and G127 or equivalent standards to ensure removal of any foreign surface matter. This may be accomplished by the manufacturer, or at the job site on a final installed system.

4. High-pressure oxygen or other oxidizer pressure systems must be disassembled for cleaning. Each component must be cleaned prior to assembly. Non-volatile cleaning agents may remain in trapped spaces, which could react with oxygen. Cleaning solutions may degrade non-metals in an assembly. Caustic and acid cleaning solutions may cause crevice corrosion in assemblies.

5. Final cleaning after assembly and before introduction of oxygen to the system, by purging the system using clean, dry gaseous nitrogen or dry air to remove contaminants or moving them to an acceptable location.

C. The ASME Designer shall specify any necessary handling of oxygen cleaned piping components such as the following:

1. Tubing should be purchased in a pre-cleaned condition.

2. Each length of tube shall be delivered plugged or capped and labeled by the manufacturer and kept sealed until prepared for installation.
3. Finished fabricated pieces should be stored in a clean dry area away from construction pathways and activities.
4. Piping components, pipe, tube, fittings, valves, and other components shall be delivered, sealed, labeled, and kept sealed until prepared for installation.
5. The interior surfaces of tubes, fittings, and other components that are cleaned for oxygen service shall be stored and handled to avoid contamination prior to assembly and brazing.
6. Components cleaned for oxygen service must be handled with clean lint and power free gloves or handling devices to maintain oil-free cleanliness of component.
7. Component cleanliness must be maintained during the assembly/construction process.
8. To maintain cleanliness during assembly, it may be necessary to assemble the system in a laminar flow cabinet, for example a Class 100 flow bench.
9. Components or systems cleaned for oxygen service must not be left in the open or unprotected. Care should be taken to avoid contamination of particulate and oil deposits on surfaces that will be in direct oxygen service.
10. Ensure all tubing has been prefabricated, properly deburred, and cleaned prior to assembly.
11. Ensure all weld slag has been removed from interior of lines.

4.0 Material Exemptions

The table below lists exemption pressures for the alloys covered in Section 4.3.1 of CGA G-4.4-2020, *Oxygen Pipeline and Piping Systems*. The exemption pressures are based on a burn criterion of less than 30 mm (1.18 in) for a specimen.

Thickness is a very important variable in component flammability. The thickness of a metal or alloy shall not be less than the minimum prescribed in the table. If the thickness is less than the prescribed minimum, the alloy shall be considered flammable and velocity limitations appropriate for the system pressure shall be observed. Exemption pressures should not be extrapolated outside the given thickness range of 3.18 mm to 6.35 mm (0.125 in to 0.250 in).

Alternatively, flammability assessments can be made using appropriate characterization techniques described in CGA G4.4-2020, Section 4.2.1, which can result in a judgment that velocity limitations are not required.

Exemption Pressure

Exemption pressure is the maximum pressure at which a material is not subject to velocity limitations in oxygen enriched atmospheres where particle impingement may occur. At pressures below the exemption pressure, ignition and burn propagation is considered unlikely to occur based on ignition mechanisms listed in CGA G4.4-2020. The exemption pressures of the alloys listed in the table below are based on industry experience and under the conditions used for the promoted ignition combustion testing per ASTM G124, *Test Method for Determining the Combustion Behavior of Engineering Materials in Oxygen-Enriched Atmospheres*.

Table 2. Exemption Pressures and Minimum Thicknesses (Normative)

Engineering Alloys	Minimum Thickness	Exemption Pressure
Brass Alloys[1]		
(all)	None specified	20.68 MPa (3000 psig)
Cobalt Alloys[2]		
Stellite 6	None specified	3.44 MPa (500 psig)
Stellite 6B	None specified	3.44 MPa (500 psig)
Copper[3]		
(all)	None specified	20.68 MPa (3000 psig)
Copper-Nickel Alloys[1,3]		
(all)	None specified	20.68 MPa (3000 psig)
Tin Bronzes		
(all)	None Specified	20.68 MPa (3000 psig)
Ferrous Castings, Non-stainless		
Gray Cast Iron	3.18 mm (0.125 in)	0.17 MPa (25 psig)
Nodular Cast Iron	3.18 mm (0.125 in)	0.34 MPa (50 psig)
Ni Resist Type D2	3.18 mm (0.125 in)	2.07 MPa (300 psig)
Ferrous Castings, Stainless		
CF-3/CF-8,CF-3M/CF-8M,CG-8M	3.18 mm (0.125 in)	1.38 MPa (200 psig)
CF-3/CF-8,CF-3M/CF-8M,CG-8M	6.35 mm (0.250 in)	2.6 MPa (375 psig)
CN-7M	3.18 mm (0.125 in)	2.58 MPa (375 psig)
CN-7M	6.35 mm (0.25 in)	3.44 MPa (500 psig)
Nickel Alloys[3]		
Hastelloy C-276	3.18 mm (0.125 in)	8.61 MPa (1250 psig)
Inconel 600	3.18 mm (0.125 in)	8.61 MPa (1250 psig)
Inconel 625	3.18 mm (0.125 in)	6.90 MPa (1000 psig)
Inconel X-750	3.18 mm (0.125 in)	6.90 MPa (1000 psig)
Monel 400	0.762 mm (0.030 in)	20.68 MPa (3000 psig)
Monel K-500	0.762 mm (0.030 in)	20.68 MPa (3000 psig)
Nickel 200	None specified	20.68 MPa (3000 psig)
Stainless Steels, Wrought		
304/304L, 316/316L, 321, 347	3.18 mm (0.125 in)	1.38 MPa (200 psig)
304/304L, 316/316L, 321, 347	6.35 mm (0.250 in)	2.58 MPa (375) psig)
Carpenter 20 Cb-3	3.18 mm (0.125 in)	2.58 MPa (375 psig)
410	3.18 mm (0.125 in)	1.72 MPa (250 psig)
430	3.18 mm (0.125 in)	1.72 MPa (250 psig)
X3 NiCrMo 13-4	3.18 mm (0.125 in)	1.72 MPa (250 psig)
17-4PH (age hardened condition)	3.18 mm (0.125 in)	2.07 MPa (300 psig)

Note: This list does not include all possible exempt materials. Other materials may be added basedonthe results of testing as described in Section 4.2.1 of CGA G-4.4-2020.

Note: These exemption pressures are applicable for temperatures up to 200 °C (392 °F).

1) Cast and wrought mill forms.

2) These cobalt alloys are commonly used for weld overlay applications for wear resistance. Use atexemption pressures above those specified in Appendix D of should be justified by a risk assessment or further testing.

3) Nickel alloys have been used safely in some applications at thicknesses less than those shown in Appendix D. Use of thinner cross sections should be justified by a risk assessment or further testing.

5.0 Organic Materials

NOTE: This section is based on Emerson Product Bulletin 59:045, Material Guidelines for Gaseous Oxygen Service, *September 2017.*

Organic materials have ignition temperatures below those of metals. Use of organic materials in contact with oxygen should be avoided, particularly when the material is directly in the flow stream. When an organic material must be used for parts such as valve seats, diaphragms, or packing, it is preferable to select a material with the highest ignition temperature, the lowest specific heat, and the necessary mechanical properties.

Lubricants and sealing compounds should be used only if they are suitable for oxygen service and then used sparingly. Ordinary petroleum lubricants are not satisfactory and are particularly hazardous because of their high heat of combustion and high rate of reaction.

The approximate ignition temperatures in 138 bar (2000 psig) oxygen for a few organic materials are shown in Table 3.

Table 3. Typical Ignition Temperatures of Organic Materials in Oxygen

MATERIAL	TYPICAL IGNITION TEMPERATURE IN 138 BAR (2000 PSIG) OXYGEN	
	°C	°F
PTFE and PCTFE	468	875
70% Bronze-filled PTFE	468	875
Fluoroelastomer	316	600
Nylon	210	410
Polyethylene	182	360
Chloroprene and Nitrile	149	300

6.0 Metals

The selection of metals should be based on their resistance to ignition and rate of reaction. Following is a comparison of these two properties for some commonly used valve materials.

7.0 Resistance to Ignition in Oxygen

Materials are listed in order from hardest to ignite to easiest to ignite:

A. Copper, copper alloys, and nickel-copper alloys — *most resistant*

B. Stainless steel (300 series)

C. Carbon steel

D. Aluminum — *least resistant*

8.0 Rate of Reaction

Materials are listed in order from slowest rate of combustion to most rapid rate of combustion:

A. Copper, copper alloys, and nickel-copper alloys — *do not normally propagate combustion*

B. Carbon steel

C. Stainless steel (300 series)

D. Aluminum — *burns very rapidly*

NOTE: Stainless steel, once ignited, burns more rapidly than carbon steel. Nevertheless, the austenitic grades (300 series) of stainless steel are much better than carbon steel because of their high resistance to ignition.

9.0 Materials for Low-Pressure Oxygen Service

NOTE: This section is based on Glenn Research Center, Glenn Safety Manual [GLP-QS-8715.1.5 Rev. C](), Oxygen. Additionally, NSS 1740.15, Safety Standard for Oxygen and Oxygen Systems*, Tables B-5 and B-6 may be useful for material selection.*

A. Gaseous Oxygen

Metals acceptable for low-pressure (nominally less than 350 psia) gaseous oxygen service include:

a. Aluminum-nickel

b. Aluminum alloys-nickel alloys

c. Copper-stainless steel

d. Copper alloys

See GLP-QS-8715.1.5 Table C.2, Some Recommended Materials for Oxygen Service, for a partial list of these materials and their applications.

B. Liquid Oxygen

Metals recommended for service with liquid oxygen include the following:

a. Nickel and nickel alloys

1) Hastelloy B nickel

2) Inconel-X

3) René 41

4) K-Monel

b. Stainless steel types

1) 304–310

2) 304L–316

3) 304ELC–321

c. Copper and copper alloys

1) Copper-Cupro-nickel

2) Naval brass

3) Admiralty brass

NOTE: Refer to ASTM MNL36, Chapter 3, Materials Information Related to Flammability, Ignition, and Combustion, for more detailed materials information.

C. Prohibited Metals

Certain metals are prohibited from being used in oxygen systems (see ASTM MNL36, Chapter 3, Restricted Alloys).

1. Cadmium

The toxicity and vapor pressure of cadmium restrict its use.

2. Titanium

Titanium metal shall not be used with liquid oxygen at any pressure or with gaseous oxygen or air at oxygen partial pressures above 30 psia. Titanium and its alloys are impact sensitive in oxygen.

3. Magnesium

Magnesium metal shall not be used in oxygen systems. In addition, its alloys shall not be used except in areas with minimal exposure to corrosive environments. Reactivity with halogenated compounds constrains its use with lubricants containing chlorine and fluorine.

4. Mercury

Mercury shall not be used in oxygen systems in any form because it is toxic; in addition, mercury and its compounds can cause accelerated stress cracking of aluminum and titanium alloys.

5. Beryllium

Beryllium and its oxides and salts are highly toxic and shall not be used in oxygen systems or near oxygen systems where they could be consumed in a fire.

D. Nonmetallic Materials

1. The primary concerns about using nonmetals in oxygen systems are their potential reactivity with the oxidant and limitations at cryogenic temperatures. Their ignition temperatures are generally lower than those for metals, and their low thermal conductivity and heat capacity make them much easier to ignite. The selection of these materials for use in oxygen is based on experience and testing of impact, ignition, and flammability characteristics. For more information, consult NASA SP-3090 and ASTM MNL36, Chapter 3, *Nonmetallic Materials*.

2. GLP-QS-8715.1.5 Table C.2, Some Recommended Materials for Oxygen Service, contains a partial list of nonmetals and their applications. Nonmetals that have been used successfully include the following:

    a. Tetrafluoroethylene (TFE) polymers (Halon TFE, Teflon™ TFE, or equivalent)

    b. Unplasticized chlorotrifluoroethylene polymer (e.g., Kel F®, Halon CTF, or equivalent)

    c. Fluorosilicone rubbers and fluorocarbons (e.g., Viton™ (The Chemours Company) fluoroelastomers), batch-tested for acceptability

d. Lubricants such as Krytox™ (The Chemours Company) and Triolube 16 (Aerospace Lubricants)

e. Table 2 in NASA RP-1113 lists ignition variability of nonmetallic materials currently used in oxygen systems and of nonmetallic materials not requiring batch-testing control, along with some use restrictions.

10.0 General Oxygen System Design Guidelines

NOTE: This section is from NSS 1740.15, Safety Standard for Oxygen and Oxygen Systems.

Alone, the use of ignition- and burn-resistant materials for components in oxygen systems will not eliminate oxygen fires. Designs shall consider system dynamics, component interactions, and operational constraints, in addition to component design requirements, to prevent conditions leading to oxygen fires. Refer to ASTM G 88 (1985) for additional system design guidelines and to Chapter 3 of this document, ASTM G 63 (1985), and ASTM G 94 (1990) for materials use guidelines.

Although it is not always possible to use materials that do not ignite under any operating condition, it is normally understood that the most ignition-resistant materials should be used in any design. The designer should also avoid ignition modes wherever possible, but what may not be clear is that the designer must also consider the relative importance of the various ignition modes when designing new or modified hardware. This means that certain ignition modes are more likely than others to result in failures, either because of the amount of soft goods present or the likelihood of a particular event leading to component heating and subsequent ignition. To reduce the risk of ignitions, any ignition failure mode that involves soft goods, contamination, or rapid pressurization must be carefully scrutinized. The following design guides are presented roughly in the order of priority described above.

A. Design, fabricate, and install per applicable codes.

B. Use filters to isolate system particulate; however, they should be placed in locations where they can be removed and inspected and where no possibility of back flow exists. A helpful practice is to check the pressure differential across the filter to aid in tracking the filter status. Use filters at the following locations:

1. Module inlets and outlets
2. Disconnect points
3. Points required to isolate difficult-to-clean passageways
4. Upstream of valve seats

C. Design component and system combination to avoid chatter.

D. Ensure proper materials certifications.

E. Design for fire containment using methods such as fire break, fire blow out, or remote operation. Use fire-resistant materials.

F. Design to allow a blowdown of the system with filtered, dry, inert gas at maximum attainable flow rates and pressures after system fabrication. This serves to purge or isolate assembly-generated particulate.

G. Design to minimize choked flow. Consider shut-off valves, metering valves, relief valves, and regulators to reduce particle impact ignition risks.

H. Avoid captured vent systems. A relief valve or burst disk that is not open directly to the atmosphere, but rather has a tube or pipe connected to the outlet, is said to have a captured vent. If a captured vent is necessary, use high ignition-resistant materials such as Monel and copper (see 403d(2)(t)).

I. Bulk oxygen installations are not hazardous (classified) locations as defined and covered in Article 500 of NFPA 70 (1993). Therefore, general purpose or weatherproof types of electrical wiring and equipment are acceptable depending upon whether the installation is indoors or outdoors. Such equipment shall be installed in accordance with the applicable provisions of NFPA 70 (1993).

J. Electrical wiring in high concentrations of GOX should be encased in hermetically sealed conduits or conduits filled with inert helium or nitrogen gas. The instruments, switches, flow sensors, and electrical devices should be designed in modular structure and hermetically sealed, and filling with nitrogen or helium is recommended.

K. Materials for electrical and electronic equipment should be selected to meet the intent of specifications found in NFPA 70 (1993). Electrical terminals should not tum or loosen when subjected to service conditions; terminal points should be protected from shorting out by eliminating foreign objects and contaminants.

11.0 Specific Oxygen System Design Guidelines

NOTE: This section is from NSS 1740.15, Safety Standard for Oxygen and Oxygen Systems.

Oxygen system designers should:

- Minimize the amount of soft goods and their exposure to flow. Soft goods exposed to flow can be readily heated through rapid compression or readily ignited through kindling chain reactions. Minimizing soft goods exposure by shielding with surrounding metals can significantly reduce ignition hazards.

- Limit gaseous oxygen pressurization rates. Soft goods (such as seals, coatings, and lubricants) are susceptible to ignition from heating caused by rapid pressurization. For example, Teflon™-lined flexible hoses are sensitive to this ignition mode, and their use with rapid pressurization applications is discouraged. Pressurization rates of valve and regulator actuators shall be minimized. And in some applications, flow-metering devices are prudent for manually actuated valves, especially for quarter-tum ball valves.

- Limit GOX flow velocities. Limiting flow velocities minimizes erosion problems and reduces the risk of particle impact ignitions. Although each material and configuration combination must be reviewed individually, fluid velocities above 30.5 m/s (100 ft/s) should receive special attention, especially at flow restrictions.

- Minimize mechanical impact. Mechanical impact ignitions can ignite large parts, and the impacts can also ignite contamination and soft goods entrapped by the impact. Relief valves, shutoff valves, regulators, and subminiature parts should be reviewed for this hazard especially.
- Minimize frictional heating in oxygen. Frictional heating, such as heating that occurs with bearings and pistons, can cause ignitions (De and Peterson 1992). Any contamination near the heated region can also be ignited. Frictional heating hazards can be reduced by carefully controlling surface finishes, coefficients of friction, alignment, and flow-induced cooling. Frictional heating has also been found to ignite materials in cryogenic applications.
- Minimize blunt flow impingement surfaces. The risk of particle impact ignitions can be reduced if potential impact surfaces are designed with shallow impact angles to reduce the kinetic energy absorbed by the impact surface upon impact.
- Eliminate burrs and avoid sharp edges. Burrs and sharp edges on equipment provide ignition sources for particle impact, and they also provide the ingredients for kindling chain combustion propagation. Removal of this material is standard shop practice and is essential to avoid oxygen-enriched ignitions.
- Design to minimize use-generated particulate during manufacture, assembly, and operation, as this particulate could be a source of particle impact ignition. Designs should have provisions to minimize particulate generation through the normal operation of valve stems, pistons, and other moving parts. This can be accomplished by using bearings, bushings, and configurations to keep particulate away from oxygen-wetted regions. Additionally, the assembly, cleaning, and maintenance practices should minimize contamination.
- Avoid rotating valve stems and sealing configurations that require rotation on assembly. Rotating valve stems and seals can gall and generate particulate.
- Minimize electrical arcing. Electrical arcs in oxygen-enriched environments can lead to heating and subsequent ignition.
- Eliminate blind passages. Long, narrow passages or blind passages are difficult to clean and to inspect for cleanliness. Additionally, they can provide a location for particulate to accumulate during operation of the equipment. This contamination can make the equipment susceptible to particle impact, rapid compression, and resonant cavity ignitions.
- Avoid crevices for particulate entrapment and resonant cavities (Phillips 1975). Cavities, especially those formed at the intersection of mating parts in assemblies, create a location where contamination can accumulate and increase ignition risks, as in blind passages.
- Design dynamic seals to minimize particulate generation. Minimize coefficients of friction and surface finishes and choose seal configurations to minimize particle generation that can cause particle impact ignitions.

- Limit fluid-induced vibrations (overall operating ranges). Vibrations can cause fretting, galling, impacting, and particle generation in components and systems. Check valve chatter and valve poppet oscillations are examples of this phenomenon. Particulate accumulations will increase the risk of particle impact ignitions.

- Consider the effects of single-point seal failures. Seals will degrade with time and use. Eventually, they may be expected to fail to seal the contained fluid. When this happens, the effects of an oxygen-enriched external environment, high velocity leakage, and loss of mechanical integrity must be addressed.

- Eliminate rotation of seals and rotation against seats. Sealed parts that require rotation at assembly (such as O-rings on threaded shafts) can generate particles which may migrate into the flow stream. Particulate generation also occurs in ball valves where operation of the valve rotates a ball on a nonmetallic seat.

  A related phenomenon that may be described as "feathering" occurs when valve stems are rotated against some nonmetallic seats such as Kel-F®. Because of the mechanical properties of some nonmetalllc materials, a thin, feather-like projection of material is extruded from the seat. The feathered material is more ignitable than the seat itself. Kel-F®' and other nonmetallic materials subject to feathering should only be used with caution for seals and seats in rotating configurations. Ball valves are not recommended for oxygen systems because of their tendency to generate particulate and their fast opening times, which create rapid pressurization of systems.

- Avoid thin walls. The walls between inner cavities or passageways and the outer surface of component housings may become so thin that stress concentrations result when pressure is introduced. Because geometries both inside and outside can be complex, it may not be obvious from drawings or even from direct inspection that such thin, highly stressed areas exist. If such walls become too thin, they may rupture under pressure loading. The energy released by the rupture can raise the temperature in the rupture zone. The failed section can expose bare, jagged metal that can oxidize rapidly and may heat enough to ignite and burn.

- Be cautious of single-barrier failures. A single-barrier failure is defined as a leak in which only the primary containment structure is breached. Such a leak introduces oxygen into a region not normally exposed to oxygen. The materials or configuration of parts in this region may not be compatible with high-pressure oxygen.

  Any situation in which a single barrier may fail should be analyzed during the design phase. The single-barrier failure analysis may consist of an engineering evaluation of the configuration, including an analysis of the compatibility of materials exposed by the failure with the high--pressure oxygen. The purpose of the analysis should be to determine if a barrier failure is credible and if exposure of incompatible materials can create a hazard. If the hazard cannot be assessed adequately by analysis, a configurational test may be performed.

- Be aware of seat shape and seals. Designs in which an O-ring seals on an unusual seat shape may cause increased wear or accelerated extrusion of the O-ring material and the generation of particulate contamination.

  Although the design of sealing interfaces is a necessary compromise, the design should use standard seat shapes as much as possible. Past experience has shown that elastomeric 0-rings are successful in static environments but are usually poor choices in dynamic environments and should only be considered in designs where the exposure to oxygen is minimized, such as line exposure. In some instances, PTFE with Viton• as a backup (which exposes the most compatible materials preferentially to oxygen) has been used for seals where elastomers must be used and cannot be limited to line exposure. Rigid plastics such as Vespel© have been used as seats in valves and regulators; however, the noncompliance of the material requires a small contact area with a hard (metal or sapphire) mating surface to achieve a seal. An alternative to rigid plastics is to use a coined metal seat if the precautions to eliminate galling, discussed above, have been taken.

- Allow sufficient seal squeeze to avoid 0-ring extrusion. Standard manufacturers' dimensions and tolerances should be incorporated into designs unless an unusual overriding design constraint demands the change. Additionally, the dimensions of all parts in the valve assembly should be carefully inspected.
- Use metal-to-metal seals in some cases. Polymeric materials cannot be used as seals in valves that control the flow of hot oxygen at high temperatures and pressures, because they lose sealing properties, are easily ignited, and wear too rapidly.

  High pressures and high flow rates can produce side loads and oscillations on the poppet seal; these can cause metal deterioration by fretting or galling. (Galling is the more severe condition, because it involves smearing and material transfer from one surface to another.) Fretting and galling can cause several problems in oxygen systems.

  The valve poppet may seize, resulting in loss of function. The frictional heat of the fretting or galling may lead to ignition of the valve. The particles generated by the fretting or galling may cause malfunction or ignition of another component downstream.

  Where possible, the valve poppet should be designed for symmetrical flow, so no oscillatory side loads are created. The symmetrical flow centers the poppet in the bore and maintains design clearances between the poppet and bore surfaces.

  For gaseous systems, it may be possible to reduce the volumetric flow rate (and thus the magnitude of oscillations and side loads) by installing an orifice. The orifice should be downstream of the poppet to minimize the pressure differential across the poppet. It is also possible to flexure-mount the poppet in the bore and to incorporate labyrinth seal grooves in the poppet surface.

To minimize the possibility of ignition, poppet and bore materials should be relatively resistant to ignition by frictional heating. Both may be hardened by nitriding or a similar process to minimize material loss by fretting or galling.

- Consider the effects of long-term operation, including the following:
  - Cold flow of seals. Cold flow is a concern, especially for soft goods with little resiliency. With applied loads, these materials permanently deform, usually resulting in sealing loss.
  - Seal extrusion (avoid extrusion-generated particulate). Generally, seals with low hardnesses tend to provide better sealing. However, the softer seals will not withstand high temperatures and pressures. When such seals fail, they often extrude, generating particulate. Pressure and thermal reversal cycles can also result in seal extrusion. Although silicone seals are not recommended, they may be found in existing oxygen systems. If found, careful examination during maintenance procedures is recommended, because excessive cross-linking of silicone elastomers in oxygen environments may occur, leading to embrittlement and degradation.
  - High-temperature substrate. The oxide is then likely to become a source of particulate.
- Design equipment so that power losses, control pressure leakage, or other loss of actuation sources return the equipment to a fail-safe position to protect personnel and property in an accident.
- Consider the effects of thermal expansion. Buckling can create component failures.

A. Cryogenic Oxygen Systems

In addition to the design considerations for high-pressure and high-temperature oxygen systems, specific considerations for cryogenic applications are described as follows. Liquid cryogens can easily vaporize and produce high-pressure regions in systems assumed to be at low pressure (liquid lockup); if these potential high-pressure conditions are not considered when designing the system, serious hazards can exist.

1. Materials Guidelines

Materials requirements are similar to requirements for GOX. One additional consideration is that vaporization of LOX occurs around heat sources such as ball bearings; this increases ignition risks and requires compensation for possible elevated pressure.

2. General System Installation Guidelines

Design considerations relating to system installations are noted below.

a. Thermal conditioning of cryogenic systems is mandatory. A bypass flow path with pressure relief valve shall be provided. Thermal conditioning can be performed with liquid nitrogen or LOX. Carefully analyze system startup for LOX pumps, as cavitation from improper chill down can increase fluid pressures and damage parts (leading to premature failure of components) and can create startup instabilities (leading to ignition from frictional heating).

b. Avoid condensation on external surfaces because the cryogen can liquefy air or freeze water and other vapors and create falling ice or other hazards.

c. Avoid condensation on internal surfaces because the cryogen can freeze water and other vapors.

- Long-term storage of LOX and extended cyclic fill operations may concentrate low volatile impurities in the storage container as a result of the loss of oxygen by boiloff. Therefore, the oxygen used based on the original specifications may not be satisfactory. Pressure relief valves or other means should be designed to prevent the back aspiration of volatile impurities into storage systems.
- The contents of vessels should be analyzed periodically for conformance to the specifications to limit the accumulation of contaminants from cyclic fill-and-drain operations. An inspection and system warmup refurbishment shutdown cycle should be established, based on the maximum calculated impurity content of the materials going through the tank or system. This should allow frozen water and gas contaminants to vaporize and leave the vessels. Where practical, a mass balance of measurable contaminants should be made for all fluids entering or leaving the system or the component.

3. Design Specifications

The concerns are similar to those for high-pressure, high-temperature oxygen, with the addition of material embrittlement because of the low temperatures. Cracking and fractures of soft goods and metals can cause premature failures.

Apply NFPA 55, Compressed Gases and Cryogenic Fluids Code, Chapter 9 Bulk Oxygen Systems to the design of bulk gas or liquid oxygen storage locations that have a storage capacity of more than 20,000 scf (566 Nm3) of oxygen.

4. Hazard Considerations

Cryogenic hazards, such as cold injuries from exposure when handling equipment with LOX, shall be considered. Additionally, oxygen-containing equipment should not be operated over asphalt pavement because of spill hazards and the potential for ignitions from oxygen-enriched asphalt, which can be readily ignited because of its shock sensitivity. When use of LOX systems over asphalt cannot be avoided, all asphalt areas under uninsulated piping should be protected to prevent contact with oxygen.

5. Component Hardware and Systems Design Considerations

Liquid lockup can occur, requiring special pressure relief protection.

Avoid fluid expansion regions in which the fluid can vaporize. If expansion is allowed to occur, the resulting fluid downstream will have two phases, gas and liquid, and the following situations could occur:

a. Increased pressure caused by vaporization.

b. High surge pressures caused by liquid hammer effects (Mechanical damage as well as rapid compression heating and ignition of soft goods can occur if fluid hammer is not eliminated in oxygen systems.)

c. Decreased performance of metering valves and other components sensitive to fluid properties.

Avoid cavitation of rotating equipment, because the high pressures generated by the rapid vaporization during cavitation can exceed the rated capability of hardware. Additionally, dynamic instabilities can be created that allow rotating shafts and impellers to wear against housings, leading to failures from frictional heating.

Avoid geysering of LOX and GOX, caused by gas bubble formation in flowing liquid systems, because this can create rapid pressurization of soft goods, and it can create a fluid hammer condition with rapid over pressurization of components, leading to bursting of pressure- containing components.

Prevent hydrostatic over-pressurization of tanks and Dewars during filling operations by using a full tricock valve system or similar overfill protection to maintain an adequate ullage area.

6. Electrical Design Guidelines

In addition to the guidance in Sections 401.b(9), (10), and (11) of this chapter, electrical wiring inside LOX tanks should be encased in hermetically sealed conduits or conduit inerted with helium or nitrogen gas. The instruments, switches, flow sensors, and electrical devices should be designed in modular structure and hermetically sealed, and inerting with nitrogen or helium is recommended.

B. Gaseous Oxygen Piping Systems

The primary concern with high-velocity flow conditions is the entrainment of particulates and their subsequent impingement on a surface, such as at bends in piping. The effects of extremes in flow velocity and pressure are also concerns. Material erosion or ignition can be caused by entrained particulate impact and abrasion, erosive effects of the fluid flow, or to both.

Until a more quantitative limit can be established, the following practices are recommended:

- Where practical, avoid sonic velocity in gases; where impractical, use the preferred materials listed in Schmidt and Forney (1975).
- If possible, avoid the use of nonmetals at locations within the system where sonic velocity can occur.

- Maintain fluid system cleanliness to limit entrained particulates, and perform blowdown with filtered, dry gaseous nitrogen (GN2) at maximum anticipated pressure and flow before wetting the system with oxygen.
- Piping systems should be designed to ensure the gaseous oxygen in the system does not exceed specified velocities. Places where fluid velocities approach 30 m/s (100 ft/s) should be reviewed for particle impact ignition sensitivity (refer to Appendix Band CGA G-4.4 1984).
- For use at pressures above 4.83 MPa (700 psig), oxygen piping and fittings should be stainless steel, nickel alloys, or copper alloys (Laurendeau 1968), because of ignition susceptibility. Monel® is approved for tubing, fittings, and component bodies (Schmidt and Forney 1975). The choice of piping and fitting materials should take into consideration the external environment.

12.0 Oxygen System Fire Prevention and Considerations

Like in air systems, there is a series of control measures that must be taken to prevent fires in oxygen services, depending on the severity of the fire hazard. Progressively more stringent practices are applied in this order: cleaning, compatible lubricants, compatible polymers and other nonmetals, and compatible metals. When oxygen concentration and pressures are low, the hazard is lowest, and cleaning may be the only control necessary. As oxygen enrichment and pressure increase, all wetted material including lubricants, metals, and non-metals must be selected more carefully. The NFPA view of oxygen compatibility (ref. NFPA 99 para. A.5.1.3.5.4) is given as,

Compatibility involves both combustibility and ease of ignition. Materials that burn in air will burn violently in pure oxygen at normal pressure and explosively in pressurized oxygen. Also, many materials that do not burn in air will do so in pure oxygen, particularly under pressure. Metals for containers and piping must be carefully selected, depending on service conditions. The various steels are acceptable for many applications, but some service conditions may call for other materials (usually copper or its alloys) because of their greater resistance to ignition and lower rates of combustion.

Similarly, materials that can be ignited in air have lower ignition energies in oxygen. Many such materials may be ignited by friction at a valve seat or stem packing or by adiabatic compression produced when oxygen at high pressure is rapidly introduced in a system initially at low pressure.

Polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) are commonly used in oxygen service. Yet even these materials begin to decompose at 200 to 300°C [400 to 600°F] and can ignite at higher temperatures.

As emphasized in ASTM Guide G63, the successful use of even the best materials depends on the design of the component and where it is used. For example, PTFE-lined flexible hose has a large surface area-to-mass ratio, and many instances involving the ignition of such hoses have been reported (Ref. Fig. 6 of ASTM G128). The use of PTFE-lined hose in high-pressure oxygen may require special provisions in the system design, such as a distance-volume piece which contains the heat of adiabatic compression.

MIL-PRF-27617 Performance Specification, *Grease, Aircraft and Instrument, Fuel and Oxidizer Resistant*

DOD-PRF-24574 (SH) Performance Specification, *Lubricating Fluid for Low and High Pressure Oxidizing Gas Mixtures*

13.0 References

There are links to external websites throughout this document that go to publicly available copies of reference material. PDF versions of the linked content are also available on the "Reference Data" SharePoint linked on the ESM Chapter 17 website. All reference listed below can be obtained via internet search, LANL's Engineering Workbench subscription, or LANL's CGA subscription.

Additionally, ASTM, CGA, NFPA, AIGA, EIGA, and NASA have published standards, guidance, and/or requirements for oxygen systems designed to minimize the control the materials and ignition of oxygen systems that may be beneficial resources.

ASTM International

- ASTM MNL36, *Safe Use of Oxygen and Oxygen Systems*
- ASTM G63, Standard *Guide for Evaluating Nonmetallic Materials for Oxygen Service*
- ASTM G72, *Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment*
- ASTM G74, *Test Method for Ignition Sensitivity of Nonmetallic Materials and Components by Gaseous Fluid Impact*
- ASTM G88, *Standard Guide for Designing Systems for Oxygen Service*
- ASTM G93, *Standard Guide for Cleanliness Levels and Cleaning Methods for Materials and Equipment Used in Oxygen-Enriched Environments*
- ASTM G94, *Standard Guide for Evaluating Metals for Oxygen Service*
- ASTM G128, *Standard Guide for Control of Hazards and Risks in Oxygen Enriched Systems*
- ASTM G175, *Test Method for Evaluating the Ignition Sensitivity and Fault Tolerance of Oxygen Pressure Regulators Used for Medical and Emergency Applications*

National Fire Protection Association

- NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*
- NFPA 53, *Recommended Practice on Materials, Equipment, and Systems Used in Oxygen-Enriched Atmospheres*
- NFPA 55, *Compressed Gases and Cryogenic Fluids Code*
- NFPA 99, *Health Care Facilities Code*

Compressed Gas Association

- CGA E-4, *Standard for Gas Pressure Regulators*
- CGA G-4.1, *Cleaning Equipment for Oxygen Service*
- CGA G-4.4, *Oxygen Pipeline and Piping Systems*
- CGA G-4.6, *Oxygen Compressor Installation and Operation Guide*
- CGA G-4.7, *Installation Guide for Stationary Electric Motor Driven Centrifugal Liquid Oxygen Pumps*
- CGA G-4.8, *Safe Use of Aluminum Structured Packing for Oxygen Distillation*

- CGA G-4.9, *Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen*
- CGA G-4.11, *Reciprocating Oxygen Compressor Code of Practice*
- CGA G-4.13, *Centrifugal Compressors for Oxygen Service*
- CGA P-8.4, *Safe Operation of Reboilers/Condensers in Air Separation Units*
- CGA P-8, *Safe Practices Guide for Air Separation Plants*
- CGA P-25, *Guide for Flat Bottomed LOX/LIN/LAR Storage Tank Systems*
- CGA PS-15, *Toxicity Considerations of Nonmetallic Materials in Medical Oxygen Cylinder Valves*
- CGA SB-2, *Definition of Oxygen Enrichment/Deficiency Safety Criteria*

Asia Industrial Gases Association

- AIGA 021, *Oxygen Pipeline and Piping Systems*

European Industrial Gases Association

- EIGA/IGC 4, *Fire Hazards of Oxygen and Oxygen Enriched Atmospheres*
- EIGA/IGC 10, *Reciprocating Oxygen Compressors For Oxygen Service*
- EIGA/IGC 13, *Oxygen Pipeline and Piping Systems*
- EIGA/IGC 27, *Centrifugal Compressors For Oxygen Service*
- EIGA/IGC 33, *Cleaning of Equipment for Oxygen Service Guideline*
- EIGA/IGC 65, *Safe Operation of Reboilers/Condensers in Air Separation Units*
- EIGA/IGC 73, *Design Considerations to Mitigate the Potential Risks of Toxicity when using Non-metallic Materials in High Pressure Oxygen Breathing Systems*
- EIGA/IGC 115, *Storage of Cryogenic Air Gases at Users Premises*
- EIGA/IGC 127, *Bulk Liquid Oxygen, Nitrogen and Argon Storage Systems at Production Sites*
- EIGA/IGC 144, *Safe Use of Aluminum-Structured Packing for Oxygen Distillation*
- EIGA/IGC 145, *Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen*
- EIGA/IGC 147, *Safe Practices Guide for Air Separation Plants*
- EIGA/IGC 148, *Installation Guide for Stationary Electric-Motor-Driven Centrifugal Liquid Oxygen Pumps*
- EIGA/IGC 154, *Safe Location of Oxygen, Nitrogen and Inert Gas Vents*
- EIGA/IGC 159, *Reciprocating Cryogenic Pump and Pump Installation*
- EIGA/IGC 179, *Liquid Oxygen, Nitrogen, and Argon Cryogenic Tanker Loading Systems*

National Aeronautics and Space Administration

- NSS 1740.15, JANUARY 1996, *SAFETY STANDARD FOR OXYGEN AND OXYGEN SYSTEMS, Guidelines for Oxygen System Design, Materials Selection, Operations, Storage, and Transportation*

- NASA/TM-2007-213740, *Guide for Oxygen Compatibility Assessments on Oxygen Components and Systems*
- GLP-QS-8715.1.5 Revision C, *Glenn Research Center, Glenn Safety Manual Chapter 5 Title: Oxygen*