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OXYGEN COMPATIBILITY FOR AEROSPACE MATERIALS

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Master's Program in Mechanical Engineering

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2022

Dedication

I would like to dedicate this work to Jesus Gonzalez, my special person, who has been supporting me and encouraging me to fly since we meet. Lastly, I would like to dedicate this paper to my dogs and chameleon, Falkor, Daisy and Camelia, who saved me from craziness during the entire process.

OXYGEN COMPATIBILITY FOR AEROSPACE MATERIALS

by

JAZMIN ABRIL ARELLANO, B.S.

THESIS

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I would like to thank my mentor and friend Dr. Chessa who guided me and impulsed me to succeed during challenging times.

Abstract

The use of oxygen for aerospace applications is bonded to the history of American rocketry. The first liquid powered rocket engine used gaseous oxygen to pressurize both gasoline as fuel and liquid oxygen as oxidizer. Research and development about oxygen compatibility with aerospace materials has been continuously performed. However, no universal test has been developed to determine the oxygen compatibility of all materials yet. A review about oxygen properties, ignition mechanisms and their unique characteristic elements in addition to metals and nonmetals commonly used in oxygen systems and materials prohibited in oxygen applications can be found in this document. The use of oxygen compatibility assessment as a tool to do proper material selection is discussed and highly encouraged. This paper attempts to facilitate the selection process for materials intended in oxygen systems.

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Chapter 1: Introduction and Background

1.1 INTRODUCTION

Aerospace industry, liquid oxygen and cold gas oxygen are bonded together. It has been almost one century since the first liquid rocket was launched. Dr. Robert H. Goddard (1882-1845) is recognized as the father of the American rocketry. He developed and launched the first American rocket powered with gasoline and liquid oxygen; the unconventional system was pressurized with gaseous oxygen. The engine was located at the top of the rocket and the fuel and oxidizer tanks were located at the bottom of the system. Illustration 1.1 is a picture of Dr. Goddard and his rocket design. His insight ideas and advanced discoveries for his time were fundamental principles to take the first human to the moon. Multiple rocket systems including Saturn V were developed by Wernher von Braun who was evidently influenced by Dr. Goddard. [1]

Dr. Goddard realized that solid rockets produce a lower exhaust velocity compared to liquid rockets. He also was aware that liquid fuels require a continuous source of oxidizer to produce trust. He decided to use oxygen not only because it is a strong oxidizer that highly supports combustion, but because oxygen can be maintained in liquid form at ambient pressures under a temperature of -297^0 F. [2]

Illustration 1.1: American rocketry pioneer Robert H. Goddard and his first liquid-fueled rocket, March 16, 1926.

Since the beginning of rocketry continuous research and development has been performed to determine the oxygen compatibility of varied materials intended for aerospace applications. Currently, test standards to determine material flammability in oxygen enriched environments have been developed, and ignition mechanisms with their unique characteristic elements were identified. The dependency between material flammability and material configuration has been also stablished. However, no universal test has been developed to determine the oxygen compatibility of all materials yet.

This paper attempts to guide the lector during the material selection process for oxygen systems. A basic discussion of ignition mechanisms and their unique characteristic ignition factors is provided. The understanding of these mechanisms and their possible consequences in oxygen systems is fundamental during material selection process. Common metallic and nonmetallic material used in oxygen systems are described in addition to materials prohibited in oxygen applications. The physical, chemical, and hazardous properties of oxygen in liquid and gaseous states are discussed. The understanding of oxygen properties besides the possible emergencies associated with oxygen is essential to determine worst case scenario during the oxygen system design and the material selection processes. The worst-case scenario of oxygen system is commonly used to drive the oxygen compatibility assessment. Information about the oxygen compatibility assessment can be found in the last chapter of this paper. The oxygen compatibility assessment is a tool that analyses individual components in oxygen systems and is highly encouraged to use during material selection process.

1.2 Oxygen Overview

Oxygen is the chemical element with symbol O and atomic number 8 in the periodic table. Oxygen has two interesting properties. Oxygen sustains life and strongly supports combustion. Around 21% of the earth's atmosphere is composed of oxygen in gaseous form. Gaseous oxygen (GOX) is odorless, colorless, and tasteless at standard pressure and temperature. Liquid oxygen (LOX) is odorless and has a light blue transparent color. In both states, oxygen is a very reactive strong oxidizer that sustains combustion. Oxygen by itself is not flammable, it is chemically stable, it does not decompose, and is not shock sensitive. However, most metallic, and not metallic materials react when oxygen's pressure, temperature or concentration is increased. Even though, they may not react with oxygen at ambient conditions. [4], [5] Personnel involved in oxygen systems handling and design shall be familiar with oxygen properties. Table 1.1 list some physical, chemical, and hazardous oxygen properties Catastrophic events are reduced or eliminated when oxygen operators and designers are properly rained.

1.2.1 Oxygen Principal Hazards

Temperature, pressure, and ignition sources are the principal dangers associated with fire hazards during oxygen handling. Emergency procedures shall be read and acknowledged, user shall be professionally trained in oxygen handling techniques, appropriate personal protective equipment shall be worn while working in any oxygen system and its surroundings. LOX, cold GOX, and uninsulated pipes transporting these fluids might cause frostbite in users when direct contact with skin occurs. LOX and GOX are higher in density than water and air respectively. LOX is eight hundred times denser than GOX. Depressions are suitable for creating an oxygen rich environment during any LOX spillage. Clothes and skin exposed to LOX accumulation become very flammable and ignitable and only takes a small ignition source such as a static discharge to create fire. More reactive materials ignite spontaneously when they come in direct contact with LOX. Porous materials such as leather and concrete will not ignite spontaneously when exposed to LOX accumulation. However, ignition in porous materials that have been previously exposed to LOX can occur with a small impact. [5] [3] Table 1.2 list relevant documentation about oxygen hazards .LOX and cold GOX management are a serious responsibility and shall never be taken for granted.

Table 1.1 Oxygen physical, chemical, and hazardous properties[5]

	Physical Properties and Chemical Properties	**Hazardous Properties**
LOX	Light blue color It is not shock-sensitive. It is chemically stable. It does not decompose	It is a cryogenic fuel that boils at ambient pressure. Frostbite risk is present when direct contact with skin occurs
	Boiling point 97.35^{0} F, Heat of fusion 76 BTU/lb., Vaporization 1.568 BTU/lb., Specific heat at constant pressure 0.405 BTU/lb-^{0}R	
LOX and GOX	Atomic weight 16 molecular weight 31.9988 Odorless, colorless, transparent fluid	It is a strong oxidizer that supports combustion. The flammability of materials increases when oxygen concentration increases.
GOX	Density 0.892 lb./ft^{3} at STP specific heat at constant pressure C_p 0.230 BTU/lb-°R, specific heat at constant volume C_v 50 BTU/lb-°R	Most materials are highly Soluble on it. Inadvertent contamination and chemical reactions might occur

1.2.2 Oxygen Personal Protective Equipment (PPE)

Personal protective equipment is designed to reduce direct human exposure to hazards and is highly encouraged. Safety glasses, face shields, safety boots, laboratory aprons, etc., are recommended to be worn while operating systems that might expose the users to an oxygen rich environment. Occupational Safety and Health Administration (OSHA) determined that an atmosphere containing at least 22% oxygen, is considered an oxygen rich environment. [1] Oxygen systems operators shall also be familiar with oxygen properties, and proficient recognizing hazards. Oxygen fires are unusual events that can lead to catastrophic events. [5], [6]

1.2.2.1 Clothes

Oxygen users shall wear low combustibility clothes with no external pockets to protect themselves from possible thermal injuries. Examples of low combustibility materials are Asbestos and glass fiber since they are both untreated textile materials and are considered 100% fire resistant in oxygen rich environments. However, they are uncomfortable to wear. Thus, well fitted fire retardant coveralls and aprons are considered a good PPE option for oxygen handling operations. Materials described as fire resistant under regular atmospheric conditions shall never be considered as burn proof in oxygen rich environments. Fire retardant clothes will rapidly burn when saturated with 30% oxygen and exposed to an ignition source. [2] Clothes that were spilled or soaked in LOX shall never be immediately removed. A good practice is to not remove clothing and avoid any possible ignition source after half an hour of being exposed to oxygen. [4]–[6]

1.2.2.2 Gloves

Due to LOX low temperatures, frostbite might occur when LOX comes in direct contact with human skin. [4]–[6]Thus, well insulated forearm cryogenic protection gloves shall be used during LOX operations to avoid direct contact with LOX. Gloves used in LOX operations shall be easy to remove in case LOX gets inside.

1.2.2.3 Footwear

Long top leather shoes shall be worn during LOX operations. Leg pants shall be worn outside the boot to prevent any LOX spillage to get inside the operator footwear. [5] Slip resistant, leather steel toe shoes are recommended to wear during normal engineering field operations.

1.2.2.4 Face Protection

Direct physical contact with cryogenics can cause serious tissue damage. [4]–[6] Face shield is highly encouraged to be worn during LOX operations. Face frostbite and permanent eye damage are prevented by using a face shield during LOX handling.

1.2.3 Oxygen System Cleaning

Oxygen systems require more than a visual inspection to determine their cleaning level. Oxygen fire hazards associated with contaminants are invisible to human eye. The cleaning processes used in oxygen systems depends on the specific material, component, and application. A single cleaning method might not be enough to meet the required cleaning level in an oxygen system. A combination of chemical and mechanical cleaning procedures is a general practice during oxygen cleaning. [4] Oxygen systems that require a high degree of cleaning might use ultrasonic energy, and deionized water in combination with different chemical agents. Ultrasonic agitation effectively removes embedded particles and lightly adhered contaminants from solid surfaces. Ultrasonic devices enhance contact between chemical agent and contaminated oxygen components. Further information in ultrasonic cleaning can be found in ASTM Practice G 131.

1.2.3.2 System Contamination

Professionally designed and well-maintained oxygen systems that were cautiously assembled might be considered within the operational cleaning limits. However, particulate contamination from regular operations such as rust or abrasion might exist. These contaminants might be highly flammable or be reactive enough to cause ignition due to friction, particle impact, or by enhancing the temperature increase during acoustic resonances. In GOX systems inadvertent oxygen contamination can occur. Colorless and odorless oxygen soluble elements such as argon and nitrogen can displace oxygen from breathing air at a lower temperature than ambient temperature causing user asphyxiation in an enclosed environment. Ignition or even explosions can occur due to flammable gases being unintentionally dissolved in oxygen. [4]

1.2.4 Oxygen Emergencies

Oxygen fires are unusual events that can be reduced with training and proper design practices. Users and designers shall be trained before operating the oxygen systems and shall be familiar with oxygen physical, chemical, and hazardous properties. They shall be confident using the proper PPE during oxygen handling procedures. Operators shall be able to identify possible hazards during regular system operations and react accordingly to emergency procedures if required.

1.2.4.1 Leaks and Spills

Fires and explosions are the principal risks associated with oxygen leaks and spills. An oxygen enriched environment drastically increases the flammability and ignitability of materials. [6] A porous material such as wood, lather, or asphalt might become impact sensitive when spilled with LOX. A very small amount of energy is required to cause a fire or explosion under these circumstances. GOX leaks can quickly transform a confined space into an oxygen enriched environment. A fire can be caused with the impingement of GOX into an organic material.

Oxygen leaks and spillages should be treated with caution since they can result in unnoticed mixtures that can lead to combustion or other harmful chemical reactions. The oxygen supply lines shall be halted or closed if possible. Any spark and heat source shall be removed or turned off. Reparations and disassembly operations shall be performed only after ventilating the area thoroughly.

1.2.4.2 Over pressurization

LOX turns into GOX after passings its critical temperature of 118.6 °C (-181.4 °F). Therefore, over pressurization can occur if GOX temperature increases in a system without pressure relief valves. Relief and vent systems dimensions shall always be considered when designing an oxygen system. [6]They shall be in accordance with expected oxygen flow to eliminate excessive back pressure. Pipe ruptures might occur if oxygen is trapped between valves and allowed to warm. Cryogenic pressure vessels and their vacuum insulated portion of the tank shall be protected from over pressurization using a proper combination of pressure relief devices. Operators shall carefully watch and listen to pressure relief devices with attention. Frost accumulated in the outer wall of a pressure vessel might be an indication of insulation damage. Pressure relief devices make higher pitch sounds when a problem is present in the system. [6]

Pressure relief devices acting constantly while pressure is also increasing is a major problem indicator. The area shall be evacuated immediately, the system turned off and the pressure vessel allowed to vent.

1.2.4.3 Cold Injury

Tissue can be severely damaged after having direct contact with LOX, cold GOX, and uninsulated pipelines transporting these materials. Emergency dependency shall be contacted immediately, oxygen cryogenic injury shall be reported. Affected individual shall be removed from any heat, spark, and any oxygen source. Injury shall not be touched, exposed to heavy water stream, or temperatures higher than 44 °C (112 °F). Frozen PPE items such as gloves and footwear shall not be removed as skin might be pulled off without notice. A warm bath not exceeding temperatures of 38.9 °C (102 °F) for injuries sizing a limb or smaller is advised by National Aeronautics and Space Administration (NASA) safety standard for oxygen systems. However, in some cases, it is safer to do nothing until qualified medical personal arrival.[6]

Table 1. Oxygen Hazards Documentation

Oxygen Hazards Relevant Information	
AIGA 048	Reciprocating compressors for oxygen service [7]
AIGA 021	Oxygen Pipeline and Piping Systems[8]
AIGA 071	Centrifugal Compressors for Oxygen Service [9]
AIGA 012	Cleaning of equipment for oxygen service[10]
ASTM Practice G 131	Standard Practice for Cleaning of Materials and Components by Ultrasonic Techniques
CGA G-4.1	Cleaning Equipment for Oxygen Service[10]
AIGA 044	Flexible Connections in High Pressure Gas Systems [11]
AIGA 066	Selection of personal protective equipment [12]
AIGA 055	Installation Guide for Stationary Electric-Motor-Driven Centrifugal Liquid Oxygen Pumps [13]
EIGA Safety Information 15,	Safety principles of high-pressure oxygen systems [14]
ASTM Symposiums	Flammability and sensitivity of materials in oxygen-enriched atmospheres

Chapter 2: History of Oxygen Fires in Aerospace

Documented history allows people to understand and learn from previous humanity experiences. Fires involving oxygen handling are not the exception. Oxygen fires are a hazard present during any LOX and cold GOX handling independently if they are used for aerospace applications or as life support aids. Oxygen fires are infrequent events with possible catastrophic consequences and shall be avoided at all costs. Correct system design practices, including material selection, and proper oxygen handling techniques highly reduce oxygen fire hazards.

2.1 APOLLO 1

Astronauts Virgil Grissom, Edward White, and Roger Chaffee lost their lives during the Apollo 204 preflight test at the Kennedy flight center in January of 1967. Review board final report and medical autopsy determined that astronauts died asphyxiated with toxic gases resultant from fire. [15], [16]

Illustration 2.1 Apollo 1 Crew Members.[15], [16]

An electrical arc that occurred in the power lines between the environmental control unit and the oxygen panel was considered the principal fire initiator. The quick fire spread increased the temperature and pressure rapidly leading to a rupture in the command module. The command module environmental control system design created an unnecessary pure oxygen environment. At the time of the accident, there were no restrictions in the amount and location of combustible materials in the command module. Subsequent investigation found multiple design, manufacturing, communication and operation deficiencies that occurred at the time of the event.

2.2 APOLLO 13

James A. Lovell, Jr, John "Jack" Swigert, Jr, and Fred Haise, Jr. Were the crew in charge of the 1970 Apollo 13 mission. It consisted in performing a safe lunar landing and explore the hilly upland Fra Mauro lunar region. However, this goal drastically changed after the loss of two out of three service module oxygen tanks. The service module provided oxygen, water and electricity to the astronauts. The second oxygen tank exploded damaging the first oxygen tank as well. A safe return to earth became the new Apollo 13 mission for the three astronauts. The astronauts were able to recreate an adapter between the command module and the lunar module lithium hydroxide canisters following Houston's mission control instructions. Thanks to the Johnson Space Center engineers set up, shown in Illustration 2.1. The Apollo 13 crew members removed carbon dioxide from the spacecraft using their available limited resources. [17]

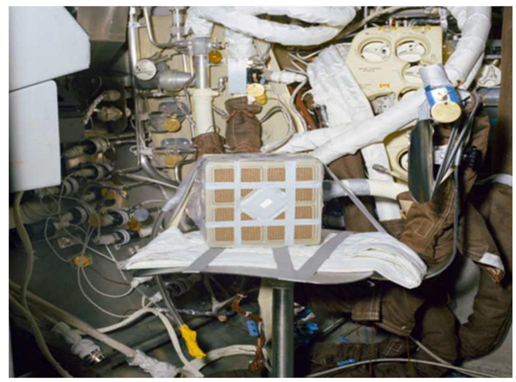

Illustration 2.2: Houston's Mission Control Adapter Setup[17]

These decisions allowed the crew members to return to home safely. However, that situation could be prevented. Apollo 13 accident review board determined that multiple changes were performed in the command module prior to the mission. Oxygen tank number two installed in the Apollo 13 service module was removed from the Apollo 10 service module to perform an upgrade. During said upgrade, tank number two was damaged unintentionally and was not working in accordance with tanks one and three during preflight operations. To overcome the malfunctioning in tank number two, the original heaters were modified, and the voltage was drastically increased. However, these design changes damaged the electrical wiring insulation, and turned the oxygen tank into an explosion waiting to happen.

2.3 The Extravehicular Mobility Unit (EMU) Fire

The extra vehicular mobility unit, or EMU, is the suit used by astronauts when performing activities outside the spacecraft and the space station. In April 1980, the EMU was under an unmanned test in Johnson Space Center. The test was performed in a large vacuum chamber and attempted to simulate the extra vehicular activities (EVA). Two technicians were performing the test procedures on the system when the fire occurred. The two technicians were burned, one required hospitalization after receiving second and third grade burns in 30% of his body.[18]

The EMU included a life support system containing two oxygen supplies, 900psi and 600psi respectively. The fire occurred when the EMU was changed to EVA mode. Further investigations were able to trace the fire until a regulator located in the second oxygen supply. The potential causes of the accident included unintentional heat in a thin wall of the regulator after being exposed to high compression, an O-ring failure due to the same high compression, and contamination particles impacting into the regulator. The aluminum regulator was melted after a few seconds in the oxygen fire. The EMU was considered total lost as shown in Illustration 2.3. The material of the oxygen regulator was changed from aluminum to a nickel and copper alloy. It also was redesigned to reduce the contaminants in its passageways.[18]

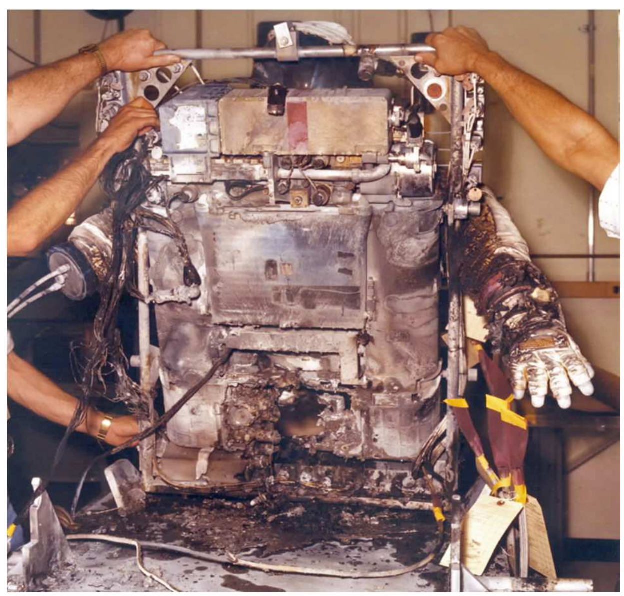

Illustration 2.3: EMU After Fire[18]

2.4 MIR SPACE STATION FIRE

February of 1997 was an unusual occasion in the MIR space station. Aleksandr Y. Kaleri, Jerry M. Linenger, and Valeri G. Korzun; Vasili V. Tsibliyev, Reinhold Ewald, and Aleksandr I. Lazutkin were the names of the cosmonauts onboard the Russian space station, exceeding three cosmonauts, the intended maximum number of persons during mission operations. During normal crew sizes, the necessary oxygen was generated by electrolytic splitting of water. Unusually enlarged crew sizes accounted for solid fuel generators from the MIR space station. These devices obtained oxygen resultant from the chemical reaction of burning canisters of solid lithium perchlorate. [19]

One of this solid fuel generators burned in flames filling out the entire station with toxic gases. The incident also blocked the access to one of the two available escape vehicles. Fortunately, the cosmonauts were able to suffocate the fire after a few minutes, and the life support systems cleared the atmosphere after few hours. After two years of analysis, it was determined that a small piece of latex glove unintentionally placed inside the canister might be the initiator of the fire.[19]

Illustration 2.4: Solid Fuel Oxygen Generator Returned from Space Station Mir[19]

2.5 SpaceX F9-29 Fire

In September of 2016 Space X mission was to take the communication Amos-6 satellite to orbit in one of their Falcon 9 space vehicles. However, the mission was postponed until January of 2017 due to a fire that resulted in the loss of both the payload and the vehicle. The analysis performed by SpaceX, NASA and the FAA among other dependencies concluded that the fire initiator was oxygen accumulation that was trapped between the helium vessels carbon fiber and aluminum layers. These super chilled helium vessels were used to pressurize the liquid oxygen and were located inside the second stage oxidizer tank. Placing the helium vessels inside the oxidizer tank is an unusual design. Liquid oxygen could be solidified when trapped between the pressure vessel layers. Investigators aimed that friction between broken fibers could be the ignition mechanism that aid the entire system to explode.[20]

Illustration 2.5: Space X F9-29 2016 Explosion [20]

Chapter 3: Oxygen Systems Ignition Mechanisms

3.1 Ignition Mechanisms Overview

This chapter attempts to provide users with a basic understanding of the ignition mechanisms associated with oxygen. Ignition mechanisms are sources of heat that can ignite system construction materials or contaminants when certain characteristic elements are present. The characteristic elements are unique for each ignition mechanism and shall be removed or lowered to prevent ignition from occurring. The understanding of ignition mechanisms and characteristic elements is imperative during proper material selection and safe system design.

The ignition mechanisms evaluation is part of the oxygen compatibility assessment (OCA) tool used by National Aeronautics and Space Administration (NASA), American Society for Testing and Materials (ASTM), National Fire Protection Association (NFPA), etc. To determine the operation risk of oxygen systems and components. The implementation of the OCA tool during material selection and designing process reduces any fire possibility and any losses tied to it. [5][21] An oxygen hazards analysis is a fundamental part of the OCA tool. In this analysis a minimum of nine ignition mechanisms shall be considered when a flammable material is encountered in a system. The possible existence of ignition mechanisms and their characteristic elements shall be evaluated and ranked from zero (impossible) to four (probable) depending on the ignition risk. Table 3.1 lists twelve ignition mechanisms. [13]

Table 3.1 *Example of Ignition Mechanisms* [4]

1.Particle Impact	5.Friction	9.Chemical Reaction
2.Heat of Compression	6.Fresh Metal Exposure	10.Spontaneous Ignition
3.Flow Friction	7.Static Discharge	11.Resonance
4.Mechanical Impact	8.Electric Arc	12.External Heat

Table 3.1 does not represent all possible ignition mechanisms. It was selected to aid users when recognizing possible ignition sources in a system. Table 3.2 lists high-risk components used in oxygen systems and the ignition mechanisms that mainly affect them. The listed ignition mechanisms and their characteristic elements are discussed in this chapter. However, oxygen system designers shall always reference the ASTM-G88 to find current information about ignition mechanisms and characteristic elements.

Table 3.2: *High Risk Components Commonly Used in Oxygen Systems*

	Ignition Mechanisms			
Components	1.Particle Impact	2.Heat of Compression	4.Mechanical Impact	5.Friction
Ball Valve	●	●		
Relief Valve			●	●
Globe Valve	●			
Butterfly Valve	●			
Flex Hose		●		
Regulator	●		●	
Check Valve			●	●
Filters	●	●		
Fittings	●			
Soft Goods	●	●	●	

3.1.1 Ignition Factors

The factors affecting the ignition of materials shall never be generalized since they depend on the material application, geometry, composition, purity, existence and condition of oxygen layers, sample condition etc., [4], [5] users shall be cautious when interpreting the data collected from ignition and combustion tests. Generalizing the results may result in an improper material selection, increasing the chances of ignition. When using testing data during material selection, designers shall verify that test conditions mimic the material's intended application as much as possible.

3.2 PARTICLE IMPACT

Ignition might happen when very small particles that travel at an extremely high velocity impact a component. [5], [6] To ignite the component, the unique characteristic elements for particle impact described in Table 3.3 shall be present and the heat generated shall be enough to ignite the particle. Particle impact is considered the most generic form of ignition for metals in oxygen systems. [5], [6] Table 3.4 lists the components found to be more susceptible to ignite with particle impact.

Table 3.3 *Unique Characteristic elements for Particle Impact* [6]

Particle Impact Characteristic Elements	
Characteristic Elements	**Description**
1. There shall be contaminant particles entering the system directly to the oxygen flow.	• Contaminant particles could be present in the system, even if it was cleaned for oxygen service. • These contaminants must be from a flammable material in majority of cases. • Construction materials such as aluminum and titanium can ignite after being impacted by inert materials such as sand.
2. There shall be a high gas velocity of 100ft/s or faster in the oxygen system	• High speed velocities can be achieved when pressure drops occur, even if the system was designed with a nominal low gas velocity. • Pressure drops that occur in flow restriction devices such as regulators, filters, valves, etc. Can increase the gas velocity within the oxygen system.
3. There is an impact point located in a 45^0 to 90^0 degree angle in the path of the contaminant particle	• A test campaign performed in the NASA White Sands Test facility that utilized modified replicas of the Space Shuttle Type II Main Propulsion system oxygen flow control valve encountered that drill points in control valves are impact points that ignite and burn when combined with the characteristic elements 1 and 2 of particle impact

Table 3.4 *Particle Impact High Risk Components* [3]

Particle Impact High Risk Mechanisms	
Ball Valve	Risk of particle generation
Globe Valve	Risk of impingement even when fully open
Regulator	High velocities are generated
Filter	Risk of impingement when misplaced
Soft Goods	Polymers impingement during gas stream

3.3 Heat of Compression

Heat of compression, rapid pressurization and adiabatic compression are the names given to the heat generation after a gas is rapidly compressed from a low temperature to a high temperature. [5] Generally, this ignition mechanisms do not affect metals. However, it is the most effective ignition mechanism for nonmetallic materials when the unique characteristic elements combination is present. Table 3.5 describes the required characteristic elements for heat of compression to ignite and burn the oxygen system.

Table 3.5 *Characteristic Elements for Heat of Compression* [4]

Heat of Compression Characteristic Elements
1. Oxygen shall be pressurized in few seconds; it could happen in less than one second for very small diameter systems
2. There shall be an exposed nonmetal close to the dead-end point of the rapidly pressurized oxygen system
3. The pressure ratio shall be enough to cause the temperature from the rapid compression to pass the autoignition temperature of the nonmetallic material

3.4 Flow Friction

Flow friction is a theoretical ignition mechanism described as heat generated after pressurized oxygen enters or flows throughout a nonmetallic material surface causing friction, erosion, or vibrations in the nonmetal. The temperature of the nonmetallic material is increased highly enough to pass its autoignition point. Polymers are the materials mainly affected by this ignition mechanism. [4], [5] No test method has been developed to test the flow friction mechanism yet. The hypothesis created after numerous ignitions had occurred in elevated pressure oxygen systems describes the unique characteristic elements for this ignition mechanism as listed in Table 3.6.

Table 3.6 *Characteristic Elements for Flow Friction* [4], [5]

Flow Friction Characteristic Elements
1. Oxygen flowing in the system shall be pressurized to at least 500Psi
2. There shall be a nonmetallic surface exposed to the oxygen flow, commonly a polymer
3. The oxygen flow shall produce friction, erosion, or vibration in the nonmetallic surface

3.5 Mechanical Impact

Mechanical impact is described as the heat that is generated after a material is impacted once or multiple times. This ignition mechanism commonly affects nonmetallic materials. However, a mechanical impact ignition is unlikely to occur in metallic materials. Solders containing lead, aluminum, titanium, magnesium, and alloys based in lithium can be ignited with mechanical impact if the characteristic elements are present. [4], [5] These unique elements are described in Table 3.7

Table 3.7 *Characteristic Elements for Mechanical Impact* [4], [5]

Mechanical Impact Characteristic Elements
1. There shall be an unstable component in the oxygen system. The nonmetal can be ignited after the temperature increase caused by being rapidly impacted multiple times by the unstable component.
2. There shall be a nonmetallic or a reactive material at the impact point

3.6 FRICTION

Friction is described as the heat generated when two or more components are rubbed together. Friction ignition affects mainly metals. Friction between metals can produce an oxidizing environment at high temperatures. The coats preventing oxidization in metals can be lost with friction producing exceedingly small particles. However, it can also affect polymers and composites if specific conditions are present. [4], [5] The increase in temperature caused by friction can elevate the temperature of exposed materials above its ignition point. Detached particles can enhance ignition acting as contaminants or as reactive particles impacting construction materials. Table 3.8 describes the characteristic elements required for friction ignition to occur.

Table 3.8 *Characteristic Elements for Friction* [4], [5]

Friction: Characteristic Elements
1. There shall be at least two or more rubbing surfaces.
2. There shall be at least high normal loading applied to the rubbing surfaces
3. High-speed friction between the rubbing surfaces

3.7 Fresh Metal Exposure

Fresh metal exposure refers to the heat of oxidation produced when unoxidized metals get in contact with an oxidizing environment. This ignition mechanism usually acts in collaboration with other ignition mechanism such as friction and particle impact. [4], [5] Fresh metal exposure can be consequence of a mechanical failure occurring in the construction material. Aluminum and titanium are metals highly affected by fresh metal exposure to an oxidizing atmosphere. No test has been developed yet to collect more data about this impact mechanism. Available characteristic mechanisms are described in Table 3.7.1 [4], [5]

Table 3.9 *Characteristic Elements for Fresh Metal Exposure* [4], [5]

Fresh metal exposure: Characteristic elements
1. There shall be a rapid oxidizing metal surface exposed to an oxidizing environment
2. The configuration of the affected metal shall have a minimum heat loss configuration
3. The layer preventing oxidation shall be rapid to destruction or removal

3.8 Static Discharge

Static discharge refers to the heat generated when a material accumulates enough static energy to ignite another material receiving the static discharge. The risks of ignition caused by a static discharge are highly reduced in high humidity atmospheres due to the thin layer of moisture that is formed in surfaces. A nonconductive material can accumulate enough static energy to ignite a material receiving the static discharge. High fluid flow with high matter particulate formation can also produce electrical static discharge. [4], [5] Static discharges are a common transfer energy process. Arcs can occur between poorly grounded dirty pipes. Static discharges also occur when two pieces of fabric clothing are quickly pulled apart. However, static discharges as all the existing ignition mechanism shall meet their unique characteristic elements to cause an ignition. These characteristic elements are described in Table 3.10

Table 3.10 *Characteristic Elements for Static Discharge* [4], [5]

Static discharge: Characteristic elements
1. There shall be charge accumulation in a nonconductive surface caused by flow or friction
2. There shall be one discharge source between surfaces with different static potentials
3. There shall be at least one conductive surface between charges surfaces
4. The environment shall be dry, or the charged surfaces shall be in a dry gas atmosphere

3.9 Electric Arc

Electric arc refers to enough electrical current arcing between a power source and a flammable material generating sufficient heat to cause an ignition. Malfunctioning devices and ungrounded components such as electrical instrumentation and electrical control equipment are a common example of this type of ignition mechanism, particularly if they are highly powered or poorly maintained. [4], [5] The characteristic elements for electric arc ignition mechanism are described in Table 3.11

Table 3.11 *Characteristic Elements for Electric Arc* [4], [5]

Electric arc: Characteristic elements
1. There shall be an ungrounded or short-circuited power source.
2. There shall be a flammable material capable to be ignited by the sparks or electrical arc

3.10 Chemical Reaction

Chemical reaction as ignition mechanism refers to the heat generated resulting from an unrelated chemical process between oxygen and other materials. The increase in temperature produced by this reaction can be high enough to cause an ignition or even a fire to occur. [4], [5] The characteristic elements for this specific ignition mechanism are not standardized as they depend on the reactants involved in the process. The possible combination of ignition mechanisms such as mechanical impact or friction with chemical reactions shall be determined by system designers. Some chemical reactions require an external source of heat to occur. However, other chemical reactions are considered imminent since the energy required is low enough that chemical reaction is assumed. Unintentional ignition can result from hydrogen fuel leaking to the oxygen side of a system.

3.11 SPONTANEOUS IGNITION

Certain liquids, porous materials or fine particle accumulations increase their temperature by experimenting internal reactions. The risk of ignition is present if the rate of heat dissipation in the material is lower compared to the heat rate ignition. Thermal runaway can occur when the material is quickly self-heated, and its temperature is highly increased and attained. Spontaneous ignition and fire can occur few minutes after thermal runaway temperature is acquired or even after several hours, days, weeks or months have happened since the thermal acquirement. [4], [5] Reactant materials such as oxidants decompose at a lower temperature compared to their ignition point. Decomposed materials can become very reactive even when they have a low reaction rate as a bulk. The effect of the reaction can be amplified if the material has a high surface area to volume ratio, and fine particle accumulations decrease the rate of heat dissipation in materials. [4], [5] No reliable test has been developed yet for this ignition mechanism. However, the available characteristic elements are described in Table 3.12

Table 3.12 *Characteristic Elements for Spontaneous Ignition* [4], [5]

Spontaneous Ignition: Characteristic Elements
1. There shall be a material with high surface area to volume ratio that decomposes or oxidates at extremely low temperatures compared to its ignition point
2. There shall be an environment with poor heat dissipation

3.12 RESONANCE

Rapid heat is generated when acoustic oscillations occur in resonant cavities. The temperature is rapidly increased with the presence of contaminant particles and high gas velocities. [4], [5] The ignition caused by resonance in oxygen systems is a largely researched topic. However, its undesirable presence has not been eliminated from designs yet because not enough design parameters exist. Table 3.13 describes the necessary characteristic elements required for a resonance ignition to occur.

Table 3.13 *Characteristic Elements for Resonance* [4], [5]

Resonance: Characteristic elements
1. Reactive materials such as flammable contaminants or particulate matter shall be present at source of heat
2. There shall be an acoustic resonance which is typically easy to hear
3. A throttling device injecting a sonic gas jet to a closed end tube or orifice shall be present

3.13 EXTERNAL HEAT SOURCES

External heat sources are any type of external heat that can increase the temperature of the system enough to produce an ignition. Some common sources of external heat are personnel smoking, welding sparks, internal combustion engine exhausts, lightening, open flame among others. [4], [5] External heat sources shall be recognized and considered when selecting oxygen system location since they can increase the temperature of a construction material above its auto ignition point. They can also facilitate chemical reactions within the system. Since external heat sources cannot be generalized, there are not unique characteristic elements for this type of ignition mechanism.

Chapter 4: Material Selection

4.1 Material Selection Overview

Oxygen systems require proper material selection and superior design practices to prevent possible system failures. Due to the variety of materials, no universal oxygen compatibility test has been developed yet. In addition to ignition and combustion tests data, the analysis results from previous oxygen system failures are used to do reliable material selection. Material behavior in oxygen systems is a widely researched topic. [22], [23] ASTM G94 describes a correlation between the location of elements in the periodic table and their combustion resistance in an oxygen enriched environment.

It was found that the groups of elements Cu, Ag, Au, and Ni, Pd, Pt are adequate for oxygen service in hazardous applications, and at the same time they are ordered in columns in the periodic table. The elements Be, Mg, Ca and Ti, Zr, Hf are grouped vertically in two separated columns in the periodic table, and at the same time they are considered improper selections for oxygen hazardous applications. [22], [23] Illustration 4.1 shows the groups of materials described by this correlation. A second correlation was found between the metals melting point and metals ignition point. The ignition point of metals is usually equal or greater than the materials melting point. Unfortunately, both correlations only apply to metals and are still under research.

The oxygen compatibility assessment tool is highly recommended for material selection when designing safe oxygen systems. A substantial amount of material test data is available for oxygen systems that operate between 150 psi and 3000 psi. However, limited material data is available for oxygen systems operating above 3000 psi. [5]

Applications with weight limitations such as the ones in aerospace industry are always looking to increase efficiency by reducing the weight of components. Special caution is required when selecting materials with little to no history of application in oxygen systems. Material temperature, pressure, and flow rate under operational and environmental conditions, in addition to material configuration and composition are some of the factors that shall be considered during material selection process. Materials and Process Test Information System (MAPTIS) is a tool used by NASA Marshall Space Flight Center to store the data obtained from standard material testing. The results are periodically published, and further information can be obtained by creating a user or organization account in the MAPTIS system. [5]

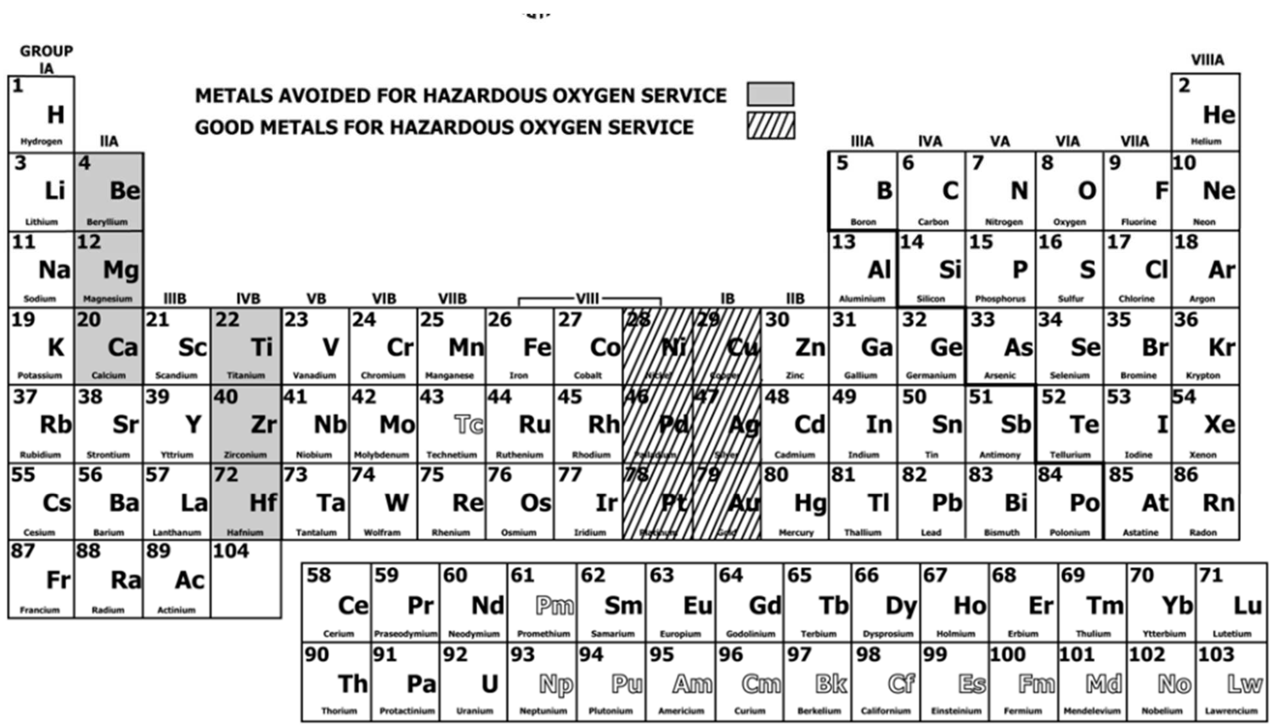

Illustration 4.1: Periodic Table Location of Some Hazardous Oxygen Service Metals[22]

4.2 Materials Control

Materials do not ignite in an oxygen rich environment unless their temperature exceeds their ignition point. The temperature of ignition depends on material properties and configuration in addition to the pressure, temperature, flow, oxygen concentration and dynamic conditions of the system. For ignition to occur, the amount of heat dissipated must be extremely low compared to the amount of the energy gained by the material. [6] Materials selected for oxygen systems require good physical properties at environmental and operational conditions. They shall be certified as good for oxygen service by the manufacturer. It is considered a good practice to corroborate supplier and vendor information. Information about materials that require batch testing for oxygen service can be obtained from the White Sands Test Facility (WSTF) materials database. [6] Material batch testing is required for several materials whose variations might cause that batches from the same material have ranges unacceptable for oxygen applications regardless of if they were manufactured at the same time, under the same initial conditions and procedures.

The flammability and combustibility of materials shall also be evaluated for oxygen service applications. A nonflammable material can be used in a system even if ignition sources exist. Components shall be tested to determine the safety margins within the oxygen system when ignition sources are found. Proper engineering design practices might minimize or even eliminate ignition sources when acknowledged. A flammable material might be used in an oxygen system if no ignition source exists. The material combustibility, flammability, configuration, physical and chemical properties in environmental and operational conditions in addition to the system dynamic configuration and oxygen saturation shall be analyzed to determine its implementation. [24] Logic process to aid oxygen systems designers to do safe material selections are extensively found in literature, Illustration 4.2 is an example of them.

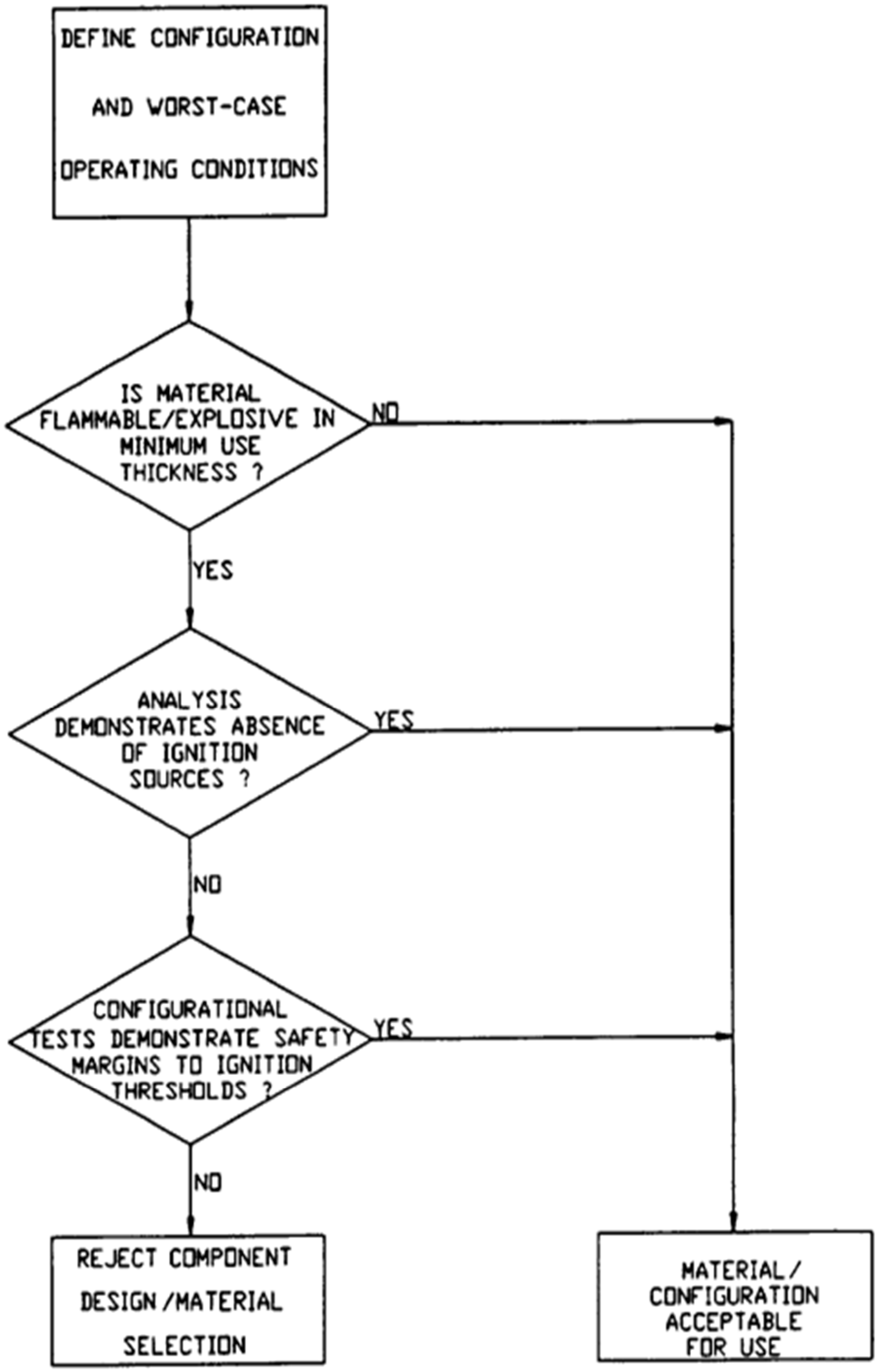

Illustration 4.2: Material Safety Logic [6]

4.2 REQUIRED TESTS

Multiple tests have been developed to determine the flammability and combustibility of materials under oxygen enriched environments. The data obtained from these tests is used to rank the materials and determine their oxygen compatibility. Combustion tests such as upward flame propagation and oxygen index shall be performed in metals and nonmetal materials, respectively, that are intended for oxygen systems. The heat of combustion test is used to determine materials damage potential. Ignition testing evaluates the possible effects of ignition mechanisms in intended materials for oxygen operations. Multiple ignition tests have been developed to determine the ignition mechanisms effects in materials. [6], [25] Table 4.1 lists the required and suggested material tests for LOX and GOX environment. Especial caution shall be used when applying test data to material selection because the flammability of material is very dependent from the material configuration. Thus, poor data interpretation might end up in improper material selection and ignition might occur.

4.2.1 Promoted Ignition in Metals in GOX

Promoted ignition test, or upward flammability test is used to determine the flammability of materials. It is considered the metallic materials combustion behavior standard test. A small rod of 0.125inches in diameter is suspended in a test chamber using a standardized easily ignited material. The test is commonly performed in a 100% oxygen environment. However, the oxygen concentration and pressure can be variated to determine the range of the flammable limits for the tested material. [27]

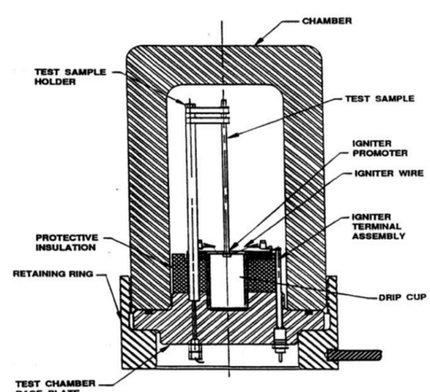

Illustration 4.3 Promoted Ignition Test Fixture Schematic [26]

The promoted ignition test has demonstrated that flammability increases when pressure is increased and decreases when material thickness is augmented. The upward flame test was standardized because it is more repeatable and the behavior of the material at different conditions is easy to observe compared to downward flame propagation. The test configuration can be observed in Illustration 4.3. Metals have demonstrated to increase their flammability propagation in the downward test. [27] Thus, material configuration and possible ignition mechanisms affecting the construction material shall be considered during material selection.

4.2.2 Oxygen index in nonmetals

Oxygen index test is used to determine the flaming combustion of materials in a flowing mixture of oxygen and nitrogen. It is considered the standard test to determine candle like combustion ranking in plastics. Nonmetallic materials with high oxygen index are preferred. The oxygen index test has demonstrated that oxygen index decreases when pressure is increased.[6]

Table 4.1 *Material Testing in LOX and GOX Environments* [27]

Required Tests for LOX and GOX Environments	
Upward Flame Propagation	Required for nonmetals for pressures ≤345 kPa (≤50 psia).
Upward Flammability of Materials in GOX	Required for nonmetals for pressures >345 kPa (>50 psia) and for all metals used in GOX and LOX
Supplemental Test for Different Material Uses	
Mechanical Impact for Materials in Ambient Pressure LOX	NASA-STD-(I)-6001A 13A
Mechanical Impact for Materials in Variable Pressure LOX and GOX	NASA-STD-(I)-6001A 13B
Gaseous Fluid Impact	NASA-STD-(I)-6001A 14
Autogenous Ignition Temperature	ASTM G72-01
Heat of Combustion	ASTM D240-02
Electrical Arc	ASTM G125-00
Frictional Heating	NASA-STD-(I)-6001A
Particle Impact	NASA-STD-(I)-6001A

4.3 METALLIC MATERIALS

Metals are the most common selection for oxygen service construction materials. They have a lower ignitability in comparison to polymers. Oxygen service construction metals are mainly ignited as a result of a polymers or contaminants chain reaction. Thus, superior design practices and proper metallic selection highly reduce the risk of ignition in an oxygen system. Ignitability and combustibility of metals depend on the material configuration, and there is not extensive data available about unconventional configurations. Ignition mechanisms shall be eliminated from thin cross sectional area sections. In general, avoiding thin cross-sectional area and finely divided configurations such as thin-walled tubing and wire meshing is considered a superior design practice. Thin cross-sectional area enhances material ignition, including metals with regular ignition resistance. Bulk metals have more ignition resistant than nonmetals. Metallic materials require high oxygen concentrations to enhance combustion. [6], [22] However, applying superior design practices is highly encouraged since products from bulk metal combustion create more damage than products from nonmetallic materials due to their high flame temperatures.

4.3.1 Nickel and Nickel Alloys

Nickel alloys are considered an excellent material selection for oxygen applications at any pressure range. Pure nickel, or nickel 200, is a desirable choice for filtering devices as it supports combustion at 10000 psi or greater pressures. Nickel based alloys have low temperature toughness at high strengths. [6], [22] Some nickel characteristics and their suggested applications are described in Table 4.2

Table 4.2 Nickel Superior Characteristics and Suggested Applications[4], [6]

Nickel
Nickel – Copper Alloys are more resistant to particle impact ignition than aluminum and Iron metal alloys
Nickel, and nickel copper alloys have better mechanical impact ignition characteristics than aluminum and titanium alloys
Compared to common metals and alloys, Nickel has superior ignition resistant properties
Nickel has superior fire propagation qualities
Nickel Suggested Applications
Oxygen Fittings and Piping, liners inside vessels, other dynamic components

4.3.1.1 Nickel -Copper Alloys

Nickel-copper alloys are part of the least ignitable selection of construction materials. Monel can be a desirable choice for aerospace applications where light weight components are always desirable. Due to its lower strength to weight ratio in comparison to aluminum. Monel components can be designed to be smaller and lighter than aluminum components while increasing the safety of the component by reducing its ignition limits. Monel is highly recommended for manually operated devices and systems where fire consequences can be catastrophic. Monel is also used to reduce the risk of particle impact ignition in high velocity gas systems. Table 4.3 List some Monel superior properties and suggested applications. Bulk Monel has history of achieving successful operations at 10000 psi. Monel 400 series and Monel K-500 submitted to upward flammability testing do not support combustion in pressures up to 10000 psi. [6], [22] Monel alloys support greater frictional loads than stainless steel, and usually have high friction resistance. Surface burning, and melting has been observed during impact test even though ignition has not occurred. [6], [22] Ignition mechanisms avoidance and proper design practices shall be applied to Monel components. Thin cross-sectional areas and finely divided configurations affect Monel performance.

Table 4.3 Monel Superior Characteristics and Suggested Applications[4], [6]

Monel	
Monel is among the best option for less ignitable oxygen service materials. Monel have excellent friction ignition resistance and particle impact ignition	
400 Series Monel is an excellent alloy for applications that require welding such as pressure vessels and piping. It has superior ignition resistance capabilities.	
Monel K-500 has superior physical properties compared to other Monel series. It is an excellent choice for applications that require high strength to weight ratio. Monel K-500 is not recommended for applications that require welding.	
Monel component suggestion	
Monel K-500	Valve stems, piston shafts
400-series Monel	Pressure vessels, valve bodies, springs, pipelines
Monel	Control valves, bypass valves, strainer mesh for pipelines

4.3.1.2 Nickel Iron Alloys

Nickel and nickel alloys have demonstrated to have high combustion resistance. Inconel are widely used Nickel-Iron alloys in aerospace applications that require high strength and welding to be allowed. The ignitability of Inconel varies with the type of alloy. Inconel 718 is commonly used as construction material for oxygen applications operating at high pressures because it possesses good mechanical properties and has higher ignition resistance than the stainless steels. Under particle impact test, Inconel 718 has greater resistant properties than most of the stainless steels, excepting stainless steel 40C that has similar particle impact ignition resistance properties than Inconel 718. Inconel 718 ignites at similar conditions than stainless steel under frictional test. However, Inconel MA754 has an exceptional ignition resistance by friction and has demonstrated to succeed the vertical burning test under a 10000-psi pressure. [6], [22] The Inconel selection depends on the desired application. Table 4.4 describes some Inconel applications and characteristics. The application of oxygen compatibility tool is highly encouraged during material selection.

Table 4.4 Inconel Superior Characteristics and Suggested Applications[4], [6]

<table>
<tr><th colspan="2">Inconel</th></tr>
<tr><td colspan="2">Inconel 625 can replace Monel 400 in high temperature applications that require welding. However, Monel has better flame and ignition resistance.</td></tr>
<tr><td colspan="2">Inconel 718 can replace Inconel 625 in high temperature applications that require welding and high strength to weight ration. However, Inconel 625 is desired for its better ignitability and flammability properties</td></tr>
<tr><td colspan="2">Inconel718 has better particle ignition resistance than most stainless steels and similar friction ignition properties than most stainless steels</td></tr>
<tr><th colspan="2">Inconel component suggestion</th></tr>
<tr><td>Inconel X-750</td><td>High strength springs</td></tr>
<tr><td>Inconel 600</td><td>Low strength springs</td></tr>
<tr><td>Inconel 625</td><td>High temperature applications that require welding</td></tr>
<tr><td>Inconel 718</td><td>Applications that require welding, high temperature ang high strength to weight ratio</td></tr>
</table>

4.3.1.3 Other Nickel based alloys

Hastelloy C-22 and Hastelloy C-276 are Nickel based alloy are both Nickel alloys that have demonstrated a high ignition resistance than Inconel 718 and the stainless steels. Hastelloy flammability resistance under oxygen rich environments is comparable to Inconel 625 resistance. C-22 and C-276 are considered good option for applications that require resistance to solvents, wet and dry chlorine, mineral acids, and hydrofluoric acids. [6], [22]

4.3.2 Copper and Copper Alloys

Copper and copper alloys such as brass and bronze are considered good options for oxygen service applications at high pressures. Excepting copper alloys that contain aluminum at concentrations of 5% or greater. Coper alloys containing aluminum increase their flammability and ignitability in oxygen enriched environments. Material selection is essential during the design process of a safe oxygen system. A superior design configuration is also necessary to maintain the copper and the copper alloys fire resistant properties. Thin cross-sectional areas and wired or meshed designs decrease flame and combustion resistant properties of these metallic materials. Under filtering applications, sintered bronze has demonstrated to have better resistant properties than stainless steels and sintered Monel 400. [6], [22] Copper has also demonstrated flame resistance in the upward flame test at pressures up to 10000 psi. Copper and copper alloys have demonstrated excellent ignition resistant properties under particle impact test, and are used as combustion chamber liners, they are considered a good material selection for high velocity gas applications. Captured vent systems are relief devices that are not directly opened to the atmosphere. Monel and copper are considered good material construction options for them. However, copper has an excessive oxidation at elevated temperatures, the low ductile oxide formed at exposed surfaces can cause contamination in oxygen systems if sloughs off. [6], [22] Some copper characteristics and suggested applications are listed in Table 4.5

Table 4.5 Copper Characteristics and Suggested Applications[4], [6]

Copper
Copper has superior particle ignition resistance.
Copper has good ignition and combustion resistant properties and is a good selection for high velocity gas applications.
Sintered bronze has superior capabilities for filter element material than stainless steel and Monel because it has better flammability resistance.
Copper component suggestion
Impingement plates, Chamber liners, captured vent systems, reliable seal at moderate to high temperatures

4.3.3 Stainless steels

Stainless steels are extensively used in oxygen applications. The range of ignitability and burn resistance is the same for all the stainless steels, except for Stainless Steel 440C which has superior characteristics. Compared to aluminum and titanium alloys, stainless steels have a higher ignition and burn resistant ratio. However, they have greater heats of combustion compared to copper and copper-nickel alloys. [6], [22] They can be good candidates for storage tanks and lines since few problems have been reported of stainless steels used for these applications. However, stainless steels might not the best option for dynamic locations such as valves, regulators, or systems with high pressure, high velocity or high flow since multiple ignitions has been reported. Stainless steels become more ignitable under thin-walled tube and wire mesh configurations. Stainless steel also has demonstrated poor resistance to ignition due to particle impact and friction under low pressure oxygen rich environments. Stainless steel particulates are also a form of contamination that might ignite component, although they are not as reactive as aluminum particulates. [6], [22] Some stainless steels characteristics and suggested components are described in Table 4.6.

Table 4.6 Stainless Steels Characteristics and Suggested Applications[4], [6]

Stainless Steels	
Low-cost material choice extensively used in oxygen service for pipelines and storage tanks	
Stainless steels have better flame and ignition resistant properties than aluminum and titanium	
Stainless steel 440C have similar particle ignition resistance properties to Inconel alloys	
Stainless components	
Avoid using stainless steels in dynamic locations such as regulators and valves. **Avoid** using stainless steels for high pressure, high velocity, or high flow applications	Valves, tubing, vessels, storage tanks and fittings.

4.3.4 Aluminum and Aluminum alloys

Aluminum is extensively used in aerospace and medical applications that pretend to reduce weight of components. Aluminum and its alloys are recognized for their tendency to resist ignition. However, upward flammability test has demonstrated that aluminum and its alloys support combustion at ambient temperature in oxygen enriched environments. Thus, special attention shall be given to components that are manufactured with aluminum or aluminum alloys. Aluminum has a widely described oxide layer protects the inner material from ignition even after the material has exceed its melting point (1220^0) in static conditions. However, the oxide layer can be compromised due to impact mechanisms such as friction and mechanical impact. [6], [22] Table 4.7 describe some aluminum characteristics and possible applications.

Aluminum shall not be used in dynamic applications such as valves, regulators, and pipelines because aluminum particulate is very reactive, and ignition might occur due to friction and particle impact. Anodized aluminum has demonstrated to reduce the ignitability of aluminum due to particle impact. [6], [22] Aluminum surfaces that are not anodized shall not be exposed to particle impact mechanisms. Failures have occurred due to oil contaminants in aluminum 6061-T6 used in oxygen service. Oil contaminants such as motor lubricated oil, and tool maker’s oil enhance the ignitability of the material. [6], [22]

Aluminum alloys are attractive options for pressure vessels and static oxygen systems because of their high strength to weight ratio. However, excellent design techniques shall be implemented to avoid aluminum particulate formation which is highly reactive and could ignite the system. Filters and other dynamic components such as valves shall be designed using a material with higher ignition and combustion resistant properties such as Monel, nickel, or copper alloys. [6], [22]

Table 4.7 Aluminum Characteristics and Suggested Applications[4], [6]

Aluminum	
Ignition temperature of aluminum and its alloys vary from 1255 F to 3175^0 F. It depends on the oxide layer protection. Special caution shall be used when selecting aluminum as construction material.	
Aluminums are easily ignited by mechanical impact and friction. Aluminum Iron alloys are also easily ignited by particle impact.	
Aluminum particulate is very reactive. It can contaminate and ignite the construction material	
Anodized aluminum reduces the particle impact ignitability of aluminum.	
Aluminum components	
Avoid using aluminum to design lines, valves, and other dynamic components	It **might** be used to design static pressure vessels where friction, particulate formation, particle impact and mechanical impact are completely eliminated

4.3.5 Iron Alloys

Most iron alloys are not recommended for oxygen service applications because they are easily ignited and does not offer any weight savings to the system. However, they are extensively used in pressurized GOX tanks and pipelines after possible ignition mechanisms are discarded. Invar 36 can be an exception because it has ignition and combustion resistant properties that are similar to the stainless steel properties. [6], [22]

4.4 Restricted Alloys

There are materials prohibited for oxygen service applications due to their poor ignitability and combustibility properties or their toxicity and vapors temperatures. Titanium, cadmium, beryllium, magnesium, and mercury are some of the materials restricted in oxygen applications. [6], [22] Materials that do not pass the oxygen compatibility assessment tool including the material ignition and combustion tests shall not be implemented in oxygen applications.

4.4.1 Titanium

Titanium is an impact sensitive material in oxygen enriched environments. Thus, titanium and titanium alloys shall be avoided or eliminated from oxygen service facilities. GOX can be safely in contact with titanium at 30 psia or lower pressures. However, tests have been demonstrated that Ignition between oxygen and titanium can occur at the low pressure of 1 psia. [6], [22] Titanium alloys have low resistance to ignition friction. LOX shall never be in contact with titanium or titanium alloys at any pressure. The combustion reaction between titanium and oxygen can propagate and completely consume the system and surroundings.

4.4.2 Cadmium

The toxicity and the vapor temperature of cadmium at a temperature of 120^0 F or higher restrict cadmium implementation in oxygen systems at any time. [6], [22]

4.4.3 Beryllium

Beryllium as pure metal, its oxides, and its salts are very toxic. They shall be eliminated and avoided from any oxygen system or any system where they could be consumed by a fire. [6], [22]

4.4.4 Magnesium

Magnesium and magnesium alloys have demonstrated to sustain combustion in oxygen enriched environments at a pressure of 1psia or lower. They shall be avoided in oxygen service systems. Magnesium also reacts with lubricants containing fluorine and chlorine. [6], [22]

4.4.5 Mercury

Mercury and its amalgamations are prohibited in oxygen service systems due to its toxicity and their tendency to cause acceleration in stress cracking in aluminum and titanium alloys. [6], [22]

4.5 Other Metals and Alloys

There are a lot of other metallic material option including new alloys that are currently under development. Recent technologies open the door to new oxygen service construction materials. However, comparing the physical, chemical, and hazardous properties of a newly proposed material as well as submitting the new material to the oxygen compatibility assessment and its corresponding ignition and combustion testing methods is required before it can be used as a safe construction material for oxygen systems.

4.6 Nonmetallic Materials

The use of nonmetals in oxygen systems shall be limited to be used only under essential requirements such as valve seals and seats. The portion of nonmetals exposed to oxygen shall be minimized. Chain reaction from nonmetallic ignition might result in fire propagation to the metallic portion in the oxygen system. Nonmetallic materials might introduce toxic combustion products in the system when ignited. Nonmetals usually become very flammable at absolute pressures of 14.6 psia or greater in oxygen enriched environments. [6], [23] In general, nonmetals ignite at extremely low temperatures and pressures compared to metallic materials.

Especial care must be applied when selecting nonmetallic materials. Polymers included plastics and elastomers, in addition to composites and lubricants are often used as nonmetallic materials for oxygen service applications. Polymers have a vast range of variation on their ignitability characteristics. It has been demonstrated that polymer ignition can be addressed with superior design practices and proper material selection. However, fully fluorinated materials are desirable because they have low heats of combustion, high ignition temperatures and high oxygen indices. [6], [23] Fluorinated materials also have good oxygen compatibility characteristics.

4.6.1 Elastomers

Elastomers are extensively used in oxygen systems as O-rings and diaphragms due to their flexibility properties. Elastomers pass the glass transition temperature at lower temperatures than room temperature and can be used to temperatures of 406^0 or more. Silicon rubber components are widely used in oxygen systems because they have lower glass transition temperatures. [6], [23]However, they have poor ignition resistance properties compared to the ignition resistant properties of fluorinated components. Silicon rubber components are usually replaced with Kalrez. Buna-N, polyurethane rubbers, neoprene rubber, and ethylene-propylene rubbers are hydrocarbon-based elastomers that burn energetically in oxygen enriched environments. [6], [23] Superior design practices shall be implemented to eliminate the presence of ignition mechanisms. Several fires have resulted from the chain reaction tied to the ignition of these components. Thus, fully fluorinated elastomers are highly recommended.

4.6.2 Plastics

Polytetrafluoroethylene (PTFE Teflon), fluorinated ethylene propylene (FEP Teflon), polychlorotrifluoroethylene (PCTFE), Kel-F ° 81 are Semi-crystalline plastics that are commonly used in oxygen service applications. Amorphous polymers such as polyimides (Vespel SP21) are also selected for oxygen applications. PTFE Teflon is usually replaced with less oxygen compatible polymers due to its low creep resistance. Even though PTFE Teflon has a great mechanical impact ignition resistance, and overall good combustion and flame-resistant properties. [6], [23]

4.6.3 Composites

Composites used in oxygen service are previously discussed materials that does not account with a polymer reinforcement. Polymeric composites might have enhanced mechanical or physical properties compared to other available materials. However, polymer reinforcement can lower the ignition resistance properties from the selected material. Glass fiber filled Teflon is a polymer reinforced composite with decreased ignition resistance properties. [6], [23]

4.6.4 Lubricants

Lubricants and greases implemented in oxygen systems shall be selected based on their oxygen compatibility properties. They are primarily based on PTFE, FEP and chlorotrifluoroethylene (CTFE) that has been halogenated or fluorinated and whose viscosity has been increased with higher-molecular-weight CTFEs. [6], [23] Lubricants with PTFE base usually utilize additives that enhance their lubricity. However, those modified fluids might compromise the oxygen compatibility characteristics from the original material. CTFE lubricants enhanced with silicon have been the main cause of corrosion formation inside oxygen systems. They allow moisture penetration in the film fluid. Those types of lubricants shall not be used for oxygen service applications.

4.6.5 Ceramics

Ceramics and glasses are considered inert materials and are not commonly used for oxygen applications. Ceramics might be applied as thermal and electrical insolation. However, they are brittle materials that can be easily fractured during operational procedures or even by mechanical impact. Deterioration in ceramic coating can compromise their insulating advantages. Thus, a high safety factor and their availability to support compressive loads is desired when selecting ceramics for oxygen systems. Pressure vessels windows and valve ball seals in oxygen service utilize special design practices to incorporate sapphire glass in their design. [6], [23] Pressure vessels have a minimum safety factor of ten. Thus, special glass requirements able to retain pressure differentials shall be meet.

Chapter 5: Oxygen Compatibility Assessment

5.1 Oxygen Compatibility Assessment Overview

The oxygen compatibility assessment (OCA) is a tool that aids designers and operators to understand and address the risks associated with oxygen systems. It shall be applied to compressed and pressurized systems that operate with oxygen. The OCA tool is intended for individual components within a system. The analyzer in charge of the OCA tool shall determine the worst-case scenario of the component properties such as temperature, pressure, flow rate, cleanliness level, and material configuration under environmental and operations conditions. The worst-case scenario conditions can be used to drive the rest of the remaining assessments in the OCA tool. The combustion and flame-resistant properties shall be determined. The induced ignition test for metals and the oxygen index test for nonmetals are data sources available for materials intended oxygen services. Once the worst-case scenario and the materials flammability is determined, the analyzer shall proceed to a detailed analysis of possible ignition mechanisms affecting the component. A huge dependency between materials flammability and materials configuration exists. Thus, especial attention shall be applied to when determining the presence of ignition mechanisms within the system because a single test capable to determine the flammability of uncommon material configurations has not been developed yet.

The kindling chain reaction is another assessment included in the OCA tool. This assessment aids the oxygen system designers to determine the possibility of a fire to propagate and burn out the oxygen system. The analyzer shall determine the materials ability to contain a fire and the possible ignition mechanisms affecting it. A chain reaction can occur if the material heat of combustion and the configuration of the material have enough energy and the required factors to ignite the surrounding materials and components. After the kindling chain has been determined by the system analyzer. The possibility of chain reaction and their consequences in the user, system and mission shall be determined. A chain reaction determines the ignition mechanisms and kindling chain possible effects. The components shall be evaluated using the worst-case scenario. Documenting the OCA tool findings and possible system improvements allows user to eliminate or reduce ignition mechanisms and facilitates comparisons between current and future operating conditions. [5], [21], [27] The assessments included in the OCA tool are described in this chapter.

5.2 WORST CASE OPERATING CONDITIONS

An increase in pressure, temperature, oxygen concentration, flow rate or even cleanliness level of the component can cause a change in the material flammability and combustibility properties. The worst-case scenario shall be the first condition to be determined by the analyzer in each component. [5], [21], [27]To quantify the worst-case operational conditions of the components a piping and instrumentation diagram is required, a flow schematic and process flow diagram are also recommended. The analysis shall determine possible improvements in the system and help to create procedures in how to operate the system after a single point failure occurs. Worst case operation conditions are also used to drive other assessment within the OCA tool. Thus, correct analysis of each component is required. Table 5.1 is a suggestion for the worst-case scenario assessment.

Table 5.1: *Worst Case Assessment Suggestion*

	Operational Conditions					**Environmental Conditions**				
Component Description	**Temperature**	**Pressure**	**Flow rate**	**Cleanliness level**	**Oxygen concentration**	**Temperature**	**Pressure**	**Flow rate**	**Cleanliness level**	**Oxygen concentration**
A										
B										
C										
D										

5.3 FLAMMABILITY ASSESSMENT

Most common materials metallic and nonmetallic become flammable in oxygen enriched environments when pressure is increased. Thin cross-sectional areas and finely divided materials such as thin-walled tubing and wire meshing increase the risk of ignition in materials. The flammability of materials depends on their configuration. Flammability data for metals can be found from the material promoted ignition test results and flammability data for nonmetals can be obtained from oxygen index material results. As a rule, metallic materials ignite at the melting point temperature or greater and nonmetallic materials in oxygen enriched environments ignite at ambient pressure or lower pressures. Thus, all nonmetallic materials operating at high pressure are considered flammables. [5], [21], [27] The OCA tool attempts to find and minimize possible ignition mechanisms affecting current material configurations in the system due to the material configuration and material flammability dependency. Cross-sectional area views for each oxygen component showing the configuration of the construction material are required to determine a proper range for the material flammability limits. The construction material shall be considered flammable if no materials have been proposed or the flammability is unknown. Table 5.2 is an example for material flammability assessment configuration

Table 5.2 Material Flammability Assessment Suggestion

<table>
<tr><th>Component Description</th><th>Material</th><th>Configuration</th><th>Test Data</th><th colspan="2">Flammability Designation</th></tr>
<tr><td>A</td><td></td><td rowspan="4">Material flammability is very dependent to component configuration.

Technical judgement shall be applied when analyzing component configuration</td><td>Oxygen index test for nonmetals</td><td>N = Nonflammable</td><td>Material will not burn if ignited</td></tr>
<tr><td>B</td><td></td><td>Promoted Combustion test for metals</td><td>F = Flammable</td><td>Material will burn if ignited</td></tr>
<tr><td>C</td><td></td><td></td><td></td><td></td></tr>
<tr><td>D</td><td></td><td></td><td></td><td></td></tr>
</table>

5.4 IGNITION MECHANISM ASSESSMENT

The ignition mechanism assessment shall evaluate the possible presence of ignition mechanisms and compare them with the flammability assessment results from all component construction materials. Ignition mechanism are heat sources that could potentially ignite a component if the characteristic elements are present. The ignition mechanism assessment shall determine the possible existence of all the unique characteristic elements required for the ignition mechanisms to ignite a component. Some of the most common ignition mechanisms and their characteristic elements are described in Chapter 3. Related ignition mechanism test data from the selected material shall be applied. Recommendations to reduce the ignition mechanisms effects shall be proposed and documented in the ignition mechanism assessment for each component. [5], [21], [27] Table 5.3 is a suggestion for the ignition mechanism assessment. There shall be one table for each ignition mechanism being evaluated. A minimum analysis of nine ignition mechanisms per component is highly encouraged.   A Material flammability shall be determined as described in the material flammability assessment section.

Table 5.3: *Ignition Mechanism Assessment Suggestion* [21]

Name of Ignition Mechanism:			
Ignition Rating	**Code**	**Criteria**	
		Characteristic Element	**Material Flammability**
Not possible	0	Not all present	Nonflammable or flammable
Remotely Possible	1	All present and some are weak	Nonflammable or flammable
Possible	2	All present and active	Flammable
Probable	3	All present and some are highly reactive	Flammable
Highly Probable	4	All Present and all are highly reactive	Flammable

5.5 KINDLING CHAIN ASSESSMENT

Kindling chain assessment is the name given to the analysis of the construction material, capability to ignite, contain fire and propagate. A kindling chain can occur if the material heat of combustion and the configuration of the material have enough energy to affect surrounding materials by igniting them or even consuming them. [5], [21], [27] The user shall analyze if the material heat of combustion and component configuration have the capability to propagate a fire and cause a complete burn out. Table 5.4 is a suggestion evaluation method for the kindling chain assessment. This analysis shall be supported with the presence of ignition mechanisms and the flammability properties of possible affected materials.

Table 5.4 Kindling Chain Assessment Suggestion

Component Description	**Material**	**Heat of Combustion**	**Flammability**	**Kindling Chain Exist**	**Possible Affected Components**	**Suggested Actions**
A			F	Yes		Additional analysis of components is required: +
B			F	No		Additional analysis of components is recommended +
C			N	Yes		Analysis of Components is Required +
D			N	No		No Further analysis in kindling chain is required -

5.6 REACTION EFFECT ASSESSMENT

The possible effects of fire in personnel, mission and system functionality are evaluated using a reaction effect assessment. The reaction effect assessment shall determine the possibility of ignition in the component. The ignition effects are ranked according to the range of fire propagation due to component ignition. [5], [21], [27] The possible presence of ignition mechanisms and kindling chain reactions affecting the evaluated component shall be determined. Since it might be hard to determine all possible failure scenarios in every component within the system, it is recommended to use the worst-case scenario assessment as the driver for the reaction effect assessment. Rection effects assessments are considered good tools to identify the hazardous components in the system and to anticipate and prevent any possible failure or injury. Table 5.5 is an example for the reaction effect logic.

Table 5. 5 *Reaction effect rating logic, based on ASTM G 63 and G 94.*[5], [21]

Rating	Code	Effect on Personnel Safety	System Objectives	Functional Capability
Negligible	A	No injury to personnel	No unacceptable effect on production, storage, transportation, distribution or use as applicable	No acceptable damage to the system
Marginal	B	Personnel-injuring factors can be controlled by automatic devices, or special operating procedures	Production, storage, transportation, distribution or use as applicable is possible by utilizing available redundant operational options	No more than one component or subsystem damaged. This condition is either reparable or replaceable within an acceptable period on site
Critical	C	Personnel may be injured operating the system, maintaining the system, or by being in the vicinity of the system	Production, storage, transportation, distribution or use as applicable impaired seriously	Two or more major subsystems are damaged-this condition requires extensive maintenance
Catastrophic	D	Personnel suffer death or multiple injuries	Production, storage, transportation, distribution or use as applicable rendered impossible-major unit is lost	No portion pf system can be salvaged -total loss

5.7 Documenting Oxygen Compatibility Assessment Data

Documenting the results from the oxygen compatibility assessments is highly recommended. Besides helping with material selection, OCA tool data can help users and designers to determine system conditions before and after operation. It can also facilitate investigations in case of system failure or user injury. A good practice in documentation is to include possible system improvements and concerns encountered during component assessments. Table 5.6 is a suggestion of the possible documentation format for the oxygen compatibility assessment.

Table 5.6 Sample of Oxygen Compatibility Assessment Results Table

Component Description	**Material**	**Flammability**	**Ignition Mechanisms**									**Kindling Chain**	**Reaction Effect**	**Additional Comments**	**OCA Result**
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**				
Component A	Metal	F	0	0	0	0	0	0	0	0	0	+			
Component B	Nonmetal	F										+			
Component C	Metal	N										-			
Component D	Metal	N										-			

Chapter 6: Conclusions and Future Work

6.1 Conclusions

Determining the compatibility of oxygen with construction materials is essential for aerospace applications. The use of LOX and cold GOX has been bonded to the aerospace industry since the beginning of the American liquid rocketry in 1926. Multiple incidents with catastrophic results had occurred due to inappropriate material selection, poor design practices, and inadequate oxygen handling techniques. Engineers, analyzers, and oxygen system users had been developing standards that allow the safe design and operation of oxygen systems.

Oxygen fires are uncommon events that can result catastrophic consequences. Oxygen properties and possible hazards shall be acknowledged before designing and operating an oxygen system. This document summarizes oxygen, physical, chemical, and hazardous properties, and highlight the importance of maintaining the oxygen system clean and well maintained. It describes the personal protective equipment required during oxygen service operations and the possible emergencies scenarios during oxygen handling.

Material selection is an essential step during the oxygen system designing process, inappropriate material selection can compromise operating personnel integrity, system functionality, and mission objective. This paper provides a description of twelve impact mechanisms and their unique characteristic elements. The understanding of ignition mechanisms is essential for proper oxygen system design due to the high dependency between material flammability and material configuration. Well-designed components can reduce or even eliminate the ignition mechanisms from a system. The existence of various ignition mechanisms including fresh metal exposure was determined after analyzing accidents and incidents that occurred in different oxygen systems. It was determined that the flammability and compatibility of the construction materials was affected by similar factors, or characteristic elements. These failure analyses were used to create theoretical ignition mechanisms that could be used to prevent future incidents. Even though, no test able to replicate the theoretical ignition mechanisms has been developed yet.

In addition to ignition mechanisms data, promoted ignition test data and oxygen index test data are used to determine the flammability of metals and nonmetals respectively. However, the possible ignition mechanisms affecting the component shall be acknowledged and eliminated if possible. Unconventional configurations such as thin cross-sectional areas, and finely divided material can drastically increase the flammability of any material. Thus, catastrophic outcomes might result from the combination of increased material flammability and ignition mechanisms.

This document includes a selection of materials recommended and commonly used in oxygen systems in addition to a list of restricted alloys for oxygen applications. Nickel and nickel alloys included Monel and Inconel as well as Copper and Copper alloys are part of the best options intended for oxygen systems since they have superior ignition resistant properties, and superior mechanical properties. Tables showing characteristics of selected materials as well as possible application were provided in Chapter 4.

No universal test able to determine the flammability all materials has been developed yet. Thus, the oxygen compatibility assessment (OCA) can be used as a tool to reduce the risks associated with inadequate material selection. The OCA tool is designed to analyze individual components. This paper describes the OCA tool assessments and provides suggestions to realize and document the analysis results. The worst-case scenario operational and environmental conditions shall be used to drive the entire assessment since it might be hard to determine all the possible component failures.

6.3 Future Work

Table 6.1 describes possible future documents that are related to oxygen compatibility for aerospace materials.

Table 6.1 Suggested Materials Oxygen Compatibility and Safety Future Work

Suggested Future Work
A future document could focus on the oxygen system component design since there is a high dependency between material flammability and material configuration.
Future research might focus on trying to replicate the theoretical ignition mechanisms in a laboratory to increase the available data and improve future oxygen systems.
Create a document to standardize the oxygen compatibility assessment procedure for future component design. It might include data tables similar to the suggested in Chapter 5 to facilitate the material selection and system design.
Create a standard cleaning procedure for oxygen service components. Create emergency procedure for possible oxygen handling emergencies

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Vita

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