Valves in Oxygen Service

By Kurt Larson Air Products 03 March 2017

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Air Products is...

A world-leading Industrial Gases company

- Supplying atmospheric and process gases and related equipment to manufacturing markets, including refining and petrochemicals, metals, electronics, food and beverage
- World's leading supplier of liquefied natural gas process technology and equipment
- Materials Technologies business, which Air Products sold in November of 2016, serves the semiconductor, polyurethanes, cleaning and coatings, and adhesives industries



Air Products Experience and Expertise

Owning and operating ASUs for +75 years



Wealth of operational knowledge feeds into all future designs for AP owned and Sale of Equipment plants



Operating experience, includes large multi-plant facilities with extensive pipelines and multiple customers More than 6000 employees in Global Operations on >750 operating plants



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Kurt Larson is..

- > 28 Years with Air Products
 - > 24 years in the Air Separation arena
 - Last 4 as Technology Manager for Process Measurement and Control
- Process Controls Engineering
 - Valve and Instruments specification
 - Control System Design and programming
 - > Plant commissioning and startup US, Mexico, South America, Asia
- Technology Manager
 - Valve and Instrumentation specialist supporting engineering, operations, procurement and Safety globally.
 - Owner of ~50 standards relating to process instrumentation and valves
 - Member of AP's Oxidizer Safety Committee last 5 years

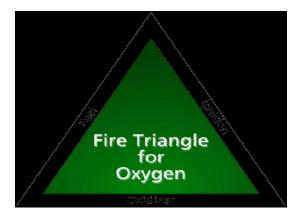
Industry and Company Standards

► G 4-4 (EIGA 13/12) Oxygen Pipelines and Piping Systems

- "The purpose of this publication is to further the understanding of those engaged in the safe design, operation, and maintenance of gaseous oxygen transmission and distribution systems. It is not intended to be a mandatory standard or code"
- G 4-14 (EIGA 200) <u>The Safe Design, Manufacture, Installation, Operation and Maintenance of Valves used in Liquid Oxygen and Cold Gaseous Oxygen</u> <u>Systems.</u>
 - "Continual improvement in the fundamental knowledge of design, material selection, manufacturing, cleaning, installation, operation and maintenance processes related to valves in liquid oxygen service"
- Air Products and others in the industry maintain their own standards with respect to Oxygen safety

Oxygen Properties

- Normal concentration in air is 21%
- Colorless, odorless and tasteless.
- Cannot be detected by human senses
- Not <u>flammable</u> but supports and accelerates combustion.
- Flammable materials, including some materials that are normally relatively non-flammable in air, burn very rapidly in high oxygen concentrations.
- Three elements necessary for an oxygen fire are an ignition source, oxygen and flammable material (fuel) - known as the "fire triangle"



Ignition Mechanisms

- Particle Impact
 - Energy generated by matter striking metal and emitting energy
- Adiabatic Compression
 - Rapid pressurization/compression results in heating
- Contamination
 - Contact with highly flammable materials or fluids
- Mechanical Energy
 - Friction, Mechanical Impact
- Others
 - Thermal Ignition, Electrical arc, etc



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Factors influencing ignition and combustion

- Pressure higher pressure increases flammability and promotes combustion
- Temperature higher temperature increase flammability and promotes combustion
- Velocity higher velocities increase risks associated with transfer of energy (ex particle impact)
- Oxygen Concentration the higher the concentration the greater the risk of combustion.

Ignition Mechanisms in LOX

- Not all the same as in GOX
 - Particle impact is not prevalent as velocities are low
 - Adiabatic compression is <u>less</u> likely to cause ignition
 - Friction ignition more likely to cause ignition
 - Mechanical impact more likely to cause ignition
 - Hydrocarbon triggers are more likely (e.g. accumulation by dry boiling)
- So the velocity curves used for GOX design are not relevant. The concept of a metal exemption pressure is also not relevant because many metals will burn if sufficiently promoted

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How to minimize risk?

- Choose highly compatible materials
 - Metals, soft goods
- Minimize Ignition mechanisms
 - Minimize soft goods, use of lubricants
- Utilize Best Practices
 - Design fit for service
 - Cleanliness
 - Operation
 - Maintenance

Choosing Metallurgy

- Burn Resistance
 - Alloys that, after exposure to an ignition event, either do not burn or tend to quench the burn resulting in minimal combustion.
- Exemption Pressures and Minimum Thicknesses
 - Alloys have been classified, via testing and industry experience, by their resistance to combustion in relation to material thickness
- Pressure/Velocity may allow use of materials beyond exemption limits

Engineering alloys	Minimum thickness	Exemption pressure
Brass Alloys 1)	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)
Copper3)	None specified	20.68 MPa (3000 psig)
Copper- Nickel ALLOYS 1) 3)	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	3.18mm (0.125 in)	8.61 MPa (1250 psig)
Inconel 600	3.18mm (0.125 in)	8.61 MPa (1250 psig)
Inconel 625	3.18 mm (0.125 in)	6.90 MPa (1000 psig)
Inconel X-750	3.18mm (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)

Pressure/Velocity Curve (EIGA 13/12)

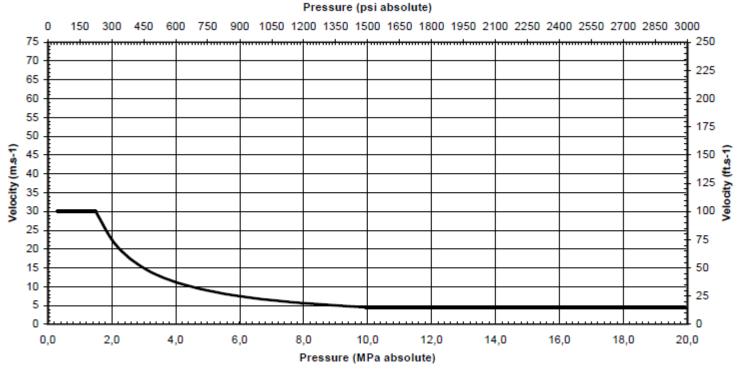


Figure 2—Impingement velocity curve

Metals - Other Considerations

- Criteria are different depending on whether metallic components are subject to direct impingement of flow
- Pressure/Velocity Criteria are less stringent for non-impingement sites as particle impact is not likely
- For a modulating butterfly valve, for example, the valve body may be considered a "non-impingement site" while the disk, portions of the seat and retainer, stem, etc would be considered subject to "impingement". Thus use of a stainless steel body may be permissible but a more burn resistant material such as Monel would be required for the internals.
- Evaluation of a valve for O2 application requires understanding of valve geometries and the minimum thicknesses of all components.

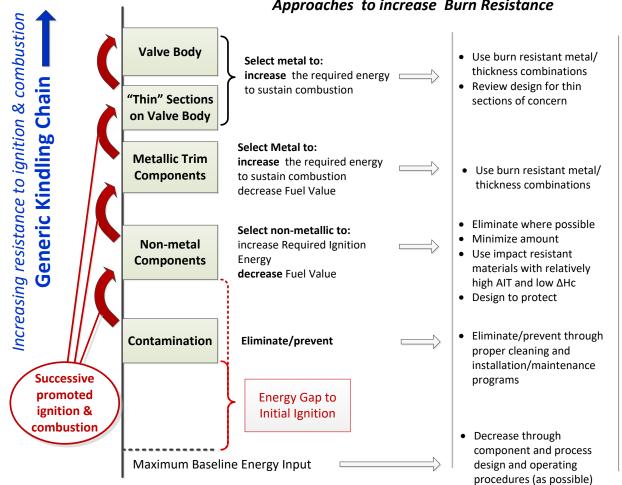
Soft Goods

- Most non-metals are less compatible with Oxygen than non-metals and may be exposed to ignition due to
 - Adiabatic Compression
 - ▶ Flexing due to vibration, friction
 - Mechanical Impact
- Best solution is to MINIMIZE.
- Where the use of non-metals is unavoidable (seals, packing, gasket, lubricants, etc), risk can reduced by taking precautions such as
 - Surrounding the non-metal with metals to serve as a heat sink
 - Keep soft goods from direct exposure to the flow stream
 - Prevent excessive movement
 - Choose materials that are physically and chemically stable at process conditions
- Preferred soft good materials include
 - Teflon, PTFE, PCTFE, Kalrez, Viton. Note: Impurities, variations in composition can severely lessen a materials burn resistance.

Lubricants

- All components in oxygen service should be designed to operate without lubrication.
- When use of a lubricant is unavoidable for assembly or operation, an oxygen compatible lubricant should be used and quantities should be minimized. Generally these are halogenated CTFE compounds. BAM and ASTM G63 provide guidance.
- The bad news is these lubricants generally do not perform as well as hydrocarbon based lubricants.
- Installation considerations can lower risks associated with ingress of less compatible lubricants.

Kindling Chain & Burn Resistance (from EIGA 200)



Approaches to increase Burn Resistance

Valve Services

- Isolation Valves
 - Operated open or closed, moved only w/o diff pressure across meaning pressure equalization is required. Material considerations are less stringent.
- Throttling valves (Manual or Automated)
 - The most severe class of valve in oxygen service due to potential for high velocities and turbulent flow.
- Check Valves
 - By nature of their function, check valve internals are subject to impingement and high velocities and should be designed in accordance with similar considerations to throttling valves
- Relief Valves
 - Again, when relieving, body and trim are exposed to high velocity and turbulence and should be designed accordingly.

Valve Styles

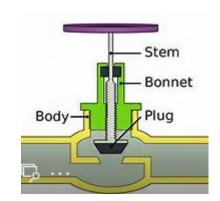
- Ball and rotating plug valves
 - These valve designs are inherently quick-opening leading to concerns with adiabatic compression. Also may have sharp leading edges. As a result, not generally preferred in GOX service. Use is more liberal in LOX.
- Butterfly Valves
 - When open, body is considered non-impingement but the disk, seat and stem are all impingement sites. Can be used in throttling service under specific operating conditions.
- Gate Valves
 - Similar construction considerations to butterfly valves but are not designed for throttling service.

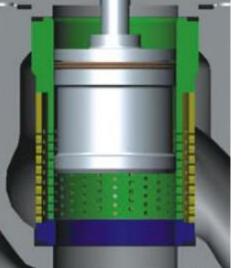
Valve Styles cont.

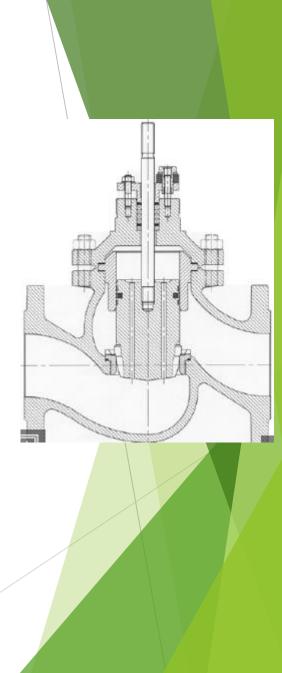
Globe Valves

- Most common design for throttling applications
- "Tortuous path" means impingement throughout the valve and common use of exemption materials.
- Specific designs require evaluation based on form and function
 - Parabolic Plug
 - Attenuation Cage
 - Balanced

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Specifier's Responsibilites

AP specified HP GOX valve which we ran at ~5% open for months.

- Clearly Define all Operating Cases
 - Pressures, Temperatures and Flowrates
 - Possible Upset Conditions
 - Consider warm cases for LOX valves
- Awareness of material considerations
- "Qualify" Manufacturers

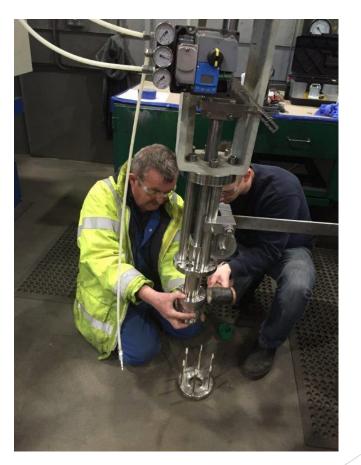


What might Qualify Mean?

- Reference list indicating experience with oxygen service
- An effective and operable quality management system capable of meeting customer technical specifications and requirements
- Resource management/human resources training/competences for oxygen service
- Lessons learnt from operations, maintenance, design and manufacturing
- Principles for selection of non-metallic materials (bearings, gaskets, packings, lubricants)
- Principles for selection of metallic materials (springs, pins, washers)
- Principles of validation of the cleaning process (qualification, cleanliness verification process, cleaning room/area organization, quality of sub-supplier material)
- Validation of the valve design
- Cascading of quality measures to sub-suppliers
- Assembling sequence, procedure, working environment for assembly process
- Material traceability metallic/non-metallic
- Standard documentation (cleanliness certificate, inspection test plan, installation and maintenance instruction, packaging-procedures and preservation, labelling and marking

Manufacturer's Responsibilities

- Selection of appropriate materials
 - Many customers may not have a clue!
 - Others (AP) would dictate materials
- Proper <u>Cleaning</u> facilities and procedures
 - From component level to final assembly
 - Judicious use of approved lubricants
 - Proper handling and packaging
- Quality control of sub-suppliers
 - Particularly soft goods



End Users Responsibilities

- Maintaining cleanliness through installation and operation
- Limit operation to defined operating cases
- Diligence in Maintenance



Thank you tell me more