Prepared by the Safety Advisory Group

Safety Info 15/08/E

Safety Principles of High Pressure Oxygen Systems

1. INTRODUCTION:

Oxygen system design should only be carried out by engineers who have professional experience and knowledge of the design principles and materials involved. There are also well established standards and regulations in many countries which must be followed where appropriate.

The following internationally recognised organisations have issued oxygen safety information which should be referred to when designing oxygen systems.

ASTM - American Society of Testing & Materials (USA)

CEN - Standardisation bodies

ISO - Standardisation bodies

NASA - National Aeronautics and Space Administration (USA)

CGA - Compressed Gas Association (USA)

EIGA - European Industrial Gases Association (Europe)

(See also paragraph 6 regarding national organisations, e.g. VBG (1a)[1], BSI (1b), NFE (1c))

Normally each time an oxygen system is planned, suitable company standards should be available which specify components and materials to be used, rather than referring to the above sources in detail. This document therefore outlines only the basic recommendations for oxygen systems.

If established company standards are not followed, or do not exist, then additional research must be carried out to avoid accidents. Note that it is the responsibility of the company and the system design engineer to ensure that safety aspects have been properly covered.

Scope and field of application

This Safety Information, "Safety Principles of High Pressure Oxygen Systems" comprises general recommendations related to the selection of components and materials for use in systems for compressed gaseous oxygen, or mixtures of oxygen and inert gases if the mixture contains more than 23.5% oxygen by volume and a pressure above 30 bar. It explains the main causes of fires in oxygen systems and gives references to important publications on oxygen which preferably should be studied by technical personnel who are writing company standards.

<u>The risks of toxic contamination in conjunction with fires in components and supply lines have not been considered in this document.</u>

[1] Refer to references at the end of the document

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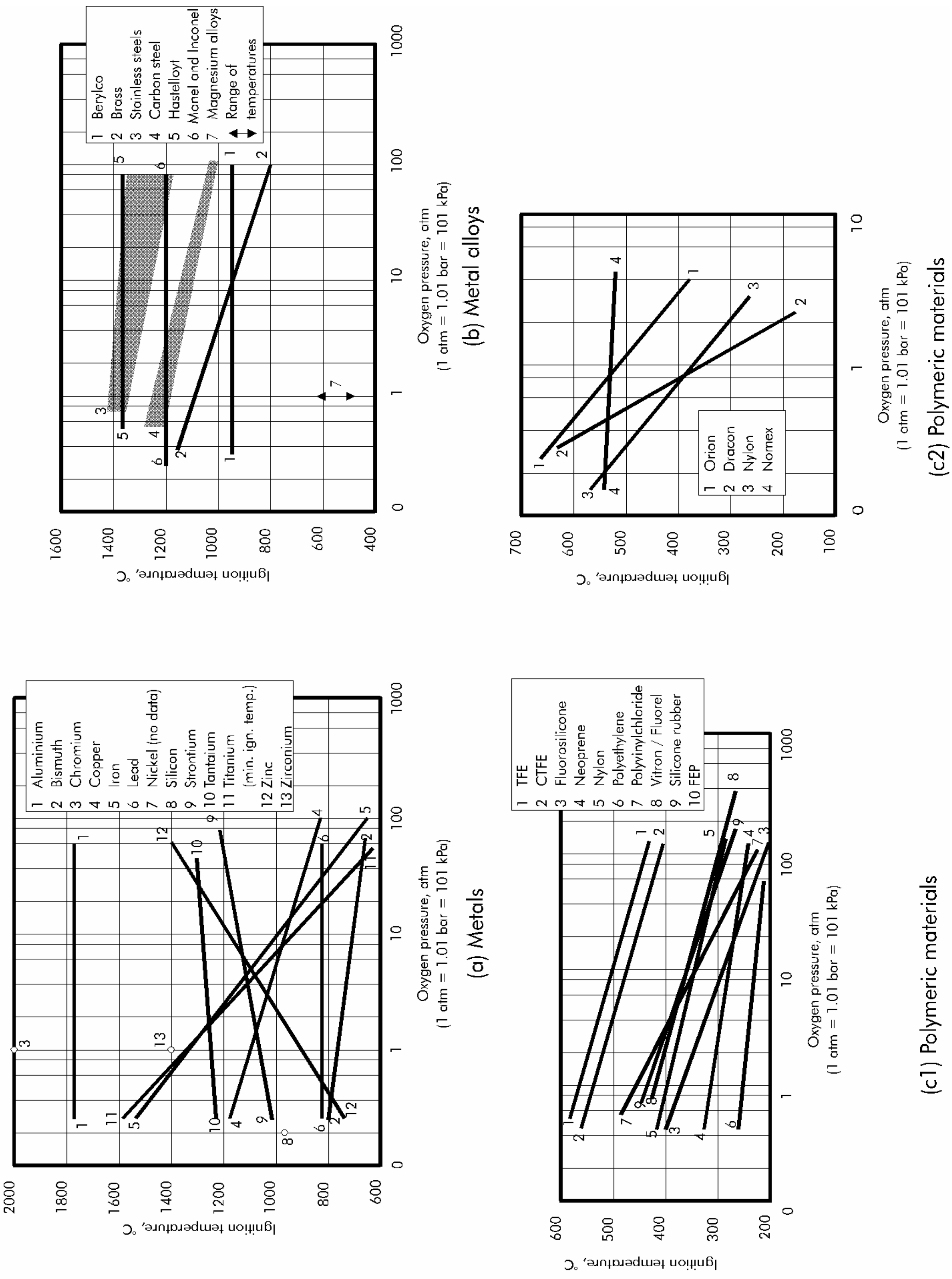

Ignition Temperatures of Materials as a Function of Oxygen Pressure

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2. OXIDISING GASES

The most common oxidising gas is oxygen (see also the oxidising properties of ozone, fluorine and nitrous oxide (**2**)). Oxygen itself is non-flammable, but it supports combustion. It is highly oxidising, reacts vigorously with combustible materials, and enhances a fire or explosion which will generate a large amount of energy in a short time.

Oxygen

Both the risk of ignition and the rate of combustion increase with higher concentrations of the oxidising gas. Higher pressure usually results in a lower ignition temperature and increased combustion rate. Furthermore a higher pressure will in the case of adiabatic compression create a higher temperature. Increased temperature will also make the risk of ignition more likely, as the amount of energy that must be added to start a fire, decreases. The ignition temperatures of polymeric materials are lower than those of metals and they become significantly lower with increasing pressure. Refer to the charts in the figure which show approximate ignition temperatures for selected metals, plastics and elastomers. For ranking of materials to be used in oxygen systems refer to testing organisations and regulating authorities according to paragraph 6.

With sufficient pressure and ignition energy, nearly all substances can be made to burn in pure oxygen, including substances which are not usually regarded as flammable, e.g. metals (compare with oxy-fuel cutting). Accidental ignition of metals in oxygen normally requires a kindling chain of reaction, i.e. ignition of impurities or non-metallic materials such as soft seat inserts in valves, O-rings etc. Organic substances e.g. oils and grease are ignited extremely easily and can function as an ignition source for other more difficult to-ignite materials.

Gas mixtures containing oxygen

For gas mixtures containing 21-23.5 % (Vol.) oxygen, the oxidising properties must be taken into consideration when regarding lubricants, sealing materials and cleaning requirements. For oxygen concentrations exceeding 23.5 % the same rules may apply as for oxygen (**3**).

3. IGNITION SOURCES

- Single or repeated violent pressure shocks (heat from adiabatic compression).
- Excessive gas velocity in pipes or components.
- Particles impacts.
- Friction between moving and stationary parts (e.g., jammed valve, rough valve handling, galling and friction energy).
- Resonance (although uncommon in industrial applications).
- Electric arcs (including static electricity or lightning.)
- Contamination with e.g. grease or oil in combination with an ignition (kindling chain of reaction).

Ignition energy in oxygen systems often comes from adiabatic compression. At customer sites e.g., high pressure cylinders should be opened against regulators or closed manifolds and hoses (**4**) with special end fittings with good heat sink used. Adiabatic compression can also be a problem at filling stations since there is a possibility of connecting returned cylinders at full pressure to the filling manifold or operating the valves in the wrong order. The hose has connections at both ends which should be designed to absorb the compression heat in the same way as the distance pieces, used with the hoses for emptying manifolds, will do. Pressure shocks can be prevented by not using valves that open quickly e.g. ball valves and by always opening manual or automatic valves slowly.

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4. CONTROLLING FIRE HAZARDS IN OXYGEN SYSTEMS

Safety philosophy of oxygen system design:

No system will be safe unless suitable materials and safe components are used: i.e. materials and components that have a trouble-free history in oxygen service or have been properly tested and where applicable approved by a recognised testing organisation.
No component will be safe unless it has been designed, manufactured and tested according to principles which ensure safe operation in oxygen service.
Design principles and material cannot be selected unless knowledge of oxygen compatibility, system design and test methods are available.
Materials must be cleaned and kept clean to ensure no contamination with flammable or non-oxygen compatible substances occurs.

Reducing the fire hazard in oxygen systems involves the control of the ignition mechanism and the propagation of the fire. For example, it is important that heat is removed from the reaction zone. The mass of non-metallic material should be kept small, and must be well embedded in surrounding metal for heat conductivity. The system or component must be cleaned for oxygen service, i.e. not be contaminated with e.g. hydrocarbons. Only tested (**5**) and approved lubricants should be used and applied in the smallest possible amounts. The system shall be designed to protect operators in case of a fire e.g. by using shields (panels) in front of valves and other components or by operating remote controlled valves from a safe distance.

Engineering guidelines regarding choice of materials:

Metallic materials:

Aluminium and *aluminium alloys* including *aluminium bronze* shall not normally be used in pipelines or other components where there is a history of ignition e.g. in regulators, valves etc. Al-seals must be well embedded. Aluminium is however considered to be an appropriate material for gas cylinders, vaporisers etc.

Pipes and components:

Selecting the metal alloy for piping systems depends on the pressure, velocity and piping configuration (impinging or non-impinging flow). Guidance for material selection is given by national authorities and in IGC Doc 13/XX.

For valves, where ignition is more likely to occur, copper, copper alloys (e.g. brass, tin bronze, Monel), Nickel, etc. are the preferred materials in high pressure oxygen systems i.e. above 30 bar. Aluminium bronzes with >2.5% Al should not be used without special consideration by experts. Specific guidance for valve material selection is given in IGC Doc 13/XX.

Cleanliness is a pre-requisite. Sections of copper alloy or similar material should be inserted where particle impact, pressure shock or extreme velocities are expected.

Internal parts of thin sections made from stainless steel should be avoided especially where adiabatic compression may occur and where non-metallic or easily ignited materials are present.

Non-metallic materials:

Materials with high ignition temperature and low combustion heat are preferred. Good design may effectively reduce the probability of a fire.

When selecting a sealing medium, as a first choice, use metallic or inorganic material which is not combustible in an oxygen atmosphere. Organic materials must be tested and approved before use in the actual operating conditions. Refer to section 6 for a survey of tests and testing organisations which are used.

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Good practice when designing and building oxygen systems:

When planning or working with high pressure oxygen systems always be aware of the great risk of reaction between oxygen and incorrect or contaminated materials. A fire will often cause extensive damage. Therefore the following five design rules should be met, as well as defining safe operational procedures.

1. Use only oxygen compatible materials and approved products. When selecting materials and dimensions, consideration must be given to pressure gas flow velocity, and piping configuration (**8**).

2. Components should only be used in the conditions (pressure, flow direction) for which they have been tested and approved. For valves upto 25mm “burn out” test data and approval (**9**) is available. For a survey of “burn out” testing see section 6.2.

3. Pipes and other components used in oxygen service shall be cleaned and degreased using a suitable solvent and procedure. Oil free sand blasting may be used for internally cleaning Carbon Steel pipes. All dangerous traces of the solvent shall be removed before oxygen is admitted. It is a good practice to do the cleaning before assembling the oxygen system and to prevent the ingress of impurities during the work. Oxygen equipment should be tested for cleanliness before being put into service.

4. Foreign particles such as mill scale, rust, dirt, pieces of PTFE tape, turnings and weld droplets must be carefully removed before system start-up. Particles shall as far as possible be arrested in filters and not be allowed to transfer from one part of the system to another. Such filters shall be cleaned after purging and prior to admission of oxygen into the system. Materials for filters must be chosen with great care as they have a very large exposed surface. Sintered bronze may be a good choice for systems which are operated at somewhat higher pressures e.g. in cylinder filling or emptying manifolds. Care shall be taken regarding material thickness, some materials that will not burn in Oxygen service at regular thickness can become combustible when the thickness is very small for example in filter mesh.

5. Although non liquefied (permanent) gases do not cause static electricity charging, the filling manifold, the hoses and the connection to gas cylinder valve shall be connected to the plant bond (earth) (**10**) in order to prevent internal electrostatic charging and sparks. The reason is that it is very difficult to avoid foreign particles especially if the same equipment is used for cylinder emptying. Foreign particles in a gas stream will increase the risk of electrostatic charging of e.g. the plastic in the inner tube of a steel braided flexible hose (**11**).

5. CONSIDERATIONS IN SHUTDOWN AND REPAIR SITUATIONS

During repair of oxygen systems the risk of oxygen enrichment and injuries due to fire must be considered. All work in confined spaces must be thoroughly planned and supervised to ensure that there is not too high oxygen concentration or oxygen deficiency after purging operations. Before welding or cutting is performed on an oxygen pipe system the oxygen supply must be shut off, the pipe section if possible blind flanged and its pressure must be relieved. A single shut off valve cannot be relied on. Double block and bleed valves shall be considered. The pipe section must be purged with an inert gas or air until the oxygen concentration has fallen to 21%. Note that during cutting work, severely rusted pipe systems can start burning even after they have been purged with an inert gas. Maintain cleanliness of oxygen systems by using lubricant-free tools etc.

The risk of oxygen enrichment or oxygen depletion during maintenance and purging operations is described in the following IGC Documents:

004/XX Fire Hazards of Oxygen and Oxygen
044/XX Hazards of Oxygen Deprivation
040/XX Work Permit
033/XX Cleaning Equipment for oxygen services

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6. SURVEY OF IMPORTANT PUBLICATIONS ON OXYGEN

Method, procedure or practice used	**Testing Organisation / Regulating Authority** **BAM [1] /VBG [2]**	**ASTM [3] /NFPA [4]**	**Other Testing Organisation or Standards e.g.** **NASA[5], BSI[10], DIN [7], *others*[14]**
1. Pneumatic Impact Test (PIT) of materials - GOX[5]	Main test method, see “Liste”[6]	G74 Standard test method	
2. Pneumatic Impact Test of components e.g. valves regulators etc. - GOX. (Burn-out test)	Main test method. Conditions for “approval“[6]	G74 Std. test method can be used also for components	TRG (DIN)[7], DIN 8546, DIN 8545, TRG770 Anlage 1 ISO 2503[8] EN 849-CEN/TC 23SC 2N 138[9]
3. Auto Ignition Temp (AIT) - GOX (high pressure)	Optional	G72 Standard test method	BS 4N 100-2: 1999 (Bomb test) [10] NF E 29-763/94[11] ISO TC 58/WG7, Oxygen compatibility
4. Oxygen Index (OI)	Optional	D2863 Standard test method	ISO 4589-1984 (DIN 22117) Standard test method
5. Heat of Combustion (HoC)	Optional	D4809 Standard test method	DIN 51900
6. Mechanical Impact Test - LOX[5] (MIT-LOX)	Optional	D2512 Standard test method	BS 4N 100-2:1999 (Lox Impact Machine)
7. Design of systems for oxygen service. (Oxygen)	Regulation/VBG 62	G88 Standard guide G63, G94 (evaluation of materials)	IGC[12] Doc 13/XX BS 4N 100-2:1999 NASA[5] (e.g. SP 3090, 8060)
8. Cleaning Methods for Materials and Equipment in Oxygen Service	Regulation/VBG 62	G93 Standard	IGC Doc 33/XX CGA Pamphlet G-4.1 - 1996
9. Fire Hazards in Oxygen Enriched Atmospheres.		NFPA Manual (53 M 19909)	IGC Doc 04/XX
10. Non metallic materials Oxygen Compatibility		BAM VBG 62	ASME

Footnotes

1) BAM- “Bundesanstalt für Materialforschung und Prüfung”, Germany.
2) VBG-”Unfallverhütungsvorschriften der Berufsgenossenschaft der chemischen Industrie”.
3) ASTM-American Society for Testing and Materials, USA.
4) NFPA-National Fire Protection Association, USA.
5) NASA-National Aeronautics and Space Administration, USA.
6) Liste der nichtmetallischen Materialen -BG Chemie (see note 2). Test results by BAM.
7) DIN- “Deutsches Institut für Normung”
TRG- „Technische Regeln Druckgase“ (DIN)
8) ISO-International Organisation for Standardization.
9) CEN-European Committee for Standardization.
10) BSI-British Standard Institute.
BS-British Standard.
11) NFE-French Standard.
12) EIGA/IGC-European Industrial Gases Association/Industrial Gases Council (Doc 13/XX).
13) CGA-Compressed Gas Association, USA.
14) a) Air Liquide, Testing Centre, France
b) DNV, Norway
c) Wendall Hull Associates, USA

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<u>Ref:</u> **<u>The following references are found in the text of the document:</u>**

(1a) VBG-Berufsgenossenschaft der chemischen Industrie (Germany).

(1b) BSI-British Standardisation Institute (United Kingdom).

(2) The same rules apply in principle to nitrous oxide systems as to oxygen. Oxidation reactions with nitrous oxide give off more heat than oxygen. On the other hand, nitrous oxide reactions require a higher activation energy, which makes them more difficult to initiate. Violent reactions can take place once the ignition is started since nitrous oxide can decompose. Hot work must not be carried out on any equipment under pressure or which have not been purged (also compare with the decomposition properties of Ozone).

(3) Reference: ASTM G88-84, "Oxygen enriched atmosphere".

(4) Reference IGC Doc. 42/XX "Prevention of Hose Failures in High Pressure Gas Systems".

(5) A list of Oxygen compatible lubricants is prepared by BAM in Germany, "<u>Liste der Nichtmetallischen Materialen</u>", can be ordered from Jedermann-Verlag KG-Fax No. + 49 6221-278 70.

(6) (not used)

(7) (not used)

(8) Ref. IGC Doc 13/XX The Transportation and Distribution of Oxygen by Pipeline.

(9) Valve manufacturers marking of oxygen compatibility may not always be relied upon. If in doubt check the test certificate from the testing organisation.

(10) Ref. ASTM G 88-84.

(11) A measured resistance of 10 M Ohm or less will prevent electrostatic charging of e.g. a pipe or hose.

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