METHODS TO AVOID AND DETECT INTERNAL CORROSION OF GAS CYLINDERS AND TUBES

Doc 62/22

Revision of Doc 62/14

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METHODS TO AVOID AND DETECT INTERNAL CORROSION OF GAS CYLINDERS AND TUBES

As part of a programme of harmonisation of industry standards, the European Industrial Gases Association (EIGA), publication, Methods to Avoid and Detect Internal Corrosion of Gas Cylinders and Tubes, has been used as the basis of an internationally harmonized gas association's publication on this subject.

This publication is intended as an international harmonised publication for the worldwide use and application by all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), EIGA, and Japan Industrial and Medical Gases Association (JIMGA). Regional editions have the same technical content as the EIGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Regional regulatory requirements are those that apply to Europe.

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Amendments to 62/14

Section	Change
	Rewrite following Harmonisation Association's review

Note: Technical changes from the previous edition are underlined

1 Introduction

There are a number of reasons for a cylinder or a tube to fail. These reasons can include but are not limited to, abuse, misuse, manufacturing flaws, and internal corrosion. A number of gases can react with moisture to produce corrosive media that could react with the cylinder or tube material and lead to a cylinder or tube failure. The number of incidents resulting from internal corrosion is relatively small compared to the number of cylinders and tubes in service because the industry follows procedures to reduce moisture in cylinders and tubes.

2 Scope and purpose

This publication provides guidance to help prevent and detect internal corrosion of compressed gas cylinders and tubes. It applies to gas cylinders, bundles of cylinders, and tubes including installations at customer sites.

NOTE—Unless noted by exception, the use of the word "cylinder" in this publication refers to both cylinders and tubes.

The main emphasis of this publication focuses on steel cylinders containing oxygen/oxygen mixtures including compressed air and carbon dioxide/carbon dioxide mixtures in the presence of moisture. Certain aspects of this publication can also apply to other gases that can react in the presence of moisture such as hydrogen chloride.

3 Definitions

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

3.1 Publication terminology

3.1.1 Shall

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

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

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

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Bundle of cylinders

Portable assembly that consists of a frame and two or more cylinders, each of a capacity up to 150 L and with a combined capacity of not more than 3000 L, or 1000 L in the case of toxic gases, connected to a manifold by cylinder valves or fittings such that the cylinders are filled, transported, and emptied without disassembly.

3.2.2 Corrosion

Reaction of the cylinder material with certain aqueous media (for example, carbonic acid formed from carbon dioxide and water).

3.2.3 Corrosive gas

Gas in a cylinder that will interact with the cylinder material in an oxidizing manner in the presence of moisture.

3.2.4 Hydraulic test

Test performed on the cylinder using an aqueous solution such as a test to check for leaks (proof test) or an expansion test (hydrostatic test).

3.2.5 Manifolded containers

Cylinders and tubes that are interconnected, supported, and held together as a unit by structurally adequate means.

4 Corrosion

There are mainly two mechanisms that promote corrosion:

- Acidic corrosion, which can be caused by gases such as carbon dioxide and sulphur dioxide that form acids when combined with water. Visual indications include area/general corrosion, line corrosion, or pitting corrosion in local areas. Typically, corrosion is located at the interface of gas/liquid (water); and
- Oxidizing gas corrosion, which can be caused by gases such as oxygen when combined with water. This corrosion is generally widespread over the internal surface of the cylinder.

5 Sources of moisture contamination

Free moisture contamination can occur from several different sources. For example, manufacture, filling, use, valving, storage, and maintenance.

5.1 Water from manufacturer’s hydraulic test

As part of a cylinder's initial acceptance procedure, a mandatory hydraulic test is performed by the manufacturer. It is essential that subsequent emptying and drying of the cylinder is undertaken so that there is no free moisture left in the cylinder. Once achieved, it is necessary to maintain this dry condition (see 5.5).

5.2 Water from product/filling operation

Certain products can contain moisture when compressed into a cylinder, for example compressed air. Additionally, some filling operations can introduce moisture into cylinders, for example if water lubricated compressors or water-ring vacuum pumps are used, without taking precautions to prevent water carry over.

NOTE—Water lubricated compressors have largely been replaced by high pressure cryogenic pumps.

5.3 Water backflow during use

Water backflow into cylinders can occur whenever the cylinder is at a lower pressure than the application (involving a fluid) to which it is connected.

5.4 Water ingress

5.4.1 Rainwater

Rainwater could enter the cylinder if the valve is left open after use, or if an unvalved cylinder is inadequately protected while in storage or transportation.

NOTE—Plastic plugs fitted to new cylinders do not always provide protection against ingress of rainwater.

5.4.2 Water immersion

If cylinders are immersed in water, and if the external pressure exceeds the internal pressure of the cylinder, there is a possibility that the water can enter the cylinder, for example through an open valve, neck threads, or an inadequately sealed valve, and contribute to corrosion. Some users such as fish farms and shipyards immerse cylinders during or after use.

5.4.3 Atmospheric humidity

Cylinders stored with their valves open or devalved cylinders that are inadequately protected against moisture ingress can "breathe". This can result in condensation of moisture from the atmosphere into the cylinder when the temperature drops, for example at night. This moisture can result in internal contamination and buildup of water following several such air ingress cycles.

5.5 Water from periodic inspection of cylinders

As part of the periodic inspection and test, cylinders are hydraulically tested, unless a suitable alternative is permitted. It is essential that subsequent emptying and drying of the cylinder is carried out so there is no free moisture left in the cylinder. Once achieved, it is essential that this internal dryness is maintained until re-use. To confirm the absence of free moisture, an internal visual inspection after drying is recommended. Organizations undertaking hydraulic testing should have a quality assurance system to ensure cylinders are adequately dried after the hydraulic test. It should be noted that a cylinder warmed or hot from the drying process can condense moisture inside as it cools if the drying process uses moist, hot gas.

NOTE—For composite cylinders with liners from AA 6061, see EIGA Doc 72, *Water Corrosion of Composite Cylinders with AA 6061 Liners* [1].[1]

6 Avoidance of cylinder corrosion

Several methods are available to reduce the likelihood of corrosion. The different methods are based upon material selection, design criteria, prevention, and detection methods. These methods can be applied as single measures or in combination depending upon the application.

6.1 Material selection and cylinder design

6.1.1 Material selection

The choice of material of construction of the cylinder can affect the cylinder's corrosion resistance. Common cylinder materials are:

- Aluminium alloys—Aluminium alloy cylinders are widely used in the gases industry because of their high corrosion resistance to a wide range of gases in the presence of water including oxygen and carbon dioxide. However, care shall be taken to minimize ingress of fluids into the cylinder when in the presence of certain contaminants, for example chlorides and soft drink syrups, as it cannot be assumed that the alloy will protect entirely against all corrosion mechanisms;

- Carbon steels and low alloy steels—Cylinders manufactured from low alloy or carbon steels are very widely used for carbon dioxide/carbon dioxide mixtures and for oxygen/oxygen mixtures including compressed air. In the presence of water, internal corrosion will occur. The rate of

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

corrosion will depend on the gas, gas pressure, and the amount of water and contaminants present;

- Stainless steels—Stainless steel cylinders are corrosion resistant for a wide variety of products. Stainless steel cylinders are very sensitive to chloride contamination. Care shall be taken when used in marine applications and with the water quality used for the hydraulic test to ensure chloride levels are compatible with the grade of stainless steel used. Their use in high pressure applications is very limited;
- Internal coating and surface treatments—Use of internal coatings, liners, and surface treatments does not ensure protection against internal corrosion and can create additional operational concerns; and
- Steels with improved toughness—Improving the toughness of the steel increases the chance of a leak instead of a burst (leak before break). This approach does not prevent corrosion but can limit the consequences should a failure occur. With the steels available today, only limited progress can be made in this area. The chance of a leak instead of a burst is increased when the pressure at the time of failure is low compared with the cylinder test pressure.

6.1.2 Cylinder design

- Corrosion allowance—Cylinder specifications such as the ISO 9809 series and ISO 11120, *Gas cylinders – Refillable seamless steel tubes of water capacity between 150 l and 3000 l – Design, construction and testing* do not contain a corrosion allowance, unlike some stationary pressure vessel codes [2, 3]. For steel cylinders, because of the potentially high corrosion rates, a normal pressure vessel corrosion allowance of approximately 1 mm to 2 mm (0.039 in to 0.079 in) is of little benefit in extending the cylinder's life and consequently is not recommended.
- Good design in welded cylinders—For some gas applications welded cylinders are used. Welded cylinders with joggle joints should be designed and manufactured so that these joints do not retain water. An alternative joint type is a butt welded joint. See ISO 4706, *Gas cylinders – Refillable welded steel cylinders – Test pressure 60 bar and below* [4].

6.2 Avoidance of water ingress

6.2.1 Single cylinders

There are different methods for protecting single cylinders from water ingress. These methods include but are not limited to:

- Closing the valve after use;
- Returning the cylinder with residual gas pressure to the filler; and
- Using a residual pressure valve (RPV) that retains a positive gas pressure inside the cylinder. A Type 1 RPV includes a non-return feature that is designed to prevent backflow from a downstream customer process. See EIGA Doc 64, *Use of Residual Pressure Valves* for more information on RPVs [5].

6.2.2 Design of bundles of cylinders and manifolded containers

For protecting the bundles of cylinders from water ingress, they shall have at least one main valve even if individual cylinders are valved. Methods for protecting a bundle of cylinders can include:

- using a main valve and closing this valve after use and returning the bundle of cylinders with residual gas pressure to the filler; or
- using a RPV as the main valve.

In the United States and Canada, in addition to bundles of cylinders, manifolded containers shall be protected from water ingress even if individual cylinders are valved. Methods for protecting manifolded containers can include, but are not limited to:

- using a main valve and closing this valve after use and returning the manifolded containers with residual gas pressure to the filler;
- sealing the filling/user connection with a vented plug or cap; or
- using a RPV as the main valve.

6.2.3 Customer installation

Customer installations should provide a non-return valve in their process if the possibility of water backfeed exists.

6.2.4 Filling operation

While most fill plants do not use water sealed or water lubricated equipment, some installations could have such equipment and this presents a risk of moisture ingress.

6.3 Moisture detection methods

Water ingress is the main reason for internal corrosion. The following are methods to indicate the possible presence of water in the cylinder.

6.3.1 Residual pressure check

Presence of residual pressure in the cylinder before filling indicates that water ingress is unlikely to have occurred.

Cylinders, bundles of cylinders, and manifolded containers found with no residual pressure and when the previous service is not known should be submitted to additional procedures (see 6.3.2, 6.3.3, 6.3.4, 6.3.5 and 6.3.6).

6.3.2 Weight check

If a significant amount of water is present, it can be detected by a cylinder weight check. This method is mainly used for liquefied gases, for example carbon dioxide when the tare weight of the empty cylinder is checked.

The sensitivity of this method depends on the size of the cylinder, the accuracy of the scale used, and the stamped tare weight.

Similar considerations may also apply to bundles of cylinders and manifolded containers. This method is not reliable for tubes.

6.3.3 Internal visual inspection

This inspection involves removing the valve from the depressurized cylinder and checking for free water. This inspection shall be carried out whenever cylinder valves are changed and in particular when changing from a conventional cylinder valve to an RPV.

6.3.4 Moisture meters

Moisture meters are used for the measurement of very low concentrations of moisture content in a gas stream from a cylinder. Moisture meters are not normally designed to determine if free water is present in the cylinder, but they may be used for this purpose if an adequate procedure is followed. The difficulties to overcome are:

- Measurements at high pressures do not provide reliable results and are not recommended;
- Aqueous liquid/vapour equilibrium in the cylinder can take time to develop a representative moisture concentration in the vapour phase;

- When several interconnected cylinders are tested simultaneously, the moisture level recorded corresponds to the average moisture concentration. However, all the contamination could be due to moisture in a single cylinder;
- Measurement is time consuming especially when high level moisture has contaminated the sensor, which will then take time to dry out; and
- Some corrosive gases can affect the moisture analysis or even destroy the instrument.

6.3.5 Cylinder evacuation

The evacuation of single cylinders, pallets containing cylinders, bundles of cylinders, or manifolded containers before filling is a common procedure for quality and for safety reasons.

When a preset vacuum is not achievable in a given time, this can be an indication that there is free water in one or more of the connected cylinders. This method is not reliable for tubes.

6.3.6 Cylinder inversion

By inverting a cylinder not equipped with a dip tube, it is possible to detect free water when the valve is opened. This approach will not detect small quantities of water. Additionally, the method is not always convenient for large cylinders where specific equipment is needed to be performed in a safe manner.

6.4 Corrosion detection methods

Although several corrosion detection methods are available such as ultrasonic testing (UT), acoustic emission testing (AET), internal visual inspection (see 6.3.3), tare weight checks, and the hammer test, none of them are entirely satisfactory for cylinder filling applications.

UT and AET are sophisticated methods involving time consuming procedures, and therefore, are not used for checking cylinders at the time of filling. For this reason, their use is restricted to periodic inspection as an alternative or as a supplement to the hydraulic test.

Internal examination is not suitable as an inline prefill inspection but is normally used when other methods indicate suspicion of corrosion.

Weight checks and the hammer test are relatively simple and inexpensive methods that detect heavy generalized corrosion but will not detect the frequently encountered localized corrosion such as line, pit, or crevice corrosion.

7 Guidance for moisture acceptance levels

Because of the risk of stress corrosion cracking (SCC) in steel cylinders, more stringent levels of moisture contamination (typically less than 5 ppm) are necessary for carbon monoxide and carbon monoxide/carbon dioxide mixtures (see EIGA Doc 95, *Avoidance of Failure of CO and CO/CO2 Mixtures Cylinders*) [6].

8 Recommendations/Conclusions

There are different ways to avoid and detect internal gas cylinder corrosion (for details, see section 6):

8.1 Using a residual pressure valve with a non-return function

A RPV including a non-return function may be attached to the cylinder. This applies to new cylinders, existing cylinders at time of retest, or at any opportunity a cylinder valve is changed, for example because of valve damage. Before fitting the RPV, ensure that the cylinder is free from moisture by internal visual inspection. The functionality of the RPVs shall be checked prior to filling in accordance with EIGA Doc 64 [5].

8.2 Cylinders without residual pressure valves

The following checks may be performed prior to filling a steel cylinder containing carbon dioxide/carbon dioxide mixtures and oxygen/oxygen mixtures that are not fitted with an RPV and could be contaminated with liquid:

- residual pressure (cylinders with a residual pressure may be considered uncontaminated);
- tare weight (for pure carbon dioxide cylinders only);
- cylinder inversion and valve opening to see if liquid is emitted (larger cylinders will require equipment specifically designed to invert cylinders); or
- moisture analysis.

8.3 Use of aluminium alloy cylinders

As indicated in 6.1.1, aluminium alloy cylinders are more resistant to corrosion in case of moisture ingress. For medical oxygen applications, it is recommended to conduct an odour test before filling to detect contamination or use cylinders equipped with a RPV and/or a valve integrated pressure regulator (VIPR) to avoid backflow contamination.

9 References

Unless otherwise specified, the latest edition shall apply.

[1] EIGA Doc 72, *Water Corrosion of Composite Cylinders with AA 6061 Liners*, European Industrial Gases Association. www.eiga.eu

NOTE—This publication is part of an international harmonization program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

[2] ISO 9809 Parts 1, 2, 3, and 4, *Gas cylinders – Refillable seamless steel gas cylinders – Design, construction, and testing*, International Organization for Standardization. www.iso.org

[3] ISO 11120, *Gas cylinders – Refillable seamless steel tubes of water capacity between 150 l and 3000 l – Design, construction and testing*, International Organization for Standardization. www.iso.org

[4] ISO 4706, *Gas cylinders – Refillable welded steel cylinders – Test pressure 60 bar and below*, International Organization for Standardization. www.iso.org

[5] EIGA Doc 64, *Use of Residual Pressure Valves,* European Industrial Gases Association. www.eiga.eu

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[6] EIGA Doc 95, *Avoidance of Failure of Steel Cylinders Containing CO and CO/CO2 Mixtures*, European Industrial Gases Association. www.eiga.eu

NOTE—This publication is part of an international harmonization program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

10 Additional references

CGA G-6.3, *Carbon Dioxide Cylinder Filling and Handling Procedures,* Compressed Gas Association, Inc. www.cganet.com

CGA G-6.8, *Transfilling and Safe Handling of Small Carbon Dioxide Cylinders*, Compressed Gas Association, Inc. www.cganet.com

EIGA Doc 83, *Recommendations for Safe Filling of CO2 Cylinders and Bundles*, European Industrial Gases Association. www.eiga.eu

ISO 7866, *Gas cylinders — Refillable seamless aluminium alloy gas cylinders — Design, construction and testing*, International Organization for Standardization. www.iso.org

ISO 16148, *Gas cylinders — Refillable seamless steel gas cylinders and tubes — Acoustic emission examination (AT) and follow-up ultrasonic examination (UT) for periodic inspection and testing,* International Organization for Standardization. www.iso.org

ISO 18119, *Gas cylinders — Seamless steel and seamless aluminium-alloy gas cylinders and tubes — Periodic inspection and testing*. International Organization for Standardization. www.iso.org