



SAFE USE OF GAS CYLINDERS IN MARINE SERVICE

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Prepared by WG-2 Gas cylinders and pressure vessels

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Amendments to 61/12

Section	Change
	Editorial to align style with EIGA Style manual
3.1	Addition of Publications terminology
3.2	Recommendation on closing cylinder valves
4.6	Additional recommendations to users
6	References updated and aligned to text
	Appendix B removed

Note: Technical changes from the previous edition are underlined

1 Introduction

The number of industrial gas cylinders which are used in areas such as off-shore oil production, on board ships, shipyards, fish farms and diving applications has increased considerably over the past few decades. The consequence of this is that these cylinders are exposed to the risks of rough handling as well as internal contamination, for example by sea water.

These conditions are generally referred to as marine environment or marine service.

A number of incidents have been reported, caused by internal corrosion of oxygen cylinders in marine service, resulting in perforation or violent rupture of the cylinder.

In addition, severe internal corrosion has been detected during routine inspections and periodic inspection.

Investigations have revealed a higher occurrence of damage to the porous material of acetylene cylinders in marine service than in industrial use.

Though the majority of the above incidents have not resulted in injuries or fatalities, it is evident that these incidents represent a potential risk of damage to both users and personnel in cylinder filling stations.

IGC Technical Note 32/82 *Detection and Prevention of Internal Corrosion of Oxygen Cylinders in Off-Shore Service* [1]¹ first examined the problem and provided recommendations to prevent and detect internal corrosion of oxygen cylinders in marine service.

This publication covers only the additional recommendation believed to be specific to gas cylinders in marine service. All inspection and prefill checks as required by transport regulations such as the *European Agreement on the Carriage of Dangerous Goods by Road*, ADR [2] shall also be performed as necessary.

By applying the recommendations of this publication, the integrity of gas cylinders in marine service should be improved and thereby reduce safety concerns.

This publication has been prepared based on the additional information collected by EIGA companies and supersedes TN 32/82 [1].

Since the recommendations in this publication have been applied, EIGA has noted a significant reduction in marine service incidents.

2 Scope

This publication applies only to those cylinders which can be identified as having a significant risk of internal contamination and/or rough handling.

It covers primarily dedicated oxygen and acetylene cylinders including bundles of cylinders used in the marine environment, but many of its recommendations may be applied also to other industrial gas cylinders in marine service.

NOTE This publication does not cover any regulatory requirements for filling, transporting, use and retesting of gas cylinders, which are outside their regional area of approval.

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

3 Definitions

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

3.1 Publications 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

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

3.1.5 Can

Indicates a possibility or ability.

4 **Oxygen cylinders in marine service**

4.1 **Nature and aspects of the problem**

Oxygen is usually supplied in either single cylinders or bundles of cylinders, with the cylinders being manufactured from either steel or aluminium alloy.

Cylinders are not designed nor intended to be exposed to corrosive products or to be used under water (except diving cylinders).

The correct use and handling of the cylinders prevents the ingress of foreign materials and therefore the risk of internal corrosion.

The main aspects, which are considered relevant, are summarized as follows:

- risk of ingress of sea water into oxygen cylinders, see 4.2;
- internal corrosion of steel cylinders in the presence of oxygen and sea water, see 4.3;
- possible inadequacy of conventional prefill inspections, see 4.4;
- possible lack of knowledge and appreciation by the users with regard to cylinder handling, see 4.5; and
- recommendations to prevent internal contamination or corrosion, see 4.6.

4.2 **Ingress of sea water into oxygen cylinders**

Cylinders and bundles of cylinders in marine use can be subject to rough handling and harsh environmental conditions not usually encountered on shore.

In addition, cylinder valves are frequently left in the open position, (even though this practice is not recommended) after the cylinder has been emptied. This is based upon a survey carried out by EIGA member companies that revealed about 25 % of the total number of cylinders supplied for offshore service are returned with the valves open.

In such conditions internal contamination of cylinders with sea water can occur in one or more of the following ways:

- exposure to sea water on the decks of supply boats;
- rough handling and carelessness resulting in cylinders being dropped or left in flooded areas;
- flooding of dry docks prior to launching of rigs or ships;
- deliberate or accidental submerging of cylinders in the sea; and
- temperature fluctuations giving rise to possible condensation of moisture from the atmosphere.

4.3 Mechanism of corrosion and corrosion rates

The corrosion rate of steel in neutral or distilled water as a result of differential aeration increases linearly with rising air pressure until the partial pressure of oxygen reaches about 0.4 bar. Further increase in air pressure results in a rapid decrease in the corrosion rate due to the formation of a passive film over the metal surface. However, in the presence of chloride solutions, such as seawater, which contains about 3.0% sodium chloride, complete passivation is no longer possible and increased oxygen partial pressure will merely result in increased corrosion rate and severe pitting damage.

The corrosion rate is influenced by factors such as temperature, chloride ion concentration and agitation, but it is governed mainly by the oxygen partial pressure [3].

A study carried out in 1970 by the University of Rhode Island, USA, on the corrosion of steel and aluminium alloy cylinders [4] demonstrated the effect of oxygen partial pressure on the pit penetration rate in the presence of seawater. The first part of the study was carried out on four alloy steel cylinders (DOT-3AA high pressure type) over a period of one hundred days at a temperature of 40°C. Each cylinder contained 0.5 litre of water. Three cylinders were filled with air to 152 bar and the fourth to 6.9 bar. Two of the high-pressure cylinders were held in the horizontal position.

The findings of the study can be summarised as follows:

- Corrosion is greatly accelerated under increased oxygen partial pressure;
- The corrosion rate is greater with sea water than with fresh water; and
- The water – oxygen gas contact area affects the corrosion rate. The degree of corrosion in the horizontal cylinders was appreciably greater than that in the vertical cylinders, due to the greater interfacial surface area between the water and oxygen.

The data obtained in the above study were plotted in conjunction with data obtained by F. La Que [5] for steels in contact with natural seawater at atmospheric pressure to establish a correlation line, see Appendix 1, which shows the pit penetration rate to be approximately proportional to the square root of the oxygen partial pressure.

Extrapolation of the correlation line indicated that the corrosion rate for a cylinder of oxygen at 172 bar contaminated with seawater could exceed 7 mm per year.

Tests were carried out by UEF Chesterfield (formerly TI Chesterfield Ltd.) on various steels in a 0.05% sodium chloride solution at 30° C in the presence of oxygen at atmospheric pressure and 170 bar. The tests were conducted over a period of fourteen days with partially immersed samples of chromium-molybdenum, manganese and nickel-chromium-molybdenum steels. The pit penetration rates, also shown in Appendix A, were calculated from the 14-day test data assuming a linear pit depth/time relationship.

The relationship may not hold over an extended period of time, but the test results seem to support the findings of the Rhode Island study. There was no evidence of any significant differences in the corrosion resistance of the steels.

This suggests that corrosion rates for low alloy steel oxygen cylinders, such as chromium-molybdenum steels, derived in the manner described above can only be regarded as approximate

since no allowance is made for frequency of filling, temperature, conditions of storage and use and other factors which will significantly influence corrosion rates. Nevertheless, the evidence does indicate that unless preventative measures are undertaken, the presence of seawater in an oxygen cylinder will rapidly deteriorate it to a point where it is no longer safe for use.

4.4 Cylinder pre-fill procedures

Cylinders returned to the filling stations are subjected to a thorough external inspection for general appearance, especially corrosion defects and damage, see EN ISO 24431 *Gas cylinders — Cylinders for compressed and liquefied gases (excluding acetylene)*— Inspection at time of filling, and EN ISO 11372 *Gas cylinders. Acetylene cylinders. Filling conditions and filling inspection* [6,7])

The external inspection cannot provide any information on possible internal contamination, but heavily externally corroded condition can indicate internal corrosion.

Whenever the risk of internal corrosion is present in the cylinder application, such as for cylinders used in marine environment, a residual pressure check should be performed before refilling and also where there is any doubt an additional internal inspection.

The presence of residual pressure is generally considered a satisfactory indication that water ingress is unlikely to have occurred during recent cylinder service.

Some companies follow the practice of tapping each individual cylinder with a hammer or metal bar and judge the condition of the cylinder based on the quality of sound produced. This test can detect heavy generalized corrosion or the presence of large quantities of water, but it will not detect localized corrosion or the presence of small quantities of water.

4.5 Information to users

As described in 4.2, an incorrect handling by the users is frequently the origin of internal contamination and of the consequent corrosion of cylinders used in marine environment.

Repeated information should be sent to customers in the form of letters, bulletins or cylinder applied warning labels, stressing the importance of precautions such as:

- maintaining a residual (positive) gas pressure in the cylinder;
- closing valves on nominally empty cylinder;
- forbidding transfilling operations;
- avoiding immersion of cylinders into water,
- advising not to hide damage to cylinders that could for example have been submerged or damaged, for example by repainting, and;
- storing empty cylinders in dedicated areas with the valves closed.

The practice of requesting users to identify cylinders, which for any reason have been submerged or damaged, has been adopted by some companies with encouraging results.

4.6 Recommendations to prevent internal contamination and corrosion

The recommendations to prevent internal contamination and corrosion include:

- Cylinders used in marine environment should be identified, for example by marking or labelling. These cylinders shall be internally visually inspected before being deployed into marine service;
- Cylinders identified for marine use should be equipped with residual pressure valves (RPV);
- Cylinders not equipped with RPV valves shall be individually checked for residual pressure prior to each refilling;

- Cylinders which are equipped with a RPV valve may be submitted to normal filling provided it is established that the cylinder has been protected for example. by the presence of a residual pressure; and
- Cylinders with no indication of residual pressure should be internally visually inspected or checked for moisture/contamination content prior to refilling.

5 Acetylene cylinders in marine service

5.1 Nature and aspects of the problem

Acetylene is usually supplied in either single cylinders or cylinder bundles fabricated of low alloy steel. The acetylene is dissolved in a solvent, contained within a porous material.

There are two types of porous materials:

- monolithic, for example, calcium silicate based; and
- non-monolithic, for example, granular charcoal based.

Acetylene cylinders in marine service can be subject to rough handling and harsh environmental conditions. Recent findings have shown that the rejection rate during internal examination has revealed a higher value especially due to top clearance than with acetylene in industrial service.

This follows over a year's investigation by EIGA member companies performing an internal examination before each filling.

The main aspects that are considered relevant are summarised below:

- pre-fill checks, see 5.2;
- frequency of periodic inspection, see 5.3;
- procedures for periodic inspection, see 5.4;
- identification of last test / test body, see 5.5; and
- information to owners / users, see 5.6.

5.2 Pre-fill checks

The requirements of EN ISO 11372 [7] shall be met, which include:

- The date of the last test and tester shall be clearly readable;
- Any cylinder due for testing shall not be filled, but submitted to periodic inspection;
- The cylinder shall not exhibit any serious abnormalities such as burns, severe corrosion, heat/fire damage or significant mechanical damage;
- The valve shall be suitable for acetylene and in a satisfactory condition. If the valve is changed any neck/core hole filters and the porous mass shall be inspected for presence of contamination or defects;
- The nature of the porous material and the type of solvent shall be established; and
- Any solvent shortage shall be replenished.

Cylinder owners can request that their authorisation is obtained prior to their cylinders being filled. In this case ownership shall be established and this authorisation obtained before filling the cylinders

5.3 Frequency of periodic inspection

The frequencies of periodic inspection for acetylene cylinders in marine service are recommended as follows:

- The initial periodic inspection shall be performed as described in EN ISO 10462:2013 *Gas cylinders. Acetylene cylinders. Periodic inspection and maintenance* [8]. Subsequent periodic inspection at a maximum period of five years after the last periodic inspection.

An example of the test programme is shown in Figure 1

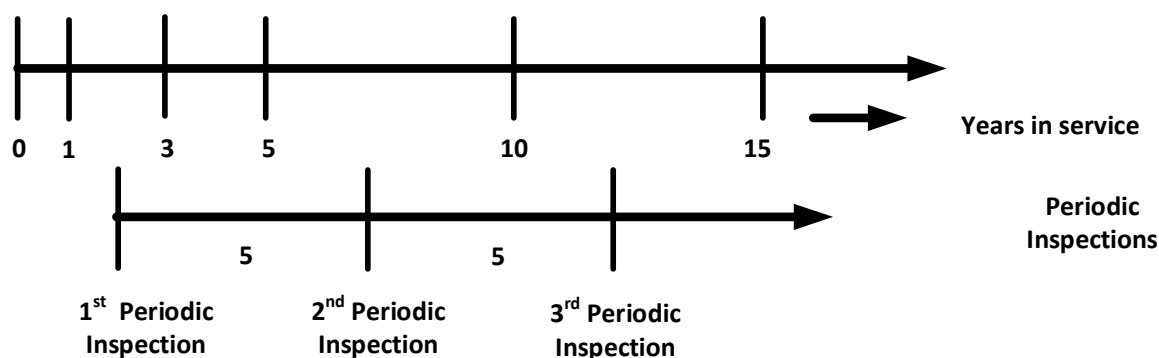


Figure 1 Example of acetylene cylinder test programme

5.4 Procedures for periodic inspection

The procedures to be used are those laid down in EN ISO 12863 [8]. The top clearance shall not exceed what is specified in EN ISO 12863 [8].

5.5 Identification of last test

In addition to any regulatory requirements for stamp marking cylinders, a clear and durable identification shall be attached to the cylinder. This shall include the date of the last test and the test body. The latter can, for example, take the form of a plastic or metallic ring fitted between the valve stem and cylinder neck. Only one test-ring shall be present. Any previous ring shall be removed and replaced by the new ring denoting that a new inspection has been successfully performed.

This approach has an additional benefit of being able to indicate that the valve has been removed in order to perform an internal inspection.

5.6 Information to owners/users

As described in 5.1 an incorrect handling by users is frequently the origin of internal contamination and the subsequent corrosion or mass damage of acetylene cylinders used in the marine environment.

Repeated information should be sent to customers in the form of letters, bulletins of cylinders applied warning labels, stressing the importance of precautions such as:

- avoiding impacts which could damage either the shell and/or porous material;
- closing valves on empty cylinders;
- maintaining the residual pressure within the cylinder;

- forbidding transfilling of cylinders;
- avoiding immersion in water;
- advising not to hide damage to cylinders that could for example have been submerged or damaged, for example by repainting; and
- storing empty cylinders in dedicated areas with the valves closed.

6 References

- [1] EIGA-IGC/TN 32/82: *Detection and Prevention of Internal Corrosion of Oxygen Cylinders in Off-Shore Service* (now withdrawn); www.eiga.eu
- [2] ADR, *European Agreement on the Carriage of Dangerous Goods by Road* www.unece.org
- [3] Herbert H. Uhlig: "Corrosion and Corrosion Control"; John Wiley & Sons, Inc.
- [4] F. C. Cichy, H. Schenck and J. J. McAniff: "Corrosion of Steel and Aluminium Scuba Tanks"; University of Rhode Island, Marine Technical Report 62.
- [5] Herbert H. Uhlig: "Corrosion Handbook"; John Wiley & Sons, Inc. Pages 383 – 388
- [6] EN ISO 24431 *Gas cylinders — Cylinders for compressed and liquefied gases (excluding acetylene)— Inspection at time of filling*; www.cen.eu
- [7] EN ISO 11372 *Gas cylinders - Acetylene cylinders - Filling conditions and filling inspection* www.cen.eu
- [8] EN ISO 10462:2013 *Gas cylinders. Acetylene cylinders. Periodic inspection and maintenance* www.eiga.eu

Appendix 1

FIGURE 1
PITTING OF CARBON AND LOW ALLOY STEELS
IN SEA WATER AGAINST OXYGEN PARTIAL PRESSURE

