SAFE USE OF GAS CYLINDERS
IN MARINE SERVICE

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KEYWORDS

- CYLINDER

- CORROSION

- SAFETY

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1   Introduction

The number of industrial gas cylinders which are used on off-shore oil production rigs, on board ships, in shipyards, in fish farms, in diving application etc., under conditions which may expose them to the risk of rough handling and internal contamination, e.g. by sea water, has considerably increased over the past few decades.

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

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

In addition severe internal corrosion has been detected during routine inspections and periodic testing operations.

Recent investigations have revealed a higher occurrence of damage to porous masses of acetylene cylinders in marine service than in industrial use.

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

IGC Technical Note 32/82 (6) first examined the problem and provided recommendations to prevent and detect internal corrosion of oxygen cylinders in marine service.

The present Document covers only the additional aspects believed to be specific to the issues herein. All normal inspection and prefill checks shall also be performed as necessary.

By applying the recommendations of this Document the integrity of gas cylinders in marine service will improve and thereby considerably reduce safety concerns.

This Document has been written in the light of the additional information collected by EIGA/AIGA companies and supersedes TN 32/82.

2   Scope

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

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

3   Oxygen cylinders in marine service

3.1   Nature and aspects of the problem

Oxygen is usually supplied in either single cylinders or cylinder bundles fabricated of alloy steel to standard specifications.

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

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

Hence the main aspects, which are considered relevant, can be summarized as follows:
• Risk of ingress of sea water into oxygen cylinders (s. 3.2)

- Internal corrosion of steel cylinders in the presence of oxygen and sea water (s. 3.3)
- Possible inadequacy of conventional prefill inspections (s. 3.4)
- Possible lack of knowledge and appreciation by the users with regard to cylinder handling (s. 3.5)
- Recommendations to prevent internal contamination or corrosion (s. 3.6).

3.2   Ingress of sea water into oxygen cylinders

Cylinders and cylinders bundles in marine use are subjected to rough handling and harsh environmental conditions not usually encountered.

In addition cylinder valves are frequently left in the open position after the contents of the cylinders are exhausted.

A survey carried out by EIGA/AIGA member companies revealed that 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 may occur in one or more of the following ways:

a) Exposure to sea water on the decks of supply boats;
b) Rough handling and carelessness resulting in cylinders being dropped or left in flooded areas;
c) Flooding of dry docks prior to launching of rigs or ships;
d) Deliberate or accidental submerging of cylinders in the sea;
e) Temperature fluctuations giving rise to possible condensation of moisture from the atmosphere.

3.3   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 (1).

A study carried out in 1970 by the University of Rhode Islands, USA, on the corrosion of steel and aluminium alloy cylinders (2) 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:

a) Corrosion is greatly accelerated under increased oxygen partial pressure;
b) The corrosion rate is greater with sea water than with fresh water;
c) 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 (4) for steels in contact with natural seawater at atmospheric pressure to establish a correlation line (Fig. 1 in 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% NaCl 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 Fig. 1 (Appendix 1), 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 as summarised in (a) and (b) above. There was no evidence of any significant differences in the corrosion resistance of the steels.

Clearly, corrosion rates for alloy steel oxygen cylinders 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.

3.4   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 ref. 7, EN 1919 and EN 1920)

The external inspection cannot provide any information on possible internal contamination, but heavily externally corroded condition may 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 in 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 may 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.

3.5   Information to users

As mentioned in paragraph 3.2 above, 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 gas pressure in the cylinder
• Closing valves on nominally empty cylinder
• Forbidding transfilling operations
• Avoiding immersion of cylinders into water

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.

3.6   Recommendations to prevent internal contamination and corrosion

The recommendations are:

• Cylinders used in marine environment should be clearly identified, e.g. by marking or labelling. Such cylinders shall be internally visually inspected before dedication into marine service.

- Cylinders identified for marine use should be preferably equipped with residual pressure valves incorporating a non-return device (RP/NR valve).
- Cylinders not equipped with residual pressure valve shall be individually checked for residual pressure prior to each refilling.
- Cylinders which have a residual pressure or are equipped with a RP/NR valve can be submitted to normal filling provided it is established, e.g. by presence of a residual pressure, that the valve device is working properly.
- Cylinders with no indication of residual pressure should be internally visually inspected of checked for moisture content prior to refilling.
- Written information in the form of leaflets, bulletins or labels applied to cylinders should be provided to users to advise them of the potential hazards of sea water contamination and of the basic precautions which should be observed (s. 3.5).

4   Acetylene cylinders in marine service

4.1   Nature and aspects of the problem

Acetylene is usually supplied in either single cylinders of cylinder bundles fabricated of alloy steel to standard specifications. The acetylene is normally dissolved in a solvent, contained within a porous mass.

There are essentially two types of porous masses:

a) Monolithic e.g. calcium silicate based;
b) Non-monolithic e.g. charcoal based.

Acetylene cylinders in marine service are 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/AIGA member companies performing an internal examination before each filling.

The main aspects that are considered relevant can be summarised below:

- Stringent pre-fill checks (s. 4.2)
- Frequency of periodic inspection (s. 4.3)
- Procedures for periodic inspection (s. 4.4)
- Identification of last test / test body (s. 4.5)
- Information to owners / users (s. 4.6).

4.2   Stringent pre-fill checks

The requirements of EN 12754 "Cylinders for Dissolved Acetylene-Inspection at Time of Filling" shall be met, in particular:

- The identity of the owner shall be established and his authorisation to fill the cylinder obtained.
- 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 mass and the type of solvent shall be established.
- Any solvent shortage shall be replenished.

4.3 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 soon as possible after the end of the first year in service and not later than three years after the cylinder has first been placed in service.
- Subsequent periodic inspection at a maximum period of five years after the last periodic inspection.

An example of the test programme may be as shown in Fig. 3 of Appendix B.

4.4 Procedures for periodic inspection

The procedures to be used are those laid down in EN 12863, "Periodic Inspection and Maintenance of Dissolved Acetylene Cylinders (7)". The top clearance shall not exceed 5 mm except if a lower value is recommended by the manufacturer of the porous mass (see Fig. 2 of Appendix B).

4.5 Identification of last test

In addition to any statutory requirements for stamp marking cylinders a clear and durable identification shall be attached to the cylinder. This should include the date of the last test and the test body. The latter may for example take the form of a plastic or metallic ring fitted between the valve stem and cylinder neck. Only one such 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.

4.6 Information to owners/users

As mentioned in paragraph 4.1 above 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 may damage either the shell and/or porous mass;
- Closing valves on empty cylinders;
- Maintaining the residual pressure within the cylinder;
- Forbidding transfilling of cylinders;
- Avoiding immersion in water;
- Forbidding hiding damage to cylinders that may for example have been submerged or damaged, e.g. by repainting.

5 Reference

(1) Herbert H. Uhlig: "Corrosion and Corrosion Control; John Wiley & Sons, Inc.

(2) F. C. Cichy, H. Schenck and J. J. McAniff: "Corrosion of Steel and Aluminium Scuba Tanks"; University of Rhode Island, Marine Technical Report 62.

(3) Compressed Gas Association, Inc., New York: "Rupture of Oxygen Cylinders in the Diving Industry"; Safety Bulletin SB-7, 1980.

(4) Herbert H. Uhlig: "Corrosion Handbook"; John Wiley & Sons, Inc. Pages 383 – 388.

(5) Garry N. Kirby: Corrosion Performance of Carbon Steel". Chemical Engineering 12 March 1979, Pages 72 – 84.

(6) EIGA-IGC/TN 32/82: "Detection and Prevention of Internal Corrosion of Oxygen Cylinders in Off-Shore Service" (now withdrawn).

(7) CEN-Standards for Transportable Gas Cylinders:

- EN 1919 "Cylinders for Liquefied Gases (excluding Acetylene) – Inspection at Time of Filling"

- EN 1920 "Cylinders for Compressed Gases – Inspection at Time of Filling"

- EN 12754 "Cylinders for Dissolved Acetylene – Inspection at Time of Filling"

- EN 12863 "Periodic Inspection and Maintenance of Dissolved Acetylene Cylinders".

Appendix A

FIGURE 1

PITTING OF CARBON AND LOW ALLOY STEELS
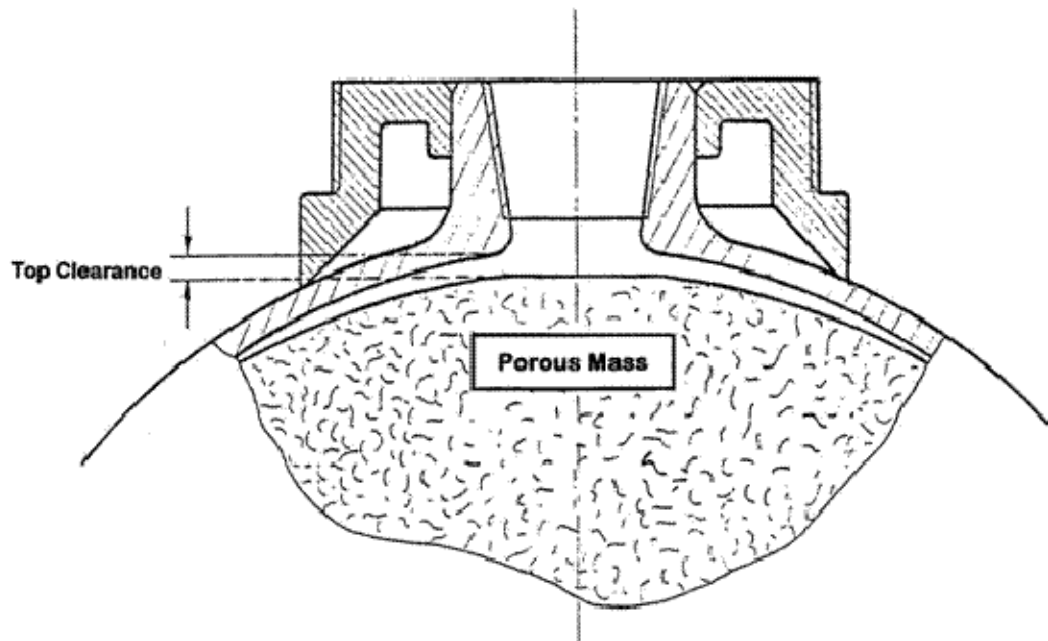IN SEA WATER AGAINST OXYGEN PARTIAL PRESSURE
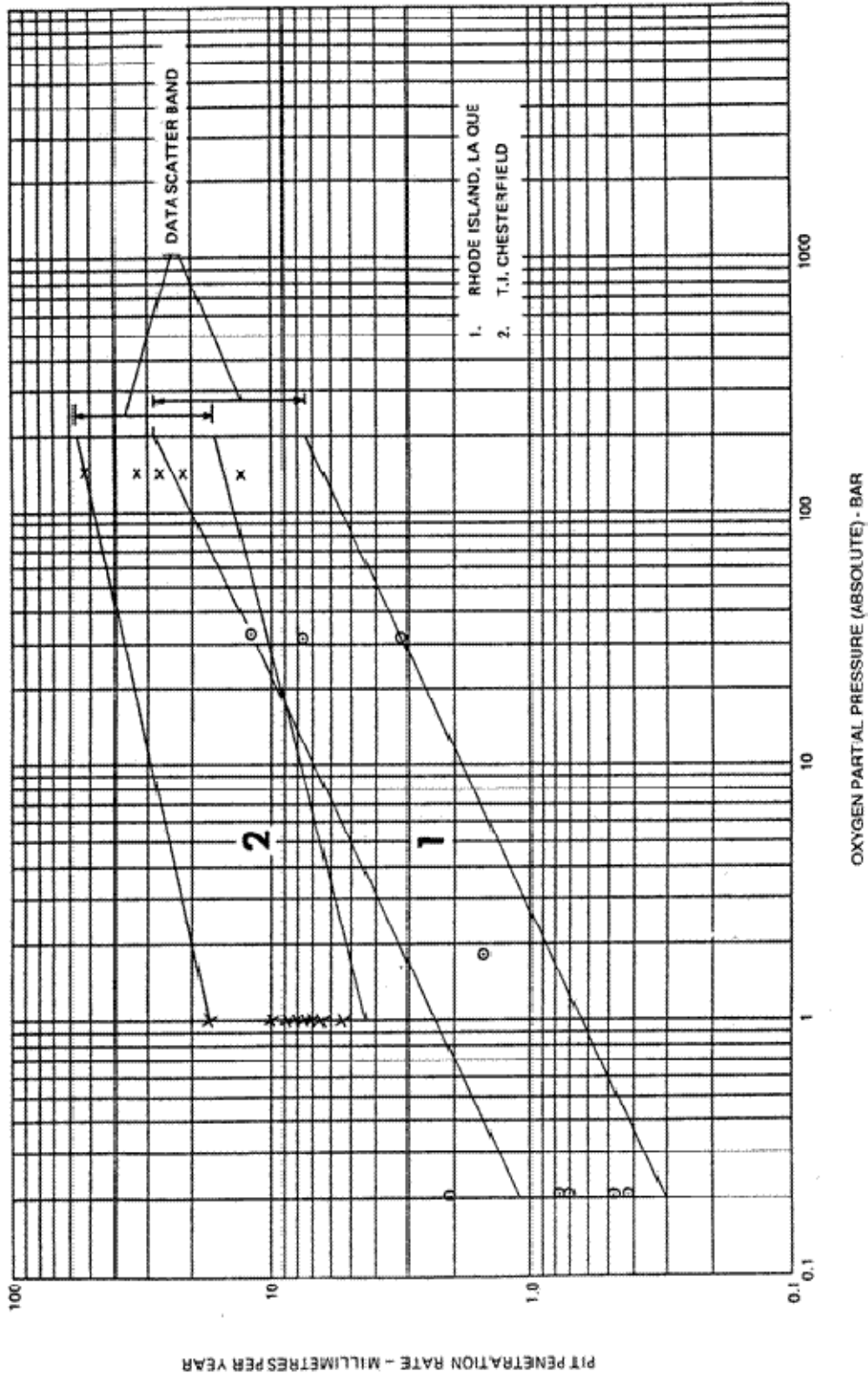
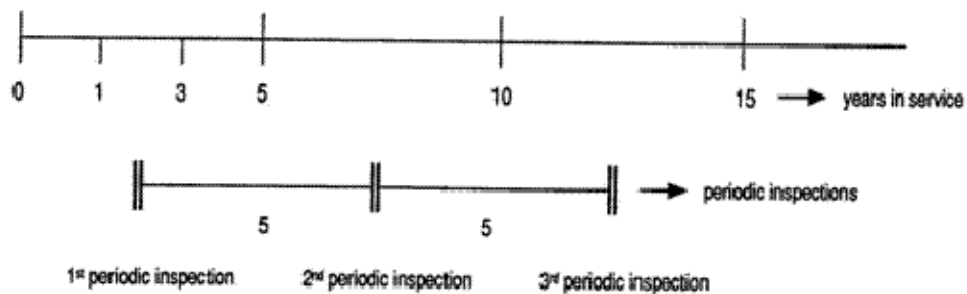# Appendix B

Figure 2   TOP CLEARANCE OF THE MONOLITHIC MASS
OF AN ACETYLENE CYLINDER

Figure 3   FREQUENCY OF PERIODIC INSPECTION