METHODS TO AVOID AND DETECT INTERNAL GAS CYLINDER CORROSION

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1 Introduction

There are a number of reasons for a cylinder to fail while in service such as from abuse, misuse, manufacturing flaws, and internal corrosion. A number of gases can react with moisture to produce corrosive media that possibly could react with the cylinder material and lead to a cylinder failure. The number of incidents resulting from internal corrosion is relatively small compared to the number of cylinders in service because the industry follows procedures to reduce moisture in cylinders.

2 Scope and purpose

This publication provides guidance to help prevent and detect internal corrosion of compressed gas cylinders. It applies to gas cylinders and bundles, including cylinder installations at customer sites.
Its main emphasis is for steel cylinders containing oxygen/oxygen mixtures and carbon dioxide/carbon dioxide mixtures in the presence of moisture. Certain aspects of this document can also apply to other corrosive gases e.g., hydrogen chloride.

3 Definitions

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

3.1 Corrosion

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

3.2 Corrosive gas

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

3.3 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).

4 Bibliography

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5 Corrosion

There are mainly two mechanisms that promote corrosion. These are:

a) Acidic corrosion, possibly caused by gases such as carbon dioxide and sulphur dioxide, which form acids when combined with water. Visual indications include area corrosion, line corrosion, or pitting corrosion in local areas; and

b) Oxidizing gas corrosion, which may be caused by gases such as oxygen when combined with water. This corrosion is generally widespread over the internal surface of the cylinder.

6 Sources of moisture contamination

Free moisture contamination can occur from several different sources, i.e., manufacture, filling, use, valving, storage, and maintenance. Water from manufacturer's hydraulic test
As part of a cylinder's acceptance procedure, a mandatory hydraulic test is performed. It is absolutely essential that subsequent emptying and drying of the cylinder is undertaken, such that there is no free moisture left in the cylinder. Once achieved, it is essential that this internal condition is maintained (see also 6.5).

6.1 Water from product / filling operation

It is possible to fill cylinders with products containing moisture. Additionally, some filling operations may introduce moisture into cylinders, e.g., if water lubricated compressors or water-ring vacuum pumps are used, without adequate precautions to prevent water carry over.

6.2 Water feedback during use

Aqueous feedback into cylinders may occur whenever the cylinder is at a lower pressure than the application (involving a fluid) to which it is connected.

6.3 Water ingress

6.3.1 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.

6.3.2 Water immersion

When cylinders are immersed in water (e.g., seawater, freshwater, etc.) and when the external pressure exceeds the internal pressure of the compressed gas, there is a chance that the aqueous material will enter the cylinder and contribute to corrosion. Some users such as fish farms, shipyards, etc., immerse cylinders either during or after use. If the valve is not shut tightly, then water will enter the cylinder, once the cylinder is empty.

Suppliers and users should take proper precautions and give special attention to cylinders in these applications.

6.3.3 Atmospheric humidity

Cylinders stored with their valves open or devalved cylinders that are inadequately protected against moisture ingress will "breathe". This involves the possible condensation of moisture from the atmosphere into the cylinder when the temperature drops, e.g. at night. This moisture will result in internal contamination following several such "air ingress cycles," though this will rarely result in a large quantity of water.

6.4 Water from periodic inspection of cylinders

As part of the periodic inspection and test, cylinders are usually hydraulically tested, (unless a suitable alternative is permitted). It is absolutely essential that subsequent emptying and drying of the cylinder is undertaken, such that there is no free moisture left in the cylinder. Once achieved, it is essential that this internal condition 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 used moist, hot gas.

7 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.

7.1 Material selection and cylinder design

7.1.1 Material selection

Aluminium Alloys:

Aluminium alloy cylinders are widely used in the gas industry. Their high corrosion resistance makes them suitable for carbon dioxide and its mixtures and for oxygen and its mixtures, even in the presence of water. However, care shall be taken to minimize ingress of fluids into the cylinder when in the presence of certain contaminants e.g. chlorides, soft drink syrups, as it must not be assumed that the alloy will protect entirely against all corrosion mechanisms.

Carbon Steels and Low Alloy Steels:

Cylinders made from low alloy or carbon steels are very widely used for carbon dioxide and its mixtures and for oxygen and its mixtures. In the presence of water, internal corrosion will occur and the rate of 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. However, due to the very high cost, their use is limited to very special applications, e.g., ultra high purity gases. They are very sensitive to chloride contamination, and care shall be taken, e.g., with the water quality for any marine applications and the hydraulic test to ensure chloride levels are compatible with grade of stainless steel used.

Internal Coating and Surface Treatments:

Some cylinders, particularly those used in the diving industry, have been internally coated/treated.

Whilst the experience with internal coatings, e.g., plastic linings, has not been entirely satisfactory, encouraging results have been obtained for internal surface treatments, e.g., phosphate treatment.

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 may 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 test pressure.

7.1.2 Cylinder design

Corrosion Allowance:

Cylinder specifications such as ISO 9809 do not contain a corrosion allowance, unlike some stationary pressure vessel codes. For steel cylinders, because of the potentially high corrosion rates, a normal corrosion allowance of approximately 1 mm to 2 mm is of little benefit to extend the cylinder's life and consequently is not recommended by the industry.

Good Design in Welded Cylinders:

For some gas applications welded cylinders are used. Welded cylinders should be designed and manufactured in such a way that joggle joints do not retain water.

7.2 Avoidance of water ingress

7.2.1 Single cylinders

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

- closing the valve at the valve manufacturer's recommended torques;
- returning the cylinder with residual gas pressure to the filler;
- using a residual pressure valve that retains a residual positive gas pressure inside the cylinder; and
- using a non-return valve that is designed to prevent back flow from a process.

7.2.2 Bundle design

Bundles shall have at least one main valve even if individual cylinders are valved. For protecting the bundle from water ingress, follow the methods listed in 7.2.1 for the main valve of the bundle.

7.2.3 Customer installation

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

7.2.4 Filling operation

Preventing moisture ingress into cylinders at the filling operation can be prevented by using equipment that is not water sealed or water lubricated.

7.3 Moisture detection methods

Water and liquids are the main reasons for corrosion. The aim of this clause is to indicate the methods available to detect the presence of water or the possibility of condensation of moisture.

7.3.1 Residual pressure check

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

Cylinders/bundles found with no residual pressure and when the previous service is not known should be submitted to special prefill procedures, e.g., weight check, internal visual inspection moisture check, evacuation, drying, etc.

7.3.2 Weight check

If a significant amount of water is present, this can be detected by a cylinder weight check. This method is mainly used for liquefied gases, e.g., 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 as above also apply to the cylinder bundles.

7.3.3 Internal visual inspection

This inspection is normally performed during periodic inspection of gas cylinders and recommended whenever the valve is removed from the cylinder.

7.3.4 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 whether or not free water is present in the cylinder, but they can be used for this purpose if an adequate procedure is followed. The difficulties to overcome are:

- Measurements at high pressures are possible though the obtained data are unreliable;
- Aqueous liquid/vapour equilibrium in the cylinder may 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 may 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 may affect the moisture analysis or even destroy the instrument.

7.3.5 Cylinder evacuation

The evacuation of single cylinders, pallets or bundles 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.

7.3.6 Cylinder inversion

By inverting a cylinder not equipped with a dip tube, it is possible to detect free water. This approach will not detect small quantities of water. Additionally, the method is not always convenient for "large" cylinders.

7.4 Corrosion detection methods

Though several corrosion detection methods are available, such as Ultrasonic Test (UT), Acoustic Emission Test (AET), internal visual inspection (see 7.3.3), tare weight checks, hammer test, etc, none of them is entirely satisfactory for cylinder filling applications.

UT and AET are sophisticated methods involving expensive and time consuming procedures, and are applicable only to single cylinders.

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 "in line" prefill inspection, but is normally used when other methods indicate suspicion of corrosion.

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

7.5 Special recommendations for some types of applications

For high strength steels with tensile strengths greater than 1100 MPa used primarily for 300 bar charging pressure cylinders, special care shall be taken to avoid the ingress of water (see 7.2).

When the presence of moisture is suspected, moisture content in the gas should be analyzed by using one of the methods described in 7.3.

8 Guidance for moisture acceptance levels

In cylinders for carbon monoxide and carbon monoxide/carbon dioxide mixtures, the water vapor content shall not exceed a value between 5 or 7 ppm, for 200 bar or 150 bar cylinders respectively.

Higher values for the water vapor content are acceptable for other gases and mixtures covered in this document. However, due to numerous parameters which need to be considered it is not possible to quote specific values. The guiding principle should be that any reasonably measurable moisture level above the low ppm level should not be considered entirely safe.

9 Conclusion

There are different ways to avoid and detect internal gas cylinder corrosion:

- A residual pressure valve (RPV) including a non-return function may be attached to the cylinder in use. This applies to new cylinders, existing cylinders at time of retest, or at any opportunity a cylinder valve is changed, e.g., because of valve damage. Before fitting the RPV, ensure that the cylinder is completely dry; and
- The following checks may be performed prior to filling a steel cylinder containing carbon dioxide or carbon dioxide mixtures not previously fitted with an RPV and which may be contaminated with liquid:
    - tare weight (for pure carbon dioxide cylinders only)
    - cylinder inversion (larger cylinders will require special equipment)
    - moisture analysis
    - residual pressure (cylinders with a residual pressure may be considered uncontaminated).