GUIDANCE NOTE 6

AVOIDANCE AND DETECTION OF INTERNAL CORROSION OF GAS CYLINDERS

REVISION 2: 2015

British Compressed Gases Association

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PREFACE

The British Compressed Gases Association (BCGA) was established in l971, formed out of the British Acetylene Association, which existed since l901. BCGA members include gas producers, suppliers of gas handling equipment and users operating in the compressed gas field.

The main objectives of the Association are to further technology, to enhance safe practice, and to prioritise environmental protection in the supply and use of industrial, food and medical gases, and we produce a host of publications to this end. BCGA also provides advice and makes representations on behalf of its Members to regulatory bodies, including the UK Government.

Policy is determined by a Council elected from Member Companies, with detailed technical studies being undertaken by a Technical Committee and its specialist Sub-Committees appointed for this purpose.

BCGA makes strenuous efforts to ensure the accuracy and current relevance of its publications, which are intended for use by technically competent persons. However this does not remove the need for technical and managerial judgement in practical situations. Nor do they confer any immunity or exemption from relevant legal requirements, including by-laws.

For the assistance of users, references are given, either in the text or Appendices, to publications such as British, European and International Standards and Codes of Practice, and current legislation that may be applicable but no representation or warranty can be given that these references are complete or current.

BCGA publications are reviewed, and revised if necessary, at five-yearly intervals, or sooner where the need is recognised. Readers are advised to check the Association's website to ensure that the copy in their possession is the current version.

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* Throughout this publication the numbers in brackets refer to references in Section 10. Documents referenced are the edition current at the time of publication, unless otherwise stated.

TERMINOLOGY AND DEFINITIONS

Corrosion	Corrosion is defined as deterioration of the cylinder material by an electrochemical reaction, when in contact with a corrosive medium, e.g. Carbon Dioxide and water (carbonic acid).
Corrosive gas	Within this document the term ‘corrosive gas’ refers to a gas which is corrosive in the presence of moisture to the cylinder material, and not necessarily to human tissue.
May	Indicates an option available to the user of this Guidance Note.
Shall	Indicates a mandatory requirement for compliance with this Guidance Note and may also indicate a mandatory requirement within UK law.
Should	Indicates a preferred requirement but is not mandatory for compliance with this Guidance Note.

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AVOIDANCE AND DETECTION OF INTERNAL CORROSION OF GAS CYLINDERS

1. INTRODUCTION

Gas cylinders are designed and manufactured for a long service life and have a history of being safe in use. However, there are a number of reasons why a gas cylinder may fail while in service, these can include abuse, misuse, manufacturing flaws, and internal corrosion.

This Guidance Note aims to provide guidance and an overview of the UK gases industry's current practices to prevent and detect internal corrosion of gas cylinders. A number of gases can react with moisture to produce corrosive media that could react with the cylinder material and lead to a cylinder failure.

The number of incidents resulting from internal corrosion is small compared to the number of cylinders in-service because the industry follows procedures to reduce moisture in cylinders and only a handful of cylinders have suffered catastrophic failure in recent years.

Failures caused by internal corrosion are frequently due to contamination of the cylinder by the customer's process. To help stop a gas cylinder failing a variety of methods and techniques to prevent and detect moisture and corrosion are described.

Further information is available within the European Industrial Gases Association (EIGA) Document 62 (4), *Methods to avoid and detect internal gas cylinder corrosion*.

2. SCOPE

This Guidance Note applies to gas cylinders, including those used at installations on customer sites.

The emphasis is for steel cylinders containing oxygen (O_2) or O_2 mixtures, and carbon dioxide (CO_2) or CO_2 mixtures in the presence of moisture. Certain aspects of this Guidance Note may also apply to other corrosive gases, e.g. hydrogen chloride (HCl). Aspects related to over-filling conditions (sometimes found with liquefied gas cylinders) or damage due to exposure to high temperatures are not covered.

Some guidance is also provided for carbon monoxide (CO) / CO_2 mixtures.

3. CORROSION

Corrosion is a complex phenomenon. At ambient temperatures corrosion of steel cylinders can only occur in the presence of an electrolyte (via the flow of an electrical current).

There are three main types of corrosion caused by the gases as defined in the scope of this Guidance Note.

They are:

3.1 Acidic corrosion

Caused by gases such as CO_2, sulphur dioxide (SO_2), etc., which form dilute acids when dissolved in an electrolyte. This type of corrosion results in general corrosion, pitting corrosion and sometimes stress corrosion.

3.2 Oxidising gas corrosion

Caused by gases such as O_2, chlorine (Cl_2), etc., which, when dissolved, form an electrolyte. This type of corrosion results in general and pitting corrosion.

3.3 Stress corrosion

Caused by gases such as CO / CO_2 mixtures which, in the presence of moisture levels greater than 5 parts per million (ppm), in certain steel cylinders will result in embrittlement. Refer to Section 8.

4. SOURCES OF MOISTURE CONTAMINATION

Several sources of free moisture contamination can be found during the life of a cylinder, i.e. use, maintenance and manufacture.

4.1 Water feedback during use

Water / liquid feedback into cylinders may occur whenever the cylinder is at a lower pressure than the application (involving a liquid) to which it is connected, e.g. in the beverage dispense industry it is possible to get feed-back from beer kegs, soft drink concentrate vessels and from pipe cleaning fluids.

4.2 Water ingress

4.2.1 Rainwater

If cylinder valves are left open after use, or if an un-valved cylinder is inadequately protected, rainwater could enter the cylinder.

4.2.2 Water immersion

Though cylinders (except those intended for underwater service) should never be immersed in water, it has been known that some users, e.g. fish farms, shipyards, etc., do not always follow this instruction. Consequently, if the valve is not shut tightly, large quantities of water will enter the cylinder, once the external pressure becomes greater than the internal gas pressure.

4.2.3 Atmospheric humidity

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

NOTE: Not all protective covers provide adequate protection against the ingress of moisture.

4.3 Water from periodic inspection and test 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 shall be carried out. Organisations undertaking hydraulic testing should have a quality assurance system incorporating procedures to ensure cylinders are thoroughly dried and inspected after the hydraulic test.

NOTES:

1. A cylinder warmed or hot from the drying process can condense moisture inside as it cools if the drying process uses moist, hot gas.
2. For composite cylinders with liners from AA6061, refer to EIGA Document 72 (6), *Water corrosion of composites with AA 6061 liners*.

4.4 Water from product or filling operation

Though not a major problem, 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. Refer to Section 5.2.4.

4.5 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 (also refer to Section 4.3).

5. AVOIDANCE OF CYLINDER CORROSION

Cylinders are more likely to be susceptible to failure if there are areas of the external surface that are damaged or corroded. In such cases, internal corrosion can only increase the possibility of failure.

Specifically stamp markings should not be excessively deep and should be carried out using well radiused lettering. Where stamp markings appear to be of excessive depth or made with sharp tools then there should be a close examination of the stamped area for any signs of cracking. Further information is available in BS EN ISO 13769 (3), *Gas cylinders. Stamp markings*.

The correct assembly of a cylinder and its valve is also important. The thread on the valve being compatible with the thread on the cylinder. The fitting of a cylinder valve shall be carried out using the correct tools and torque settings. Frequent, and especially incorrect torque settings, increase wear on the valve threads and can contribute towards stress corrosion cracking in the neck area. For further information refer to BS EN ISO 13341 (2), *Gas cylinders — Fitting of valves to gas cylinders.*

To reduce the incidence of internal cylinder corrosion, several preventative methodologies are used. These are based upon material selection, design criteria, prevention and detection methods. They can be applied as single measures or in combination depending upon the application.

5.1 Material selection and cylinder design

5.1.1 Material selection

Aluminium alloys
Aluminium alloy cylinders are widely used in the gas industry because of their high corrosion resistance to a wide range of gases in the presence of water including O_2 and CO_2. However, care shall be taken to prevent the ingress of fluids into the cylinder as in the presence of certain contaminants, e.g. chlorides and soft drink syrups, it cannot 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 CO_2 and its mixtures and for O_2 and its mixtures. In the presence of water, internal corrosion will occur and the rate of corrosion will depend on the gas, the gas pressure and the amount of water and contaminants present, e.g. under abnormal conditions corrosion rates of about 1 mm per month can be experienced.

Stainless steels
Stainless steel cylinders are corrosion-resistant for a wide variety of products. Mainly due to economic considerations, their use is often limited to very special applications, e.g. ultra high-purity gases. However, they are very sensitive to chloride contamination and care should be taken, e.g. when used in marine applications and with the quality of the water used for the hydraulic test, to ensure that chloride levels are compatible with the grade of stainless steel used.

Internal coating and surface treatments
Some cylinders have been internally coated / treated, particularly those used in the diving industry.

Internal coatings, e.g. plastic linings, have not been entirely satisfactory (and are no longer provided for use with diving cylinders), but encouraging results have been obtained for other internal surface treatments, e.g. nickel plating and phosphating (on steel cylinders).

NOTE: For plastic linings, if there is an inadequate bond between the lining and the cylinder wall, or defects in the lining, e.g. porosity or cracks, this can provide a hidden area where corrosion may occur.

5.1.2 Cylinder design

Corrosion allowance

Cylinder specifications do not normally contain a corrosion allowance, though a very few companies do request an extra wall thickness for special applications. However, in view of potentially high corrosion rates, a normal corrosion allowance of 1 mm to 2 mm is of little benefit to extend the cylinder's life, and is therefore 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 in such a way that the joints do not retain water. An alternative joint type is a butt welded joint.

5.2 Avoidance of water ingress

5.2.1 Single cylinders

For single cylinders, valve design can help to minimise the ingress of water during use. When the cylinder is not being used to supply gas, always close the valve.

A residual pressure valve incorporates a device which retains a residual positive gas pressure inside the cylinder. This positive pressure prevents the possible ingress of external (humid) air into the cylinder.

Non-return valves are designed to prevent backflow from the customer's process into the cylinder, refer to Section 4.

Some valves combine the function of a residual pressure and a non-return valve, thus both of the above advantages are gained.

NOTE: For further information on residual pressure valves refer to EIGA Document 64 (5), *Use of residual pressure valves*.

Operating experience has demonstrated clear benefits from the use of valves of this type, and their use is strongly recommended, especially for cylinders used in gas services where corrosion is likely, such as beverage dispense applications.

5.2.2 Bundle design

Bundles should have at least one main valve, even if individual cylinders each have a valve. The valve outlet should be horizontal or facing down. The exact nature of the valve will be dependent on technical aspects revolving around filling / emptying rates.

In most applications, the incorporation of a residual pressure / non-return valve will reduce the risk of backflow.

When the bundle is not being used to supply gas, always close the main valve.

5.2.3 Customer installation

Customer installations should be equipped with a non-return valve in their process if the possibility of backflow contamination exists. However, it should not be assumed that these alone provide adequate protection. Therefore, special precautions should be taken for those applications where a risk of backflow contamination exists. These can be taken by providing safeguards such as suitable valve design, as outlined in Section 5.2.1.

5.2.4 Filling operation

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

With the modern cylinder filling systems used in the UK, cylinders are filled with moisture-free gases via pumping and subsequent evaporation of cryogenic liquids.

However, filling is also performed by the compression of gases. In these cases, particular attention should be paid to the drying procedure, where water sealed gasometers or water lubricated compressors are used.

One additional potential source of contamination is the use of water ring vacuum pumps for cylinder purging, though risk here is minimised by using adequate engineering design and control procedures.

Once a cylinder has been filled the valve is to be closed. It is recommended that the outlet is sealed, e.g. by the use of plastic plugs or wrapping in tape. The main purpose of the seal is to prevent contamination of the valve outlet, but it will have the secondary benefit of giving the customer confidence that the cylinder is being delivered in a condition where it is ready for use, and will provide evidence that the contents have not been tampered with.

6. DETECTION METHODS

6.1 Moisture detection methods

Water and liquids will create an aqueous environment and their presence is the primary cause of initiating and then continuing a corrosive reaction. This section indicates the methods available to detect the presence of water or the possibility of condensation of moisture.

6.1.1 Residual pressure check

The 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 should be submitted to one or more of the special pre-fill procedures, i.e. weight check, internal visual inspection, moisture check, evacuation, drying, etc.

6.1.2 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, e.g. CO_2, when the tare weight of the empty cylinder is checked.

The sensitivity of this method depends on the water capacity of the cylinder, the accuracy of the scale used and the stamped tare weight. However, cylinder tare weights are normally only specified to 100 grams and it has been shown that as little as 5 grams of water could be enough to destroy a gas cylinder. For a weight check to be effective it has to address these factors and be sensitive enough to register these levels of contamination.

NOTE: According to BS EN 1968 (1), *Transportable gas cylinders. Periodic inspection and testing of seamless steel gas cylinders*, Section 12.3, Table 1, the maximum allowable deviation in cylinder tare weight can vary between 50 - 400 grams.

Similar considerations also apply to cylinder bundles.

NOTE: Weigh scales used for the filling of gas cylinders require to be properly maintained and regularly calibrated.

6.1.3 Internal visual inspection

This inspection is normally performed during the periodic inspection and test of gas cylinders and should also be undertaken whenever the valve is removed, e.g. for repair, for change of gas service, or if exchanging a normal valve for a residual pressure valve.

This method relies on the person carrying out the inspection being capable of detecting small quantities of moisture, and therefore requires the person to have attested eyesight and an effective light source to illuminate the inside of the cylinder.

6.1.4 Moisture meters

Moisture meters are used for the measurement of the moisture content in a gas stream from a cylinder, at very low concentrations.

Moisture meters are not normally designed to determine whether or not free water is present in the cylinder. The difficulties are:

- Measurements at high pressure are possible, but they do not provide reliable results and are therefore not recommended.

- Aqueous liquid / vapour equilibrium takes considerable time to develop a representative moisture concentration in the vapour phase.

- When several cylinders are connected together, the moisture level recorded corresponds to the average level. This may be due to moisture contamination from just a single cylinder.

- Measurement is time consuming, especially when a high level of moisture has saturated the sensor, which then will take time to dry out.

NOTE: As some corrosive gases may affect the moisture analysis or even destroy the measuring instrument, the cylinder should be purged with inert gas to remove the corrosive gas before carrying out the analysis. However, it should be noted that this procedure can result in a lower moisture figure than was actually present.

6.1.5 Cylinder evacuation

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

When a pre-set vacuum is not achievable in a given time, this may be an indication that there is free water in one or more of the connected cylinders.

6.1.6 Installation of a dip tube

A dip tube installed in CO_2 mixture cylinders can indicate small amounts of water in the cylinders, provided the end is close to the bottom of the cylinder and there is residual pressure left to perform a controlled blow-off before refilling.

6.1.7 Cylinder inversion

By inverting a cylinder it is possible to detect free water. This approach will not detect small quantities of water. However, the method is not always practicable e.g. for large cylinders, and is not an option if a dip tube is fitted.

6.2 Corrosion detection methods

Though several corrosion detection methods are available, such as ultrasonic test (UT), acoustic emission test (AET), internal visual inspection, tare weight checks, hammer test, etc., none of them is entirely satisfactory for cylinder filling applications.

UT and AET are sophisticated methods involving relatively expensive and time-consuming procedures and are applicable only to single cylinders. For this reason their use is generally restricted to periodic inspection and test as an alternative, or as a supplement, to the hydraulic test.

Internal examination is not practicable as an ‘in-line’ pre-fill inspection, but is normally used when other methods indicate suspicion of corrosion. Refer to Section 6.1.3.

Weight checks (refer to Section 6.1.2) and the hammer test are relatively simple and inexpensive methods for detecting extremely heavy generalised corrosion, but they will not detect localised corrosion such as line, pit or crevice corrosion.

7. SPECIAL RECOMMENDATIONS FOR SOME TYPES OF APPLICATIONS

For high strength steels with tensile strength (Rm) $\geq$1100 N/mm^2 special care should be taken to avoid the ingress of water (refer to Section 5.2). This requirement reflects the higher corrosion rates sometimes experienced with such steels.

When the presence of moisture is suspected, the moisture content in the gas should be analysed by using one of the methods described in Section 6.1.

8. GUIDANCE FOR MOISTURE ACCEPTANCE LEVELS

Due to the risk of stress corrosion cracking in steel cylinders containing CO and CO / CO_2 mixtures only very low levels of moisture contamination are acceptable. The water vapour content should not exceed a value above 5 ppm by volume.

NOTE: Additional information is available in EIGA Document 95 (7), *Avoidance of failure of CO and CO / CO2 mixtures cylinders*.

A higher level of water vapour may be acceptable for other gases or mixtures, but each gas or mixture should be considered on its own merits with due regard given to the possible effects on the material used in the construction of the cylinder. The guiding principle should be that the higher the moisture content, the more likely it is that corrosion will occur.

9. ACTION ON FINDING CORROSION

Where contamination is found then the cylinder should be assessed by a gas cylinder Inspection Body, authorised by the UK Competent Authority. Inspection Bodies should closely examine the cylinder and initially reject the cylinder if any corrosion can be seen.

NOTE: Inspection Bodies can outsource specific inspection techniques, e.g. the use of UT, but will still retain overall responsibility for assessing the condition of a cylinder.

Cylinders initially rejected on visual examination can be returned to service if the Inspection Body can demonstrate that the corrosion seen is within the limits set by the rejection criteria detailed in standards, such as BS EN 1968 (1), and appropriate action is taken to stop and prevent further corrosion occurring.

NOTE: Where corrosion has occurred and after appropriate action has been taken to stop and prevent further corrosion occurring, then a check should be carried out to determine if the wall thickness remains within allowable limits.

Gas cylinders which are rejected as no longer fit for continued service are to be rendered unserviceable by the methods detailed in standards, such as BS EN 1968 (1).

10. REFERENCES

	Document Number	Title
1.	BS EN 1968	Transportable gas cylinders. Periodic inspection and testing of seamless steel gas cylinders.
2.	BS EN ISO 13341	Gas cylinders. Fitting of valves to gas cylinders.
3.	BS EN ISO 13769	Gas cylinders. Stamp markings.
4.	EIGA IGC Document 62	Methods to avoid and detect internal gas cylinder corrosion.
5.	EIGA IGC Document 64	Use of residual pressure valves.
6.	EIGA IGC Document 72	Water corrosion of composites with AA 6061 liners.
7.	EIGA IGC Document 95	Avoidance of failure of CO and CO / CO2 mixtures cylinders.

Further information can be obtained from:

Health and Safety Executive	www.hse.gov.uk
British Standards Institute (BSI)	www.bsigroup.co.uk
European Industrial Gases Association (EIGA)	www.eiga.eu
British Compressed Gases Association (BCGA)	www.bcga.co.uk

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