300 BAR HIGH STRENGTH SEAMLESS STEEL GAS CYLINDERS

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Amendments from 124/11

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	Editorial to align with EIGA Style Manual
3	New Section, Definitions
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9	Reference section added and references updated.
Appendix A	Redrawn

Note: Technical changes from the previous edition are underlined

1 Introduction

For more than one hundred years, the seamless steel cylinders used for the supply of industrial gases has proved to be invaluable to the gas industry. During this time, a high level of safety has been achieved. At the same time, there has been continuous technical improvements with respect to the cylinder's gas capacity, weight and filling pressure.

The further development of high strength steels (ultimate tensile strength (UTS) > 1100 MPa) along with improved toughness of the steel has allowed a technological step forward with the increase in the operating pressure of the steel cylinder from 200 bar, to pressures of 300 bar and higher. The advantage is a higher gas/cylinder weight ratio.

It is of prime importance that these cylinders have at least the equivalent level of safety as traditional cylinders. The design requirements are defined in EN ISO 9809-2, *Gas cylinders. Refillable seamless steel gas cylinders. Design, construction and testing. Quenched and tempered steel cylinders with tensile strength greater than or equal to 1100* MPa [1][1].

NOTE For hydrogen 300bar cylinders the design requirements are covered by EN ISO 9809-, *Gas cylinders -- Refillable seamless steel gas cylinders -- Design, construction and testing -- Part 1: Quenched and tempered steel cylinders with tensile strength less than 1 100 MPa* due to the tensile strength limitation [2].

2 Scope and purpose

This publication highlights safety aspects for high strength 300 bar seamless steel gas cylinders with respect to existing standards and regulations or those in preparation, and to give recommendations for their continued safe operation.

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.

4 Development of cylinder steels

Since the first high-pressure gas cylinders were manufactured around the beginning of the twentieth century, various types of steels have been used. Initially carbon steels and low-carbon steels were the

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

common materials. The properties of these types of steels are achieved via a normalising heat treatment.

With working pressures, typically between 100 bar and 150 bar the weight of such an early industrial 40l cylinder, having a nominal gas capacity of 6 m^3 and a wall thickness of approximately 7.5 mm, was more than 70 kg.

Further progress towards thinner, lighter and more efficient cylinders was achieved mainly by the use of steels of increased yield and tensile strengths. Yield strength is the basic value used in the design of gas cylinders and it thus determines the final weight of the cylinder. A typical value of yield strength for such steels is 350 MPa.

Around 1935 carbon-manganese steel was introduced. The yield strength increased slightly to about 400 MPa.

An important technical improvement was the introduction of quenched and tempered chromium-molybdenum steels which was generally accepted from 1960 onwards. In Europe, this led to an almost doubling of the yield strength from 400 MPa to 755 MPa. This change in steel properties permitted an increase of cylinder working pressure from typically 137 bar to 200 bar resulting in an increase in the gas capacity, with a lower cylinder weight.

Since then 200 bar has been the standard cylinder working pressure in most European countries.

The weight of a typical 50 l, 200 bar industrial gas cylinder with a nominal gas capacity of 10 m^3 is about 60-65 kg.

The yield strength of “normal strength” chromium-molybdenum steel has since been further increased from 755 to 850 MPa which is a figure approved and used in many countries.

Since the 1990s, cylinder manufacturers have offered cylinders made from so called “high strength steels” with yield strength of around 1000 MPa with resulting in an increase of gas content to weight ratio and enabling an increase in filling pressure to 300bar without an excessive increase in weight.

The mass of a 300 bar working pressure, 50 l industrial gas cylinder is around 75 kg when designed to Council Directive 84/525/EEC *of 17 September 1984 on the approximation of the laws of the Member States relating to seamless, steel gas cylinders* [3]. With EN ISO 9809-2 the mass of a 50l is now approximately 65 kg [1].

5 Existing experiences with 300 bar cylinders

5.1 Cylinders made from normal strength steels

300 bar cylinders have long been available for special applications, however, when made from the same material as 200 bar cylinders. They were very inconvenient because of their weight, for example an empty 50 l cylinder with a nominal gas capacity of 15 m^3 weighs approximately 94 kg. Therefore, their wide-scale adoption was not attractive. These cylinders have been used for air, nitrogen, argon and occasionally for oxygen. They are still used for hydrogen, because of the need to use limited strength steel. (UTS < 950MPa).

5.2 Cylinders made from high strength steels

There is considerable experience in using high strength steel for industrial gas cylinders. They are mainly used for permanent gases excluding hydrogen. For the approval of cylinders using this high strength steel, additional prototype tests such as the flawed fatigue, impact test and burst testing have been developed and are required in standards such as EN ISO 9809-2 [1].

This high strength steel is also being used for lower pressure e.g. 200bar cylinders to reduce weight.

6 300 bar high strength cylinders

6.1 Critical material properties, standardisation and testing of high strength steel cylinders

The primary aim of introducing a 300 bar high strength cylinder was its reduced weight compared to those in section 3, and thus its higher technical efficiency, i.e. its content/weight ratio. However, the overall objective for design and materials properties of any gas cylinder is for it to be safe under all expected service conditions. This especially applies to those at 300 bar, as they contain approximately 50% greater stored energy.

The ability of a gas cylinder to absorb impact/shock conditions whilst in service under high strain rates or low temperature conditions is of paramount importance. It is essential that if (for whatever reason) the cylinder ruptures, it should behave in a ductile manner adhering to the traditional “leak-before-burst” philosophy.

High efficiency cylinders require stronger materials and this means increasing their yield strength. However, increased yield strength normally means that greater attention should be paid to:

- toughness;
- ductility;
- resistance to fatigue; and
- corrosion resistance.

To obtain an optimum balance between these factors requires refinement in material quality, production methods and quality control. The extra requirements placed on these new steels with a tensile strength above 1100 MPa have been intensively discussed within the cylinder design committees of ISO TC58.

6.1.1 Fundamental design

For the basic design of high strength cylinders, the Lamé Von-Mises formula has been widely accepted, see EN ISO 9809-2 [1].

This formula most accurately describes the behaviour of a gas cylinder under pressure. It is based on very thorough experimental work coupled with several decades of safe user-related experience.

6.1.2 Metallurgical considerations

The toughness requirements, at the higher strength levels, can be achieved by either modifying the chemistry of the current chromium-molybdenum type family of steels, the heat treatment cycle or possibly both. A number of steels with differing chemistry are being used for high strength steel cylinders.

The chemistry changes are aimed at either improving the inclusion morphology within the steel or increasing the strength of the matrix, and sometimes both. Cylinder manufacturers have adopted different heat treatment schedules which result in a range of mechanical properties.

The sensitivity of high-strength cylinders’ behaviour under fatigue conditions increases with an increase in the size of defect retained in a cylinder after manufacture. Hence non-destructive testing of such cylinders shall be included in any design and production recommendations.

6.1.3 Tests during manufacture

EN ISO 9809-2 [1] includes an ultrasonic examination of such cylinders at time of manufacture.

The appropriate test(s) to establish an acceptable level of safety, the relevant point(s) in the production process at which they should be carried out and the number of cylinders to be tested all need to be considered. In particular, transverse Charpy impact data are required, as well as burst/fatigue values for the cylinder, not only in its "as new" condition, but also in the presence of controlled flaw geometries.

6.1.4 Periodic inspection and test

For the periodic inspection and test there are no additional requirements compared to cylinders made from normal steels, provided that the flawed fatigue test results at the cylinder prototype stage are acceptable. The retest requirements are detailed in EN 1968 *Transportable gas cylinders. Periodic inspection and testing of seamless steel gas cylinders* [4].

6.2 Cylinder sizes – ergonomic/ weight aspects

By increasing the filling pressure from 200 to 300 bar, the contents of the cylinder increases by about 35 to 45% depending on the compressibility factor of the gas concerned. Consequently, the efficiency (gas weight / cylinder empty weight plus gas weight) of the cylinder will have no significant increase, if the same type of steel is used. However, by using high strength steels (UTS 1100 MPa) instead of normal steel, which result in an increase of yield strength of 15 – 20%, (and the same filling pressure), the cylinder efficiency will increase by between 4% and 6 % (example for nitrogen).

6.3 Gases suitable for 300 bar operation

The group of suitable gases for high strength steel cylinders operating at a pressure of 300 bar includes: argon, nitrogen, helium, krypton, neon, oxygen, and their mixtures. Mixtures of these gases with carbon dioxide need special consideration to avoid condensation at low temperature. For oxygen at high pressures some special precautions are necessary. Because of potential hydrogen embrittlement risks EN ISO 11114 -1 *Gas cylinders. Compatibility of cylinder and valve materials with gas contents. Metallic materials* limits the tensile strength (UTS) for hydrogen cylinders to a maximum of 950 MPa [5]. Provided these limits are followed, the use of hydrogen at 300 bar working pressure is possible. Speciality gases are not considered in this publication.

6.4 Corrosion

In theory, two general areas of concern should be noted as far as the cylinders' contents are concerned. These are general corrosion and stress corrosion cracking (SCC). The most relevant single factor for corrosion is the presence of water in liquid form, especially with carbon dioxide. Also, oxygen or oxygen-rich gases will enhance general corrosion, as will the presence of acidic gases such as sulphur dioxide and carbon dioxide and dissolved salts, for example, sodium chloride. Chloride ions have been particularly damaging even in low alloy, low strength steels.

There is an increased risk for high strength steels of stress corrosion cracking with acidic gases in the presence of water.

Cylinder valves that have a residual pressure device incorporated into their design are one possibility to prevent moisture ingress. However validated production processes e.g. bake-out and vacuum prior to filling can be used.

While it is possible to have lighter cylinders made from high strength steels designed for lower pressure, for example 200 bar, the resulting thinner walls can require additional consideration of the effects of external or internal metallurgical defects, damage in use, as well as corrosion.

7 Valves for 300bar cylinders

Guidance on design, construction, testing requirements of cylinder valves is given in EN ISO 10297 *Gas cylinders — Cylinder valves — Specification and type testing* [6]. Compatibility of metallic and non-metallic materials is described in EN ISO 11114 -1 and EN ISO 11114 -2 *Transportable gas cylinders. Compatibility of cylinder and valve materials with gas contents. Non-metallic materials* [5,7].

The most common taper threads for connection of valves to gas cylinder in Europe are specified in EN ISO 11363-1 *Gas cylinders. 17E and 25E taper threads for connection of valves to gas cylinders. Specifications* [8]. The connection between the valve and the cylinder is the same as that for 200 bar cylinders. Consequently, attention shall be paid when fitting cylinder valves to ensure that the valve outlet corresponds to the intended working pressure of the cylinder.

NOTE Other connections are described in PD ISO TR 11364 *Gas cylinders. Compilation of national and international valve stem/gas cylinder neck threads and their identification and marking system* [9].

The suitability of materials and design for oxygen and oxidising gases shall be proved by using the adiabatic compression test detailed in EN ISO 10297 [6].

Cylinder valves and pressure regulators for 300 bar are commercially available. For reasons of safety and to comply with national regulations and standards in most countries the valve outlet connections for 300 bar differ from those for 200 bar.

There are three safe recommended possibilities for 300bar cylinders:

- Use cylinder valves with specific 300 bar outlet connections;
- Use cylinder valves, which are equipped with a built-in pressure reducer that reduces the outlet pressure from 300 bar to e.g. 200bar. These valves are equipped with an outlet connection appropriate to the reduced pressure.
- Use a valve with an integrated pressure regulator (VIPR) with a low-pressure outlet.

8 Safety considerations

8.1 Cylinder handling

Filled 300 bar cylinders can be considerably heavier than their 200 bar equivalent water capacity cylinder and a risk assessment should be carried on the manual handing of these cylinders. The mass of gases at various pressures filled into a 50 l cylinder are given in Appendix 1.

8.2 Safety measures during filling operation

All cylinders shall be subject to a prefill inspection, for example, EN ISO 24431 *Gas cylinders. Seamless, welded and composite cylinders for compressed and liquefied gases (excluding acetylene). Inspection at time of filling* [10], including a functional test of the cylinder “residual pressure valve”.

8.3 Recommendations for introduction period, customer information/ labelling

For all cylinders operating at 300 bar, customers should receive appropriate information in advance of the new cylinders being supplied. Information provided to the customer shall include details of how to identify the new type of cylinder and gas content.

The cylinder shall be labelled in accordance with the applicable legal requirements. In addition, it is recommended that some other form of identification gives notice of the higher pressure.

8.4 Recommendations for retesting and maintenance

When cylinders of different test pressures are being retested at the same facility procedures shall be in place to segregate cylinders of different test pressures to ensure cylinders are tested at the correct pressure.

After testing it shall be ensured that correct valve is fitted to the cylinder, see Section 7.

NOTE The above also applies to new cylinders.

9 References

[1] EN ISO 9809-2, *Gas cylinders. Refillable seamless steel gas cylinders. Design, construction and testing. Quenched and tempered steel cylinders with tensile strength greater than or equal to 1100* MPa www.cen.eu

[2] EN ISO 9809-, *Gas cylinders -- Refillable seamless steel gas cylinders -- Design, construction and testing -- Part 1: Quenched and tempered steel cylinders with tensile strength less than 1 100 MPa* www.cen.eu

[3] Council Directive 84/525/EEC *of 17 September 1984 on the approximation of the laws of the Member States relating to seamless, steel gas cylinders* www.europa.eu

[4] EN 1968 *Transportable gas cylinders. Periodic inspection and testing of seamless steel gas cylinders* www.cen.eu

[5] EN ISO 11114 -1 *Gas cylinders. Compatibility of cylinder and valve materials with gas contents. Metallic materials* www.cen.eu

[6] EN ISO 10297 *Gas cylinders — Cylinder valves — Specification and type testing* www.cen.eu

[7] EN ISO 11114 -2 *Transportable gas cylinders. Compatibility of cylinder and valve materials with gas contents. Non-metallic materials* www.cen.eu

[8] EN ISO 11363-1 *Gas cylinders. 17E and 25E taper threads for connection of valves to gas cylinders*. *Specifications* www.cen.eu

[9] PD ISO TR 11364 *Gas cylinders. Compilation of national and international valve stem/gas cylinder neck threads and their identification and marking system* www.iso.org

[10] EN ISO 24431 *Gas cylinders. Seamless, welded and composite cylinders for compressed and liquefied gases (excluding acetylene). Inspection at time of filling* www.cen.eu

Appendix 1 - Mass of gases at various fill pressures