300 BAR HIGH STRENGTH SEAMLESS STEEL GAS CYLINDERS

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- CYLINDER

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1 Scope and purpose

The aim of this document is to highlight 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.

2 Introduction

The seamless steel cylinder used for the supply of industrial gases in small quantities has proved invaluable to the gases industry for more than a hundred years. During this time a high safety standard has been achieved. At the same time there have been continuous technical improvements with respect to its 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 allowed a technological step forward: the increase in the operating pressure of the steel cylinder from 200 bar, to pressures of 300 bar and above. The advantage is a higher gas/cylinder weight ratio.

Many cylinder manufacturers offer high strength 300 bar steel cylinders, which have been approved by their respective national authorities and/or Notified Bodies. It is of prime importance that these cylinders have at least the same standard of safety as the cylinders in current use. Several international bodies, among them Working Group 14 of ISO/TC 58/SC3, CEN TC23/SC1/WG1 and the IGC Working Group 2, have defined the necessary safety criteria and have established the requirements for the steel properties, wall thickness, test procedures etc.

3 Present Status

3.1 Development of cylinder steels

Since the first high-pressure gas cylinders were manufactured around the turn of the twentieth century, various types of steels have been used. In the beginning carbon steels and low-carbon steels were the common materials. The properties of these steels are achieved via a normalising heat treatment.

The working pressure was typically between 100 and 150 bar. Such cylinders were manufactured up to around 1960, though they are still being manufactured in other parts of the world. The weight of such an industrial 40l cylinder, with a nominal gas capacity of 6 m^3 and a wall thickness of approx. 7.5 mm, was more than 70 kg.

Progress towards thinner, lighter and more efficient cylinders has been achieved mainly by the use of steels of increased yield and tensile strengths. Yield stress is the basic value used in the design of gas cylinders and it thus indirectly determines the weight of the cylinder.

Around 1935 carbon-manganese steel was introduced but still in the normalised condition. The yield stress was slightly higher at about 400 Mpa.

An important technical improvement was the introduction of the quenched and tempered chromium-molybdenum steel which was generally accepted from 1960 onwards. In Europe this led to an almost doubling of the yield stress from 400 Mpa to between 700 to 755 Mpa. This permitted an increase of the working pressure to 200 bar along with an increase in the gas capacity at an even lower cylinder weight than before.

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

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

In recent years the yield stress of the original Cr-Mo steel has been further increased to 850 Mpa which is a figure approved and used in many countries.

The step from 150 bar to 200 bar was relatively uncomplicated as in most cases the same gas supply equipment could be used for both pressures and thus also the same valve connection threads for both pressure stages.

Since the 1990's cylinder manufacturers have offered cylinders with a yield stress of around 1000 Mpa and with an increase of gas content to weight ratio.

These steels are used to develop yet another significant step in the cylinder development chain: industrial gas cylinders with a 300 bar working pressure.

The weight of a 300 bar working pressure, 50l industrial gas cylinder is around 75 kg when designed to EEC Directive 84/525. Further developments at CEN and ISO have reduced this weight even more.

3.2 Existing experiences with 300 bar cylinders

3.2.1 Cylinders made from normal strength steels

300 bar cylinders have already been available for special applications. They are made from the same material as the 200 bar cylinders and thus they are very inconvenient because of their weight, e.g. an empty 50 l cylinder with a nominal gas capacity of 15 m^3 weighs approx. 94 kg. Therefore their large-scale application was not attractive. These cylinders were used for air, nitrogen, argon and occasionally for oxygen.

3.2.2 Cylinders made from high strength steels

Experience with high strength, high pressure industrial gas steel cylinders has been gathered for over a decade, mainly in Europe, North America and Australia. The cylinder most frequently used has a nominal water capacity of 50 l, working pressure of 300 bar and a weight of approx 67 kg.

There are more than a million cylinders in operations, some of them for at least 15 years. They are mainly used for permanent gases, excluding hydrogen.

The cylinders are used either with normal 300 bar valves outlet or with valve with integrated pressure regulator (VIPR). For the approval of this cylinder, additional prototype tests are now required as in EN1964-2 and ISO 9809-2, such as flawed fatigue and burst testing.

4 300 bar High Strength Cylinders

4.1 Critical properties/standardisation/testing of high strength cylinders

The primary aim of introducing a 300 bar high strength cylinder was its reduced wall thickness compared to those in clause 3.2.1., and thus its higher technical efficiency, i.e. its content/weight ratio. However, the overall objective for design/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, on account of having approximately 50% higher 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. In particular, it is essential that if (for whatever reason) the cylinder ruptures, it should behave in a ductile manner fulfilling in a "leak-before-burst" philosophy.

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

- toughness
- ductility
- resistance to fatigue
- corrosion resistance

To obtain an optimum balance between these factors required refinements in material quality, production methods and quality control. The extra requirements put on these new steels with a tensile strength above 1100 Mpa have been intensively discussed within ISO TC58 and CEN TC23. An ISO standard and a European standard for the cylinder design have been issued.

For the basic design of high strength cylinders the Lamé Von-Mises formula was widely accepted at ISO (see ISO 9809-2) and latterly at CEN (see EN 1964-2).

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

The toughness requirements, at the higher strength levels, can be arrived at by either modifying the chemistry of the current Cr-Mo type family of steels, or the heat treatment cycle (or possibly both). Already a number of steels with differing chemistry are being used for cylinders at 300 bar.

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

The sensitivity of high-strength cylinders to how they behave 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 must be included in any design recommendations.
ISO 9809-2 and EN 1964-2 include an ultrasonic examination (UE) 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 and the number of cylinders to be tested all need to be considered. These have been addressed within ISO/TC58 and CEN/TC23 and are reflected in the relevant ISO and CEN standard. 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 geometry’s.

For the periodic cylinder retest there are no additional requirements compared to 200 bar cylinders, provided that the flawed fatigue test results at the cylinder prototype stage are acceptable. The retest requirements are detailed in a CEN standard EN1968.

4.2 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. But the mechanical properties, by using high strength steels (UTS 1100 MPa), only increase by about 15-25%

Consequently the same size cylinder at 300 bar will weigh more than the present 200 bar cylinder, e.g. a 50 l cylinder with argon will weigh an extra 10 to 15 kg if designed to EN or ISO standards.

The gas companies have had to consider additional ergonomic aspects when introducing the 300 bar cylinder.

It is possible to have cylinders with the same high strength steels but at lower pressure (e.g. 200bar), water capacity and diameter.

For such cylinders, the resulting wall thickness needs special consideration since the effects of external/internal defects, or damage, can be much more significant, because of the relatively low wall thickness.

4.3 Gases suitable for 300 bar operation

The group of suitable gases for cylinders operating at a pressure of 300 bar includes: argon, nitrogen, helium, krypton, neon, oxygen, and their mixtures. Mixtures of these gases with CO_2 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 IGC document 100/03 limits the tensile strength for hydrogen cylinders to 950 MPa max. Provided these limits are followed, the use of hydrogen at 300 bar working pressure is also possible. Speciality gases are not considered in this document. For the compressibility data of some of the above mentioned gases, see Appendix 1.

4.4 Corrosion problems

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 CO_2. Also oxygen or oxygen-rich gases will enhance general corrosion, as will the presence of acidic gases such as SO_2, CO_2 etc. and dissolved salts, e.g. NaCl (chloride ions have been particularly damaging in even low alloy, low strength steels). There is a risk of stress corrosion cracking with acidic gases in the presence of water.

Moreover, the entire mechanism of SC/corrosion attack is not yet exactly defined though a number of key parameters play a crucial role in the eventual behaviour. The role of the internal surface condition needs to be fully understood, particularly the effects of crevices. The critical defect sizes/shapes are clearly established, these ought to be then built into any design specification and the relevant periodic inspection requirements for such high strength cylinders.

5 Valves for 300 bar Cylinders

General rules on design, construction, testing requirements and compatibility of metallic and non-metallic materials are compiled in several documents prepared by the CEN/ISO committees of CEN TC23/SC2 and ISO TC58/SC2. These documents do not include any limitation of any specific requirement for 300 bar. Thus they are fully valid for a 300 bar working pressure. Valve tests, according to these documents, have to be performed at a given pressure defined by the working pressure, for instance the adiabatic compression test has to be at 1.2 times the working pressure.

The valve to cylinder connection is the same as that for normal 200 bar cylinders.

The suitability of materials for oxygen and oxidising gases may be checked by using the adiabatic compression test to be performed for type approval of valves.

When introducing 300 bar cylinders, close attention must be paid to avoid the dangerous confusion between 200 bar and 300 bar equipment.

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

There are three safe recommended possibilities:

1) Use a cylinder valve with specific 300 bar outlet connections.

2) Use cylinder valves with usual 200 bar outlet connections, but with an built-in pressure reducing valve to regulate the outlet pressure below 200 bar.

3) Use a valve with an integrated pressure regulator (VIPR) with a low pressure outlet.

The “New European Valve Outlet Connection” (NEVOC) document/or ISO5145 prepared by IGC-WG2 and ISO TC58/SC2 respectively, include special 300 bar delivery outlet connections.

6 Safety Considerations

6.1 Safety measures during filling operation

To overcome many of the above-mentioned problems of corrosion (see clause 4.4) the filler has to ensure that the cylinders and the gas being filled are kept “dry” at all times. The degree of “dryness”, for a given cylinder pressure, needs to be established particularly in the presence of the type of aggressive gases given in 4.4. Especially for high strength cylinders, careful prefill inspections and special measures are essential to exclude the possibility of moisture migrating into the cylinder between two filling cycles or to remove any moisture from the cylinder before filling.

6.2 Safety measures for the construction of a 300 bar filling station

With the exception of oxygen, the construction of a filling station for technical gases does not require special consideration. The manufacture and mounting of the required components (valves, gaskets, pipes etc.) up to a range well above 300 bar, typically around 400 bar to cater for the developed pressure, is the present state of the art.

Compared to 200 bar devices, the risk of an ignition with oxidising gases is higher, thus additional safety measures must be taken with filling stations. Some details on the behaviour of materials in contact with oxygen are given in the IGC document 13/02 “Oxygen pipeline systems”. Most metallic and non-metallic materials compatible with 200 bar may also be suitable for 300 bar. However, special attention has to be given to design features, such as heat conductivity, ignition temperature or adiabatic compression. Some key recommendations are:

1) maximum flow rate
2) smoothen sharp edges in mouldings/castings
3) avoid dead spaces
4) install well embedded gaskets and gland packings
5) use automatic welding processes to avoid weld bulges
6) selection of suitable materials for the piping system, vaporisers, pumps and filling racks need thorough consideration
7) quick connectors need thorough selection and very regular maintenance routines

For a further detailed evaluation see IGC 13/02

6.3 Recommendations for introduction period, customer information/special labelling

For all cylinders operating at 300 bar, customers must receive appropriate information in advance of the new cylinders that are supplied for the first time.

Information to the customer must ensure that it identifies the new type of cylinder, gas content, etc.

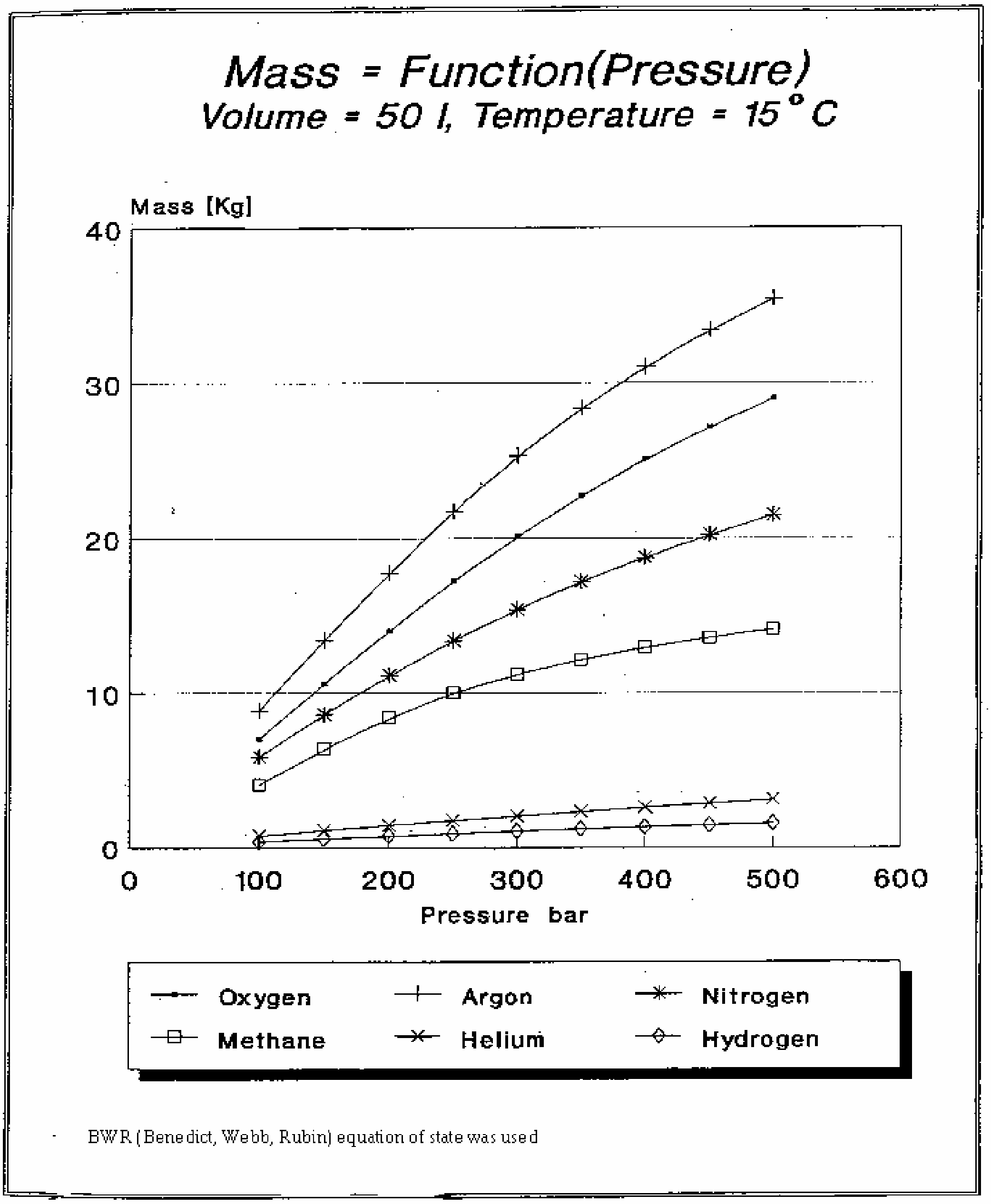
The cylinder must be labelled in accordance with the necessary statutory requirements. In addition, it is recommended that some other form of identification gives notice of the higher pressure.

7 References

EEC Directive 84/525:	“Council Directive of 17 September 1984 on the approximation of the laws of the Member States relating to seamless steel gas cylinders”
IGC Document 100/03 (Former TN26/81)	“Hydrogen Cylinders and Transport Vessels”
EN849	“Cylinder Valves – Design and Testing”
ISO 10297	“Cylinder Valves – Design and Testing”

ISO TR 12391 Parts 1,2,3, 4	“Proposals for toughness requirements for high strength steels”
ISO 9809-2	“Gas cylinders – Refillable seamless steel gas cylinders --- Design, construction and testing --- Part 2: Quenched and tempered steel cylinders with tensile strength greater than or equal to 1100 MPa”.
EN1964-2	“Specification for the design and construction of refillable transportable gas cylinders from 0.5 Litre up to and including 150 Litres
EN1968	“Transportable gas cylinders --- Periodic Inspection and testing of seamless steel gas cylinders”.
IGC Document 13/02	“Oxygen Pipeline Systems”
IGC Document 97/03	Valve outlet connections for Gas Cylinders (NEVOC)

APPENDIX 1



BWR (Benedict, Webb, Rubin) equation of state was used