INTERNATIONAL STANDARD

# ISO 11114-4

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# Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents —

## Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement



*Bouteilles à gaz transportables — Compatibilité des matériaux des bouteilles et des robinets avec les contenus gazeux —*



*Partie 4: Méthodes d'essai pour le choix de matériaux métalliques résistants à la fragilisation par l'hydrogène*

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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11114-4 was prepared by Technical Committee ISO/TC 58, *Gas cylinders*.

ISO 11114 consists of the following parts, under the general title *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents*:



— *Part 1: Metallic materials*

— *Part 2: Non-metallic materials*



— *Part 3: Autogenous ignition test in oxygen atmosphere*

— *Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement*

## Introduction

It is widely recognised that compressed hydrogen and some hydrogen bearing gases can have an embrittling effect on metallic materials, especially steels. This embrittling effect has resulted in the failure of hydrogen cylinders (including some bursts) that has led gas cylinder users and manufacturers to adopt specific measures.

The adoption of these measures has eliminated all known failures of hydrogen cylinders from this embrittlement phenomenon.

The basic recommendation was to minimise the stresses in the cylinder wall (see ISO 11114-1) and eliminate harmful defects.

This tensile strength limit of 950 MPa was developed for quenched and tempered gas cylinders of 34 Cr Mo 4 type steels using steelmaking practices, chemistry and manufacturing techniques typical of those used during the early 1980s and successfully used for filling pressures up to 300 bar. This practice has been in widescale use up to the current time. Other higher pressures, although at lower tensile strength limits, have also been used.

In recent years, improvements in steelmaking, e.g. by reducing the sulphur and phosphorus contents, have indicated the possibility of increasing the tensile strength limit of 950 MPa for embrittling gas service, as a result of improvements in the fracture toughness of the material.



Experimental work has shown that the relevant parameters affecting hydrogen embrittlement are the following:

a) microstructure resulting from the combination of the chemistry and the heat treatment;

b) mechanical properties of the material;

c) applied wall stress;

d) internal surface imperfections resulting in local stress concentrations;

e) characteristics of the gas contained (composition, quality, pressure, etc.).

When developing this part of ISO 11114 only the material aspects, a) and b) above, were considered. Other essential features, c) and d), are covered by the relevant parts of ISO 9809.

This part of ISO 11114 specifies test methods to identify steels which, when combined with the cylinder manufacturing requirements specified in ISO 9809 (all parts), will result in cylinders suitable for use in embrittling gas service.

However, some low alloy steels other than 34 Cr Mo 4 may require tensile strength lower than 950 MPa to be suitable for the manufacture of gas cylinders for embrittling gas service.

These tests have been developed following an extensive world-wide programme which incorporated laboratory and full scale tests.

# Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents —

# Part 4: **Test methods for selecting metallic materials resistant to hydrogen embrittlement**

## 1 Scope

This part of ISO 11114 specifies test methods and the evaluation of results from these tests in order to qualify steels suitable for use in the manufacture of gas cylinders (up to 3 000 l) for hydrogen and other embrittling gases.

This part of ISO 11114 only applies to seamless steel gas cylinders.

The requirements of this part of ISO 11114 are not applicable if at least one of the following conditions for the intended gas service is fulfilled [1]):



— the working pressure of the filled embrittling gas is less than 20 % of the test pressure of the cylinder;

— the partial pressure of the filled embrittling gas of a gas mixture is less than 5 MPa (50 bar) in the case of hydrogen and other embrittling gases, with the exception of hydrogen sulphide and methyl mercaptan in which cases the partial pressure shall not exceed 0,25 MPa (2,5 bar).

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4287, *Geometrical product specifications (GPS) — Surface texture: Profile method — Terms, definitions and surface texture parameters*

ISO 7539-1:1987, *Corrosion of metals and alloys — Stress corrosion testing — Part 1: General guidance on testing procedures*

ISO 7539-6:2003, *Corrosion of metals and alloys — Stress corrosion testing — Part 6: Preparation and use of pre-cracked specimens for tests under constant load or constant displacement*

ISO 9809-1, *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*

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 1 100 MPa*

1) In such cases the cylinders may be designed as for ordinary (non embrittling) gases.

 

ISO 9809-3, *Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing — Part 3: Normalized steel cylinders*

ISO 11114-1:1997, *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic materials*

ISO 11120, *Gas cylinders — Refillable seamless steel tubes for compressed gas transport, of water capacity between 150 l and 3 000 l — Design, construction and testing*

## 3 Terms, definitions and symbols

### 3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply. Some of the definitions used are based upon those in ISO 7539-1:1987.

**3.1.1**
**embrittling gases**
gases listed in ISO 11114-1:1997, Table A.3, group 2 and Table A.12, group 11

**3.1.2**
**hydrogen rupture pressure**, $P_{H2}$
maximum pressure recorded during the hydrogen rupture pressure test

**3.1.3**
**helium rupture pressure**, $P_{He}$
maximum pressure recorded during the helium rupture pressure test



**3.1.4**
**hydrogen embrittlement index**
maximum value of the ratio $P_{He}/P_{H2}$ as a function of the pressure rise rate

**3.1.5**
**environmentally-assisted cracking**
synergistic effect on a metal caused by the simultaneous action of a particular environment and a nominally static tensile stress, which results in the formation of cracking

**3.1.6**
**threshold stress**
stress above which a crack will initiate and grow, for the specified test conditions

**3.1.7**
**plane strain stress intensity factor**, $K_1$
function of applied load, crack length and specimen geometry having dimensions of stress × length

NOTE $K_1$ uniquely defines the elastic stress field intensification at the tip of a crack subjected to opening mode displacements.

**3.1.8**
**threshold stress intensity factor for susceptibility to environmentally-assisted cracking**, $K_{1H}$
stress intensity factor above which an environmentally-assisted crack will initiate and grow, for the specified test conditions under conditions of high constraint to plastic deformation, i.e. under essentially plane strain conditions

**3.1.9**
**HAC**
hydrogen assisted cracking

### 3.2 Symbols

For the purposes of this document, the following symbols apply.

$a$ effective crack length measured from the crack tip to the loading plane

$a_0$ average value of $a$

$B$ specimen thickness

$e_m$ the mean disc thickness

$E$ modulus of elasticity

$K_{IAPP}$ applied elastic stress-intensity

$K_{1H}$ threshold stress intensity factor

$m$ elastic displacement per unit load

$P$ applied load

$P_r$ actual rupture pressure

$P_r'$ corrected rupture pressure



$P_r'_{H2}$ corrected hydrogen rupture pressure

$P_r'_{He}$ theoretical helium rupture pressure corresponding to the same pressure rise rate as for the hydrogen test, calculated by regression from the corrected helium rupture pressure



$R_m$ actual value of tensile strength

$R_{P0,2}$ average of measured yield stress of three specimens from the test cylinder representing the HAC test specimen's location at room temperature

$V$ crack-mouth opening displacement (CMOD) defined as the mode 1 (also called opening-mode) component of crack displacement due to elastic and plastic deformation, measured at the location on a crack surface that has the greatest elastic displacement per unit load, $m$

$W$ effective width of a compact specimen, measured from the back face to the loading plane

$Y$ stress intensity factor coefficient derived from the stress analysis for a particular specimen geometry, which relates the stress intensity factor for a given crack length to the load and specimen dimensions

## 4 General requirements

The test methods as described in Clause 5 are valid for working pressure up to 300 bar. For higher working pressures additional verification shall be undertaken.

The tests shall be performed for selecting steels for hydrogen cylinders. Chromium–molybdenum steels, quenched and tempered with a guaranteed maximum actual ultimate tensile strength of 950 MPa, do not need to be tested and can safely be used for the construction of hydrogen cylinders. For carbon–manganese steels, different limits may apply (see ISO 9809-1).

The tests described in Clause 5 are “qualification tests” for a given steel. This means that the tests need not be repeated for each “type” of cylinder once a steel has been qualified for a specific design strength level.

The test samples shall be taken from a representative cylinder or from a piece of tube (for long cylinders according to ISO 11120), representative of the relevant manufacturing process including heat treatment.

The test samples shall have a mechanical strength not lower than the maximum intended tensile strength to be used for the cylinders to be manufactured. If it is intended later to increase the maximum strength of the steel, a new qualification test shall be performed.

With respect to the possible variation of the chemical composition, the chemistry of the steel tested shall be recorded in the qualification test report and the difference in chemistry for the steels actually used for the cylinders shall not exceed the "permissible difference" according to ISO 9809-2. In addition, for sulphur and phosphorus, these permissible differences are limited to 0,005 % and 0,010 %, respectively. In no case shall the phosphorus content of either the qualification or the production cylinders exceed 0,015 %.

With respect to the heat treatment, the manufacturer shall specify the relevant temperatures and times, and the quenching conditions (if relevant). Any modification to the heat treatment needing a new type approval according to ISO 9809-2 requires a new qualification test.

For the qualification of a given steel for the manufacturing of gas cylinders, method A, B, or C can be used (see 5.1, 5.2 and 5.3, respectively). Additionally, tensile tests shall be carried out (see 5.4).

## 5 Test methods

### 5.1 Disc test (method A)



#### 5.1.1 Principle of test

A mounted test piece in the shape of a disc is subjected to an increasing gas pressure at constant rate to burst or to crack. The embrittling effect of hydrogen is evidenced by comparing the hydrogen rupture pressures $P_{H2}$ with the helium rupture pressures $P_{He}$, helium being chosen as a reference gas.



The ratio $P_{He}/P_{H2}$ shall be determined.

The lower this ratio, the better will the steel type behave in the presence of hydrogen. This ratio is dependent on the pressure rise rate, which shall remain constant during the whole test.

NOTE 1 Hydrogen rupture pressures also depend on the hydrogen purity. Oxygen or traces of water vapour can partially inhibit the hydrogen embrittlement effect.

NOTE 2 The test can be carried out with any other embrittling gas or gas mixture (e.g. $H_2S$, hydrides). The embrittlement index of the considered gas will then be defined similarly.

#### 5.1.2 Test conditions and procedure

##### 5.1.2.1 Sample disc

The sample disc shall be flat and ground (or machined to an equivalent surface finish), and shall have the following characteristics.

Dimensions:

- Diameter: $58\,^{0}_{-0,5}$ mm.
- Thickness: 0,75 mm ± 0,005 mm.
- Flatness: less than 1/10 mm deflection.

 

Surface condition (both sides):

— Roughness: $Ra$ value (see ISO 4287) less than 0,001 mm. The roughness of the samples used for both $H_2$ and He tests shall be equivalent.

— No trace of oxides.

The following operations shall be performed to verify the sample quality:

— Immediately after the final preparation and prior to the testing, store the samples in a dry atmosphere, e.g. a desiccator.

— Degrease the sample and check thickness at 4 points taken 90° apart to define a mean thickness.

— Determine the disc's hardness (e.g. Vickers) over its outer circumference to verify that machining has not altered the original material properties.

#### 5.1.2.2 Cell and other apparatus

The cell (see Figure 1) is composed of 2 stainless steel flanges embedding the disc. A volume of approximately 5 $cm^3$ is provided below the disc. Above the disc a high-strength steel ring is mounted ($R_m \geqslant$ 1 100 MPa). The internal diameter is 25,5 mm and the ring curvature radius at the mounting diameter level is 0,5 mm.



Gas discharges can occur after disc bursting either through the lower flange or upper flange discharge port to the atmosphere. This permits the evacuation of the installation and a check of the hydrogen purity and freedom from either oxygen ($O_2 <$ 1 µl/l) or water vapour ($H_2O \leqslant$ 3 µl/l) [2]. It also permits regulation of the gas flow and adjustment of the pressure rise rate.



The sealing device shall be an elastomer O-ring for helium testing, and for hydrogen testing at rates of more than 10 bar/min. For hydrogen testing at rates not exceeding 10 bar/min, indium O-rings shall be used.

For the flange assembly, ten high-strength steel bolts should be used, size typically M10 or equivalent. The tightening torque shall be 30 N·m for elastomer O-rings and 100 N·m for indium O-rings.

Hydrogen and helium shall be stored in high-pressure containers connected to the test cells. A flow control valve between the high-pressure container and the cell shall be used to adjust the pressure rise rate.

#### 5.1.2.3 Test procedure

For a satisfactory outcome of the test performances, the following operations shall be carried out.

— Evacuation of the cell by pumping to eliminate any traces of air or moisture absorbed by the walls. Purging with the gas to be used, followed by vacuum pumping, can also be used to improve the cleaning efficiency.

— Check of the gas purity before testing.

— Adjustment of the gas flow to achieve the appropriate pressure rise rate.

— Isolation of the cell (at the start of pressure rise).

The rate of pressure rise shall be monitored for the duration of the entire test. It shall be regular and kept as constant as possible, neglecting the gas compressibility factor with pressure.

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2) 1 µl/ = 1 ppm. The use of ppm is deprecated.