INTERNATIONAL STANDARD

ISO 16111

First edition
2008-11-15

Transportable gas storage devices — Hydrogen absorbed in reversible metal hydride

Appareils de stockage de gaz transportables — Hydrogène absorbé dans un hydrure métallique réversible

Reference number
ISO 16111:2008(E)

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Published in Switzerland

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Foreword

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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 16111 was prepared by Technical Committee ISO/TC 197, *Hydrogen technologies*, with participation by Technical Committee ISO/TC 58, *Gas cylinders,* Subcommittee SC 3, *Cylinder design.*

This first edition cancels and replaces ISO/TS 16111:2006, which has been technically revised.

Introduction

As the utilization of gaseous hydrogen evolves from the chemical industry into various emerging applications, such as fuel for fuel cells and internal combustion engines and other specialty hydrogen applications, the importance of new and improved storage techniques has become essential. One of these techniques employs the absorption of hydrogen into specially formulated alloys. The material can be stored and transported in a solid form, and the hydrogen later released and used under specific thermodynamic conditions. This International Standard describes the service conditions, design criteria, type tests, batch tests and routine tests for transportable hydride-based hydrogen storage systems, referred to as “metal hydride assemblies” (MH assemblies). Types of MH assemblies may serve as: fuel cell cartridges; hydrogen fuel storage containers; high-purity hydrogen supplies and others.

Transportable gas storage devices — Hydrogen absorbed in reversible metal hydride

1 Scope

This International Standard defines the requirements applicable to the material, design, construction, and testing of transportable hydrogen gas storage systems, referred to as “metal hydride assemblies” (MH assemblies) which utilize shells not exceeding 150 l internal volume and having a maximum developed pressure (MDP) not exceeding 25 MPa (250 bar). This International Standard only applies to refillable storage MH assemblies where hydrogen is the only transferred media. Storage MH assemblies intended to be used as fixed fuel-storage onboard hydrogen fuelled vehicles are excluded. This International Standard is intended to be used for certification purposes.

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 7225, *Gas cylinders — Precautionary labels*

ISO 7866, *Gas cylinders — Refillable seamless aluminium alloy gas cylinders — Design, construction and testing*

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*

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

ISO 10297:2006, *Transportable gas cylinders — Cylinder valves — Specification and type testing*

ISO 11114-4, *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement*

ISO 11119-1, *Gas cylinders of composite construction — Specification and test methods — Part 1: Hoop wrapped composite gas cylinders*

ISO 11119-2:2002, *Gas cylinders of composite construction — Specification and test methods — Part 2: Fully wrapped fibre reinforced composite gas cylinders with load-sharing metal liners*

ISO 14246, *Transportable gas cylinders — Gas cylinder valves — Manufacturing tests and inspections*

ISO 14687, *Hydrogen fuel — Product specifications*

ISO 16528-1, *Boilers and pressure vessels — Part 1: Performance requirements*

UN Recommendations on the Transport of Dangerous Goods. Model Regulations

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
absorbed
taken and held through the formation of bonding interactions within the bulk of the material

3.2
burst pressure
highest pressure reached in an MH assembly during a burst test

3.3
design stress limit
total stress loading allowed on the shell wall

NOTE In MH assemblies, the shell design takes into account the gas pressure plus other stresses, such as pressure exerted by expansion of the hydrogen absorbing alloy.

3.4
fuel cell cartridge
article that stores fuel for discharge into the fuel cell through a valve(s) that controls the discharge of fuel into the fuel cell

3.5
fuel cell cartridge
MH assembly, which stores hydrogen for use as a fuel in a fuel cell

3.6
full flow capacity pressure
gas pressure at which the pressure relief device is fully open

3.7
hydrogen absorbing alloy
material capable of combining directly with hydrogen gas to form a reversible metal hydride

3.8
internal component
structure, matrix, material or device contained within the shell (excluding hydrogen gas, hydrogen absorbing alloy and metal hydride)

NOTE Internal components may be used for purposes such as heat transfer, preventing movement of the hydrogen absorbing alloy/metal hydride and/or to prevent excessive stress on the shell walls due to hydride expansion.

3.9
internal volume
water capacity of the shell

3.10
maximum developed pressure
MDP
highest gas gauge pressure for an MH assembly at rated capacity and equilibrated at the maximum service temperature

NOTE The MDP term was specifically selected for MH assemblies to avoid confusion with the MAWP and the service pressure used in other ISO International Standards.

3.11
metal hydride
solid material formed by reaction between hydrogen and hydrogen absorbing alloy

3.12
metal hydride assembly
MH assembly
single complete hydrogen storage system, including shell, metal hydride, pressure relief device (PRD), shut-off valve, other appurtenances and internal components

NOTE 1 The MH assembly extends only to, and includes, the first shut-off valve.

NOTE 2 A fuel cell cartridge is a type of MH assembly.

3.13
normal operating conditions
range of pressures, temperatures, hydrogen flow rates, hydrogen quality, etc., specified for all use and filling operations

3.14
normal service conditions
range of pressures, temperatures, hydrogen flow rates, hydrogen quality, etc., specified for all normal operating, transportation and storage conditions

3.15
pressure relief device
PRD
device intended to prevent the rupture of an MH assembly in the event of overpressure or exposure to fire

NOTE A pressure relief device may be "pressure-activated", set to activate at a certain pressure. Alternatively, a pressure relief device may be "thermally-activated", set to activate at a certain temperature. A pressure relief device may also be both "pressure-activated" and "thermally-activated".

3.16
pressure relief valve
PRV
reseatable PRD

3.17
rated capacity
maximum quantity of hydrogen deliverable under specified conditions

3.18
rated charging pressure
RCP
maximum pressure to be applied to the MH assembly for refilling

NOTE The RCP is not necessarily equal to the equilibrium plateau pressure of the hydrogen absorbing alloy.

3.19
reversible metal hydride
metal hydride for which there exists an equilibrium condition where the hydrogen absorbing alloy, hydrogen gas and the metal hydride co-exist

NOTE Changes in pressure or temperature will shift the equilibrium favouring the formation or decomposition of the metal hydride with respect to the hydrogen absorbing alloy and hydrogen gas.

3.20
rupture
structural failure of a shell resulting in the sudden release of stored energy

3.21
shell
enclosure of any shape (cylindrical, prismatic, cubic, etc.) designed to contain the hydrogen gas, metal hydride and other internal components of the MH assembly

NOTE A shell may be a cylinder, a pressure vessel or other type of container.

3.22
stress level at MDP
sum of all the stresses on the shell wall caused by the metal hydride at rated capacity, hydrogen gas at MDP and any other applicable mechanical loadings

3.23
test pressure
required pressure applied during a pressure test for qualification

4 Service conditions

4.1 Pressures

4.1.1 Maximum developed pressure (MDP)

The MDP shall be determined by the manufacturer from the metal hydride's temperature–pressure characteristics at the maximum service temperature. In no case shall the MDP exceed 0,8 times the test pressure of the shell. The MDP shall not exceed 25 MPa (250 bar).

4.1.2 Rated charging pressure (RCP)

The RCP shall be specified by the manufacturer in order to prevent charging at a pressure that could result in the shell wall stress exceeding the design stress limit.

4.1.3 Stress level at MDP

The stress level at MDP shall be determined by the manufacturer from the hydrogen absorbing alloy's packing and expansion properties, the MDP within the MH assembly, and other applicable mechanical loadings.

4.2 Rated capacity

The manufacturer shall state the rated capacity of the MH assembly by units of mass of hydrogen.

4.3 Temperature ranges

4.3.1 Operating temperature range

The minimum and maximum temperature for normal operating conditions to which the MH assembly is rated shall be specified by the manufacturer.

4.3.2 Service temperature range

The minimum and maximum temperature for normal service conditions to which the MH assembly is rated shall be specified by the manufacturer. At a minimum, this range shall be of at least from −40 °C to 65 °C and shall include the entire operating temperature range.

4.4 Environmental conditions

The MH assemblies are expected to be exposed to a number of environmental conditions over their service life, such as vibration and shock, varying humidity levels, and corrosive environments. The manufacturer shall specify the environmental conditions for which the MH assembly was designed.

4.5 Service life

The service life for the MH assemblies shall be specified by the manufacturer on the basis of use under service conditions specified herein. The service life shall not exceed that specified by the standard to which the shell is designed as per 5.3.

4.6 Hydrogen quality

The minimum quality of the hydrogen gas that shall be used to fill an MH assembly shall be specified by the manufacturer according to ISO 14687 or as appropriate.

NOTE If the quality of the hydrogen gas is considered a critical issue to avoid performance degradation of the MH assembly, the manufacturer may consider including the information on the product label.

4.7 Special service conditions

Any additional service conditions that shall be met for the safe operation, handling and usage of the MH assembly shall be specified by the manufacturer.

5 Design considerations

5.1 General

The MH assembly shall be designed and constructed to prevent leakage of hydrogen or metal hydride particles under normal conditions of storage and transport.

5.2 Material selection

5.2.1 General

The MH assembly components shall be made of materials that are suitable for the range of conditions expected over the life of the MH assembly. Components that are in contact with gaseous hydrogen and/or metal hydride material shall be sufficiently resistant to their chemical and physical action under normal service conditions to maintain operational and pressure containment integrity.

Hydrogen absorbing alloys and/or metal hydride materials that are classified as Type I explosive materials according to the UN Recommendations on the Transport of Dangerous Goods shall not be used in an MH assembly.

5.2.2 External surfaces

The MH assembly shell, shut-off valve, PRDs and other appurtenances shall be resistant to the environmental conditions specified in 4.4. Resistance to these environmental conditions may be provided by using materials inherently resistant to the environment or by applying resistant coatings to the components. Exterior protection may be provided by using a surface finish giving adequate corrosion protection (e.g. metal sprayed on aluminium or anodizing) or a protective coating (e.g. organic coating or paint). If an exterior coating is part of the design, the coating shall be evaluated using the applicable test methods specified in Annex B. Any coatings applied to MH assemblies shall be such that the application process does not adversely affect the mechanical properties of the shell or performance and operation of other components. The coatings shall be designed to facilitate subsequent in-service inspection and the manufacturer shall provide guidance on coating treatment during such inspections to ensure the continued integrity of the MH assembly.

5.2.3 Compatibility

The compatibility of MH assembly materials with process fluids and solids, specifically embrittlement due to the exposure to hydrogen, shall be considered. Guidance on compatibility of materials with gases is given in ISO 11114-1 and ISO 11114-2. Materials necessary for the pressure containment and structural integrity of the MH assembly and its internal and external appurtenances shall be resistant to hydrogen embrittlement, hydrogen attack and reactivity with contained materials and maintain their integrity for the service life of the MH assembly. Recognized test methods, such as those specified in ISO 11114-4, shall be used to select metallic materials resistant to hydrogen embrittlement where required for pressure or structural integrity. Consideration shall be given to the impact that temperature may have on hydrogen embrittlement.

Consideration shall be given to all of the chemical species that may be present during the charged, partially charged and discharged states and their potential reactivity with the MH assembly material. The MH assembly materials shall be selected so as the combination does not endanger the MH assembly integrity.

NOTE The susceptibility to hydrogen embrittlement of some commonly used metals is summarized in ISO/TR 15916. Additional guidance regarding hydrogen compatibility is found in Annex A.

5.2.4 Temperature

The MH assembly materials shall be suitable for the service temperature range specified in 4.3.2.

5.3 Shell design

5.3.1 Shells with internal volume greater than 120 ml

The MH assembly shell shall be designed and tested according to ISO 7866, ISO 9809-1, ISO 9809-3, ISO 11119-1, ISO 11119-2, or standards registered in accordance with ISO 16528-1, as applicable. Shells designed and tested in accordance with ISO 9809-1 shall have a tensile strength less than 950 MPa. Shells designed and tested in accordance with ISO 11119-1 or ISO 11119-2 that use seamless steel liners conforming to ISO 9809-2 or to ISO 9809-1 shall have a tensile strength less than 950 MPa.

The shell shall not exceed 150 l internal volume, and the MDP shall not exceed 25 MPa (250 bar). The maximum combined stresses for the loads described in 5.4 as well as the operating and service temperature ranges for the MH assembly shall not exceed the limits prescribed by the standard to which the shell is designed.

NOTE 1 Shells can be designed and tested according to one of the International Standards specified above, even where the shell internal volume is less than that covered by the scope of that International Standard.

NOTE 2 An equivalent gas pressure calculated to be equal to the stress level at MDP can be used as the design hydraulic test pressure for determining minimum shell wall thickness.

5.3.2 Shells with internal volume of 120 ml or less

For MH assemblies with an internal volume of 120 ml or less, the shell design shall be deemed to be appropriate if the shell meets 5.3.1 or the MH assembly meets the following design and test criteria:

a) the pressure in the MH assembly shall not exceed 5 MPa (50 bar) at 55 °C when the MH assembly is filled to its rated capacity; and

b) the MH assembly design shall withstand as required by 6.2.3, without leaking or bursting, a minimum shell burst pressure of 2 times the pressure in the MH assembly at 55 °C when filled to rated capacity, or 1,6 times the pressure in the MH assembly at the maximum service temperature when filled to rated capacity, or 200 kPa (2 bar) more than the MDP of the assembly at 55 °C when filled to rated capacity, whichever is greater.

5.4 Design strength

The shell design shall take into account the stress level at 1,25 times MDP. Consideration of components contributing to the stress level at MDP shall include but not be limited to:

— 1,25 × MDP;

— thermal stress, including dissimilar rates of thermal expansion and contraction;

— weight of internals in any possible MH assembly orientation;

— shock and vibration loading;

— maximum stress due to hydrogen absorbing alloy expansion;

— other mechanical loadings.

To verify that the design stress limit is not exceeded, the MH assembly design shall be subjected to the hydrogen cycling and strain measurement test described in 6.2.6.

NOTE The process of introducing and subsequently removing hydrogen in the hydrogen absorbing alloy typically causes it to expand and contract. In turn, this can result in large stresses inside the alloy's particles that cause them to fragment into smaller particles, a phenomenon known as decrepitation. After several charge/discharge cycles, the average particle size may have significantly decreased. Stresses on the MH assembly walls may be derived from expansion of the hydrogen absorbing alloy during hydrogenation and from changes in the packing configuration due to decrepitation over the service life of the MH assembly. The magnitude of the expansion/contraction phenomena will vary greatly as a function of the hydrogen absorbing alloy used.

5.5 Overpressure and fire protection

5.5.1 General

The MH assembly shall be protected with one or more PRDs of the non-reclosing type, such as fusible triggers, rupture disks and diaphragms, or of the re-sealable type, such as spring-loaded PRVs. The MH assembly and any added component (e.g. insulation or protective material) shall collectively pass the fire test specified in 6.2.2. The PRD shall conform to the requirements of 5.5.2 and 5.5.3 and the additional requirements of the competent authority of country of use, as applicable.

For MH assemblies with an internal volume of 120 ml or less, other means may be used to protect from overpressurization, such as venting through a feature integral to the shell. MH assemblies that use an alternative means of relieving pressure shall meet the acceptance criteria of the fire test specified in 6.2.2.

5.5.2 PRD activation pressure

The pressure of actuation of pressure-activated PRDs shall be specified by the manufacturer and shall be greater than the MDP but less than 1,25 times the MDP. In no case shall the pressure of actuation of a pressure-activated PRD exceed the test pressure of the shell. For PRVs, the full flow capacity pressure shall also be specified, and shall not exceed the test pressure of the shell.

5.5.3 PRD activation temperature

The temperature at which any thermally actuated PRD is set to activate shall be specified by the manufacturer and correspond to an equilibrium pressure inside the MH assembly of less than 1,25 times the MDP. In no case shall the temperature of actuation of a temperature-activated PRD result in an equilibrium pressure inside the MH assembly that exceeds the test pressure of the shell. The PRD shall have a pressure rating greater than the MDP at all temperatures less than or equal to 10 °C above the maximum service temperature. In no case shall the PRD activate at a temperature lower than the maximum service temperature.

