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Transportable gas storage devices — Hydrogen absorbed in reversible metal hydride

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

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Foreword

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ISO 16111 was prepared by Technical Committee ISO/TC 197, *Hydrogen technologies*.

Introduction

As the utilization of gaseous hydrogen evolves from the chemical industry into a fuel for various emerging 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 later released and used under specific thermodynamic conditions. This standard will describe the service conditions, design criteria, type tests, and routine tests for these canisters.

Transportable gas storage devices — Hydrogen absorbed in reversible metal hydride

1 Scope

This standard addresses the safe design and use of transportable hydrogen gas storage canisters including all necessary valves, relief devices, and appurtenances, intended for use with reversible metal hydride, hydrogen storage systems. This standard only applies to refillable devices where hydrogen is the only transferred media. Transportable gas storage devices do not include devices intended as fixed on-board fuel storage for hydrogen fuelled vehicles.

The requirements of this standard are not intended to constrain innovation. The manufacturer may consider materials, designs or constructions not specifically dealt with in this document. Components used in transportable hydrogen gas storage devices may not be within the size limitations of the standards referenced in this document. These alternatives shall be evaluated as to their ability to yield acceptable results when subjected to testing equivalent to that prescribed by this standard.

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 7866:1999 *Gas cylinders — Refillable seamless aluminium alloy gas cylinders — Design, construction and testing*

ISO 9809-1:1999 *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 9809-3:2000 *Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing — Part 3: Normalized steel cylinders*

ISO 11114-1:1997/Cor. 1999 — *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1 Metallic materials*

ISO 11114-2:2000 - Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials

ISO 11114-4:2005 - 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 11119-1:2002 *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 13769:2002 *Gas cylinders — Stamp Markings*

ISO 14687: 1999/Cor. 1:2001 - *Hydrogen Fuel — Product Specification*

ISO/TR 15916:2004 – Basic considerations for the safety of hydrogen systems

ISO/TS 16528:2002 *Boilers and pressure vessels — Registration of Codes and Standards to promote international recognition*

3 Terms and definitions

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

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

3.2
canister
single complete hydrogen storage system, including shell, metal hydride, safety devices, shut-off valve and other components (e.g. for heat exchange, to prevent excessive stress on the shell walls due to hydride expansion, etc.). The canister extends only to and includes the first shut-off valve

3.3
design stress
sum of the stresses on the shell wall caused by the metal hydride material at rated capacity, hydrogen gas at maximum developed pressure and any other applicable mechanical loadings

3.4
full flow capacity pressure
gas pressure at which the pressure relief device is fully open

3.5
hydrogen absorbing alloy
material capable of combining directly with hydrogen gas to form a reversible metal hydride.

3.6
maximum developed pressure (MDP)
highest gas gauge pressure for a fully charged canister equilibrated at the maximum service temperature

3.7
metal hydride
solid material formed by reaction between hydrogen and hydrogen absorbing alloy. A reversible metal hydride is a metal hydride for which there exists an equilibrium condition where the hydrogen absorbing alloy, hydrogen gas and the metal hydride co-exist. 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

3.8
normal operating conditions
range of conditions, such as pressure, temperature, H_2 flow rate , H_2 impurities and etc., which the product might be exposed to during all use and filling operations

3.9
rated capacity
stated deliverable quantity of hydrogen specified by the manufacturer

3.10
rated charging pressure (RCP)
maximum pressure allowed to be applied to the product for refilling as stipulated by the manufacturer

3.11
rupture
structural failure of a shell resulting in the rapid and violent release of stored energy in such a manner that it may pose a safety hazard to people or property.

3.12
shell
enclosure designed to contain the hydrogen gas, metal hydride and other internal components of the canister

3.13
transportable
designed to be mobile and not intended to be used in a fixed, permanent installation

4 Service Conditions

For each canister design, a set of service conditions shall be defined by the manufacturer that, at a minimum, includes the following:

4.1 Pressures

4.1.1 Maximum Developed Pressure

The MDP shall be determined from the metal hydride's temperature-pressure characteristics at the maximum service temperature.

4.1.2 Rated Charging Pressure (RCP)

The RCP shall be stipulated to prevent charging at a pressure that could result in the shell wall stress exceeding the design stress. The RCP shall be given in units of MPa.

4.1.3 Design Stress

The design stress shall be determined from the alloy packing and expansion properties, the maximum developed pressure within the canister and other applicable mechanical loadings.

4.1.4 Pressure Relief Device Activation Pressure

For pressure-activated pressure relief devices (PRDs), the pressure of actuation shall be specified and shall be greater than the maximum developed pressure. For pressure relief valves (PRV) the full flow capacity pressure shall also be specified.

4.2 Rated Capacity

The manufacturer shall state the rated capacity of the canister by mass (SI units) of hydrogen

4.3 Temperature ranges

4.3.1 Operating Temperature Range

The minimum and maximum temperature stipulated under normal operating conditions.

4.3.2 Service Temperature Range

The minimum and maximum temperature stipulated for the product during any normal service condition. This range shall include the operating temperature range and at a minimum shall be from –40 °C to +75 °C.

4.3.3 Pressure Relief Device Activation Temperature

The temperature at which any thermally-actuated PRD is set to activate shall be greater than the maximum service temperature and shall be stipulated.

4.4 Environmental Conditions

Canisters are expected to be exposed to a number of environmental conditions over their useful lifetimes, such as vibration and shock, varying humidity levels and corrosive environments. If a canister is to be used in service where specific environmental conditions are beyond those accounted for in the required tests, then additional testing shall be performed to verify performance under those environmental conditions.

4.5 Service Life

The service life for the canisters 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 code or standard to which the shell is designed, constructed and certified and in no case shall exceed 20 years. See Section 9 concerning requalification of canisters.

4.6 Hydrogen Quality

The recommended quality of the hydrogen gas that is used to fill a canister shall be specified by the manufacturer, such as per ISO 14687: 1999 “Hydrogen Fuel – Product Specification” and its Technical Corrigendums, and ISO 14687 Technical Specifications for fuel cell applications as applicable.

4.7 General

Special Service Conditions - If there are any additional service conditions that need to be specified by the manufacturer regarding the safe operation, handling and usage of these canisters, it shall be clearly defined.

5 Design Considerations

5.1 Shell Requirements

The shell shall be designed and certified according to ISO 7866, ISO 9809-1, ISO 9809-3, ISO 11119-1, ISO 11119-2 or standards registered in accordance with ISO 16528, as applicable, or as required by the authority having jurisdiction. The stress loading exerted on the shell at maximum allowable operational pressure, as defined by the appropriate standard to which it was qualified, shall be greater than or equal to the design stress.

5.2 Design Strength

The process of introducing and subsequently removing hydrogen in the alloy storage material causes it to expand and contract. This, in turn, can result in large stresses inside the alloy particles that cause them to fragment into smaller ones, a phenomenon known as decrepitation. After several charge/discharge cycles, the average particle size may have significantly decreased. Stresses on the canister walls may derive from expansion of the hydrogen absorbing alloy during hydrogenation and from changes in the packing configuration with decrepitation over its service life. The magnitude of the expansion/contraction phenomena will vary greatly as a function of the hydrogen absorbing alloy used. Other mechanical loadings due to, for instance thermal stresses, weight of materials, methods of mounting, etc., shall be considered when defining the overall stress levels.

The shell design shall account for the total stress loadings, including:

- the Maximum Developed Pressure;
- thermal stress, including dissimilar rates of thermal expansion and contraction;
- weight of internals in any possible canister orientation;
- shock and vibration loading;
- maximum stress due to solid material expansion;
- other mechanical loadings.

To verify that the stress levels on the shell are not exceeded, the canister design shall be subjected to the hydrogen cycling and vibration test described in section 6.4.

5.3 Material Selection

Canister components shall be made of materials that are suitable for the service life with the range of conditions expected during normal service. Components which are in contact with gaseous hydrogen and/or metal hydride material shall be sufficiently resistant to their chemical and physical action at service conditions to maintain operational and pressure containment integrity. The following items shall be considered for all systems:

5.3.1 External Surfaces

Canister shells, valves, PRDs and other components shall be subjected to an environmental exposure or corrosion test as required by their individual qualification requirements. 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, anodizing); or a protective coating (e.g. organic coating, paint). If exterior coating is part of the design, the coatings shall be evaluated using the test methods acceptable to the authority having jurisdiction. Any coatings applied to canisters 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 inspection to ensure the continued integrity of the canister.

5.3.2 Compatibility

Compatibility of canister materials with process fluids and solids, specifically embrittlement due to exposure of hydrogen, should be considered. Materials necessary for the pressure containment and structural integrity of the canister and its internal and external appurtenances shall be sufficiently resistant to hydrogen embrittlement, hydrogen attack and reactivity with contained materials to maintain their required integrity for the life of the canister. The susceptibility to hydrogen embrittlement of some commonly used metals is summarized in ISO/TR 15916. Test methods specified in ISO/DIS 11114-4 shall be used to select metallic materials resistant to hydrogen embrittlement where required for pressure or structural integrity. Additional guidance regarding hydrogen compatibility is found in Annex A. Also if charged with gases or materials that are capable of combining chemically with each other or with the canister material, the materials must be selected so as the combination does not endanger the canister integrity.

5.3.3 Temperature

The effect on the canister material of prolonged, repeated or transient exposure of the temperature extremes defined in section 4.3.2 shall be considered.

5.4 Alloy Loading of Canister

Quality control and assurance procedures shall be in place to ensure the consistent loading of the hydrogen-absorbing material into the canister. Any change in material, manufacturing process or installation procedure shall require repeating the hydrogen cycling and vibration test, fire test and drop test.

5.5 Overpressure and Fire protection

The canister shall be protected with one or more pressure relief devices of the self-destructive type, such as fusible trigger, rupture disks and diaphragms, or of the re-sealable type, such as spring-loaded PRVs. The canister and any added component (e.g. insulation or protective material) shall collectively pass the fire test specified in section 6.1. Pressure relief devices shall be approved to a standard acceptable to the authority having jurisdiction in the country of use.

For canisters with an internal volume of less than 0.125 litres, another means may be used to protect from overpressurization, such as venting through a feature integral to the shell. Canisters that use an alternative means to PRD's shall pass the fire test specified in section 6.1.

5.6 Shutoff Valves

The canister assembly shall incorporate a shutoff valve that can be closed when the assembly is disconnected from the refill or gas-consuming equipment. The shutoff valve shall be required to conform to an applicable published standard.

5.6.1 Integral Valve Protection

Canister designs that use an integral method of valve protection that is not meant to be removed for canister operation, such as the use of a shroud, collar or recessing the valve in the canister assembly, shall meet the requirements of the drop test in Section 6.2.

5.6.2 Removable Valve Protection

Canister designs that use a removable means of valve protection that is meant to be removed for canister operation, such as a cover or cap, shall meet the requirements of the drop test in Section 6.2 with the protective means in place and meet the requirements of the valve impact test in Section 6.5 without the protection means in place. The canister shall be labelled in accordance with Section 10.2.1.

6 Type/Qualification Tests

The following tests shall be performed to qualify the canister design. The data for all tests conducted shall be acquired using calibrated instruments.

6.1 Fire Testing

Fire testing shall be performed on all new canister designs to demonstrate that the fire protection system, such as pressure relief devices and/or integral thermal insulation specified in the design, will prevent the rupture of the canister under the specified fire conditions. Any significant change to the design, for example changes in: diameter or length; PRD; shell-type; means of particulate containment or metal hydride, shall necessitate repeating the fire testing.

Exception: A manufacturer can use data and engineering calculations, based on previous fire testing results on existing designs, to show that a new design does not require fire testing.

Precautions shall be taken to insure safety of personnel and property during fire testing in the event that canister rupture occurs.

6.1.1 General Requirements

6.1.1.1 Sample Preparation

Canisters shall be filled to rated capacity with hydrogen. The canisters tested shall be representative of production canisters.

6.1.1.2 Data Monitoring and Recording

Temperature and pressure of the canister shall be monitored remotely and recorded at intervals of every 15 seconds or less. A manual valve shall be installed to allow venting of the canister in the event of a test equipment or system malfunction.

In addition to the pressure and temperature readings, the following information shall also be recorded for each test:

- canister manufacturer
- canister part or model number
- unique identifier;
- PRD-type and rating;
- PRD location and orientation;
- date of test;
- canister pressure;
- canister orientation (vertical, horizontal or inverted);
- ambient temperature;
- estimated wind condition/direction;
- names of witnesses;
- time of activation of pressure relief device; and
- elapsed time to completion of the test.

Exception: For canister designs that preclude monitoring pressure during the fire test, a statement of justification for not monitoring pressure during the fire test shall be given, a means for determining activation of the PRD shall be provided and additional safety precautions shall be taken to safely carry out the fire test.

6.1.1.3 Test Setup

Fire tests shall be conducted on at least three canisters in each orientation of intended use and/or transportation. In the case where canisters are to be used and transported in a single orientation, only testing in that orientation will be required. For canister designs for which the orientation of use and transportation are not specified, at least three canisters shall be fire tested in at least the vertical and horizontal orientation.

Canisters, over their entire width, shall be subjected to a heat source of a maximum length of 1,65 m. Canisters longer than 1,65 m or equipped with multiple PRDs with a spacing greater than 1,65 m, shall be subjected to a partial engulfment fire test in the horizontal orientation. If a canister is longer than 1,65 m and is fitted with a pressure relief device at one end, the opposite end of the canister shall be subjected to the fire source.

If the canister is fitted with pressure relief devices at both ends, or at more than one location along the length of the canister, the fire source shall be centred midway between the pressure relief devices that are separated by the greatest horizontal distance.

For canisters less than 0,30 m in length, install a temperature-indicating device within 0,05 m of but not in contact with the canister surface near each end. For canisters longer than 0,30 m, install a temperature-indicating device at each end and one at the midpoint. Temperature-indicating devices are permitted to be inserted into small metallic blocks (less than 0,025 m per side).

6.1.1.4 Fire Source

The canisters shall be tested either by direct (bonfire) or indirect (chimney) flame impingement method. For short canisters (less than 1,65 m long), the fire source shall totally engulf the test apparatus described in (6.1.1.3 Test Setup). Any fuel may be used for the fire source provided it supplies uniform heat sufficient to maintain the specified test conditions for a minimum of 20 min. The selection of a fuel should take into consideration air pollution concerns. The arrangement of the fire shall be recorded in sufficient detail to ensure that the rate of heat input to the canister is reproducible.

6.1.2 Direct Flame Impingement

Sufficient fuel shall be supplied to ensure a burn time of at least 20 min. The canister shall be placed in the test orientation with the canister at least 0,100 m above the fuel or at a sufficiently greater height to ensure total flame engulfment. Metallic shielding shall be used to prevent direct flame impingement on tank valves, fittings, and/or pressure relief devices. The metallic shielding shall not be in direct contact with the specified fire protection system (pressure relief devices or tank valve).

6.1.3 Indirect Flame Impingement

The canister shall be placed in a test apparatus that is designed to contain the test subject and provide a controlled and reproducible rate of heat input without localized overheating. The apparatus can be constructed of any suitable material capable of withstanding the test environment. The fire source shall be installed to provide heat to the chimney and test specimen in a uniform manner.

Immediately following ignition, the fire shall produce a flame entirely engulfing the test apparatus. The temperature of at least one temperature-indicating device shall indicate a temperature of at least 590 °C within 5 min of ignition. One temperature-indicating device shall maintain an average temperature of at least 590 °C for the duration of the test.

6.1.4 Acceptance Criteria

The canister design is deemed to have passed the test if, for all valid tests, either of the following critieria is met in the same manner:

- the internal pressure vents to zero gauge pressure without rupture of the canister, as defined by section 3.11;
- the canister withstands the fire for a minimum of 20 min without rupture.

Any failure or inconsistency of the fire or heat source during a test shall invalidate the result, and a re-test shall be required. Any venting through or failure of the shell, a valve, fitting or tubing during the test that is not part of the intended protection system, shall invalidate the result and a re-test shall be required.

6.2 Drop test

All canister designs shall meet the requirements of the drop test. Any significant change to the design, for example changes in shell-type or means of particulate containment, shall necessitate repeating the drop test.

6.2.1 General Requirements

The surface onto which the canisters are dropped shall be a smooth, horizontal concrete pad or flooring. The container shall be allowed to bounce on the concrete pad or flooring after the initial impact. No attempt shall be made to prevent this secondary impacting. A guide rail for posture maintenance may be used. Several canisters shall be drop tested at ambient temperature with different drop orientations.

6.2.2 Sample Preparation

All canisters used for these tests shall include their valve protection in accordance with Section 5.6 and have an equivalent weight (± 2 %), packing density and internal structure as production canisters. Ballast material may be used. The canisters shall not be pressurized.

6.2.3 Test Procedure

One or more canisters shall be drop tested in accordance with the following conditions. One canister is permitted to be used for all drop tests.

a) One canister shall be dropped vertically on the end containing the valve assembly, with the lower end at a height of 1,8 m. One canister shall be dropped vertically on the on the end opposite the valve and the lower end shall not be less than 1,8 m. The manufacturer may use the same non-charged canister for all two tests.

b) One canister shall be dropped at a 45 ° angle on head from a height such that the center of gravity is at 1,8 m; however, if the lower end is closer to the ground than 0,6 m, the drop angle shall be changed to maintain a minimum height of 0,6 m and a center of gravity of 1,8 m.

c) One canister shall be dropped from a height of 1,8 m horizontally onto a 0,038 m steel apex (resulting in a height of at least 0,025 m), with the steel apex in the upward position, see Figure 1. The canister shall land at right angles to and on the rounded edge (curvature radius 5,0 mm ± 0,2 mm) of the steel apex, impacting approximately in the center of gravity of a canister. In order to prevent movement of the steel apex by the collision of a canister, the steel apex shall be fixed to concrete pad or flooring. The canister shall strike the steel apex before striking the concrete pad or flooring.

d) When the valves, relief devices and appurtenances are set on both ends of the canister, "45 ° angle on head" shall be read as "45 ° angle on weakest end".

6.2.4 Acceptance criteria

The valve shall be intact and functioning properly after that drop test.

All canisters that have undergone the drop impact tests shall be visually inspected and all apparent damage recorded, subjected to the leak test (Section 6.3) and then be hydrostatically pressurized to destruction. The canisters shall meet the acceptance criteria of 6.3 and the recorded burst pressures shall exceed 85 % of the minimum shell burst pressure.

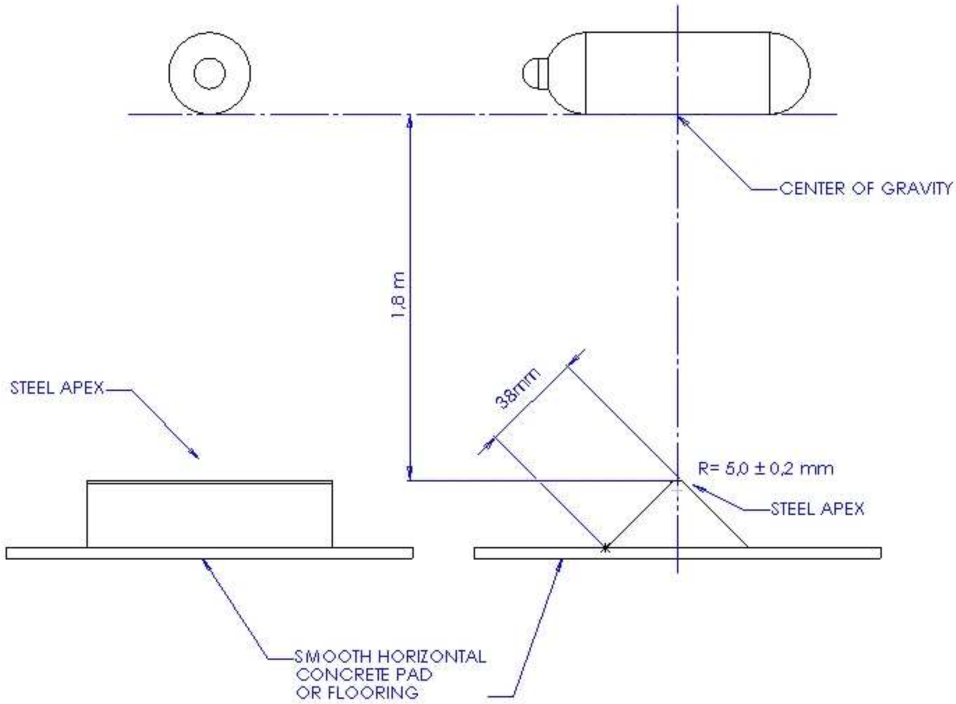

Figure 1- Canister drop test onto an apex.

6.3 Leak Test

6.3.1 General Requirements

The canister shall be charged with either hydrogen, helium or a blend of the two to its rated charging pressure. Before placing the canister in an enclosed area to perform the leakage test, it is recommended to test for the presence of major leaks using a soap bubble solution, or by other adequate means, on all possible leak locations.

The entire canister shall be monitored for leakage.

6.3.2 Acceptance Criteria

The total leakage rate shall be less than 10 cm^3/h (standard conditions: 0 ℃ and 101.325 kPa). If hydrogen gas is not used, the leakage rate shall be converted into an equivalent hydrogen leakage rate.

6.4 Hydrogen Cycling and Strain Measurement Test

Hydrogen cycling and strain measurement testing shall be performed on all new canister designs to demonstrate that the design stress limits of the shell are not exceeded during use. Any significant change to the design, for example changes in: shell-type or specifications; means of particulate containment or metal hydride-type (hydrogen absorbing alloy), shall necessitate repeating the hydrogen cycling and strain measurement testing. Manufacturers can use data and engineering calculations, based on previous cycling and strain measurement testing, to demonstrate that the new design does not require additional testing.

Precautions shall be taken to ensure safety of personnel and property during testing in the event that canister failure or hydrogen release occurs.

6.4.1 General Requirements

The canisters tested shall be representative of production canisters. Each canister shall be adequately instrumented with strain gages to determine the maximum local strain that the shell experiences on cycling. With metal hydride canisters, the strain may not be uniform throughout the canister. The number and location of the strain gages required to ensure that the highest strain experienced by the shell may be determined from engineering models based on knowledge of the design, including the internal configuration and geometry, alloy distribution, and etc. If engineering models cannot accurately determine the points of expected highest strain, then the number and locations of required strain gages shall be empirically determined by extensively instrumenting at least two canisters with strain gages and performing the test. Based on the results, further testing may be performed using fewer strain gages that are strategically placed to monitor for the highest strain levels experienced by the shell.

At a minimum, it is recommended that hoop strain be monitored on cylindrical and dome sections of canisters, that bending strain be monitored on flat sections of canisters and for strain concentration points (such as corners and edges), that the appropriate strain in areas around the concentration point be monitored and an appropriate concentration factor is used to estimate the strain at the concentration point.

The strain gages shall be protected from damage during extended testing and exposure to the cycling environment, for example by use of a chemically resistant epoxy. Periodically during and at not less than at the start and end of cycling, the strain gages shall be calibrated to ensure proper functioning. If any strain gage is found to not be properly functioning, it shall be replaced.

The strain at shell design stress shall be determined either by engineering calculations based on the shell design and material properties or empirically by internally applying either a pneumatic or hydrostatic pressure up to an equivalent gas pressure and measuring the strain. For any shell where the strain gages are applied to an outer layer and not directly to the shell or liner in contact with the metal hydride and hydrogen gas (such as type II, III and IV fiber-wrapped composite tanks) or for any shell that has been intentionally subjected to plastic deformation (i.e. autofrettage), the strain at design stress for each gage shall be determined empirically prior to cycling the canisters with hydrogen. All strain gages shall be calibrated and the calibration periodically checked during testing.

6.4.2 Test Procedure

For canisters that, by design, may only be transported and used in a single orientation, at least five canisters shall be tested in that orientation. For canister designs that do not preclude use in more than a single orientation, at least three canisters shall be tested in each of two orientations perpendicular to each other: with the canister axis horizontal and with the canister axis vertical. The canisters shall be hydrogen charge cycled from not more than 5% of rated capacity to not less than 95% of rated capacity. The rated charging pressure shall be used for charging and the temperatures shall be held within the operating temperature range. The cycling shall be continued for at least 50 cycles and until the acceptable results defined in 6.4.3 are met. If the measured strain on consecutive cycles exceeds that at design stress or plastic deformation of the shell material occurs, the testing shall be discontinued.

At a minimum, a measurement for each strain gage shall be recorded on every cycle while at the maximum state of charge condition.

After the 5th complete cycle and then at 50 cycle intervals, with the canisters charged to not more than 5% of rated capacity, each canister shall be subjected to one of the following vibrational sequences while in the orientation of cycling:

- a sinusoidal waveform with a logarithmic sweep between 7 Hz and 200 Hz and back to 7 Hz traversed in 15 min. This cycle shall be repeated 12 times for a total of 3 hours for each. The logarithmic frequency sweep is as follows: from 7 Hz a peak acceleration of 1 g_n is maintained until 18Hz is reached. The amplitude is then maintained at 0,8mm (1,6 mm total excursion) and the frequency increased until a peak acceleration of 8 g_n occurs (approximately 50 Hz). A peak acceleration of 8 g_n is then maintained until the frequency is increased to 200 Hz.

- only for canisters with a mass greater than 100 kg, the following vibration sequence may be used as an alternate to the above sequence. Simple harmonic motion with a vertical amplitude of 0.8 mm with a 1.6 mm maximum total excursion, frequency to be varied at a rate of 1 Hz/min between the limits of 10 Hz to 55 Hz. The entire range of frequencies and return must be traversed in 95 +/- 5 min.

6.4.3 Acceptable Results

The acceptable results are that for each strain gages, either the maximum measured strain is not greater than 50% of the strain at design stress or that for 50 consecutive cycles, there is no trend of increasing strain. If for any strain gage, the strain for consecutive cycles exceeds the strain for the shell at design stress or if the shell experiences plastic deformation, the test shall be considered to be failed and a redesign required.

To determine that there is no trend of increase in strain, the data for each strain gage with a maximum strain greater than 50% of the strain at design stress shall be analyzed by a least squares linear regression method, according to the equation:

$$a = \frac{\left(\sum_{i=j}^{j+N} y_i x_i\right) - N\overline{yx}}{\left(\sum_{i=j}^{j+N} x_i^2\right) - N\overline{x}^2}$$

where: x is the cycle number, $\overline{x} = \frac{1}{N}\sum_{i=j}^{j+N} x_i$ (average cycle number), N the number of consecutive cycles analyzed and not to be less than 50, y the measured strain and $\overline{y} = \frac{1}{N}\sum_{i=j}^{j+N} y_i$ (the average strain). The canister shall be cycled until, for a period including not less than 50 consecutive cycles, the coefficient a is less than or equal to zero (0) for all strain gages that have a strain reading greater than 50% of the strain at design stress. This criterion shall be met by all strain gages on a canister for the same period of consecutive cycles.

6.5 Valve Impact test

In accordance to Section 5.6, canister designs that employ a removable means of valve protection shall be subjected to the impact test.

6.5.1 Sample Preparation

Three sample canister assemblies of each design and size shall be subjected to this test. For the purpose of this test, ballast may be used in place of hydrogen absorbing alloy or the shell may be left empty. They shall not be pressurized with gas during the impact test.

6.5.2 Test Procedure

A hardened steel ball with a Brinell hardness of 248 of adequate size and mass shall be used as the impact object. Each sample and the impact ball shall be conditioned for at least 4 hrs at -40 ℃, and within 5 min after conditioning be subjected to two impacts in accordance with the Table 1 and as follows: Each sample shall be rigidly anchored and the impact ball shall be allowed to free fall an appropriate distance to impart the required energy to the side of the valve. Then the valve and canister assembly shall be rotated 180 degrees and a second side impact shall be conducted.

Following the two impacts, each sample shall be visually inspected for damage and subjected to a leakage test at 1,5 times the rated charging pressure. After conducting the valve impact test, the sample shall be subjected to the leak test described in section 6.3 and not exhibit a leakage rate of more than 1 scch.

Table 1: Ball impact requirements for valves

Canister Type (V= internal volume in litres)	Impact Joules
V ≤ 0,35 litres	1,02
0,35 litres < V ≤ 10 litres	6,8
10 litres < V ≤ 25 litres	13,5
25 litres < V ≤ 100 litres	27,1
100 litres < V	162,7

6.5.3 Acceptance Criteria

The main canister shutoff valve shall withstand impacts in accordance with this Section without damage that would cause leakage and the valve connection (inlet threads) shall remain intact without cracking. Valve shall be operative and leak free (handwheel may break).

Exception:

If leakage or damage is observed following the impacts, each canister assembly shall incorporate a cover or cap and be retested in accordance with section 6.2 and be marked in accordance with Section 10.2.1.

7 Routine Tests and Inspections

To verify compliance with these requirements, the manufacturer shall maintain production controls and perform the required inspections. The manufacturer shall maintain records of the quality control program on each canister for not less than 10 years. The program shall include at least the following:

Each completed canister shall be subjected to and meet the acceptance criteria of the leakage test of Section 6.3.

For all shells used in the manufacture of canisters in accordance to this standard, all of the appropriate documentation verifying that the shell was manufactured, tested and qualified in accordance to the appropriate shell code or standard shall be obtained and maintained by the canister manufacturer. The canister manufacturer shall perform incoming inspection of shells to the degree necessary to ensure that the shell meets specifications.

8 Filling Procedures and Inspections

8.1 General

Initial filling and refilling of metal hydride canisters shall only be performed using procedures specified by the manufacturer. At a minimum, the manufacturer shall specify the rated charging pressure and minimum and maximum operating temperatures.

8.2 Equipment

The initial fill and refill equipment shall be designed and constructed to meet the requirements of the authorities having jurisdiction.

8.3 Information for inclusion in initial fill and refill procedures

8.3.1 Inspection prior to initial filling and refilling

Manufacturer shall specify inspection procedures to be carried out prior to initial filling and prior to refilling of the canister. Items to be inspected shall include whether the canister is within service date, labels are legible and secure, damaged or missing components in the interface, and damage to the shell or valve, evidence of tampering or abuse. Criteria shall be provided as to when refilling is allowed or when canisters shall be removed from service.

8.3.2 Charging Specifications

The manufacturer shall provide the following information, for the initial filling and refilling of the canisters:

- safety precautions and potential hazards to be aware of;
- a method for determining when the rated capacity described in Section 4.2 has been achieved;
- minimum and maximum pressure range (maximum pressure shall not exceed the rated charging pressure);
- minimum and maximum temperature range;
- other special conditions required for initial filling and refilling.

8.3.3 Inspections and Checks after Initial Filling and Refilling

Manufacturer shall specify an inspection procedure to be carried out after the initial filling and after refilling of the canister. Items to be inspected shall include leakage of hydrogen from the canister and damaged or missing components in the interface (e.g. damage to threads, damaged o-rings or seals).

9 Requalification Procedures

The canister is permitted to be requalified in accordance with the requirements of the code or standard to which the shell was originally designed and certified or in accordance with a method acceptable to the authority having jurisdiction. Caution: certain procedures (e.g. hydrostatic testing) allowed for cylinder or pressure vessel requalification may not be appropriate for metal hydride canisters.

10 Marking, labelling, and documentation

10.1 Marking

The canister shall be stamped or permanently marked with "ISO 16111-RCP" where RCP is the rated charging pressure in units of MPa, manufacturer's identification, date of manufacture and a unique identification number or as required by the authority having jurisdiction. In cases where the RCP is less than 1 MPa, the RCP shall be marked with up to two decimal places (0,xx).

10.2 Labelling

Precautionary labelling shall be in accordance with ISO 7225 Gas Cylinders – Precautionary Labels. The manufacturer shall include an appropriate UN identification number and description (see Annex B for guidance), part or model number and other cautions and hazard warnings pertinent to the metal hydride canister as appropriate. Labels shall not obscure any permanent shell markings.

10.2.1 Labelling concerning removable valve protection

Labelling shall include the following, or the equivalent, “WARNING: Valve may be damaged if subjected to impact. KEEP VALVE PROTECTION IN PLACE WHEN NOT CONNECTED FOR USE.”

10.3 Documentation

The following documentation shall be available from the canister manufacturer.

10.3.1 Material Safety Data Sheets

Material Safety Data Sheets (MSDS) covering both the hydrogen gas and the contained solid material shall be provided for inclusion with all product shipments. The MSDS shall include safety and handling requirements to be followed in case of hydrogen leakage and/or breach of the storage system, exposing the solid material.

10.3.2 Users or operating manual

A users or operating manual shall be provided that specifies service conditions, hydrogen quality, fill procedures, disposal and recycling information and/or other pertinent limitations on use.

10.3.3 Qualification Test Reports

Qualification reports verifying compliance with the requirements of this standard shall be made available to users upon request.

Annex A
(informative)

Material Compatibility for Hydrogen Service

A.1 Material Compatibility for Hydrogen Service

Components in which gaseous hydrogen or hydrogen-containing fluids are processed, as well as all parts used to seal or interconnect the same, shall be sufficiently resistant to the chemical and physical action of hydrogen at the operating conditions.

A.2 Metals and Metallic Materials

Users of this standard should be aware that engineering materials exposed to hydrogen in their service environment may exhibit an increased susceptibility to hydrogen assisted corrosion via different mechanisms such as hydrogen embrittlement and hydrogen attack.

Hydrogen embrittlement is defined as a process resulting in a decrease of the toughness or ductility of a metal due to the permeation of atomic hydrogen.

Hydrogen embrittlement has been recognized classically as being of two types. The first, known as internal hydrogen embrittlement, occurs when the hydrogen enters the metal matrix through material processing techniques and supersaturates the metal with hydrogen. The second type, environmental hydrogen embrittlement, results from hydrogen being absorbed by solid metals from the service environment.

Atomic hydrogen dissolved within a metal interacts with the intrinsic defects of the metal typically increasing crack propagation susceptibility and thus degrading such basic properties as ductility and fracture toughness. There are both important material and environmental variables that contribute to hydrogen-assisted fracture in metals. The material microstructure is an important consideration as second phases, which may or may not be present due to compositional and processing variations, may affect the resistance of the metal to fracture. Second phases, such as ferrite stringers in austenitic stainless steels, may also have a specific orientation leading to profound anisotropic response in the materials. In general, metals can also be processed to have a wide range of strengths, and the resistance to hydrogen-assisted fracture is known to decrease as the strength of the alloy is increased.

The environmental variables affecting hydrogen-assisted fracture include pressure of hydrogen, temperature, chemical environment and strain rate. In general, the susceptibility to hydrogen-assisted fracture increases as hydrogen pressure increases. The effect of temperature, however, is not as systematic. Some metals such as austenitic stainless steels exhibit a local maximum in hydrogen-assisted fracture susceptibility as a function of temperature. Although not well understood, trace gases mixed with the hydrogen gas can also affect hydrogen-assisted fracture. Moisture, for example, may be detrimental to aluminum alloys since wet oxidation produces high-fugacity hydrogen, while in some steels moisture is believed to improve resistance to hydrogen-assisted fracture by producing surface films that serve as kinetic barriers to hydrogen uptake. A so-called inverse strain rate effect is generally observed in the presence of hydrogen; in other words, metals are less susceptible to hydrogen-assisted fracture at high strain rates.

At temperatures close to ambient this phenomenon can affect metals with body centered cubic crystal lattice structure, e.g. ferritic steels. In the absence of residual stress or external loading, environmental hydrogen embrittlement is manifested in various forms, such as blistering, internal cracking, hydride formation, and reduced ductility. With a tensile stress or stress-intensity factor exceeding a specific threshold, the atomic hydrogen interacts with the metal to induce sub-critical crack growth leading to fracture.

Hydrogen embrittlement can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection, and operating in high-pressure, high temperature hydrogen.

Many low-alloyed structural steels may suffer from hydrogen attack at temperatures as low as 200 ℃. T his is a non-reversible degradation of the steel microstructure caused by a chemical reaction between diffusing hydrogen and the carbide particles in the steels that results in the nucleation, growth and merging of methane bubbles along grain boundaries to form fissures.

Hydride embrittlement occurs in metals such as titanium and zirconium and is the process of forming thermodynamically stable and relatively brittle hydride phases within the structure.

Clad welding and welds between dissimilar materials often involve high alloy materials. During operation at temperatures over 250°C hydrogen diffuses in the fusion line between the high alloy weld and the unalloyed/ low alloy base material. During shutdown, the material temperature drops. The reduced solubility and diffusibility of hydrogen breaks the weld by disbonding.

The following are some general recommendations for managing the risk of hydrogen embrittlement.

— Select raw materials with a low susceptibility to hydrogen embrittlement by controlling chemistry (e.g. use of carbide stabilizers), microstructure (e.g. use of austenitic stainless steels), and mechanical properties (e.g. restriction of hardness, preferably below 225 HV, and minimization of residual stresses through heat treatment). Use test methods specified in ISO/DIS 11114-4 to select metallic materials resistant to hydrogen embrittlement. The API Publication 941 shows the limitations of various types of steel as a function of hydrogen pressure and temperature. The susceptibility to hydrogen embrittlement of some commonly used metals is summarized in ISO/TR 15916.

— Clad welds and welds between dissimilar materials used in hydrogen service should be ultrasonically tested at regular intervals and after uncontrolled shutdowns in which the equipment may have cooled rapidly.

— Minimize the level of applied stress and exposure to fatigue situations.

— When plating parts, manage anode/cathode surface area and efficiency, resulting in proper control of applied current densities. High current densities increase hydrogen charging.

— Clean the metals in non-cathodic alkaline solutions and in inhibited acid solutions.

— Use abrasive cleaners for materials having a hardness of 40 HRC or above.

— Use process control checks, when necessary, to mitigate risk of hydrogen embrittlement during manufacturing.

A.3 Polymers, Elastomers, and other non-metallic materials

Most polymers can be considered suitable for gaseous hydrogen service. Due account should be given to the fact that hydrogen diffuses through these materials much easier than through metals. Polytetrafluoroethylene (PTFE or Teflon®) and Polychlorotrifluoroethylene (PCTFE or Kel-F®) are generally suitable for hydrogen service. Suitability of other materials should be verified. Guidance can be found in ISO 11114-2, ISO/TR 15916 and the NASA document NSS 1740.16.

A.4 Other references

Further guidance on hydrogen assisted corrosion and control techniques may be found through the following standards and organizations:

A.4.1 American Society for Testing and Materials (www.astm.org)

ASTM **B577-93** 01-Apr-1993
Standard Test Methods for Detection of Cuprous Oxide (Hydrogen Embrittlement Susceptibility) in Copper

ASTM **B839-94** 01-Nov-1994
Standard Test Method for Residual Embrittlement in Metallic Coated, Externally Threaded Articles, Fasteners, and Rod-Inclined Wedge Method

ASTM **B849-94** 01-Nov-1994
Standard Specification for Pre-Treatments of Iron or Steel for Reducing Risk of Hydrogen Embrittlement

ASTM **B850-98** 01-Nov-1998
Standard Guide for Post-Coating Treatments Steel for Reducing the Risk of Hydrogen Embrittlement

ASTM **E1681-99** 10-Apr-1999
Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials

ASTM **F1459-93** 01-Nov-1993
Standard Test Method for Determination of the Susceptibility of Metallic Materials to Gaseous Hydrogen Embrittlement

ASTM **F1624-00** 01-Aug-2000
Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique

ASTM **F1940-01** 01-Nov-2001
Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners

ASTM **F2078-01** 01-Nov-2001
Standard Terminology Relating to Hydrogen Embrittlement Testing

ASTM **F326-96** 01-Nov-1996
Standard Test Method for Electronic Measurement for Hydrogen Embrittlement from Cadmium-Electroplating Processes

ASTM **F519-97** 01-Nov-1997
Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environments

ASTM **G129-00** 01-Aug-2000
Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking

ASTM **G142-98** 01-Nov-1998
Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen Containing Environments at High Pressure, High Temperature, or Both

ASTM **G146-01** 01-Feb-2001
Standard Practice for Evaluation of Disbonding of Bimetallic Stainless Alloy/Steel Plate for Use in High-Pressure, High-Temperature Refinery Hydrogen Service

ASTM **G148-97** 01-Nov-1997
Standard Practice for Evaluation of Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique

A.4.2 The National Association of Corrosion Engineers (www.nace.org)

NACE **TM0177-96** 23-Dec-1996
Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking in Hydrogen Sulfide (H2S) Environments

NACE **TM0284-96** 30-Mar-1996
Standard Test Method - Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking

A.4.3 The American Petroleum Institute (www.api.org)

API **RP 941** 01-Jan-1997
Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants.

API **934** 01-Dec-2000
Materials and Fabrication Requirements for 2-1/4Cr-1Mo & 3Cr-1Mo Steel Heavy Wall Pressure Vessels for High Temperature, High Pressure Hydrogen Service

A.4.4 American Welding Society (http://www.aws.org/)

ANSI/AWS **A4.3-93** 01-Jan-1993
Standard Methods for Determination of the Diffusible Hydrogen Content of Martensitic, Bainitic, and Ferritic Steel Weld Metal Produced by Arc Welding

A.4.5. The American Society of Mechanical Engineers (www.asme.org)

ASME Boiler and Pressure Vessel Code

ASME/ANSI B31.3 Chemical plant and petroleum refinery piping

ASME/ANSI B31.1 Power piping

A.4.6 ASM International (www.asminternational.org) and the Society of Automotive Engineers (http://www.sae.org/)

SAE/AMS **2451/4** 01-Jul-1998
Plating, Brush, Cadmium - Corrosion Protective, Low Hydrogen Embrittlement

SAE/AMS **2759/9** 01-Nov-1996
Hydrogen Embrittlement Relief (Baking) of Steel Parts

SAE/USCAR **5** 01-Nov-1998
Avoidance of Hydrogen Embrittlement of Steel

A.4.7 International Standards Organization (www.iso.ch)

ISO **15330** 01-Oct-1999
Fasteners -- Preloading test for the detection of hydrogen embrittlement -- Parallel bearing surface method

ISO **15724** 01-Jan-2001
Metallic and other inorganic coatings - Electrochemical measurement of diffusible hydrogen in steels - Barnacle electrode method

ISO **2626** 01-Oct-1973
Copper - Hydrogen embrittlement test

ISO **3690** 01-Mar-2000
Welding and allied processes -- Determination of hydrogen content in ferritic steel arc weld metal

ISO **3690 /Amd1** 01-Jan-1983
Amendment 1 - Welding - Determination of Hydrogen in Deposited Weld Metal Arising from the Use of Covered Electrodes for Welding Mild and Low Alloy Steels

ISO **7539-6** 1989
Corrosion of metals and alloys – Stress corrosion testing - Part 6: Preparation and use of pre-cracked specimens

ISO **9587** 01-Oct-1999
Metallic and other inorganic coatings -- Pretreatments of iron or steel to reduce the risk of hydrogen embrittlement

ISO **9588** 01-Oct-1999
Metallic and other inorganic coatings -- Post-coating treatments of iron or steel to reduce the risk of hydrogen embrittlement

ISO **TR 15916** 15 Feb 2004
Basic considerations for the safety of hydrogen systems

ISO/DIS **11114-4** 2003-07-15
Transportable gas cylinders – Compatibility of cylinders and valve materials with gas contents – Part 4: Test methods for hydrogen compatibility with metals

A.4.8 Standards from European Standards Organizations

BS **7886** 01-Jan-1997
Method of Measurement of Hydrogen Permeation and the Determination of Hydrogen Uptake and Transport in Metals by an Electrochemical Technique

DIN **8572-1** 01-Mar-1981
Determination of Diffusible Hydrogen in Weld Metal - Manual Arc Welding

DIN **8572-2** 01-Mar-1981
Determination of Diffusible Hydrogen in Weld Metal - Submerged Arc Welding

Annex B
(informative)

Applicable Hazard Classifications and Designations found in the UN Model Regulations for the Transport of Dangerous Goods

An appropriate hazard classification and proper shipping name acceptable to the authority having jurisdiction shall be used. The List of Dangerous Goods in the 13th edition of the UN Model Regulations on the Transport of Dangerous Goods includes an entry for metal hydride hydrogen storage systems:

UN No.	Name and description	Class or Division	Subsi-diary Risk	UN Pack-ing Group	Special Provi-sions	Limited Quanti-ties	Packaging And IBC's		Portable Tanks	
							Packing Instruc-tions	Special Provi-sions	Portable Tank Instruc-tions	Portable Tank Special Provis-ions
3468	HYDROGEN IN A METAL HYDRIDE STORAGE SYSTEM	2.1			321	NONE	P099			

Packing Instructions P099: Packaging requirements to be determined by authority having jurisdiction.

Special Provision 321: These storage systems shall always be considered as containing hydrogen.