Modeling of Current Standards for Selecting Pressure Vessel Steels (DOT Packaging) to Transport Hydrogen-Bearing Gases*

PHASE I Report to

The US Department of Transportation, Office of Hazardous Materials Safety Administration, Engineering and Research, Mark Toughiry

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By

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Abstract

This report details the results of the first phase of an analysis of the current standards for selecting pressure vessel steels to transport hydrogen-bearing gases conducted by the Applied Chemicals and Materials Division of the National Institute of Standards and Technology for the Pipelines and Hazardous Materials Agency of the Department of Transportation.

The goals of the study were:

Conduct a thorough survey of the status of standards for selecting pressure vessel steels by conducting a literature review, a survey of industrial stakeholders, a review of regulatory requirements and limits for 34CrMo4 steel and gas composition, a review of the range of 34CrMo4 steel (vessel materials used domestically and internationally), and a review of current test methods;

Develop a research plan that outlines the steps needed to generate a model that includes homogeneous and inhomogeneous material properties, environmental conditions, stress, strain, and loading conditions, which will be used to compare the conditions evaluated through the test methods currently included in the ISO Standard 11114-4 to in-service conditions; and

Conduct a rudimentary comparison between the failure mechanisms that result from the three accepted test methods and in-service failures.

The survey covered ISO Standard 11114-4 for test methods, ISO 9809-1, 2, US DOT 49 CFR §178, and ISO/TR 22694 for manufacturing of seamless steel cylinders, CGA-C5, C6, C18, and C20, ISO 6406 and 16148 for periodic inspection of cylinders.

A research plan has been developed that includes a physics-based model of fracture that will be robust enough to accurately incorporate the conditions of the three approved test methods for qualifying these cylinders. A minimum number of measurements with these test methods will be performed to validate the model.

The comparison found that none of the three approved test methods represented in-service conditions, and none of the tests were robust enough to guarantee a valid test and failure in a short time, with the appropriate failure mechanism.

Keywords: Hydrogen-assisted cracking, hydrogen embrittlement, ISO 11114-4, pitting, pressure vessel, structural steel.

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Abbreviations

ε^p	Equivalent plastic strain
θ_L	equilibrium between lattice site occupancy
θ_T^c	trapping site occupancies, carbides
θ_T^d	trapping site occupancies, dislocations
θ_T^{gb}	trapping site occupancies, grain boundaries
δ_n, δ_t	Normal and tangential displacement constants
Δ_n, Δ_t	Normal and tangential cohesive zone displacements
ΔH	Free energy difference
ΔK	Stress intensity range
ϕ	Fracture energy in air
$\theta_{(L, T)}$	Hydrogen coverage (at lattice and trapping sites)
AISI	American Iron and Steel Institute
ASME	American Society of Mechanical Engineers
B	Specimen thickness
W	Specimen width
$C_{(H, L, T)}$	Hydrogen concentration (total, lattice, trapping)
CMOD	Crack mouth opening displacement
CT	Compact tension
D	diffusion coefficient
D_{eff}	Effective diffusion coefficient
DOT	Department of Transportation
EIGA	European Industrial Gases Association
FBH	machined flat bottom hole
h	hours
HEI	Hydrogen embrittlement index
ID	Internal diameter
ISO	International Standards Organization
ISO TC58/WG7	ISO Technical Committee 58, Working Group 7

J_{IC}	Plane-strain fracture toughness
K_{1H}	Threshold stress intensity factor
K_{app}	Applied stress intensity factor
$K_{critical}$	Critical stress intensity factor
KD-10	ASME Boiler and Pressure Vessel Code, as it applies to vessels in hydrogen service
K_{IAPP}	Applied elastic stress intensity factor
K_{Ic}	Critical plane-strain stress intensity factor in an inert environment
K_{Ix}	Mode I stress intensity factor
$K_{measured}$	Measured stress intensity factor
ksi	Kips (thousands of pounds) per square inch
K_{TH}	Threshold stress intensity factor for hydrogen-assisted cracking
K_{THa}	Threshold stress intensity factor for crack arrest at a fixed displacement
m	meter
min	minute
mm	millimeter
N_T	Trap site density
NASA	National Aeronautics and Space Administration
OD	Outer diameter
p	Hydrostatic stress or pressure
Pa	Pascal
ppm	Parts per million
P_r'	Rupture pressure
$P_r'_{H2}$	Rupture pressure in hydrogen gas
$P_r'_{He}$	Rupture pressure in helium gas
psi	Pounds per square inch
R	Ideal gas constant
R_a	Average surface roughness
R_m	Actual value for the tensile strength (average of two tests)
s	Second

SSRT	slow strain-rate tensile tests
T	Temperature
T_n	Normal traction stress
UE	ultrasonic examination
UTS	ultimate tensile strength
V_H	Partial molar volume of hydrogen
WOL	Wedge opening loading
YP	Yield point

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Executive Summary

The construction of transportable gas cylinders is covered by ISO 11114 [1], and part 4 prescribes test methods for the selection of steels resistant to hydrogen embrittlement. There are three test methods specified in ISO 11114-4 [2], and one of the objectives of this report is to evaluate those test methods from a theoretical test methodology perspective. The second objective of this report is to determine a “best” test method to select and qualify steels that have an ultimate tensile strength greater than 950 MPa (138 ksi) for the construction of seamless steel gas cylinders. The goal is to determine the “best test” that is relevant to in-service conditions, especially when applied to particular high strength steels. This report pertains to 35 CD 4 steel, also known as 34CrMo4 and 35 CD 4 Cr-Mo, and AISI 4135 steel. These are known generally as quench-and-temper steels, where the strength of the steel can be varied by altering quench and temper treatments.

Industry is most concerned with two primary failure scenarios that have been determined to be the most relevant and plausible and therefore require further review. The first failure scenario considers a cylinder with a flaw that passes inspection but grows until failure from successive filling cycles which occur between inspection intervals. The other failure scenario is a filled cylinder that experiences hydrogen diffusing into the wall over time and weakening the grain boundaries, which leads to a through-crack in a steel that does not have adequate resistance to hydrogen embrittlement. The current test methods, one where a thin disk of material forms a bubble and bursts, one where rising load either does or does not lead to crack advance in a pre-cracked specimen, and one where an initial strain is imposed on a pre-cracked specimen and the crack either advances or does not in a set amount of time, do not adequately cover both failure scenarios.

Therefore, suggested modifications were determined for each test method. However, since none of the test methods results in a valid test under in-service conditions, a model will be developed that can relate the test conditions, which include loading, strain, environmental factors, and hydrogen diffusion, of each test method back to in-service conditions. This allows an accurate comparison of the test methods and will point toward a single, best test method.

Introduction

This report describes the work performed by the Applied Chemicals and Materials Division (ACMD) at the National Institute of Standards and Technology (NIST) under the interagency agreement DTPH5615X00015/0001 for the Office of Hazardous Materials Safety Administration, a part of the United States Department of Transportation (DOT). The work is the first phase of a proposed multiphase project aimed at providing the scientific basis to enable the harmonization of techniques used for selecting steels resistant to hydrogen embrittlement for the pressure vessels used to store and transport pressurized hydrogen and other hydrogen-bearing gasses. The first phase of the work, which is covered in this report, includes a review of the current approaches used for selecting steels, the development of a modeling framework to provide an unbiased comparison of current techniques and future techniques, and a simple analysis of the three techniques currently recommended by the ISO 11114-4 committee [2], the standards body that determines the test method or methods for qualifying materials for use in transportable cylinders for hydrogen-bearing gas applications. Proposed phase II work is comprised of a physics-based model of fracture that incorporates hydrogen diffusion in the microstructures of the steels used for transportable gas cylinders, and includes environmental effects on stresses and strains. Measurements from the three test methods currently accepted by the ISO 11114-4 standard will be used to validate the model [2].

Hydrogen gas is widely used in the chemical processing industry and is expected to play a significant role as a transportation fuel in the near future. Because hydrogen gas is highly flammable, it poses significant challenges associated with safe distribution and storage. Gas cylinders are used to transport and store pressurized hydrogen and some hydrogen-bearing gases, but it is widely recognized that these gases can have an embrittling effect on cylinder construction materials, potentially leading to in-service cylinder failure. There are two possible failure scenarios that are safety concerns for the industry. The first is a crack or flaw that has grown in the ensuing time from when the cylinder was last inspected, and upon filling the crack opens up and failure occurs. The other scenario is a filled cylinder that experiences hydrogen diffusing into the wall over time and weakening the grain boundaries, which will eventually cause a through-crack in the steel that does not have adequate resistance to hydrogen.

In the United States, the Department of Transportation (DOT) relies on ISO 11114-4 as a basis for the qualification of steels for pressure vessels such as cylinders, tubes and tank car tanks that are used to transport hydrogen [2]. ISO Standard 11114-4 prescribes three optional test methods for selecting steels resistant to hydrogen embrittlement, but long-standing questions exist around the harmony and suitability of the methods to predict embrittlement for in-service conditions. For example, the extremely severe conditions imposed by some methods differ significantly from the actual in-service conditions, and may not appropriately or consistently evaluate the pertinent embrittlement mechanisms. There is also concern around how test data taken in one set of conditions can be used to predict embrittlement in conditions with different gas chemistries and operating conditions.

The approach used in the ISO 11114-4 standard [2] is to use any of the three accepted methods, with the desired output of determination of hydrogen embrittlement. However, each of the three test methods measures a different property, or makes a measurement that is related to a different property. Therefore, each test method does not necessarily reflect the same failure mechanism, and the failure mechanism corresponding to a test method may not, in turn, correspond to the failure mechanism or mechanisms observed in the field. Accordingly, harmonization of results based upon three test methods is unlikely. Determination of a single test method is highly desirable, particularly in the case of safe and reliable use of steels with UTS > 950 MPa.

A wide variety of laboratory test methods have been used to evaluate and qualify steels to construct pressure vessels and to establish the maximum permissible stress levels or maximum allowable hydrogen gas pressures.

The primary objectives of this report are to determine a "best" test method for qualification of materials that have a UTS greater than 950 MPa (138 ksi) for application of seamless steel gas cylinders for hydrogen-bearing gases, and to evaluate the currently-specified three test methods in the ISO 11114-4 standard [2] from a theoretical test methodology viewpoint. The intent is that the "best test" reflect, or is relevant to, in-service conditions.

There are two possible failure scenarios that are safety concerns for the industry. The first is a crack or flaw that has grown in the ensuing time from when the cylinder was last inspected, and upon filling, the crack opens up and failure occurs. The other scenario is a filled cylinder that experiences hydrogen diffusing into the wall over time and weakening the grain boundaries, which will eventually cause a through-crack in a steel that does not have adequate resistance to hydrogen. A revised ISO Standard 11114-4 should address these concerns.

Furthermore, we recommend that a single test method be used to qualify a steel for the following reasons:

1. It will allow direct comparison between steels that currently perform well (baseline steel qualification) and new, higher-strength steels proposed for use.
2. It will enable development of a model that can interpolate from the test condition to the in-service conditions with inputs on fugacity (pressure), diffusivity, temperature, initial flaw geometry and size, and loading conditions (e.g., the model will be able to combine static and dynamic loading to account for off-nominal conditions that may occur during service).

Review of Current Methods for Selecting Pressure Vessel Steels

The ISO 11114-4 document [2] is the worldwide standard for test methods that qualify steels for seamless cylinders carrying pressurized hydrogen-bearing gases. The subsequent sections will discuss regulatory requirements, details of the test methodologies contained within the standard, a literature review relevant to these test methods, and a survey of industrial codes and standards for design and periodic inspection of transportable pressure vessels. The range of in-service conditions that exist in the field are discussed in the first section, because the in-service conditions are one of the primary factors for determining the relative merits of each test methodology.

In-Service Conditions

The in-service conditions are partly defined by US DOT regulations [3, 4], and partly by design codes. Additionally, limitations of inspection technologies allow for cracks and pits to exist that are below detection, but may become large enough for detection during the next 5-to-10-year use cycle. Reasonable assumptions must be made to generate a worst-case, but probable scenario for starting flaw sizes, maximum stresses and strains, and likely failure modes.

The in-service conditions for portable hydrogen gas-containing pressure vessels are as follows:

1. Maximum pressure, ranges from 130 bar to 1000 bar (2000 psi to 14500 psi), depending on the special permits for the cylinders or tubes
2. Temperature range from –40 to 65 °C
3. Operating pressures are 2/3 of design pressure (based on the test pressure of ~0.6 multiplied by the burst pressure)
4. 5 to 10 years between inspections, depending on the design standard or the U.S. DOT Special permits for the cylinders [5]

If a worst case is considered: a cylinder that was last inspected 4.75 years ago would be filled to 150 bar (2200 psi) on a day that is –40 °C, then is shipped to Arizona where it sits on the dock for months and bakes in the summer sun, whereupon it reaches 65 °C. The ideal gas law tells us that the pressure in that cylinder would rise to 217 bar (3191 psi). That pressure is nearly the design pressure. Now assume that there was an undetectable flaw (0.28 mm deep in a 6 mm wall thickness) at the time of the last inspection. Perhaps that cylinder was filled and emptied weekly prior to this latest fill. That would mean that it has experienced 247 pressure cycles since its last inspection, conceivably opening up a fresh crack surface for the hydrogen to dissociate and through which it will migrate to the stress concentration at the crack tip. All this has occurred without exceeding any condition that was anticipated for in-service conditions, so a new steel would need to have flaw tolerances sufficient to compensate for these conditions.

The kinetics of the mechanisms involved in potential hydrogen damage during storage must be considered for safe operation of seamless steel gas cylinders and tubes. A new cylinder or tube will have an oxide layer on the interior surface that largely precludes hydrogen adsorption and dissociation and/or diffusion into the metal. Repeated use and storage of hydrogen will chemically reduce the oxide, stripping that layer over time and will subsequently produce water within the vessel. That time interval will be a function of the thickness of the original oxide layer and the pressure of gas inside the cylinder or tube, the temperature of storage, and the amount of time at pressure. If there is enough time, pressure, and temperature, the oxide layer may be sufficiently thinned such that hydrogen does adsorb, dissociate, and can diffuse to an existing crack (this may be in the form of a corrosion pit or a flaw from manufacturing). The amount of water produced by chemical reduction of the oxide layer by hydrogen will also be dependent upon the same conditions, and may or may not be enough for enhanced internal corrosion.

Regulatory Requirements and Limits for Steel Cylinders

The inspection of gas cylinders, and the specifications within the codes for inspections, provides details that limit the flaw sizes and define the wall thicknesses of seamless gas cylinders. This section extracts some details that are, in turn, pertinent to the requirements of a single measurement method for qualification of steels for transportable seamless cylinders for hydrogen-bearing gases.

a. Temperature -40 °C to 56 °C
b. Dedicated gas service: Outside of North America, cylinders are dedicated for hydrogen service by regulation, and within North America, industry practice is to dedicate cylinders to hydrogen service, but there is no regulation for dedicated service.
c. Although industry does not normally track the numbers of fills a cylinder sees, certain special permits require that practice.
d. Inspections are every 5–10 years: See CGA C-6 [6], 49 CFR 180.209 [5], and ISO 6408[7]
    1. Visual inspection, *and*
    2. Hydrostatic testing to 5/3 of the service pressure *or*
    3. Ultrasonic testing
e. Conditions that disqualify a cylinder for continued service [CGA-C5 [8], -C6 [6], -C20 [9]]
    1. For hydrostatic testing: 10% expansion of the volume
    2. For ultrasonic testing, refer to Table 1 of CGA C20-2014 [9]
    3. For visual inspection (internal and external), wall thickness must be ≥ 95 % of the original wall thickness based on visual detection of flaws, which include:
        a. Draw marks
        b. Surface pitting
        c. Out of roundness
        d. Dents
        e. Evidence of fire or excursion in service beyond temperature limits
        f. Visual defects – cracks, draw marks, folds in fabrication (inside neck or base)
        g. Wall loss

Review of current test methods and in-service conditions

Test methods that are currently accepted for qualification of steels for use as transportable seamless cylinders for hydrogen-bearing gas applications are defined in ISO 11114-4: 2005 [2], which references ISO 7539-6 [10] for specimen preparation. Design of such cylinders is found in ISO 9809-1 [11], 2 [12]. Details of each test method, advantages, and disadvantages are given. Advantages of each test method come from internal documentation from the ISO TC58/WG7. Disadvantages come from internal documentation from the ISO TC58/WG7and the opinions of the authors.

Method A

Burst test with disc specimen to obtain hydrogen embrittlement index (ratio or $P_r'_{He}/ P_r'_{H2}$, where P_r' is the rupture pressure, normalized to 0.75/average thickness of the disk)

- Disc specimen: Diameter = 58 mm, Thickness = 0.75 mm
- No flaws present and smooth surfaces: R_a < 0.001 mm
- Pressure introduced and increased at rates evenly distributed between 0.1 and 1000 bar/min.
- Rupture Pressure, P_r' normalized to 0.75 P_r/disk thickness
- Hydrogen Embrittlement Index (HEI) ($P_r'_{He}/ P_r'_{H2}$) must be $\leq$ 2 to qualify a steel
- HEI ($P_r'_{He}/ P_r'_{H2}$) plotted vs pressure rise rate
- High purity H_2 at 150 Bar and having a purity of 99.9995 %, $O_2 \leq 1$ ppm, $H_2O \leq 3$ ppm – Or- 99.9999 % $O_2 \leq 0.1$ ppm, $H_2O \leq 0.5$ ppm
- He purity (H_2O, 3 ppm)
- 15 tests total are run; 6 in helium and 9 in hydrogen
- Regression of $P_r'_{He}$ is used
- <u>No</u> regression of $P_r'_{H2}$ is used
- Specimen failure due to: rupture or leaking crack (often this occurs at clamped edge(s) rather than in the dome)
- Two longitudinal specimens tensile tested per ISO Standard 9809-1 [11]

2.1.a. Advantages:

- *Simple, low cost, easy to run/operate*
- Some statistical information from number of tests performed, although those statistics are NOT USED
- Good steel ranking
- Measures "classic" hydrogen embrittlement in the form of loss of ductility
- *Proponents claim that it is reliable, based on documented empirical history*

2.1.b. Disadvantages:

- *Failure exhibits large-scale plasticity, not relevant to in-service use, as cylinders are designed and operated well below the yield strength (Maximum in-service stress is approximately 40 % of the yield strength)*
- *Sample is only 1/8 of wall thickness, and steel microstructure is not typically homogeneous from OD to ID*

- No flaws introduced: any failure condition or cause for removal from service would have to assume a 5% flaw or reduction in wall thickness
- No design information derived
- Unable to determine how conservative the test is compared with in-service conditions
- This test cannot be run with some hydrogen-bearing gases of interest, as there is a phase change in some gases at a lower pressure than that stipulated in the test method

Method B

Fracture test with compact tension (CT) specimen employing step-wise rising load and 20 minute dwells between load increments equivalent to ΔK = 1 MPa·m^{½}. Determines the minimum value of stress intensity factor that results in crack initiation/propagation, referred to as K_{1H} (crack initiation).

   - Traditional CT specimen; 2 specimens tested (specimens diametrically opposed from cylinder wall)
   - No flattening of specimen is allowed
   - Crack initiation and growth monitored by DCPD (direct current potential drop) method
   - High purity H_2 at 150 bar and having a purity of 99.9995 %, $O_2 \leq$ 1 ppm, $H_2O \leq$ 3 ppm, or H_2 = 99.9999 % $O_2 \leq$ 0.1 ppm, $H_2O \leq$ 0.5 ppm
   - Fatigue pre-cracked in H_2
   - Stress intensity factor of 1 MPa·m$^{1/2}$ held for 20 mins and increased in 1 MPa·m$^{1/2}$ increments alternating with 20-min dwells until failure
   - Load increased at a rate of 2×10^{-3} kN·s^{-1}
   - K_{1H} calculated as K_{1H}= YP/BW$^{1/2}$ from ISO Standard 7539-6 [10]
   - Values of K_{1H} for both specimens must be $\geq$ 60/950 x R_m (MPa·m$^{1/2}$) to qualify the steel. R_m is equal to the average of two tensile strength values. The strength ratio maintains the same critical flaw size for new steels >950 MPa (138 ksi) UTS.
   - Two longitudinal tensile specimens adjacent to CT specimens and tested per ISO Standard 9809-1 [11]

2.2.a. Advantages:

- Traditional CT specimen (taken circumferentially with crack orientation along central cylindrical axis)
- Failure occurs upon loading, representing a worst-case in-service condition
- Low-level plasticity is similar to an in-service crack advance event, simulating loading upon filling
- Valid K_{1H} measurement is useful for design, and is an intrinsic material property
- Test represents hydrogen-assisted cracking (HAC)

2.2.b. Disadvantages:

- Modern steels may be more ductile than appropriate for valid K_{1H} test (J-integral test may be more appropriate for modern, higher-toughness steels)

- More expensive and complicated to run—need high-pressure chamber with loading capabilities
- The test is continued to failure at stress intensity levels that are well beyond those observed in service

Method C

Constant displacement test to measure the stress intensity at crack arrest in presence of gaseous hydrogen, referred to as $K_{THarrest}$. Sometimes referred to as the bolt-load test (e.g., constant displacement with modified wedge opening loaded WOL specimen).

- WOL specimen; 3 specimens tested from 3 locations 120° apart.
- Specimens are pre-cracked according to ISO Standard 9809-1 [11]
- Specimens loaded to K_{1APP} = (60)*(R_m/950): by constant displacement. The strength ratio maintains the same critical flaw size for new steels >950 MPa (138 ksi) UTS.
- High purity H_2 at minimum of 150 bar having a purity of 99.9995 %, $O_2 \leq 1$ ppm, $H_2O \leq 3$ ppm
- Fatigue pre-cracked in H_2
- Specimen tested at least for 1000 hours at room temperature
- SEM used to determine crack growth and taken at locations perpendicular to pre-crack at 25 %, 50 %, 75 % of the specimen width, *B*
- Pass/Fail based on the average crack growth: Pass ≤ 0.25 mm, Fail > 0.25 mm
- Two longitudinal tensile specimens adjacent to the CT specimens are to be tested per ISO Standard 9809-1 [11]

Advantages:

- WOL specimen (specimen orientation similar to that of "B" with 3 taken at 120^0 clocking)
- Measures hydrogen-assisted cracking

Disadvantages:

- Comparatively long test, lasting a minimum 1000 hours
- No control on the size of the plastic zone
- No measured output other than by post-mortem examination
- A null test provides no data; steel behavior outside of this very limited test condition is unknown, including the issue of incubation time
- This test artificially induces a plastic zone of uncontrolled size that a crack must grow through in order to have crack propagation; the size of the plastic zone may influence the incubation time
- Does not measure $K_{THarrest}$

Test Methodology Discussion

Ideally, a test method should be conducted at conditions as closely as possible to those encountered during service. However, this can rarely be done, because most in-service conditions provide for years of reliable service, particularly for the case of steel, seamless, gas pressure vessels (cylinders and tubes). Any test method that uses only the stresses and strains that are at the maximums of in-service conditions for these vessels would take years to conduct, and, therefore, would be of little practical use. The next best scenario would be to achieve the same theoretical conditions with a combination of mechanical testing and physics-based modeling.

Barring that, an ideal test completes in a reasonable amount of time and provides the same conditions as the most likely failure mode of a vessel in service. The ISO 11114-4 was begun, however, on the premise that it should contain suitable test methods, or a test method, to evaluate resistance to hydrogen embrittlement. Hydrogen embrittlement can have a broader definition when considering a general audience, but the hydrogen community generally separates hydrogen embrittlement from hydrogen cracking. The hallmark of hydrogen embrittlement is loss of ductility at strains above those that correspond to the ultimate tensile strength, whereas the hallmark of hydrogen-assisted cracking is crack growth at lower stresses than what is seen without the presence of hydrogen. The potential field-failure of these steels relates much more closely to hydrogen-assisted cracking than it does to hydrogen embrittlement.

Most gas cylinders are removed from service before an actual failure occurs, a prudent procedure. Gas cylinders are removed when a cylinder over-expands as a result of wall thinning (case 1) from manufacturing or corrosion, or when a flaw that is 5 % or more of the wall thickness is detected (case 2), typical of corrosion-induced cracking or growth of a manufacturing flaw. A Case 1 field failure is not likely because non-destructive measurement of wall thickness is extremely reliable and design stresses are so low that obtaining a condition of stress above the yield strength is improbable.

Consider the two competing ways that failure might occur; the first case is crack advancement. This case is dealt with below. The other case is hydrogen damage at a constant load, and the crack does not necessarily advance, but grain boundaries weaken. Although, there are cylinders that have been in service for many decades that continue to pass inspection time and again, the use of higher-strength steels could not preclude this possibility. This might be similar to a modified version of Method C, where the load is constant, rather than the displacement.

Another potential failure is from fracture upon filling (pressurization) of the cylinder with a flaw present [13]. This scenario is measured by Method B. Failure from a stress condition above the tensile strength of the steel, which is what is measured by Method A, is extremely unlikely—the least likely failure mode of the three accepted tests in ISO Standard 11114-4 [2].

In either case, for hydrogen damage to occur, hydrogen must dissociate from H_2 to H and adsorb on a metal surface, then diffuse to a site of high potential energy, such as trapping sites or high strain (typically because of high stress). Methods B and C provide a fresh metal surface for easy (low-activation-energy) adsorption at much lower stresses than Method A. Method A requires breaking of the native oxide layer at stresses near the UTS, a phenomenon observed in many tensile-test studies of steels in hydrogen gas.

There are two fundamental issues with use of constant displacement (Method C). One is that as a crack advances, *the stress decreases*, which is not the physical case of a pressurized gas cylinder "holding" pressure while the crack grows into the wall. The other issue is that when a specimen is loaded to a constant displacement, the plastic zone ahead of the crack tip differs from that of a constant load, and is particularly different from that of an inner-wall crack in a pressurized cylinder. The plastic zone caused by constant-displacement loading is likely the origin of the variation in incubation time seen in WOL tests.

The stress intensity factor provided by Method B will be slightly more conservative than the stress intensity factor generated by a quantitative version of Method C (K_{THa}). However, plane stress conditions are likely to prevail when testing for K_{1H} (Method B) with thin specimens such as these, which leads to less conservative results than would be generated with plane strain conditions (edge effects minimized). A suitable finite element model can quantify the difference between the two for both the typical and most extreme in-service conditions of gas cylinders. If Method C is run under such conditions that K_{THa} is determined, then the result of that test is equivalent in value, for design purposes, to that of Method B.

Method C has a few disadvantages compared with Method B. A null test for Method C may not be valid for the type of steels used for gas cylinders, where the null result implies that the stress intensity is at least as large as K_{Appl} (the stress intensity associated with initial loading). The intact oxide layer found when there is no fresh surface (no crack advance for the null test case) inhibits dissociation, adsorption, and diffusion of hydrogen to the crack-tip process zone, raises an additional concern about this test method in the null case. Perhaps a longer incubation time or higher initial load might have resulted in crack growth and a toughness below that prescribed in the standard.

Although no test method is designed to account for the chemical reduction of the oxide layer in the presence of hydrogen, it is possible that the chemical reduction of the oxide layer could be calculated by use of chemical and statistical thermodynamics. This scenario applies to the variable incubation time in Method C.

Method A would be an excellent discriminator for the most severe type of hydrogen embrittlement, the type ascribed to stresses exceeding the ultimate tensile strength. This test method could cause extreme bending near the clamp, where dislocations would be generated early in the test and continue until failure.

The most significant issue with Method A is that it is not representative of likely in-service failure modes. Additionally, the mixing of statistics in Method A is not sound. The use of 6 repeat tests for helium, followed by regression of those results, is sound. The use of 9 tests in hydrogen gas, combined with the choice of the maximum value of those 9 tests, relative to the regression line of the helium tests, is not sound. A regression should also be done on the 9 (preferably 6, the same number as the helium tests) hydrogen tests, and a number of evenly spaced points could then be used for the embrittlement index (ratio). A hypothetical issue arises where a manufacturer might want to qualify a steel with this test method. Since the method uses what is essentially the greatest positive "outlier" from a set of 9 data points, the manufacturer could just perform a few more hydrogen tests under the conditions where the outlier occurred, thereby artificially lowering the maximum embrittlement index down to an acceptable level. The use of a ratio of the pressure at failure in hydrogen compared with that in helium would be a one-to-one comparison, if it were based on comparable stress states in both cases. However, it is known that the disk shape at failure is different when tested in helium and hydrogen [14]. This means that the stress states differ between the two pressurizing gases because the time-dependent material response in the presence of hydrogen changes the mechanics of the test. Therefore, the use of a pressure ratio is inappropriate until the difference in stress states is known. Method A would be acceptable only if re-designed such that failure occurs at the center of the disk, where the stress field is well-known (biaxial). Addition of a pre-defined crack at the center of the disc would result in a known triaxial stress state at the crack tip.

There are issues of inhomogeneity of the steel (see images from Metallurgical Evaluation DOT 3AA cylinder, DTPH56-07-P-000007) through the thickness of the cylinder wall. Method A does not stipulate that samples be taken from different regions of the thickness and tracked to see if certain regions fail at higher or lower stresses. This issue could be even more significant in the case of other hydrogen-bearing gases, where lower test pressures would be required because of phase changes in such gases. Such tests would require thinner specimens that would represent even less of the through-thickness microstructure.

As described in the previous section, none of the ISO Standard 11114-4 test methods in its current form can convincingly predict the behavior of these steels over the course of years of service [2]. There are certain modifications to each test method, however, that may improve their relevance.

Recommendations for Improvement of the Three Currently Accepted Test Methods

Method A:

Create a controlled flaw at the center of the disk

Add strain measurement, such as a grid pattern and imaging of the disc as it forms into a bubble and subsequently fails

Model the differences in stress between helium and hydrogen pressurization, because hydrogen attack of the steel results in a different bubble shape from that derived by helium

Method B:

J_{1H} or K_{1H} in strength range > 950 MPa (138 ksi) to give crack length vs energy

Perform 2 tests, one at 150 bar and one at the maximum in-service pressure, to cover entire scope of the ISO 11114-4 standard and to determine the pressure sensitivity of combined steel and test methodology [2]. If this is too expensive and/or time consuming, test at the maximum in-service pressure.

Predetermine the diffusivity of the steel, and conduct tests at a strain rate commensurate with the time required for the hydrogen to diffuse through the specimen.

Method C:

Conduct test with a CMOD gage and an instrumented bolt to obtain quantitative data. Apply a range of displacements to the bolt so as to guarantee crack growth, and, therefore, K_{THa}.

Perform 2 suites of tests, one at 150 bar and one at the maximum in-service pressure, to cover the entire scope of the ISO 11114-4 standard [2] and to determine pressure sensitivity of combined material and test methodology. If this is too expensive and/or time consuming, test at the maximum in-service pressure.

Add an uncertainty to the result such that the measured quantity must be above the agreed-upon toughness threshold value ($K_{critical}$) when accounting for uncertainty ($K_{measured}$ – uncertainty ≥ $K_{critical}$): this accounts for the dependency of K_{TH} on K_{app}

Recommendations for an ideal qualification method for ISO 11114-4: A qualification method that would accurately represent a material behavior in service is attainable by developing a physics-based model that is informed by a mechanical test that measures the steel's response to stress in the presence of hydrogen. Look-up tables would be provided for ferritic steels that are inclusive of possible candidates for hydrogen-bearing pressure vessels. The model would require data on the permeability, diffusivity, and concentration of hydrogen in representative steels and microstructures under a range of stress states. The mechanical test that would provide the final piece of information to assess the suitability of the steel could be any such test that applies a quantifiable stress state in a pressurized hydrogen environment. We would recommend that there are additional advantages to a modified Method B. It is:

a. Based on fracture
b. Energy-based: J_{IC} or K_{1H}: same as K_{TH} in this strength range (≥ 950 MPa), but gives crack length versus energy for both design and modeling inputs: also allows for smaller specimen dimensions which helps with thin-walled vessel steels

    However, as K values increase for higher-strength steels, the plastic zone is larger than what would be found in service, particularly for a cylindrical geometry with internal pressure. That larger plastic zone also attracts more hydrogen than the in-service case, increasing the risk of hydrogen-assisted cracking where it would not otherwise exist.

c. Low systematic uncertainty
d. Relatively fast
e. Relatively inexpensive

Literature Review

A search of the technical literature was performed for published papers related to quench-and-temper type steels and hydrogen, which included, but was not limited to the terms "pressure vessel steels" or "A516" or "CrMo" or "4130." A goal of this exercise was to elucidate the history as found in the literature that has brought the industry to its present circumstance; that is, what were the precipitating factors for developing in the ISO 11114-4 Standard and the test methods prescribed by the standard.

The cylinder failures that occurred in Europe beginning in the late 1960s and 1970s have been described by Barthelemy [15], Irani [16], and in a report from the European Industrial Gases Association (EIGA) [17]. Over 100 hydrogen transport cylinders failed, especially those that experienced frequent fill cycles (several per week) [16]. Of failures in the United Kingdom, most failed during or immediately following filling and in the knuckle (region of high curvature where the bottom of the cylinder meets the wall) region [18]. Rare instances of vessels exploding were reported [17]. Failures initiated at corrosion pits and exhibited extensive intergranular cracking [15]. The problems were prevalent in Europe, but not in the US where lower-strength steels were employed. A report published in 1981 by EIGA attributed these failures to the higher-strength (unspecified) steels, stress concentrators found in the geometry of the cylinders and welds [15, 16], and fatigue [16, 17].

Prior to these incidents and others taking place at NASA [19, 20], there was very little awareness about the effect of hydrogen on ferritic steels in industrial applications [17, 20]. Beginning in the 1960s and through the 1980s, research was conducted to better understand the effects of hydrogen gas on the integrity of metals in the US [21-23], as well as Europe. Ultimately, standards were developed in Europe, the U.S., and Japan that required tests to be conducted in or with hydrogen gas for the use of steels for transporting hydrogen gas. Research indicated that the failures were from intergranular corrosion, which was known to be exacerbated by sulfur and phosphorous at the grain boundaries[17]. Additional findings included stress concentrations at highly-curved surfaces and manufacturing defects at the surfaces. Recommendations included restricting the ultimate tensile strength of the steels used to 950 MPa, controlled microstructure, restricting phosphorous and sulfur content, seamless construction, and close attention to stress concentrations, whether from the geometry, inclusions, or surface defects [17].

The research generated a better understanding of the degrading effects of hydrogen on ferritic steels, but the tests that would qualify steels for hydrogen use needed to be developed. Fidelle et al. developed a disk pressure test that was designed to study hydrogen gas embrittlement and permeation [24] starting in the late 1960s. With the advent of failures in hydrogen pressure vessels, the disk pressure test was advocated as a possible choice for determining which materials were susceptible to hydrogen embrittlement. Originally [24], the disk pressure test was repeated three times for a particular material and condition, and Fidelle reported a reproducibility between 1 % and 25 %, depending upon the "quality" of the material. Reproducibility for ultra-high-strength materials was reported to be 5 % to 10 %. He also reported that the rupture characteristics of the disk changed, depending on the pressurizing agent. That observation indicates that maximum stresses occurred in different regions for specimens tested in hydrogen gas and in helium gas. Fidelle also reported that the failure pressure in He was not related to the material's tensile strength, only the ductility. When reviewing the attributes of the test, Fidelle states, "…it is possible to **compare** (emphasis added): (a) various materials under given processing or service conditions, and (b) the effects of various processing or service conditions on a same material…". Furthermore, he states, "…if laboratory experiments cannot exactly duplicate reality, it is important to know hydrogen entry rate and distribution in order to simulate it adequately." In 1988, Fidelle employed the disk pressure test to develop a theory of hydrogen embrittlement by **comparing** results under a variety of controlled conditions and materials [14]. Fidelle also reported that a flaw introduced onto the specimen greatly increases the material's susceptibility to hydrogen embrittlement [14].

Concurrent with the work of Fidelle on disk pressure tests, Loginow and Phelps [23] were also conducting research on steels for hydrogen pressure vessels. They used a wedge opening loading (WOL) test to measure the K_H (which relates to K_t, the threshold stress intensity in the presence of hydrogen) of various steels at various stress intensities (30 % to 95 % of the K_{Ic} for that steel in air) and hydrogen gas pressures. The specimens were machined and precracked, such that the crack would grow in the rolling direction. The pins were instrumented with strain gages to act as load cells during the test. With the instrumented pin, it is possible to calculate the initial critical flaw size that allows the onset of fracture in hydrogen [23]. Some interesting findings include that there did not appear to be a relationship between the length of time the specimen was held in pressurized hydrogen gas (incubation time) and the mechanical or metallurgical properties (See Table 6 from Loginow and Phelps below [23]). Rather, they concluded that the kinetics of the hydrogen permeating the oxide layer at the crack tip appeared to be the controlling factor. According to Loginow and Phelps, crack blunting from the loading stress intensity does not prohibit initiation of crack growth in hydrogen. The crack initiated ahead of the precrack, but in the plastic zone. Several hundred hours of exposure time were sufficient for the crack to propagate and arrest. Furthermore, a propensity for crack propagation in hydrogen increased with increasing strength; no correlation was observed with the fracture toughness (K_{1x}) of the material in air.

Table 6 Values of K_H for steels exposed to hydrogen at various pressures

Steel	Yield Strength, ksi	K_H, ksi $\sqrt{\text{inch}}$ 3000 psi (21 MN/m^2)	6000 psi (41 MN/m^2)	9000 psi (62 MN/m^2)	10,000 psi (69 MN/m^2)	14,000 psi (97 MN/m^2)
Resistant Steels						
Type 304	34				NCP-62	
A516	42				NCP-75	
A106	50					NCP-50
HY-80	85				NCP-106	NCP-81
Steels With Moderate Susceptibility						
A372, N&T	85	76	63	67	59	63
A372, Q&T-1100	87	64	50	64		40
4130	92	80	62	41	29	47
4145, Q&T-1100	97	66	61	50	55	28
A372, Q&T-900	101				50	
4147, Q&T-1235	105	88	85	60		42
A517, gr. F	110	78	61	70	64	74
4147, Q&T-1200	113	112	37	41		27
Steels With Appreciable Susceptibility						
4147, Q&T-1170	126	35	27	22		21
HY-130	136	33	29		22	
4145, Q&T-1050	153	20	17			

NCP - No crack propagation at indicated stress-intensity levels.

Table is from Loginow and Phelps [23].

Oriani and Josephic [25] found that the WOL test could generate a crack following a short incubation time of minutes when loaded in low-pressure hydrogen gas. Furthermore, only minutes were needed for additional crack propagation upon increasing the hydrogen gas pressure.

More recently, Nibur et al. [18] found that the incubation time was not significantly impacted, whether the loading of a WOL specimen was done in air or in inert gas. They also observed that the vast majority of the specimens tested exhibited crack growth after incubating in hydrogen for a few hundred hours, many within a few hours if the applied stress intensity was twice the stress intensity at crack arrest.

Al-Anezi et al. [26] preloaded a specimen in bending and then exposed the specimen to a H_2S-containing solution to test a pressure vessel steel for susceptibility to stress-oriented hydrogen-induced cracking (SOHIC). The intergranular cracking was similar to the crack observed in other examples of hydrogen-induced cracking [26, 27]. Another variation of the WOL test was incorporated into the ASME Boiler and Pressure Vessel Code, as it applies to vessels in hydrogen service (KD-10) [28]. The Code allows for Constant Load or Constant Displacement to be applied to a pre-cracked specimen, which is held for 1000 h in hydrogen gas that is pressurized to the design pressure. Similar to the ISO Standard 11114-4 [2], crack extension ≤ 0.25 mm qualifies a steel for hydrogen-bearing pressure vessels according to KD-10.

Many other tests have been considered for qualifying steels for hydrogen pressure vessels [17, 29, 30]. These include tensile (notched and smooth specimens), impact toughness (Charpy V-notch), fracture toughness (rising load/displacement, constant load, stepwise loading), and fatigue[31], the last two with either compact tension or bending specimens. Also, tests that are relevant to steels that will experience hydrogen gas pressures of over 1000 bar in service have become particularly desirable [29, 30] to qualify steels for the tube trailers that will be necessary initially for transporting hydrogen fuel. Lighter weight tubes and/or higher pressures are essential for minimizing the cost of the fuel transportation.

Nibur et al. [18] present an argument for the rising-displacement test (K or J), rather than the constant-displacement test (WOL). They found that the rising-displacement test better represents in-service failure conditions (failing during or immediately following filling).

Fatigue tests on pressure vessel steels have been conducted by several laboratories, in air [32], in hydrogen gas [33-35], and full scale (cyclically loading full-sized cylinders) tests in hydrogen [36]. Fatigue crack growth tests have been incorporated into KD-10 [28]. However, at the present time, fatigue mechanisms are not considered pertinent to the ISO TC58/WG7 committee (high-pressure cylinders and tubes).

Important points found from the literature review include determination of the fracture modes of early gas cylinder failures from the 1970s, realization of why the issues were different during that time between Europe and North America, and how different researchers approached the problem and the range of possible solutions that they identified.

Industry Survey

Seamless steel cylinders for hydrogen gas and hydrogen-bearing gases are periodically re-qualified for service under DOT regulations [4] and by ISO standards [7, 37, 38]. The DOT regulations for periodic inspection refer to Compressed Gas Association standards such as CGA-

C5 [8], C-6 [6], C-18 [39] and C-20 [9]. The ISO standards for periodic inspection of seamless steel cylinders and tubes are ISO 6406 [7] and ISO 16148 [37]. DOT special permitting can qualify cylinders for gases that are ultra-dry and non-corrosive (portable, high-pressure cylinders), and the steels used for these cylinders would be investigated for use for hydrogen-bearing gases under the ISO 11114-4 standard [2]. In North America, cylinders are not dedicated by regulation to service of one type of gas, but it is industry practice to restrict them to a particular gas. Re-qualification is done by visual inspection for dents, bulges, scratches, and corrosion, followed by either hydrostatic testing or ultrasonic scanning. Hydrostatic testing is conducted at 5/3 of the rated pressure of the cylinder, and the expansion of the cylinder following pressurization is measured. A measure of 10 % permanent expansion warrants rejection of that cylinder for further use. During the manufacturing of seamless steel cylinders under ISO 9809-1&2 [11, 12], ultrasonic examination (UE) is used for measurement of wall thickness, as well as any side wall flaw that is deeper than 5 % of the wall thickness. Additionally, the applied UE, capable of detecting a notch depth of 5 % of the wall thickness, will detect any isolated pitting corrosion with depths equal to or greater than 10 % of the wall thickness. In the US, the calibration for UE includes a machined flat bottom hole (FBH) on the ID of a cylinder with the following dimensions: diameter = 3.2 mm (1/8") for all seamless steel cylinders that have an OD<102 mm (4") and diameter = 6.4 mm (1/4") for seamless steel cylinders that have an OD≥102 mm (4"); depth = 10 % of the minimum design wall thickness (t_{min}) for all cylinders. In ISO standards (e.g., 9809-1&2 [11, 12] and 6406 [7]), a machined V-notch depth of 5 % of the wall thickness has been used for detection of a side wall crack with depths greater or equal to 5 % of the wall thickness, as well as pitting corrosion with depths greater or equal to 10 % of the wall thickness. Research was conducted during development of ISO 6406 to prove that a V-notch depth of 5 % of the wall thickness generates the same back-reflection signal of an UE-shear wave as a FBH with a depth of 10 % of the wall thickness. Therefore, in most U.S. documents for UE of seamless gas cylinders the standard is a 10 % FBH, whereas in ISO 6406 the accept/reject criterion is a 5 % V-notch [7].

The ISO TC58/WG7 was established as a result of the 1995-1999 Joint EIGA-WG2/ECMATG Project. Test methods were compared to determine their efficacy in detecting hydrogen embrittlement in order to facilitate the selection of steels for safe and reliable seamless steel cylinders for containment of hydrogen gas where the ultimate tensile strength of such cylinders can exceed 950 MPa (138 ksi). The three acceptable test methods in ISO 11114-4 were determined based on this report, where steel that corresponded to 1980s vintage was measured. This steel was used because that vintage of steel was found to be safe if heat treated to an ultimate tensile strength of 950 MPa or lower, and known to potentially fail if heat treated to greater than 950 MPa (138 ksi). A key feature of this test project was that data were also acquired for fatigue crack growth of CT specimens and full cylinder fatigue tests.

Although the test standard does not stipulate that a test method provides design data, some members of the ISO TC58/WG7 expressed that design data from a standard test would be desirable.

Another item expressed by the ISO TC58/WG7 members was the desire for all three accepted test methods to provide the same results from the viewpoint of passing or failing a steel for service in hydrogen-bearing gases. It is unlikely that this will occur, even given the fact that the ISO TC58/WG7 attempted to harmonize the results of the three test methods. Fundamentally, the three tests measure (or attempt to measure) three different properties. Method A attempts to measure hydrogen embrittlement. Method B attempts to measure plane-strain fracture toughness in research-grade hydrogen at a specified gas pressure, a measure of hydrogen-assisted cracking attributable to a rising load. Method C, a pass/fail test, assesses the resistance to the initiation of crack growth in a research-grade hydrogen environment at a specified gas pressure, a specified initial stress intensity, and given a specified incubation time. Ideally, the wedge opening loading test is performed at constant displacement and measures the threshold stress intensity at crack arrest, and measures hydrogen-induced cracking. Therefore, the three test methods cannot, in all likelihood, produce consistent results for passing or failing a steel.[1]

The accepted test method should reflect in-service conditions, which none of the three methods do currently. Large-scale plasticity occurs during testing with Methods A and B, and Method C either loses load during crack growth (constant displacement test) or is challenging to obtain meaningful data without generating a large plastic zone (constant load test).

The ISO TC58/WG7 has reviewed the three accepted test methods many times and has had testing done at a number of laboratories to determine the efficacy and/or the shortcomings of each method.

The Background for the standard states that the main effect of hydrogen is embrittlement of the metal; that is, increased susceptibility to mechanical failure.[2] The results of embrittlement were loss of ductility (determined by Method A), decrease of static load-bearing capability (determined by Method C), and a decrease in fatigue life.

Test conditions for Method B are given, including the rate at which load is increased. It appears that there is a 20-minute dwell time between load steps (equivalent to a stress of 1 $\text{MPa}\cdot\text{m}^{1/2}$ and a relatively slow loading rate of $2\text{x}10^{-3}$ $\text{kN}\cdot\text{s}^{-1}$). The desired K_{IH}, 60 $\text{MPa}\cdot\text{m}^{1/2}$ (55 $\text{ksi}\cdot\text{in}^{1/2}$), which correlated with the UTS of 950 MPa (138 ksi), was based upon Method C tests conducted by Praxair.

For Method C the value of applied stress intensity, K_{IAPP}, began as the same as the minimum value of desired K_{IH}, but has since been proposed to increase to 1.2 times that, and subsequently to 1.5 times. Method C is defined as successful when no crack growth is observed (a null test), although testing by Sandia National Laboratories showed that the assumption that

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[1] The three test methods are not universally accepted and independent use of the methods could potentially result in a conflicting qualification or disqualification of a particular steel. This conflicts with the purpose and scope of the ISO 11114-4 standard, which is to provide a universally accepted set of test methods.

[2] Hydrogen embrittlement is given a very broad definition by the ISO TC58/WG7. Typically, hydrogen embrittlement is defined as loss of ductility for strains at or beyond the ultimate tensile stress. Other effects are characterized as hydrogen-assisted fracture or hydrogen-assisted fatigue. It seems remiss that the ISO TC58/WG7 does not include hydrogen-assisted fracture as part of its broad definition of hydrogen embrittlement.

K_{TH} is equal to K_{IAPP} upon a null test may not be valid for quench and tempered steel with a UTS above 950 MPa (138 ksi) [40].

Various types of tensile testing have been considered. Slow strain-rate tensile tests, SSRTs, are used extensively worldwide, and are very well-accepted. Deciding upon a slow enough strain rate that would effectually represent hydrogen embrittlement (experts define this as at least 75% of the theoretical maximum effect of hydrogen embrittlement at equilibrium conditions, as defined by Sievert's Law) could be easily found in the literature. For instance, a strain rate of 10^{-4} has been shown to meet this requirement. However, this type of testing has been consistently rejected by the ISO TC58/WG7. One reason given is that sensitivity and reproducibility were poor, particularly for high strain rates. However, high strain rates would not be used in a sensible version of a SSRT. Measurement of reduction of area results in relatively high uncertainty, though, and SSRT measures of "classic" hydrogen embrittlement, the loss of ductility at or above the ultimate tensile strength, is not a likely condition found in field failures of gas cylinders.

Other test methods have been considered by the ISO TC58/WG7, and most tests found in the literature are variations of Methods A, B, or C, are difficult to run, have high uncertainty, or are prohibitively expensive.

Strengths and weaknesses of test methods were discussed by the Working Group. The approach of the ISO TC58/WG7 was from an empirical and historical standpoint of test methodology, and the strengths and weaknesses discussed are valid within that framework. Since our approach to test methodology was based upon measurement theory and likely mechanisms from failures that could occur in the field, comments on the strengths and weaknesses will only be given for select issues. Furthermore, DOT cylinder specifications, Article KD-10 [41], and the ISO Standard 9809-1, -2, [11, 12] and ISO 11120 [42] ensure that large-scale plasticity is not seen in-service. A test that is designed for mechanical environments more severe than the in-service conditions will naturally disqualify steels that may be perfectly suitable, even when considering an additional safety factor.

A potential inconsistency is seen in Method A. The Standard does not stipulate where fracture must occur. The stress state for fracture at the dome is very different from that at the clamp. Therefore, the stress state from one specimen to another, even for a given steel, may not be comparable with this Method.

The statement was made that both fracture mechanics tests can be conducted at pressures significantly lower than the 300 bars given in the scope of the standard, and this may raise doubts on reliability. This relates to the pressure sensitivity of the material. Those tests could easily be re-defined to be run at 300 bars, or at the maximum service pressure, which is what the revised draft of the ISO 11114-4 requires. The doubts on reliability are odd, though, because numerous documents going back to the 1970s conclude that a threshold value for the effect of pressure is in the range of 50 to 100 bar. Granted, this is for carbon and low-alloy steels with UTS below 1000 MPa (145 ksi), but the pressure sensitivity would not be expected to change much if the UTS were even a few hundred MPa higher. The design specifications in ISO 9809-1 & 2 [11, 12] allow seamless steel with UTS up to 1200 MPa (174 ksi), provided that the ratio of burst pressure to test pressure is greater than or equal to 1.6. Therefore, if that requirement can be met, as well as resistance to hydrogen embrittlement that is equivalent (by wall stress) to that of accepted steels with UTS less than 950 MPa (138 ksi), then new, higher-strength steels should qualify for service with hydrogen-bearing gases.

Research Plan

Physics-based Computational Modeling

Regardless of the modifications to any or all of the three test methods, there remain disparities between a laboratory test that can be performed in a reasonable amount of time and in-service conditions. Physics-based computational modeling will be employed to compare the loading conditions, hydrogen mechanisms, and failure modes of each test method to the others and to in-service conditions. It is only by modeling these behaviors that the best laboratory approximation to in-service conditions and probable failures can be determined.

We will develop a physics-based hydrogen diffusion and fracture model composed of three main components, which are: (1) a hydrogen transport model that predicts the concentration of hydrogen at any point in the steel, (2) a hydrogen-induced decohesion model, which accounts for macroscopic embrittlement, and (3) a fracture model to initiate and grow a crack.

To model how hydrogen diffuses through the steel, this proposal leverages the work done by Sofronis and McMeeking [43]. This transport equation, used by many authors [44-46], has been shown to accurately predict the state of hydrogen concentration in the steel. To model fracture (initiation) and growth, this work will use the cohesive zone fracture method [47]. Furthermore, defining the surface energy, or fracture energy of the cohesive zone, as a function of hydrogen coverage, incorporates the effect of hydrogen on the steel's susceptibility to fracture. This has shown to be effective for modeling fracture initiation [44, 48].

Hydrogen Transport: In cylinder steels, hydrogen can reside at either normal interstitial lattice sites (NILS) or trap sites. Following the work of Novak et al. [49], the equilibrium between lattice site occupancy, θ_{L}, and the three trapping site occupancies ($\theta_{\mathrm{T}}^{\mathrm{c}}$, $\theta_{\mathrm{T}}^{\mathrm{gb}}$ and $\theta_{\mathrm{T}}^{\mathrm{d}}$ for carbides, grain boundaries and dislocations, respectively) is governed by Oriani's theory [50]. The governing hydrogen transport equation is based on the influence on diffusion of both hydrostatic stress and plastic strain. The final form of the hydrogen transport equation [49], which is an extension of Fick's law, is

$$\frac{D}{D_{\mathrm{eff}}}\frac{\partial C_{\mathrm{L}}}{\partial t} = D\nabla^2 C_{\mathrm{L}} - \nabla\cdot\left(\frac{DV_{\mathrm{H}}}{3RT}C_{\mathrm{L}}\nabla p\right) - \left(\sum_j \alpha^j\theta_{\mathrm{T}}^j\frac{\partial N_{\mathrm{T}}^{\mathrm{j}}}{\partial\varepsilon^{\mathrm{p}}}\right)\frac{\partial\varepsilon^{\mathrm{p}}}{\partial t}, \tag{1}$$

where D is the diffusion coefficient, D_{eff} is an effective diffusion coefficient related to D, C_{L} is the NILS hydrogen concentration, V_{H} is the partial molar volume of hydrogen, R is the gas constant, T is the temperature, α^j is the number of trapping sites per trap type j, $N_{\mathrm{T}}^{\mathrm{j}}$ is the trap-site density for trap type j, p is the hydrostatic stress or pressure and ε^{p} is the equivalent plastic strain. Motivated by the work of Kumnick and Johnson [51], the trap-site density for dislocations ($N_{\mathrm{T}}^{\mathrm{d}}$) changes with plastic strain, whereas the remaining lattice-site density and trap-site densities remain constant.

Fracture: The initiation and growth of cracks will be modeled with the cohesive zone approach. A cohesive zone is a zero-thickness finite element that is inserted in the crack path in a finite element simulation with a specific constitutive model that dictates the crack opening response.

The constitutive model, seen in equation (2), defines the normal traction (stress) T_n as a function of crack opening displacement Δ_n:

$$T_\mathrm{n} = \frac{\phi}{\delta_\mathrm{n}}\left(\frac{\Delta_\mathrm{n}}{\delta_\mathrm{n}}\right)\exp\left(-\frac{\Delta_\mathrm{n}}{\delta_\mathrm{n}}\right)\exp\left(-\frac{\Delta_\mathrm{t}^2}{\delta_\mathrm{t}^2}\right), \qquad (2)$$

where ϕ is the fracture energy in air (unique to the steel), δ_n and δ_t are the normal and tangential displacement constants of the cohesive zone at which the maximum traction occurs, and Δ_n and Δ_t are the normal and tangential cohesive zone displacements [52]. The maximum traction can be found through $\partial T_\mathrm{n}/\,\partial\delta_\mathrm{n} = 0$ and is usually set to be equal to the yield strength of the steel. A similar formula exists for the tangential response of the cohesive zone but is not included here.

Fracture energy and hydrogen coverage: Based on a first-principles study, Jiang and Carter [53] calculated the ideal surface energy in Fe and Al systems, or otherwise stated, the energy required for decohesion under the influence of varying levels of hydrogen. Serebrinsky et al. [48] showed that the quadratic function

$$\phi(\theta) = (1 - 1.04670 + 0.01687\theta^2)\phi \qquad (3)$$

fits the surface energy data reported by Jiang and Carter, where $\phi(\theta)$ is the surface energy, ϕ is the surface energy of the steel without the influence of hydrogen, and lastly θ is the hydrogen coverage, which is based on the Langmuir-McLean isotherm [48]

$$\theta = \frac{C_\mathrm{h}}{C_\mathrm{h} + \exp(-\Delta H/RT)}, \qquad (4)$$

where C_h is the total concentration of hydrogen $C_\mathrm{h} = C_\mathrm{L} + C_\mathrm{T}$, ΔH is the free energy difference between the surface and bulk steel, R is the gas constant and T is the ambient temperature. The cohesive zone model for fracture can now be rewritten to incorporate the embrittling influence of hydrogen by replacing the fracture energy ϕ in (2) by $\phi(\theta)$ in (3).

Novelty of approach: This model is unique because it combines three important physically motivated computational features to model hydrogen diffusion and embrittlement in steel pressure vessels. These features are (1) the hydrostatic-stress-driven hydrogen diffusion model [54] that predicts the NILS and trap site hydrogen concentrations [50], (2) the cohesive zone fracture model that simulates crack initiation and growth, and (3) the hydrogen-induced decohesion model [48] that defines the energy required to create a new surface, or fracture, as a function of hydrogen coverage.

Modeling of the tests outlined in ISO 11114-4: The model will require calibration of the four primary components: constitutive deformation response, hydrostatic-stress-driven hydrogen diffusion, cohesive zone fracture model that simulates crack initiation and growth, and the hydrogen-induced decohesion response. The hydrostatic-stress-driven hydrogen diffusion will be the most difficult component to calibrate, and therefore will likely be calibrated based upon theory rather than experimental results (although this could be measured by experiments at neutron and synchrotron beam lines). Once the model components are created, integrated, and calibrated, the full model will be used to predict the response of each of the three methods described in the ISO 11114-4 standard [2].

Disc test (Method A): In this test, a polished thin circular disk is clamped around the edges and increasingly pressurized on one side of the disk with hydrogen gas until the disc fails, anywhere from the center of the dome to the edge of the disc. Once the initial conditions and boundary conditions described in Method A are input to the model, the model will be able to characterize the following material responses spatially: elastic and inelastic deformation, hydrogen concentration, and "damage" accumulation. In this case, damage refers to a parameter with a critical value that indicates crack initiation and growth (cohesive zone fracture coupled with the hydrogen-induced decohesion model).

Fracture mechanics test (Method B): In this test, a CT specimen is subjected to an increasing load in the presence of hydrogen. The test is completed once the crack grows a given amount or the specimen fractures. Once the initial conditions and boundary conditions described in Method B are input to the model, the model will be able to characterize the following material responses spatially: elastic and inelastic deformation, hydrogen concentration, and "damage" accumulation, as defined above in Disc test (Method A).

Resistance to hydrogen-assisted cracking (Method C): In this test, a CT specimen is loaded to a specified displacement. The specimen is then placed in gaseous hydrogen. The test is completed after a specified amount of time. Once the initial conditions and boundary conditions described in Method C are input to the model, the model will be able to characterize the following material responses spatially: elastic and inelastic deformation, hydrogen concentration, and "damage" accumulation, as defined above in Disc test (Method A).

Modeling in-service conditions of transportable gas cylinders: The full model will also be used to predict the response of a cylinder typical of those found in-service. Specifically, gas cylinders having no flaws, as well as flaws of varying geometry and percentage of the wall thickness, will be modeled to produce baseline comparison metrics for the results produced in the activities laid out in **Modeling of the tests outlined in ISO 11114-4**.

Comparing simulated results of Methods A, B, and C with in-service conditions: The results of the simulations of methods A, B, and C will be compared with simulated results of the in-service conditions to identify areas of similarity or difference. More specifically, is the compressible gas cylinder steel deforming, i.e., developing plastic strain, like the in-service case? Is the distribution of hydrogen in the steel and the embrittling effect similar to that of the in-service conditions? Furthermore, comparisons between the methods will be made in an attempt to elucidate the differences in deformation response produced by each. In other words, the relative conservatism, which is based on the difference between the stress level of the test condition and that of the stress level of the in-service condition, of each of the three acceptable test methods will be evaluated. In this way a full understanding of each test method may be attained. Finally, parametric studies may be performed using the full model to determine under what conditions Method A, as example, might compare well to the in-service conditions; e.g., induce a crack of 5% specimen thickness.

Improving ISO 1114-4 standard through modeling and simulation: The results from the simulations of the three test methods and in-service conditions, comparisons between simulations of each of the three tests and in-service conditions, and simulation informed modifications to the test methods will be used to guide improvement of the current standard.

Phase II justification – narrative

The ISO TC58/WG7 has been debating over the three accepted test methods for close to 20 years, without consensus on a single test. The testing approach thus far has not focused on the probable failure modes and conditions that could be seen in-service, should a failure actually take place (which is unlikely because these cylinders are designed to have such low stresses). The testing approach did not attempt to connect the conditions of stress and potential flaws that can occur in the field with the conditions of each test. In order to do that, and to provide a quantitative measure of how far beyond in-service conditions are the stresses and hydrogen uptake for each test method, a model is needed. That model must be robust enough to be able to provide consistent and accurate treatment of all three test methods, such that the proponents of each method can be assured that their method is not misrepresented. Outputs of the model can vary, but one output that could be helpful is to calculate the stresses needed to run a test to completion for each method and compare those stresses to the maximum in-service stress. Another could be to calculate what flaw size, as a percentage of the wall thickness, each test method would require in order for that test to complete at in-service stress. Once the model has been developed sufficiently to be able to compare the stress/strain fields and stress-assisted hydrogen diffusion for each test method to in-service stresses and geometry, we would be well positioned to take the model to the point where it can inform the decision on qualifying a steel for hydrogen service. The model would be calibrated for accepted steel with less than or equal to 950 MPa UTS, and for steel that is being used under DOT special permit that has UTS greater than or equal to 1050 MPa, but has not yet been qualified for hydrogen service, so that with K_{1H} data that is acquired in pressurized hydrogen gas, the model can predict how that steel will behave under in-service conditions.

Key data required for model calibration include:

- Full strain tensor, which will allow various geometries to be modeled
- Baseline crack-tip strain field (in air) for CT geometry
- Crack-tip strain field at various levels of stress (ΔK) in hydrogen, potentially at various gas pressures (might not need more than one pressure)
- Diffusivity of hydrogen through microstructural components
    - These will be on clean metal surfaces
    - Vary gas pressure, or fugacity
    - Measure stress component
    - Activation energy
    - Calculate geometric component (gas cylinder geometry attracts less hydrogen than CT geometry)

The only data piece that would be missing from this model would be consideration of the adsorption, dissociation, and possible diffusion through an oxide layer (complete or partial) of hydrogen. This would be part of Phase III, because these type pf measurements would be challenging and would involve collaboration with others. The number of steps in this process would include, but not be limited to:

- Hydrogen adsorbs on the surface

- Surface energy and temperature cleaves the H-H bond
- H diffuses through partial to full oxide layer
    - Kinetics
    - Activation energy
- Determine whether there is a critical concentration of hydrogen to cause localized damage

Summary and Conclusions

Summary of the literature/industry review: A review of the literature provided us with the context for developing the ISO Standard 11114-4 [2]. A spike in cylinder failures from the late 1960s to the early 1980s for cylinders made of higher strength steels (> 950 MPa) had the gas industry and governments reconsidering how steels were chosen for refillable pressure vessels for hydrogen gas service. Historical information was studied and tests were conducted to enable selection of safer, more reliable steels. Tests similar to Methods A and C were established in the literature by the mid-1970s, making those tests logical choices to include in the Standard.

A review of the documents from the ISO Technical Committee 58/Working Group 7 revealed a long history of healthy discussion, disagreement, and consensus-building. While members clearly championed the Method they preferred and questioned the value of the other two methods, the standard has obviously served the community well with a halt to in-service accidents. However, just as clearly, it will be necessary to reassess the three test Methods if higher-strength steels are to be employed for hydrogen gas service. While never losing sight of the goal of safe, reliable service, now is the time to establish a test for steel selection that is based on in-service conditions and failure mechanisms.

Methods A, B, and C with respect to in-service conditions: Limiting the UTS of the pressure vessel steel to ≤ 950 MPa and any qualifications made with Methods A, B, and C from the ISO 11114-4 Standard [2] have proven to avert in-service failures and accidents, despite each testing very different aspects of hydrogen damage. Higher rates of hydrogen diffusivity would be expected at temperatures above room temperature, while tests are now conducted only at room temperature. Methods B and C are conducted at hydrogen gas pressures of 150 bar, although a 10 % over pressurization is permitted and the pressure will rise even higher in hot environments. The scope of the Standard includes pressures up to 300 bar, so tests could be conducted at 300 bar, if these steels are used for hydrogen applications at 300 bar. Methods A and C have significant plasticity introduced, although these gas cylinders operate well below the yield strength of the steel. Furthermore, the failure mechanism of Method A does not represent the manner in which failures are possible in these cylinders.

A look-up table and toughness test in pressurized hydrogen gas would be the most efficient means of determining the suitability of a new steel for hydrogen-gas service. With a physics-based model, it is possible to account for the microstructure, the hydrogen concentration, and the hydrogen diffusivity with respect to the stress intensity factor and temperature. An actual fracture toughness test conducted in pressurized hydrogen gas would provide the necessary data point that combines all the pertinent factors to enable a go/no go decision. Diffusivity measurements would need to be made under a number of conditions, such as temperature, clean surface, traps unfilled, traps filled, etc. Neutron-beam studies can provide data on the strain fields at the crack tip and hydrogen concentrations at various loading conditions. A test chamber developed at NIST that is capable of applying a mechanical force in the presence of pressurized hydrogen gas and is compatible with neutron sources will enable this measurement to take place.

Considerations for other hydrogen-bearing gases: Does each test method measure a likely failure mode of other hydrogen-bearing gases? Can that method be modified for that? Are test conditions such that other hydrogen-bearing gases cannot be measured with that method? For instance, gases that change phase at a pressure well below test conditions (such as silane)? Can that test be modified to account for peculiarities of other hydrogen-bearing gases? Are issues with gases such as H_2S known well enough, relative to behavior of pure hydrogen, to be accounted for, or is testing required for each?

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