MATERIALS FOR LIQUID HYDROGEN, LIQUID AMMONIA AND LIQUID CARBON DIOXIDE CONTAINMENT SYSTEMS ADVISORY

April 2025

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OVERVIEW

OBJECTIVE

The International Maritime Organization (IMO) has set an ambitious goal for the maritime industry to reach net-zero greenhouse gas (GHG) emissions by 2050, with a 40 percent reduction in carbon dioxide (CO_2) emissions expected by 2030. The shipping industry could potentially achieve these targets by either capturing CO_2 emissions or using alternative fuels.

A key aspect of the developing carbon capture value chain is the need to transport and use or sequester captured CO_2. While companies have historically transported CO_2 by pipeline, ship transport offers a potentially more feasible and cost-effective option. On vessels with limited storage space, it is preferred to liquefy CO_2, as its liquid form occupies significantly less volume than its gaseous form.

Among the various alternative marine fuels, hydrogen and ammonia are receiving substantial interest from shipowners. Both are zero-carbon fuels, as they contain no carbon in their molecules. If produced using renewable energy sources and consumed properly, hydrogen and ammonia can be net-zero fuels, generating no CO_2 from production to consumption (Well-to-Wake). These characteristics make ammonia and hydrogen desirable as alternative fuels.

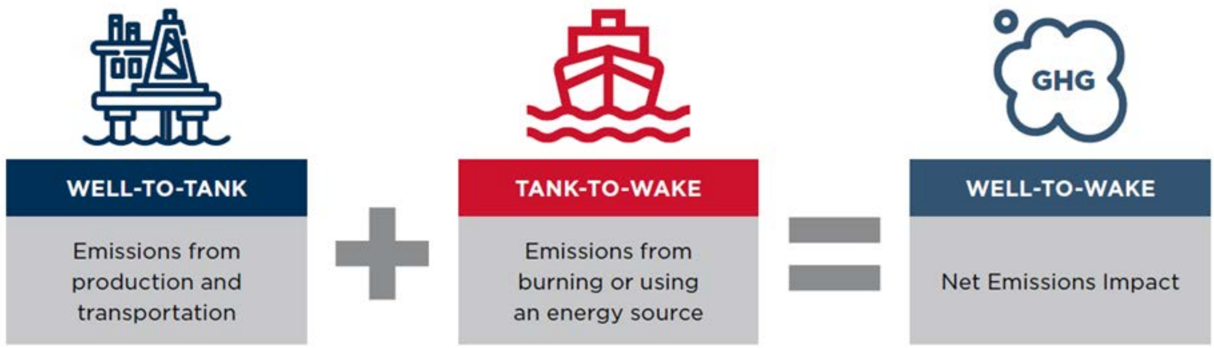

Figure 1: Well-to-Wake emissions concept.

These three liquefied gases – liquid hydrogen (LH_2), liquid ammonia (LNH_3) and liquid carbon dioxide (LCO_2) – must be stored in a tank system aboard the ship, and each presents distinct material challenges. As part of the American Bureau of Shipping's (ABS) efforts to support maritime decarbonization initiatives, this advisory provides guidance on material selection for the cargo and fuel containment systems of these liquefied gases.

INTRODUCTION

This advisory focuses on material selection for tanks storing LH_2, LCO_2 and LNH_3. The characteristics of each liquefied gas are discussed and will later be considered in the context of material selection. Table 1 below summarizes some relevant properties of each of the three liquids.

	LH_2	LCO_2	LNH_3
Boiling Point (° C)*	-253	-78**	-33
Density (kg/m^3)	70.8	1,101	696
Flammability Range	4.0–75.0%	Non-flammable	14.8–33.5%***

*At atmospheric pressure

**Does not have a boiling point; sublimation point is used instead.

*** (DL Fenton et al., 1995)

Table 1: Properties of liquefied gases.

HYDROGEN

Hydrogen naturally occurs as a compound in water or methane. As a gas, it is colorless, odorless and non-toxic. It is extremely light, with a density of 70.8 kilograms per cubic meters (kg/m^3). Due to its very low boiling point of -253° C at atmospheric pressure, hydrogen must be transported under cryogenic conditions to remain liquid.

Hydrogen's flammability represents a risk that must be accounted for. With a flammable range of 4–75 percent, hydrogen has a much wider range than that of other fuels (e.g., 5–15 percent for natural gas). Hydrogen also has a very low ignition energy of 0.02 millijoule (mJ), making stringent fire safety and leak prevention measures essential. Finally, since large volumes of hydrogen will be needed to power a ship, supply issues and costs associated with increasing production pose major challenges to the implementation of hydrogen as a marine fuel.

Currently, one liquefied hydrogen carrier is in service: the *Suiso Frontier*, built by Kawasaki Heavy Industries. It is 116 meters (m) in length and has a storage tank with a capacity of 1,250 m^3 (HESC, 2024).

CARBON DIOXIDE

Carbon dioxide is a non-flammable gas that becomes toxic in high concentrations at room temperature and atmospheric pressure. The triple point of CO_2 presents some unique considerations for maritime shipping. At -56.6° C and 0.52 megapascal (MPa), pure CO_2 exists simultaneously as a solid, liquid and gas. Carbon dioxide can also enter a supercritical state, exhibiting characteristics of both liquid and gaseous phases, at the critical point at about 7.2 MPa and 31° C. As shown in Figure 2, liquid and gaseous CO_2 can easily transition to a solid if the pressure and temperature change, which must be avoided during LCO_2 transportation.

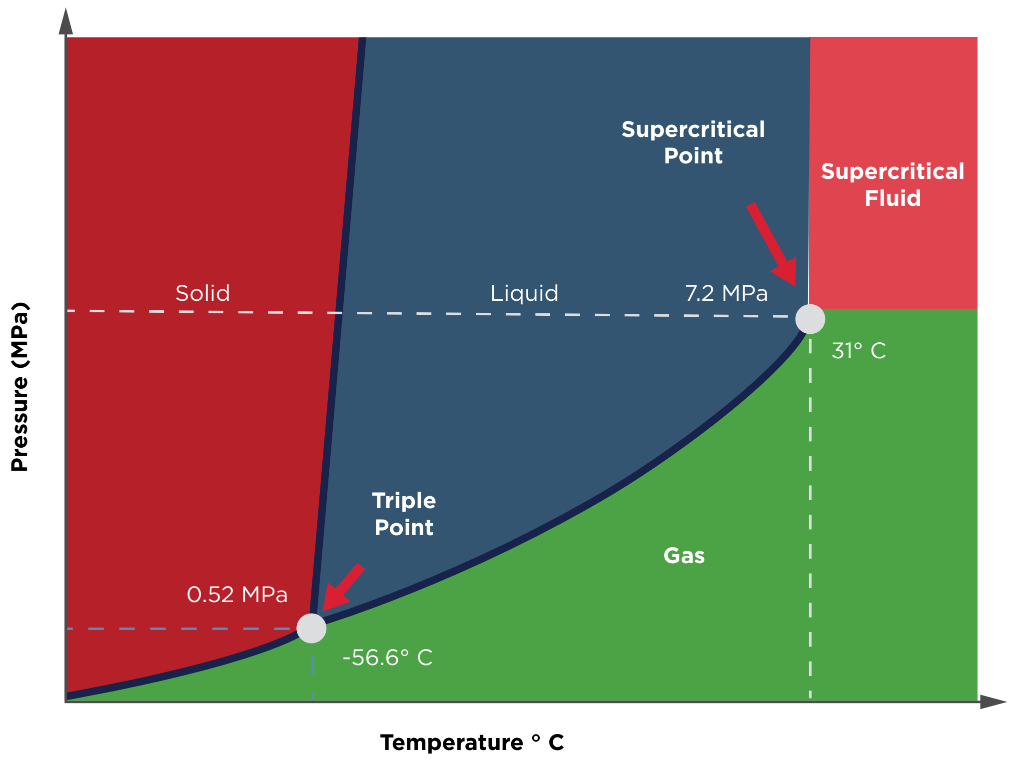

Figure 2: Phase diagram of pure CO_2.

Carbon dioxide must be pressurized to reach and maintain a liquid state. Depending on the transportation and storage conditions, different levels of pressure may be required to liquefy and handle the CO_2. Because CO_2 can exist as a liquid at various temperature and pressure combinations, multiple shipping conditions are possible, as shown in Table 2.

	Low-pressure	Medium-pressure	High-pressure
Operating Pressure (MPa)*	0.7–0.8	1.5–2	4.5
Operating Temperature (° C)	-50	-25	10
Advantages	Leverages liquefied petroleum gas experience and allows larger quantities to be transported over longer distances.	Commercially mature concept.	Low CO_2 conditioning costs. Most appropriate for direct injection from the ship.
Disadvantages	Requires more insulation to avoid solidification around the triple point.	A complicated tank design may not be economically feasible for large vessels.	More costly tank design.

*Adapted from (Al Baroudi et al., 2021)

Table 2: Comparison of CO_2 shipping conditions.

AMMONIA

Ammonia can be used as a fuel or medium to carry hydrogen due to the number of hydrogen atoms in its chemical composition. According to the International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) and the International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels (IGF Code), when used as fuel or cargo, it may be anhydrous or contain water. Ammonia poses serious safety concerns, as it is toxic, explosive and highly corrosive.

Leaked ammonia is hazardous to humans. At low concentrations, ammonia can be irritating to the eyes, skin and lungs. At high concentrations, it becomes immediately life-threatening. It may also be deadly to marine life.

Ammonia has a density of 696 kg/m^3 and a boiling point of -33° C. When fully refrigerated, it is generally stored at its boiling point but can also be stored at a higher temperature under pressure. Anhydrous ammonia or impurities within the ammonia can accelerate corrosion and induce stress corrosion cracking (SCC).

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TANKS FOR LIQUEFIED GASES

INTRODUCTION

According to the IGC and IGF Codes, there are two popular types of cargo/fuel containment systems: independent type and membrane type. Tanks that are self-supporting and independent of the ship structure are referred to as independent tanks. This is distinct from membrane tanks incorporated directly into the ship structure. In this section, both types of tanks will be discussed.

INDEPENDENT TANKS

Independent tanks are freestanding, completely self-supported structures that are not part of the ship's structure and do not contribute to the hull strength. They are often attached to the ship using skirts or other supporting structures. Independent tanks can have varying shapes, such as prismatic, spherical, cylindrical, bi-lobed, tri-lobed and others.

Prismatic tanks are self-supporting and can be built to match the hull shape, maximizing cargo space. Spherical tanks are advantageous due to their marginally lower installation costs, reduced stress concentrators and minimized losses due to a lower surface-to-volume ratio. Despite these advantages, spherical tanks are more difficult to manufacture and do not optimize ship cargo space as effectively as other tank shapes. Cylindrical tanks are easier to build, but their size is more limited. The tank can be designed to be bi-lobular or even tri-lobular to increase capacity.

According to the IMO IGC and IGF Codes, there are three categories of independent tanks: Type A, Type B and Type C. Figure 3 illustrates the geometry of each type.

Figure 3: Independent tank types.

TYPE A TANKS

In practice, Type A tanks can be used to transport large quantities of ammonia. Type A tanks typically have prismatic geometry, are made of flat panels and are covered with external insulation. According to the IGC and IGF Codes, the design vapor pressure of these tanks must be less than 0.07 MPa when constructed primarily of plane surfaces. A complete secondary barrier is required if the cargo temperature at atmospheric pressure is below -10° C. This secondary barrier is a layer of material designed to protect the ship's hull from leaks or cold temperatures, in addition to the primary barrier. If the cargo temperature at atmospheric pressure is above -55° C, the hull structure may act as a secondary barrier. Any secondary barrier must be able to contain a leaked fluid for fifteen days.

TYPE B TANKS

These tanks can be spherical (often referred to as "Moss-type" tanks) or prismatic. When constructed primarily of plane surfaces (as in the case of prismatic tanks), the design vapor pressure should be less than 0.07 MPa. They have partial secondary barriers (e.g., drip trays) to capture and drain leaked fluid. If the cargo temperature at atmospheric pressure is below -10° C, a partial secondary barrier with a small leak protection system shall be provided.

TYPE C TANKS

Type C tanks can be cylindrical or lobed, are pressurized and do not require a secondary barrier. Recently, new non-cylindrical pressurized tank designs have been approved, offering flexibility to adapt the inner hull form like prismatic tanks, thereby increasing the tank capacity. Type C tanks may be insulated with insulation panels or by a vacuum insulation system (the latter only for non-lobed tanks). The ABS *Guidance Notes on Strength Assessment of Independent Type C Tanks* covers these types.

Type C tanks can be used for all three liquefied gases discussed in this advisory. Currently, they are the only applicable solution for LCO_2 storage, as they can maintain the appropriate vapor pressure to keep the CO_2 as a liquid (Al Baroudi et al., 2021) while avoiding solid formation. Bi-lobed and cylindrical tanks can be used for LCO_2, with the design pressure generally increasing as tank volume decreases. Vacuum-insulated Type C tanks are a promising option for the cryogenic temperatures required of LH_2. Small or medium quantities of ammonia can be transported in Type C tanks.

MEMBRANE TANKS

Currently, membrane tanks are the most popular containment system for liquefied natural gas carriers. Membrane tanks are desirable for other liquefied gases due to their ability to maximize the use of the available cargo space available on a ship. These tanks consist of a thin primary barrier, or membrane, which is separated from the ship's hull by an insulation system. A complete secondary barrier is required if the cargo temperature is below -10° C. Membrane tanks can be used for ammonia and LH_2.

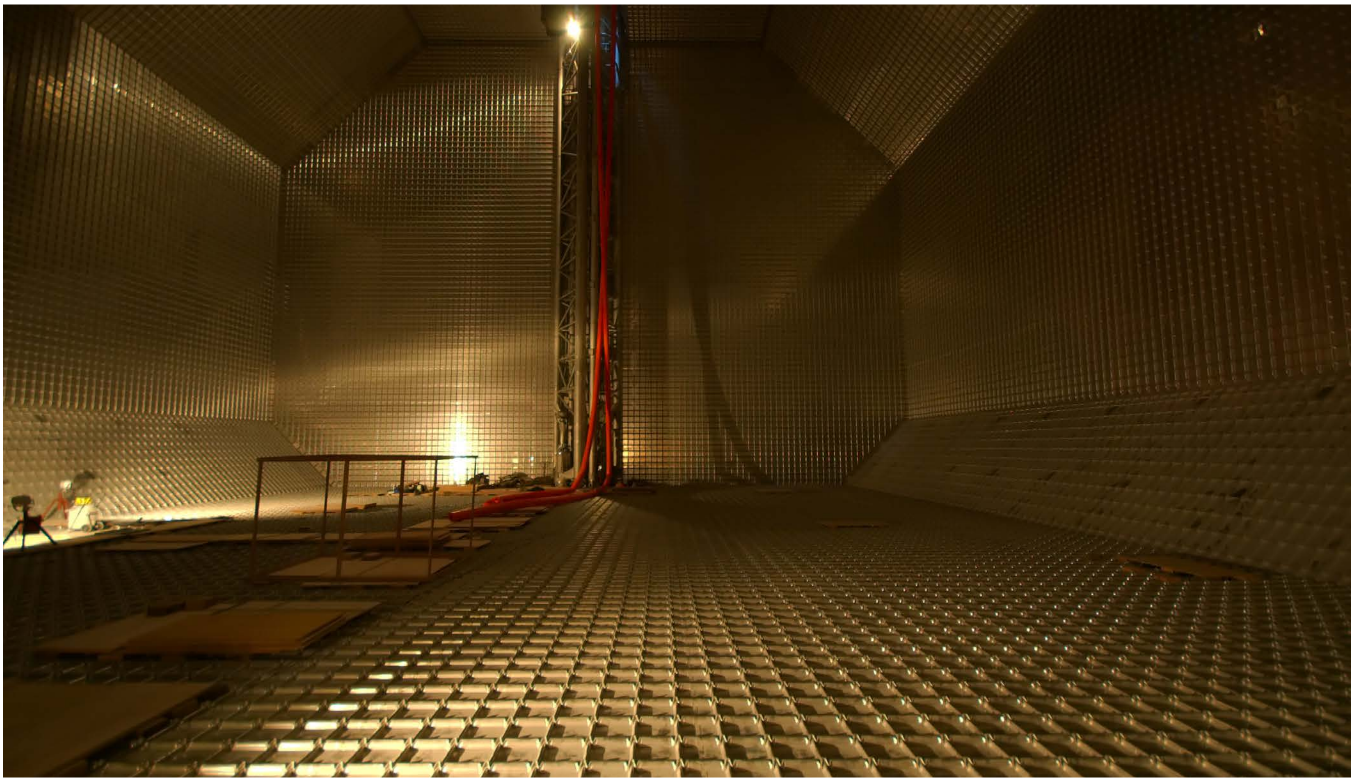


Figure 4: Interior of a membrane tank.

TECHNICAL CHALLENGES

Two main material challenges associated with LH_2 are cryogenic embrittlement, which occurs at the extremely low temperatures required to keep it a liquid, and hydrogen embrittlement (HE). Cryogenic temperatures cause some materials to lose their ductility, making them brittle. This challenge is undesirable for cargo and fuel containment system materials, as brittle materials may fail rapidly and without much warning. Hydrogen embrittlement causes similar issues but through a different mechanism. Due to its small atomic size, hydrogen atoms can diffuse into the metal matrix, weakening the metal and causing brittleness or cracking. The exact mechanism by which HE may occur can vary depending partially on the operating conditions and on the material itself.

Current research on LCO_2 shows that, in the absence of impurities, LCO_2 does not pose many challenges to the materials containing it. Impurities, which can be picked up from the capture process or the source, have the potential to affect material integrity. However, there is limited knowledge of the effects of these impurities. Impurities will also affect the triple point of CO_2, which may change the pressure level required to maintain the liquid state, increasing the risks of corrosion, acid formation and the formation of toxic substances.

The IGC Code provides specifications for both pure and impure ammonia as cargo, recognizing that impurities can influence corrosion rates. Ammonia is highly corrosive, and SCC is a major concern for ammonia containment systems. Due to its toxicity, the containment system must be gas-tight to prevent leaks through the tank wall.

FABRICATION

PRESSURE TESTING

All cargo tanks and process pressure vessels shall be subjected to hydrostatic or hydropneumatic pressure testing in accordance with the ABS *Marine Vessel Rules* (MVR), Part 5C, Chapter 8, Section 4 (MVR 5C-8-4), as applicable to the tank type.

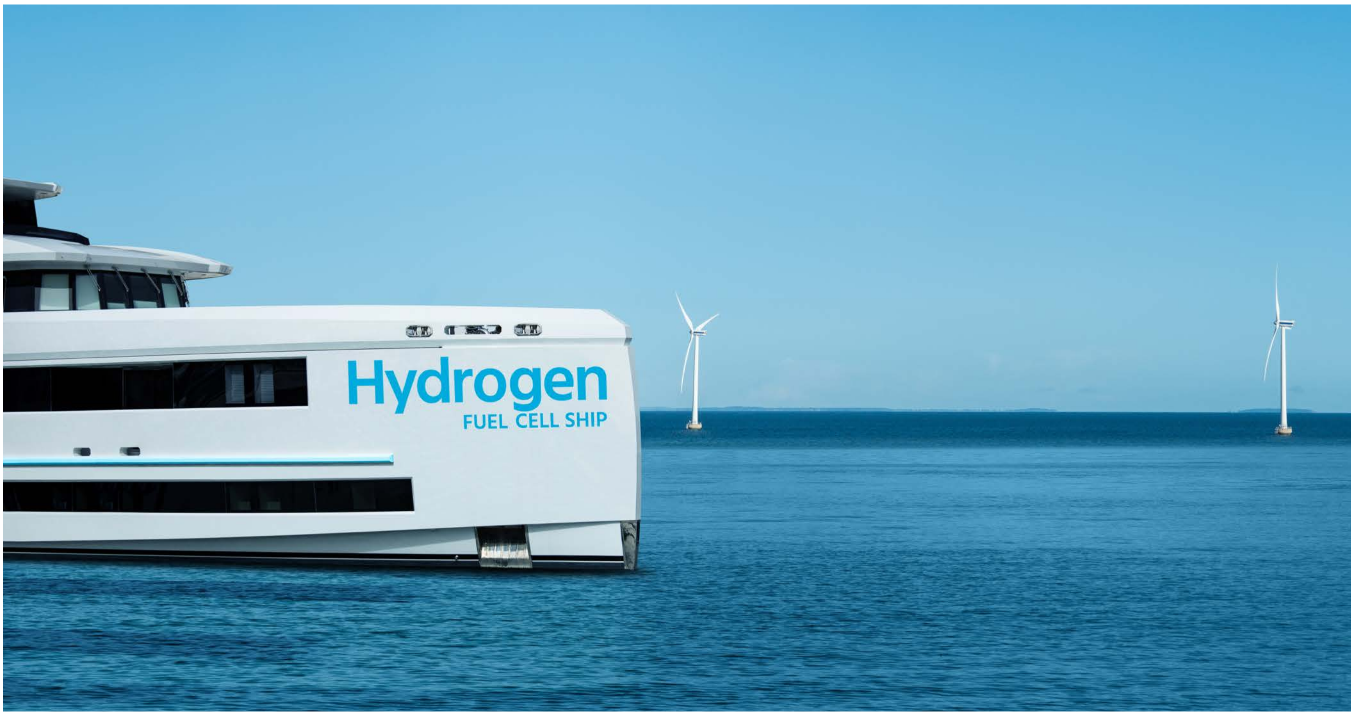
MECHANICAL PROPERTY TESTING

Cargo tanks are required to undergo testing to help ensure that they are safe and suitable for service. The ABS MVR 5C-8-6 specifies general test requirements for mechanical property testing including tensile tests, Charpy V-notch tests, bend tests, microsection, macrosection and hardness testing. These tests must be carried out in accordance with recognized standards and to the satisfaction of the Administration.

LIQUID HYDROGEN

For LH_2, several tests are required to verify material properties. The American Society of Mechanical Engineers (ASME) B31.12 specifies fabrication and erection requirements for LH_2 piping and low-temperature toughness tests on both LH_2 and gaseous hydrogen piping and pipelines. While these specifications apply primarily to piping, some provisions may also be relevant to tanks and containment systems.

The ASME B31.12 further outlines testing procedures, which should follow Chapter GR-3, Part IP and PL of the ASME B31.12, the ASME Boiler and Pressure Vessel Code (BPVC), Section IX and the American Petroleum Institute (API) Standard 1104. If additional requirements are specified in the engineering design, those testing provisions should also be followed. A ship carrying LH_2 in bulk should comply with the IGC Code, as amended by resolution MSC.370(93). Annex 18 of Resolution MSC.420(97), *Interim Recommendations for Carriage of Liquefied Hydrogen in Bulk*, specifies additional requirements for LH_2.



LIQUID CARBON DIOXIDE

In the ABS *Requirements for Liquefied Carbon Dioxide Carriers*, all materials used for the independent Type C tanks must comply with Section 5C-8-6 of the ABS MVR. These materials must undergo tensile tests, toughness tests, bend tests (for welds), and if required by the Administration, macrosection and microsection observations and hardness tests. Charpy V-notch testing and post-weld heat treatment (PWHT), or alternative methods such as engineering critical assessment and mechanical stress relieving by pressurization, are also required for materials intended for LCO_2 service.

LIQUID AMMONIA

Type C tanks for LNH_3 are often required to undergo PWHT. However, for larger tanks that cannot undergo PWHT, mechanical stress relieving by pressurization may be used as an alternative to heat treatment, subject to the following conditions:

1. Steels with a ratio of yield stress to ultimate tensile strength greater than 0.8 shall generally not be mechanically stress relieved. If, however, the yield stress is raised by a method giving the steel high ductility, slightly higher rates may be accepted upon consideration in each case.
2. The thickness of the tank's shell and heads shall not exceed 40 millimeters (mm). Higher thicknesses may be accepted for parts that are thermally stress-relieved.

An alternative to PWHT will be discussed in a subsequent section.

FORMING

Caution should be exercised during forming for tanks where SSC is a potential risk. Forming can induce strain hardening of a material, which increases its yield strength, making it more susceptible to SCC. For brevity, this section focuses only on forming requirements for LH_2.

LIQUID HYDROGEN

The ASME B31.12 code for hydrogen piping specifies that components may be formed by any hot or cold method suitable for the material, intended service and the severity of the bending or forming process. Cold working can reduce resistance to HE, while hot working improves HE resistance. The finished surface must be free of cracks and substantially free from buckling, and the thickness after bending or forming should meet or exceed the engineering design requirements. Heat treatment is generally required after forming, and ASME B31.12 specifies the appropriate temperatures and durations for this process.

Note that this code applies specifically to piping for LH_2 service and may not cover considerations for LH_2 tanks. The International Organization for Standardization (ISO) 20421-1 *Cryogenic vessels — Large transportable vacuum-insulated vessels Part 1: Design, fabrication, inspection, and testing* provides additional specifications for the forming, testing and welding of cryogenic tanks. For tanks with maximum allowable working pressures up to and including 1.2 MPa, the Compressed Gas Association Code (CGA) H-3 applies.

The General Requirements of ASME B31.12 contain definitions and requirements for materials, welding, brazing, heat treating, forming, testing, inspection, examination, operation and maintenance.

Bolted flange connections on hydrogen piping should be avoided where welded connections are feasible.

WELDING AND WELD CONSUMABLES

GENERAL

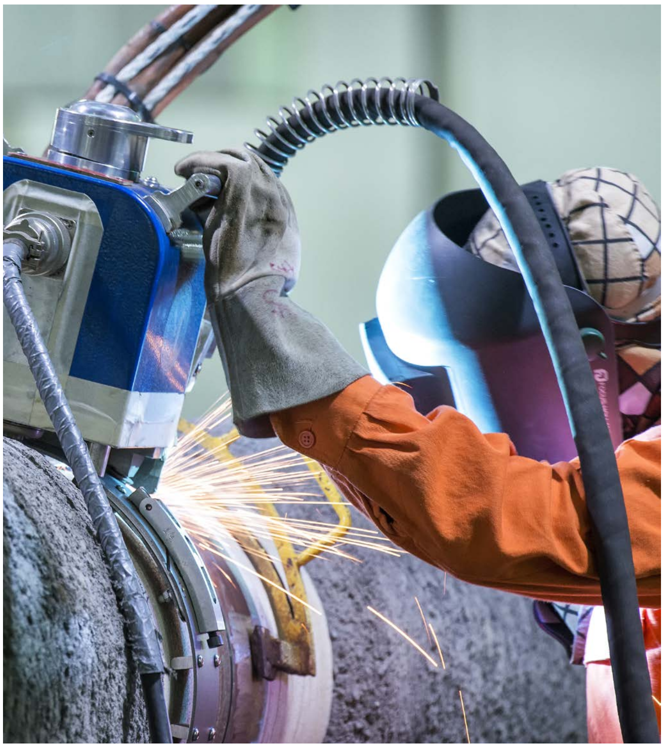
The ABS MVR Part 5C-8-4/20 reiterates the requirements for the construction and welding of independent tanks. Filler metals should conform to the requirements of the ASME BPVC, Section II, Part C and Section IX or a proprietary specification agreed to between the employing contractor and the owner.

LIQUID HYDROGEN

The ASME B31.12 for LH_2 piping permits the following welding processes:

- Manual Welding: Shielded metal arc welding, gas tungsten arc welding (GTAW), plasma arc welding (PAW)
- Semiautomatic Welding: Gas metal arc welding (GMAW), flux core arc welding (FCAW)

Mechanized welding methods include automated or operator-controlled functions. Processes with filler metal



include GTAW, GMAW, FCAW, PAW and submerged arc welding. The processes without filler metal shall be performed using a GTAW or PAW process. Manual torch brazing is acceptable as well. Additional welding or brazing processes may be used when permitted by the engineering design or the owner. ABS is working with other industries to develop requirements for mechanical tests for welding metal in LH_2 service.

According to Annex 18 of MSC.420(97), all welded joints of the cargo tank shells should be of the in-plane butt-weld full penetration type to prevent hydrogen leakage. For dome-to-shell connections only, tee welds of the full penetration type may be used, provided the results of the welding procedure tests support their use.

Finally, welding requirements for hydrogen environments are specified in the ASME BPVC and the American National Standards Institute (ANSI)/ASME B31.3. Post-weld annealing may be required to restore a microstructure susceptible to HE, especially in the heat-affected zone (HAZ). Type 347 stainless steel is very sensitive to cracking during welding, (National Aeronautics and Space Administration, 1997), so proper welding precautions must be followed when using this material.

LIQUID CARBON DIOXIDE

Welding requirements for LCO_2 are limited, as it is a newer aspect of the industry. The ABS *Requirements for Liquefied Carbon Dioxide Carriers* specify that welding procedure specifications (WPS) must be qualified with PWHT, which may include either local or full-scale heat treatment. Construction related to the CO_2 tank and piping welding and testing must be in accordance with the ABS MVR 5C-8-4, subsections 5, 6 and 20.

Some high-manganese steels have been considered for LCO_2 service, but suitable filler metals for such steel have not yet been developed. ABS collaborates with other industries to develop filler metals with the necessary properties.

LIQUID AMMONIA

The ABS *Requirements for Ammonia Fueled Vessels* specify that the materials in general should comply with ABS MVR Part 2. Fuel containment systems, welding procedures, stress relieving and non-destructive testing plans must be submitted to ABS for approval. The API Standard 625, API 620 and other standards, including ASME B31.3, cover low-temperature storage tanks (pressure less than 0.1 MPa) and other standards, including ASME B31.3. For pressurized storage with pressure greater than 0.1 MPa, ASME Section VIII Divisions 1 and 2 are applicable (Challa, 2023).

CORROSION TESTS

LIQUID HYDROGEN AND LIQUID CARBON DIOXIDE

Corrosion in LCO_2 environments is complex due to the interactions between the impurities present in the LCO_2 specification at varying temperatures and pressures.

Currently, no specific corrosion test standards are available for LH_2 or LCO_2. However, ABS MVR Part 5C-8-4/3.5 specifies that a suitable corrosion allowance may be required if the cargo is corrosive, such as when LCO_2 contains corrosive impurities. Other ways to mitigate corrosion, including scavenging against oxidizing agents or corrosive impurities, can also be applied.

LIQUID AMMONIA

Corrosion is a significant concern for ammonia tanks. The IMO Sub-Committee on Carriage of Cargoes and Containers (CCC) 7, Appendix 2, specifies compatibility test requirements for ammonia service. The American Society for Testing and Materials (ASTM) B858 can be applied to copper alloys, though not specifically to high-manganese austenitic steel. Consequently, the following additional non-standard tests should be performed:

- Specimens should be prepared in accordance with ISO 7539-2 and ISO 16540. Two specimens, one welded and one base metal, should be immersed in four ammonia environments for 30 days. After immersion, all specimens should be examined for SCC under an optical microscope with proper magnification. The location and number of cracks should be reported and, if necessary, confirmed by a dye penetrant test. For welded joints, the crack location should be described by location in the base metal, HAZ or weldment.

Ammonia SCC can be visually difficult to detect, as the dye penetrant and radiographic techniques are not always successful with detecting small cracks. Acoustic emission testing and ultrasonic examination can be used to pinpoint potentially susceptible areas without removing a tank from service or its insulation. For surface-breaking cracks, wet fluorescent magnetic particle inspection with an alternating current yoke is considered the most sensitive detection method. However, this method requires qualified individuals to interpret the results. Risk-based inspection programs, fracture mechanics analyses and field inspection histories can minimize the risk of catastrophic failure due to ammonia SCC. Specific measures for preventing ammonia SCC are detailed in the ABS MVR Part 5C-8-17, subsections 12.2-12.8.

ENGINEERING CRITICAL ASSESSMENT

Post-weld heat treatment is commonly used to relieve residual stresses and reduce the risk of material cracking, especially for carbon steels. However, an alternative approach may be acceptable if the tank is too large to perform PWHT for all the welds. During design, PWHT may be waived in lieu of a satisfactory engineering critical assessment (ECA) approved by the classification society or recognized standards. The International Association of Classification Societies (IACS) Unified Requirements (UR) W1 addresses material thicknesses 40-50 mm toughness requirements, PWHT and/or the option of ECA.

The fracture mechanics approach uses mathematical methods to describe the force required to initiate and propagate a crack in a specific material, as well as the material's resistance to crack growth. In BS 7910, a failure assessment diagram (FAD) is used to evaluate the fracture strength of cracked structures. This involves the calculation of:

- A fracture parameter, K_r, based on the ratio of the elastic crack driving force to the material's fracture toughness
- A plastic collapse parameter, L_r, defined as either the ratio of applied load to the limit load or, equivalently, the ratio of reference stress (characterizing the increase in stress in the vicinity of a flaw) to the yield strength

Flaw assessment for ECA is performed in accordance with BS 7910, which currently applies to steel and aluminum. It is important to note that ECA is not a substitute for good workmanship, although it may allow for larger defects.

Furthermore, an ECA must be conducted before manufacturing begins. If the ECA result is unsatisfactory, the tank must be redesigned to meet the ECA requirements, or it must receive PWHT. For more information on ECA, see the ABS *Guide for Liquefied Gas Carriers with Independent Tanks* and the ABS *Guidance Notes on Fracture Analysis for Marine and Offshore Structures*.

Among the three liquid gases discussed in this advisory, PWHT and ECA are most relevant to ammonia and LCO_2 tanks, as they may be built using carbon steel. Engineering critical assessment may also be applied to LH_2 tanks to verify their low-temperature fracture resistance.

MATERIALS FOR LIQUID HYDROGEN

INTRODUCTION

Materials for LH_2 must be able to retain their properties in cryogenic conditions and resist HE. Material selection will also depend on the liquefaction pressure and temperature. Therefore, safety factors for hydrogen systems should be based on material tests conducted under similar conditions to those experienced in service (Sandia National Laboratories, 2008).

At cryogenic temperatures, metals with face-centered cubic (FCC) microstructure are preferable, as FCC materials exhibit better resistance to ruptures in cold environments (Kim et al., 2023). This is due to the higher number of slip planes, planes of atoms that can slide over one another, found in FCC structures, which promote more ductile behavior. Ductility arises from the easy movement of dislocations (defects or irregularities in the metal microstructure). The close-packed active slip planes in FCC materials allow this movement, whereas body-centered cubic (BCC) materials lack this close-packed structure. As a result, higher shearing stresses are required to cause slips in BCC materials, making dislocations harder to move. When this happens, dislocations pile up, hindering the movement of atoms, which can increase the material's yield strength, leading to brittle behavior.

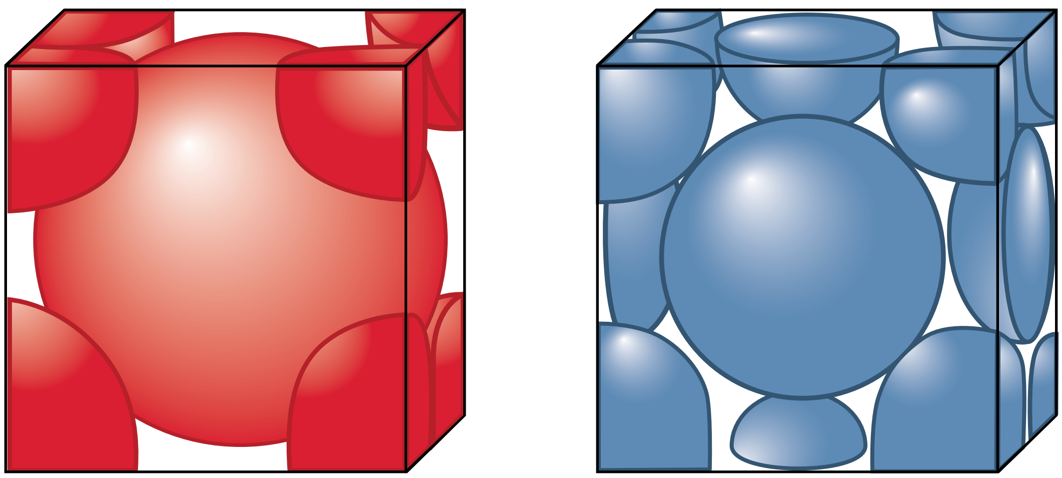


Figure 5: Difference between material microstructures. Body-centered cubic (left), and face-centered cubic (right).

Hydrogen embrittlement occurs when a material is subjected to sufficiently high stress, and hydrogen content is over a critical level, which varies depending on the alloy (Chen et al., 2024). Due to their small size, hydrogen molecules slip into the metal matrix and settle in the grain boundaries, causing a loss of ductility and toughness in the metal, which can lead to cracking and accelerating fatigue. When a crack forms, hydrogen diffuses toward the crack tip, causing it to sharpen and grow under cyclic loading (Murakami et al., 2008). While the effects of hydrogen are often detrimental, some FCC materials have exhibited improved yield strength and ductility after exposure to hydrogen (Chen et al., 2024). Hydrogen embrittlement is theorized to occur via several mechanisms, but the precise cause warrants further research.

There are a few ways to mitigate HE. Generally, alloys with higher strength tend to be more susceptible to HE (Chen et al., 2024), so lower-strength alloys are more favorable. Brittle hydrides, formed in alloys that contain zirconium, niobium, titanium and magnesium, are theorized to promote HE, so avoiding materials with these elements may help prevent embrittlement. Additionally, surface coatings offer an extrinsic approach to preventing HE while introducing hydrogen traps within the alloy microstructure provides an intrinsic solution (Chen et al., 2024).

POTENTIAL MATERIALS

Stainless steel has been widely used for LH_2 tanks as far back as 1955 due to its FCC microstructure. The chromium-nickel-manganese 200 and chromium-nickel 300 steels are preferred, as higher nickel and chromium contents enhance low-temperature performance. However, some 300-series steels can revert into a martensitic microstructure, a very hard microstructure, when stressed, particularly when loaded above their yield stress at low temperatures. This transition can reduce the steel's ductility.

The low-carbon stainless steel variants 304L and 316L (which contains more molybdenum than 304L) have traditionally been used for liquid hydrogen tanks, as both can maintain their properties at low temperatures, are more easily welded than their higher-carbon counterparts, 304 and 316, and are less prone to sensitization (chromium-carbide precipitation, which makes the material more susceptible to corrosion). Although several LH_2 tanks have been built for land-based and road/rail transportation, there is limited official guidance on the appropriate steel grades for marine transportation.

Stainless steel grades 316, 316L and 310S are desirable choices for HE resistance (Liu et al., 2023). The HE resistance of these stainless steels can be further improved by grain refinement, refining the surface to make it less rough and possibly by surface coatings, cathodic protection, ion implantation and laser peening (Qiu et al., 2021). However, these materials generally exhibit lower strength than low-alloy steels, necessitating thicker tank walls, higher manufacturing costs and greater component weight.

Ceramic coatings, known as "barrier coatings," have been used to prevent HE in gaseous hydrogen pipeline applications. Aluminum oxide, titanium aluminum nitride and titanium carbide show promise for preventing the entry of hydrogen into the metal matrix (Wetegrove et al., 2023), although limited information is available regarding their application for cryogenic LH_2 tanks.

It is important to note a potential trade-off between cryogenic properties and HE resistance. For example, cold working increases the strength of austenitic stainless steels (Bertsch et al., 2021) but may increase susceptibility to HE. While increasing nickel content improves cryogenic performance, stainless steel with high nickel and nitrogen content is more susceptible to HE under gaseous conditions. More research is required to determine if this trade-off applies to LH_2 conditions (Liu et al., 2023). Additionally, a modern trend in manufacturing austenitic stainless steel is to use nitrogen in place of the more expensive nickel to promote the formation of the austenite microstructure. However, this practice decreases the steel quality and should be considered during the selection of austenitic stainless steels.

Aluminum alloys can also be used for LH_2 storage. Like stainless steels, they have FCC microstructures and lack a ductile-to-brittle transition temperature, meaning they retain their ductility and high impact toughness, even at low temperatures. The current preferred alloys for LH_2 services include the aluminum-magnesium 5000 series, aluminum-manganese 3000 series, aluminum-magnesium-silicon 6000 alloys, aluminum-zinc-magnesium 7000 alloys and strain-hardened aluminum-copper-magnesium 2000 series. Aluminum alloy 5086 is recommended by NASA for lining LH_2 storage tanks (Sekaran et al., 2014). It is important to note that alloys like 5086 come in various tempers, which can affect their mechanical properties.

One of the biggest challenges of using aluminum is the knowledge and skill level required to perform quality welding and fabrication. Aluminum is far more susceptible to cracking during welding and to defects compared to most steels if incorrect procedures and practices are employed. When hydrogen is introduced, microcracks in the weld toe can increase the likelihood of HE. High-strength aluminum alloys are very sensitive to HE, and higher amounts of alloying elements can promote SCC and may increase HE.

Various methods may be employed to reduce the risk of HE in aluminum alloys, including anodizing to inhibit film formation, acid radical suppression and sodium silicate solution inhibition. Coatings like nickel act as hydrogen barriers, while cadmium coatings encourage hydrogen to recombine and bubble out of the material. Other promising coatings include platinum, copper, gold, tin, tin-lead alloys, metal oxides and titanium nitride.

Additionally, grain refinement and heat treatment both help enhance HE resistance. Multi-level nanomaterials have also been proposed to prevent HE. Soft mold forming or additive manufacturing can eliminate the need for welding in high-stress areas, such as nodes, and may reduce the risk of hydrogen cracking (Chen, 2021). Friction stir welding has also demonstrated the potential to offer enhanced resistance to HE. More recent techniques use homogenization to promote the appearance of zircon nanoparticles, which can reduce hydrogen mobility in the metal matrix and increase HE resistance. However, as mentioned earlier, some methods for preventing HE come at the expense of mechanical properties (Safyari et al., 2023).

Titanium alloys are known for their exceptional cryogenic performance and have been used extensively by NASA for hydrogen tanks. While properties like elongation, impact toughness and fracture toughness decrease with temperature, these can be improved by reducing the content of carbon, hydrogen, oxygen, and other interstitial elements and minimizing the exposure to chlorine. Currently, the commonly used “space alloys” are OT4 and BT5-1 for Russia and TA7 and alpha-Ti for the United States, while the TC4 E1I alloy was mainly used in the Apollo projects (Qiu et al., 2021). Hydrogen has even been proposed as a temporary alloying element to enhance the formability of titanium alloys (Chen et al., 2024).

Due to its high cost, it is unlikely that an entire LH_2 storage tank would be constructed of titanium, but it might be used for LH_2 conduits, valves, fittings or cargo pipes. However, titanium alloys may also be susceptible to HE.

APPROVAL PROCEDURE

Section 6 of the ABS *Requirements for Liquefied Hydrogen Carriers* specifies that any materials directly exposed to hydrogen during normal operations must meet the design requirements appropriate for the application, operating conditions and environment. Materials that are or can come into contact with cryogenic fluids are to be in accordance with ISO 21010. Materials exposed to high oxygen concentrations need to be oxygen-resistant, as described in 5C-8-17/17 of the ABS MVR. This is especially critical for insulation materials, as oxygen will condense in the insulation that is exposed to air due to the lower temperature. Therefore, the insulation must be non-combustible to reduce the risk of fire.

The ABS MVR Part 2-1-4/13 states that austenitic low-carbon (less than 0.10 percent carbon) stainless steels and aluminum alloys are to be used for service temperatures below -165° C. Toughness tests for service temperatures of -254° C and below will be subject to special consideration.

Both ASME B31.12 and ANSI/American Institute of Aeronautics and Astronautics (AIAA) G-095A provide lists of materials that are suitable for hydrogen service. Table 3 below is adapted from the latter and enumerates which materials are suitable for LH_2 service.

Material	LH_2	Notes
Aluminum and its alloys	Yes	
Austenitic stainless steels with > 7% Nickel (304, 304L, 308, 316, 321, 347)	Yes	Some make martensitic conversion if stressed above yield point at low temperature
Carbon steels	No	Too brittle for cryogenic service
Copper and its alloys (brass, bronze, copper-nickel)	Yes	
Grey, ductile or cast iron	No	Not permitted for hydrogen service
Low-alloy steels	No	Too brittle for cryogenic service
Nickel and its alloys	No	Susceptible to HE
Nickel steels (2.25%, 3.5%, 5% and 9% nickel)	No	Ductility lost at LH_2 temperatures
Titanium and its alloys	Yes	Susceptible to HE

Source: ANSI/AIAA G-095A

Table 3: Suitable materials for LH_2 service.

MATERIALS FOR LIQUID CARBON DIOXIDE

INTRODUCTION

Most current research on the interaction between metals and LCO_2 focuses on pipeline conditions, where the fluid usually flows in a supercritical state. As a result, some of the findings observed in pipelines may not apply to tanks, particularly findings related to multiphase flow effects on corrosion. However, valuable information can still be drawn from this research to inform the understanding of LCO_2 storage on board vessels.

CHARACTERISTICS OF LIQUID CARBON DIOXIDE

Liquid CO_2 shipping is covered under the IGC Code. Liquid CO_2 has a distinct triple point, which is critical for shipping purposes. The CO_2 must not change phase from liquid to solid during transportation, operations, or during loading and unloading. Measures must be taken to prevent this transition and maintain the appropriate pressure and temperature conditions for LCO_2. Additionally, measures must also be taken to avoid leakage, and its associated pressure drop.

The presence of impurities in captured LCO_2 presents numerous challenges for containment systems. These impurities can generally be grouped into two categories:

- Impurities that have thermophysical effects on the phase boundary (nitrogen, oxygen, argon, methane and hydrogen)
- Impurities that promote corrosion (oxygen, water, sulfur oxides (SO_x), nitrous oxides (NO_x), and hydrogen sulfide (H_2S))

Impurities that shift the phase boundary must be monitored, kept to a minimum or eliminated completely. The presence of impurities with thermophysical effects increases the risk of dry ice formation, which can cause issues for the containment system components.

Corrosion is a serious concern for a tank's structural integrity and, consequently, the vessel's safety. Among the numerous present impurities in captured LCO_2, free water, SO_x, NO_x and oxygen have been the most extensively studied. However, at least 20 impurities can contribute to corrosion effects. Experiments show that reducing the content of these impurities by using scavengers lowers the corrosion rate (Rutters et al., 2016).

However, the relationship between impurities and corrosion is not always straightforward. One study demonstrated that impurities' effect on steel's corrosion rate is complex when multiple contaminants are present. For example, in a system containing CO_2 and 3,000 parts per million (ppm) of sulfur dioxide (SO_2), steel corrodes at a rate of 1.50 mm/year. When 500 ppm of oxygen is added to the CO_2-SO_2 system, the corrosion rate drops to 0.52 mm/year (Xu et al., 2018). The results of this study are shown in Table 4 below. Note that the type of material used will also affect the corrosion rate (AP1 5LX65 is a carbon-manganese steel, and 2Cr13 is a low-alloy steel):

Steel	Liquid CO_2			Supercritical CO_2		
	CO_2	$CO_2 + SO_2$*	$CO_2 + SO_2 + O_2$**	CO_2	$CO_2 + SO_2$	$CO_2 + SO_2 + O_2$
2Cr13	0.01	0.07	0.62	0.005	0.10	1.32
X65	0.02	1.50	0.52	0.01	0.95	1.54

*3,000 ppm SO_2 was added
**500 ppm oxygen was added

Table 4: Steel corrosion rates in the presence of impurities (units in mm/year) (Xu et al., 2018).

Other impurities like methanol and glycol may influence the corrosion risk differently. These substances may trigger a shift in the conditions that cause water to precipitate out of the LCO_2, thereby creating an environment conducive to CO_2 corrosion. Additionally, some impurities may interact with other impurities to form compounds that promote the formation of strong acids, causing more severe corrosion. Hydrogen sulfide is another dangerous impurity known to accelerate corrosion and induce a form of HE known as sulfide stress cracking. Due to the wide variety of impurities and their complex effects, further research is needed to fully understand the impact of impurities on the lifespan of captured CO_2 tanks. This is why it is essential to thoroughly understand the specifications of the captured LCO_2 intended to be carried or transported before designing the tanks, containment systems, processing systems and treatment systems that contain the impurity scavengers.

The design pressure of the LCO_2 system can also affect the corrosion rate. In low- and medium-pressure systems, liquefaction and refrigeration reduce light elements, such as hydrogen, nitrogen and methane, to levels aligned with their solubility in LCO_2, resulting in a purer LCO_2 specification. In contrast, high-pressure systems do not remove these light elements, so the resulting post-liquefaction LCO_2 specification remains similar to the pre-liquefaction composition.

Other critical factors for material selection for carbon capture systems include the ability to prevent rapid and sudden failure, resist stress corrosion or H_2S-related cracking, and effectively arrest running fracture.

POTENTIAL MATERIALS

Carbon-manganese steels are currently the most cost-effective and viable materials for LCO_2, and new low-temperature (LT) grades are under development, and some have entered production. According to IGC 17.21.5, all materials used in cargo tanks and cargo piping systems shall be suitable for the lowest temperature that may occur in service.

Carbon steels are widely used in CO_2 pipelines and may apply to tanks. Low nickel alloy steel, such as ASTM A203 Grade E, may also be an option. In a case study performed by the Association for Materials Protection and Performance (AMPP), 3.5 percent nickel steel, 7 percent nickel steel and 9 percent nickel steel were also deemed suitable for LCO_2 storage tanks (AMPP, 2023). Carbon and stainless steel can be used in the same system for economic considerations.

APPROVAL PROCEDURE

High-purity CO_2 is covered under the IGC Code, Section 17.21. The precise triple point temperature of the specific CO_2 cargo must be determined before loading, and the purity of the cargo must be accounted for when adjusting the cargo instrumentation. The ABS *Requirements for Onboard Carbon Capture and Storage* specify that the alarm must be set to sound at least 0.05 MPa above the triple point for the specific CO_2 being carried. The IGC Code further states that any material used in the cargo system must be suitable for the lowest temperature during the service. Reclaimed quality CO_2 is addressed in IGC Code Section 17.22, with the requirements of 17.21 still applicable. IGC Code Section 17.22 requires construction materials of the cargo system to account for the possibility of corrosion due to impurities.

The ABS *Guide for Liquefied Carbon Dioxide Carriers* outlines fundamental requirements for materials used in the construction of cargo systems, namely:

- Where it is impractical to carry out PWHT over the whole tank due to its large size, local PWHT is acceptable and is to be performed in accordance with recognized standards.
- A material with specified minimum yield stress above 410 MPa will require consultation with and approval from the ABS Materials department before use. Steels with yields above 410 MPa may be subject to additional fracture toughness in consideration of the base metal and welds.
- For selected materials, the corrosion allowance must be suitable for the corrosive properties of the cargo and is to be submitted for evaluation by the ABS Materials department.

Note: according to IACS UR W1, exemption to PWHT stress relief based on an alternative approach, such as ECA, is to be approved by the classification society or shall be recognized standards.

According to MSC.1 Circ 1599, high-manganese austenitic steel may be used for cryogenic service for high-purity and reclaimed quality CO_2. The steel should be fine-grained and fully killed, with hot rolling followed by controlled cooling as needed. Its use is limited to plates with thicknesses between 6 and 40 mm. For thicknesses above 40 mm, the Administration may give special consideration. These materials should meet the requirements in IGC and IGF Codes and other recognized standards, such as ISO 21635:2018 or ASTM A1106/A1106M-17.

MATERIALS FOR LIQUID AMMONIA

INTRODUCTION

Ammonia storage has been a common practice for nearly half a century, mainly within the agricultural industry. Historically, ammonia was stored in pressurized bullets or Horton spheres. However, today, it is often stored at low pressures at -33° C.

In recent years, there has been a growing interest in using ammonia as a zero-carbon fuel, necessitating the construction of large maritime ammonia tanks. The IGC Code is the main IMO guidance for ammonia.

CHARACTERISTICS OF LIQUID AMMONIA

Pure anhydrous ammonia itself does not typically cause SCC. The issue arises when oxygen is present, even at a concentration as low as 1 ppm. The IGC Code advises keeping the dissolved oxygen content below 2.5 ppm to prevent ammonia SCC.

Interestingly, the presence of water can reduce SCC. According to the National Association of Corrosion Engineers (NACE) TR5A192, adding 0.2 weight (wt) percent water to air-contaminated ammonia completely prevented SCC in carbon steel. However, water alone cannot entirely solve the problem, as it does not prevent cracking in condensation areas or where the water is not constantly present in ammonia at a certain critical concentration. To combat SCC where water cannot be tolerated, 0.025 percent hydrazine can be added as an oxygen scavenger, removing the oxygen from ammonia and inhibiting SCC (Loginow et al., 1989).

Ammonia condensation must also be prevented by using condensing systems and maintaining the appropriate pressures and temperatures to protect the tank from SCC.

The IGC Code requires that ammonia tanks, especially those made of steel other than stainless steel, must be cleaned thoroughly before loading. Ammonia may also cause polymerization with materials such as propylene oxide, so the tanks must be thoroughly cleaned after removing the ammonia.

POTENTIAL MATERIALS

Ammonia tank walls are constructed from all-welded carbon-manganese steel that is either normalized or thermo-mechanically controlled processed. These materials are impact-tested at -40° C (Stress Corrosion Cracking of Steel in Liquefied Ammonia Service - A Recapitulation, 1989). In some cases, nickel steel may also be used. Liquid and gaseous ammonia have high chemical compatibility with SS316 (Machaj et al., 2022). However, SS316 is not currently covered in the IGC Code, possibly due to its high cost compared with other materials.

Certain materials should never be used to construct ammonia tanks due to their reactivity with ammonia, including mercury, silver, gold and thallium, as they may form explosive compounds with ammonia. Similarly, galvanized steel should not be used, and copper, brass and zinc alloys should be avoided or used where contact is minimal due to their rapid degradation in ammonia.

To minimize the risk of corrosion from anhydrous ammonia, the IGC Code, as amended by Resolution MSC.370(93), specifies that carbon-manganese steel used in tank construction should have:

- Fine-grained quality
- Specified minimum yield strength not exceeding 355 MPa
- An actual yield strength not exceeding 440 MPa

One of the following measures should also be taken:

- Use a lower-strength material with a specified minimum tensile strength not exceeding 410 MPa
- Conduct PWHT
- Maintain carriage temperature near -33° C, but in no case above -20° C
- Ensure the ammonia contains no less than 0.1 wt percent water, and the master shall be provided with documentation confirming this

If carbon-manganese steels exceed these yield properties, PWHTs are required. Tensile and yield properties of welding consumables should exceed those of the tank material by the smallest practical amount. Carbon-manganese steels that do not meet these requirements are prohibited from carrying ammonia under the IGC Code. Nickel steels can also be used if the nickel content does not exceed 5 percent. However, if the transport temperature is below -20° C, a higher nickel content may be used. Aluminum 5083-O can be considered in some applications, though its higher cost may be a limitation.

The NACE TR5A192 report identifies that the steels in the cold-worked, welded and stressed conditions are the most susceptible to ammonia SCC. Among these, nickel alloy steels and carbon-molybdenum steels are more vulnerable than standard carbon steels. Post-weld heat treatments can reduce SCC, and frequent inspections and repairs of steel surfaces in contact with ammonia are critical to maintaining tank integrity (Loginow et al., 1989).

APPROVAL PROCEDURE

For Type C tanks constructed from carbon and carbon-manganese steels, the IGC Code mandates that PWHT is required when the design temperature is below -10° C. However, according to the IACS UR W1-1975, an exemption to the standard post-weld stress relief heat treatment may be granted, provided an alternative approach, such as ECA, is approved by the classification society or follows recognized standards.

Under the ABS *Requirements for Ammonia Fueled Vessels*, materials should generally comply with the ABS *Rules for Materials and Welding (Part 2)*. Additionally, materials for fuel containment must be in accordance with 5C-13-7/4 of the ABS MVR. The use of alternative metallic materials may be used for ammonia service subject to IMO Guidelines MSC.1/Circ.1622, as amended by MSC.1/Circ/1648.

CURRENT RESEARCH

New materials, such as high entropy alloys and gradient structural materials, are being explored to meet the specific challenges associated with LH_2 storage. These materials have demonstrated excellent hydrogen resistance while retaining good strength, but they are not yet commercially available on a large scale. Additionally, because they have had limited application outside the laboratory, their actual performance as a maritime LH_2 tank is not fully understood (Liu et al., 2023).

While these advanced materials offer promising potential, welding consumables suitable for liquified gas containment systems still require research and development. Currently, welding consumables for LH_2 lack the appropriate low-temperature toughness required for cryogenic use. Additionally, consumables for LCO_2 need to be developed that possess high strength and adequate toughness. Further research into optimizing welding procedures is also critical to ensuring the integrity of cryogenic storage systems.

Hydrogen embrittlement has been well-documented for as long as hydrogen has been used. Still, the precise mechanism by which it occurs at cryogenic temperatures is not yet fully understood. Understanding the method of HE at cryogenic temperatures in marine applications is essential in understanding how to prevent it.

Large-scale transportation of captured LCO_2 on board ships is still a new concept. Therefore, the challenges of storing captured LCO_2 are not fully understood. Further research on the effects of impurities on tank materials, including how the interaction of various impurities affects materials and how the complex interactions affect the impurities themselves, is needed. Developing standards for acceptable impurity concentrations may also be necessary; current industry specifications vary widely. ABS is working with other industry and research parties to understand the effects of impurities and the acceptable concentration levels of each.

APPENDIX I — REFERENCES

ABS REFERENCES

ABS *Marine Vessel Rules*

ABS *Guidance Notes on Strength Assessment of Independent Type C Tanks*

ABS Guide for Liquefied Gas Carriers with Independent Tanks

ABS *Guidance Notes on Fracture Analysis for Marine and Offshore Structures*

ABS *Requirements for Liquefied Hydrogen Carriers*

ABS *Guide for Liquefied Carbon Dioxide Carriers*

ABS *Requirements for Onboard Carbon Capture and Storage*

ABS *Requirements for Ammonia Fueled Vessels*

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IMO International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels (IGF Code)

IMO Resolution MSC.370(93). Amendments to the International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code), adopted May 22, 2014.

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ASME Boiler and Pressure Vessel Code

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APPENDIX II – ABBREVIATIONS

ABS American Bureau of Shipping

AIAA American Institute of Aeronautics and Astronautics

AMPP Association for Materials Protection and Performance

ANSI American National Standards Institute

API American Petroleum Institute

ASME American Society of Mechanical Engineers

ASTM American Society for Testing and Materials

BPVC Boiler and Pressure Vessel Code

CCC IMO Sub-Committee on Carriage of Cargoes and Containers

CGA Compressed Gas Association

CO_2 carbon dioxide

ECA engineering critical analysis

FAD failure assessment diagram

FCAW flux core arc welding

FCC face-centered cubic

GMAW gas metal arc welding

GTAW gas tungsten arc welding

HAZ heat affected zone

HE hydrogen embrittlement

IGC Code International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk

IGF Code International Code of Safety for Ships Using Gases or other Low-Flashpoint Fuels

IMO International Maritime Organization

ISO International Organization for Standardization

LCO_2 liquid carbon dioxide

LH_2 liquid hydrogen

MVR Marine Vessel Rules

NACE National Association of Corrosion Engineers

NASA National Aeronautics and Space Administration

NO_x nitrogen oxide

PAW plasma arc welding

ppm parts per million

PWHT post-weld heat treatment

SCC stress corrosion cracking

SO_x sulfur oxides

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