

CRYOPUMPING-RESISTANT LH2 STORAGE VESSEL**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims priority to United States Provisional Patent Application Serial No. 63/522,651, filed on June 22, 2023, which is herein incorporated by reference in its entirety.

GOVERNMENT RIGHTS

[0002] This invention was made with government support under Grant Number DE-EE0009387 awarded by the Department of Energy. The government has certain rights in the invention.

BACKGROUND**Field**

[0003] Embodiments of the present disclosure generally relate to a cryogenic vessel for storing liquid hydrogen.

Description of the Related Art

[0004] Hydrogen is an energy source that is an alternative to conventional fossil fuels. For example, some modes of transportation, such as cars, are powered by hydrogen fuel cells. Hydrogen also has applications in other industrial applications, such as the Haber-Bosh process to produce fertilizer. As demand for hydrogen increases, due in part to the development of more efficient hydrogen powered vehicles and machines and consumer adoption thereof, there is a need to store hydrogen in industrial quantities.

[0005] Hydrogen gas has a low density. To efficiently store industrial quantities of hydrogen gas, the hydrogen gas is liquefied. However, liquefied hydrogen gas is extremely cold which places stress on its container. For example, the boiling point of liquefied hydrogen gas at one atmosphere of pressure is about -253 °C (20 °K). Therefore, liquid hydrogen is typically stored at conditions close to ambient pressure and a temperature of approximately 20 Kelvin.

[0006] Storage of liquid hydrogen requires insulation to reduce heat transfer between the liquid hydrogen and the outside environment. Without insulation the liquid hydrogen would rapidly change phase into gaseous hydrogen (commonly referred to as boil-off) and the outside of the storage vessel would be cold enough to liquefy or freeze most components of air such as nitrogen and oxygen.

[0007] Liquid hydrogen is sufficiently cold to cause component gases in the air, such as nitrogen or oxygen gas, to condense and freeze in the presence of liquid hydrogen, such as on the walls of the vessel containing the liquid hydrogen. Condensing and freezing of an atmospheric gas transfers heat to the liquid hydrogen which causes the liquid hydrogen to boil-off. The boiled-off hydrogen gas may have to be vented, which results in losses. As a result, some liquid hydrogen containment vessels include a vacuum insulation to avoid heat loads caused by the condensation or freezing of an atmospheric gas.

[0008] Conventional liquid hydrogen storage vessels are formed from a double steel walled vessel with a vacuum insulation. The inner steel vessel wall storing the liquid hydrogen is suspended from the outer steel vessel wall. Insulation material is located between two vessel walls in a vacuum condition. With all insulation materials the evacuation of air prevents convection heat transfer and also prevents liquefaction of gases in the insulation space against the cold inner container and the resulting heat transfer that would reduce the insulation effectiveness.

[0009] The outer steel vessel walls of the liquid hydrogen storage vessels are limited in size due to the tendency of steel walls to buckle due to the vacuum load of the vacuum insulation. Therefore, the outer container must be designed to withstand the pressure difference caused by evacuating the insulation space, which could cause the outer container to buckle and collapse inwards.

[0010] While vacuum-jacketed insulation is cost effective for smaller storage vessels, it can be cost-prohibitive for very large storage vessels to design the outer container for vacuum. Fuel tanks of rockets are often insulated with a

single layer of foam due to weight constraints, but they have very high boil-off rates, very short storage time measured in hours, experience adsorption of water vapor and gases that can cause damage to the foam, and the formation of ice on the outside surface. This behavior is not acceptable for multiple fill cycles or long-term storage.

[0011] Therefore, what is needed in the art is a method of insulating large liquid hydrogen gas storage vessels which is cost effective.

SUMMARY

[0012] The present disclosure generally relates to a cryogenic vessel for storing liquid hydrogen.

[0013] In one embodiment, a liquid gas storage container is described. The liquid gas storage container includes an inner shell forming a cavity and an outer shell forming an insulation volume between the inner shell and the outer shell. A first insulation layer is disposed within the insulation volume and around the inner shell. The first insulation layer is formed of a closed-cell insulation material. A second insulation layer is disposed within the insulation volume between the first insulation layer and the outer shell.

[0014] In another embodiment, a liquid gas storage container is described. The liquid gas storage container includes an inner shell forming a cavity and an outer shell forming an insulation volume between the inner shell and the outer shell. A first insulation layer is disposed within the insulation volume and around the inner shell formed of a closed-cell insulation material. A second insulation layer is disposed within the insulation volume between the first insulation layer and the outer shell. A membrane layer is disposed between the first insulation layer and the second insulation layer.

[0015] In another embodiment, a liquid gas storage container is described. The liquid gas storage container includes an inner shell forming a cavity and an outer shell forming an insulation volume between the inner shell and the outer shell. A first insulation layer is disposed within the insulation volume and around

the inner shell formed of a closed-cell insulation material. A gas is disposed within the insulation volume between the first insulation layer and the outer shell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only exemplary embodiments and are therefore not to be considered limiting of its scope, may admit to other equally effective embodiments.

[0017] Figure 1 illustrates a schematic cross-sectional side view of a liquid hydrogen storage container, according to embodiments described herein.

[0018] Figure 2 illustrates a schematic cross-sectional side view of a liquid hydrogen storage container, according to embodiments described herein.

[0019] Figures 3A illustrates a close-up view of a portion of the walls forming the liquid hydrogen storage container of Figure 1, according to embodiments described herein.

[0020] Figures 3B illustrates a close-up view of a portion of the walls forming the liquid hydrogen storage container of Figure 2, according to embodiments described herein.

[0021] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DETAILED DESCRIPTION

[0022] The present disclosure generally relates to a cryogenic vessel for storing liquid hydrogen. More specifically, the disclosure relates to a cryogenic

vessel with multiple insulation layers which reduce cryopumping and enable lower cost manufacturing and maintenance of large liquid hydrogen storage containers. The cryogenic vessels include a first layer of insulation comprising a closed-cell polymeric foam capable of condensing and preventing run-away cryopumping due to reduced permeability. Additionally, the cryogenic vessels include a second layer of insulation comprising perlite or glass microspheres that can reduce a flow permeability to below 40 Darcy, thereby reducing run-away cryopumping due to reduced permeability. Advantageously, the cryogenic vessel of the present disclosure can provide enhanced storage capability compared to conventional cryogenic vessels, in which the cryogenic vessels can provide about 25 years to about 60 years of cold storage capabilities.

[0023] A storage vessel that can insulate liquid hydrogen without a vacuum and without liquefaction of gases against the cold surface would significantly reduce the cost of large-scale liquid hydrogen storage compared to conventional liquid hydrogen storage containers. In the embodiments described herein, the inner shell contains the liquid hydrogen product. The space between the outer shell and the inner shell contains at least two layers of insulation. The insulation adjacent to the inner shell is known as the inner insulation layer. The insulation between the inner insulation layer and the outer shell is known as the outer insulation layer.

[0024] The outer insulation layer is filled with gas to maintain the pressure in the insulation space close to the atmospheric pressure outside of the outer vessel such that external pressure on the outer vessel is substantially reduced. This reduces the cost of the outer vessel. As the inner vessel contracts due to the cold liquid hydrogen product, or if the gas condenses, additional gas is supplied to the outer insulation layer to prevent a decrease in pressure. The contraction of the inner vessel may be dependent on the radius of the inner vessel multiplied by the temperature difference between an ambient temperature and the inner vessel temperature. At least one embodiment utilizes a low-thermal conductivity gas such as nitrogen or argon within the insulation space, e.g., inner insulation layer and/or the outer insulation layer.

[0025] The insulation layer structure described herein can be used in any application that stores or conveys cryogenic liquids, such as pipes. For example, the insulation layer structure described herein can store liquid helium or liquids with a higher temperature. Spherical liquid gas storage containers are illustrated, however, the insulation layers, membranes, and shell structures described herein may also be used for cylindrical storage containers, or storage containers with other shapes.

[0026] When the liquid hydrogen product must be stored at a pressure significantly above ambient pressure the most-straightforward geometry is a sphere, but non-spherical pressure vessel shapes (with generally rounded geometry) are possible. When the liquid hydrogen product can be stored at or near ambient pressure vessels of other shapes, such as a cylinder, may be used. The insulation spaces may have consistent thicknesses throughout to reduce interface temperature variations. .

[0027] Figure 1 illustrates a schematic cross-sectional side view of a liquid gas storage container 100. The liquid gas storage container 100 includes an inner shell 102 which forms a cavity 104. The cavity 104 is formed by an inner surface 122 of the inner shell 102. The cavity 104 is configured to hold liquid hydrogen or another liquid gas. The cavity 104 may have a volume of greater than 3,000 m³, such as greater than 4,000 m³, such as greater than 5,000 m³, such as greater than 6,000 m³, such as greater than 6,500 m³, such as greater than 7,000 m³, such as greater than about 10,000 m³, such as greater than about 50,000 m³, such as greater than about 75,000 m³, such as greater than about 100,000 m³, such as greater than about 150,000 m³, such as greater than about 200,000 m³. In some embodiments, the volume is about 5,000 m³ to about 250,000 m³, or greater, such as about 100,000 m³ to about 200,000 m³. The inner shell 102 is formed of a cryogenic metal material, such as a cryogenic steel or another cryogenic metal alloy capable of being utilized at temperatures of about 20 Kelvin. The inner shell 102 may be substantially spherical. In some embodiments, the inner shell 102 may be cylindrical with hemispheres at either end or may have a cross-section which is polygonal, but with rounded corners. Without being bound by theory, rounded corners can provide reduced stress

concentration compared to sharp corners, in which rounded corners can provide reduced stress cracking of insulation.

[0028] An outer shell 106 is formed around the inner shell 102. An insulation volume 105 is formed between the inner shell 102 and the outer shell 106. The insulation volume 105 includes at least two insulation layers, such as a first insulation layer 108 and a second insulation layer 110. The first insulation layer 108 is disposed around the inner shell 102, such that the first insulation layer 108 is wrapped around the inner shell 102 and covers an outer surface 120 of the inner shell 102. The first insulation layer 108 is attached to the outer surface 120 of the inner shell 102. The first insulation layer 108 is chemically bonded to the outer surface 120, in which the chemical bond can include forming a bond using an epoxy bond and/or forming a bond via a reaction between the first insulation layer 108 and the outer surface 120. The first insulation layer 108 is a closed-cell insulation material. Closed-cell foams include polyethylene, polyurethane, polyisocyanurate, and polystyrene foams.

[0029] Closed-cell foams are formed by cells that have thin polymeric membranes arranged in polyhedral shapes, e.g., about 0.01 mm to about 1.0 mm, such as about 0.01 mm to about 0.5 mm, about 0.05 mm to about 0.1 mm, or about 0.07 to about 0.1 mm. The cells are filled with gas such as a blowing agent, which is a gas that is used to expand the cells in the foam. For example, a blowing agent can include an unsaturated organic compound such as hydrofluoroolefin. At room temperature atmospheric gases, such as nitrogen, can diffuse into the cells, in which the blowing agent diffuses out.

[0030] When the outer surface 120 of the inner shell is cooled down, gases in the cells of the first insulation layer 108 proximal to the outer surface 120 also cool. The gases can liquefy and/or solidify. When the gases liquefy and/or solidify, the pressure in the cell drops, creating a pressure difference across the cell wall of the closed-cell foam. The pressure differential can be about 0.01 atm to about 1 atm, e.g., about 0.01 atm to about 0.5 atm, about 0.01 atm to about 0.1 atm, or about 0.01 atm to about 0.05 atm. When the cell wall of the closed-cell foam is permeable to gases, the gas will diffuse from surrounding

cells with higher pressure into the cell with low pressure, and can liquefy. This process can continue until the cells proximal to the outer surface 120 are substantially filled with liquefied and/or frozen gases. Upon warming of the outer surface 120, such as during maintenance, the liquefied and/or solidified gases will vaporize, and can rupture the cells.

[0031] To prevent damage the closed-cell foam can be cooled to cryogenic temperatures, thereby reducing and/or preventing diffusion of gases into a cell of the closed-cell foam due to reduced permeability of the closed-cell foam. Without being bound by theory, by reducing permeability of the closed-cell foam the likelihood of rupture when warming the closed-cell foam is reduced. Moreover, and without being bound by theory, the first insulation layer 108 can reduce complications of insulation performance damage upon warming the inner shell 102.

[0032] The first insulation layer 108 is filled with a first gas, such as a blowing agent, nitrogen or a nitrogen containing mixed gas. For example, the first insulation layer 108 can initially be filled with a first gas of hydrofluoroolefin, in which after a period of time, *e.g.*, seconds, minutes, hours, days, years, or decades, the first insulation layer 108 can be filled with a second gas of nitrogen. In some examples, the first insulation layer 108 may be filled with air with concentrations similar to those found in ambient air. The first insulation layer 108 is used adjacent to the inner shell 102 and the first insulation layer 108 is thick enough so the temperature at the outer surface 128 of the first insulation layer 108 is above the condensation temperature of the gas in the second insulation layer 110, *e.g.*, about 77 Kelvin (the point at which nitrogen boils or liquefies).

[0033] The closed-cell insulation material which forms the first insulation layer 108 has a cell size (diameter) of less than about 1 μm to about 1 cm, such as 0.1mm to about 1.0mm. For example the pore diameter of the closed-cell insulation mater can be about 10 μm to about 100 μm . The first insulation layer 108 has a first conductivity of about 0.0001 W/(m-K) to about 0.050 W/(m-K), such as about 0.010 W/(m-K) to about 0.040 W/(m-K), such as about 0.010

W/(m·K) to about 0.030 W/(m·K), such as about 0.015 W/(m·K) to about 0.030 W/(m·K), such as about 0.020 W/(m·K) to about 0.030 W/(m·K).

[0034] A second insulation layer 110 is also disposed within the insulation volume 105. The second insulation layer 110 is disposed between the first insulation layer 108 and the outer shell 106. The second insulation layer 110 is disposed on an outer surface 128 of the first insulation layer 108 and inside of an inner surface 124 of the outer shell 106. The cross-section of the inner surface 124 of the outer shell 106 is substantially circular. The second insulation layer 110 has a thermal conductivity, which is optionally higher than the thermal conductivity of the first insulation layer 108. The second insulation layer 110 may be a gas, foam, aerogel, expanded perlite, glass microspheres or another insulation with low thermal conductivity. The glass microspheres can include a diameter of about 1 nm to about 100 μm , e.g., about 1 nm to about 10 μm , about 500 nm to about 10 μm , or about 500 nm to about 1 μm . The second insulation layer 100 may be a closed-cell foam.

[0035] In at least an embodiment, the second insulation layer 110 can include perlite having a flow permeability of about 40 Darcy to about 50 Darcy. In at least an embodiment, the second insulation layer 110 can include glass microspheres having a flow permeability of about 3 Darcy to about 10 Darcy. In at least an embodiment, the second insulation layer 110 can include a mixture of perlite and glass microspheres. The mixture can include about 1 wt% to about 99 wt% of perlite and about 1 wt% to about 99 wt% of glass microspheres. For example, the mixture can include about 60 wt% to about 99 wt% of perlite and about 1 wt% to about 40 wt% of glass microspheres. As a further example, the mixture can include about 80 wt% to about 99 wt% of perlite and about 1 wt% to about 20 wt% glass microspheres. The mixture can include a flow permeability of about 6 Darcy to about 45 Darcy, e.g., about 6 Darcy to about 40 Darcy, about 6 Darcy to about 30 Darcy, about 6 Darcy to about 20 Darcy, or about 10 Darcy to about 20 Darcy. Without being bound by theory, a second insulation layer having a flow permeability of about 6 Darcy to about 40 Darcy can reduce run-away cryopumping, thereby increasing efficiency of temperature insulation of the second insulation layer 110.

[0036] The second insulation layer 110 is filled with a second gas, which may be a single gas or a combination of gases combination. The second gas may be over 50% nitrogen, over 50% argon, or over 50% of a combination of nitrogen and argon when measured by partial pressures. In some embodiments, the second gas combination may be over 60% of one or a combination of nitrogen and argon, such as over 70% of one or a combination of nitrogen and argon, such as over 80% of one or a combination of nitrogen and argon, such as over 90% of one or a combination of nitrogen and argon. The nitrogen and/or argon concentration within the first insulation layer 108 may be maintained by exposing the first insulation layer 108 to a nitrogen and/or argon gas source. In some examples, dry air may be utilized. A nitrogen and/or argon gas may be used in the second insulation layer 110 during formation of the second insulation layer 110 onto the outer surface 128 of the first insulation layer 108.

[0037] The hydrogen or helium gas concentrations are reduced within the second insulation layer 110 due to the highly conductive qualities of hydrogen and helium compared to nitrogen and argon.

[0038] The second insulation layer 110 has a second conductivity of about 0.010 W/(m·K), to about 0.100 W/(m·K). The thermal conductivity of the first insulation layer 108 may be 2 times less than the thermal conductivity of the second insulation layer 110, such as 3 times less than the thermal conductivity of the second insulation layer 110, such as 4 times less than the thermal conductivity of the second insulation layer 110, such as 5 times less than the thermal conductivity of the second insulation layer 110, such as 7 times less than the thermal conductivity of the second insulation layer 110, such as 10 times less than the thermal conductivity of the second insulation layer 110.

[0039] At least two insulation layers are disposed between the inner shell 102 and the outer shell 106, e.g., within the insulation volume 105. There is a first insulation layer 108 which may be a closed-cell foam, which can prevent run-away cryopumping. There is also a second insulation layer 110 suitable to reduce manufacturing costs and a supply of gas to maintain a pressure within

the outer insulation layer. The gas in the second insulation layer 110 is a gas or mixture of gases with relatively low conductivity that would liquefy at liquid hydrogen temperatures of around 20 K. The temperature of the outer edge of the first insulation layer is above the condensation temperature of the gas or mixture of gases in the second insulation layer to prevent condensation and run-away cryopumping. The pressure is maintained substantially above full vacuum to reduce cost of the outer vessel. The pressure within the second insulation layer 110 is maintained at about 0.5 atmospheres to about 2 atmospheres, such as about 0.5 atmospheres to about 1.5 atmospheres, such as about 0.75 atmospheres to about 1.25 atmospheres, such as about 0.8 atmospheres to about 1.2 atmospheres, such as about 0.9 atmospheres to about 1.1 atmospheres, such as about 0.95 atmospheres to about 1.05 atmospheres, such as at about 1 atmosphere. The pressures within the first insulation layer 108 may be about 1.0 atmospheres at a first surface thereof, but reduces in pressure to about 0.2 atmosphere or less, to about 0.1 atmosphere or less, near the inner tank 102.

[0040] Optionally, an interleaving layer can be disposed between the first insulation layer 108 and the second insulation layer 110. The interleaving layer can include a composite, cement, metal, polymer, foam, or a combination thereof. The interleaving layer can include a thickness of about 0 mm to about 200 mm, e.g., about 10 mm to about 150 mm, about 50 mm to about 150 mm, or about 50 mm to about 100 mm. Without being bound by theory, the interleaving layer can arrest crack formation and increase strength of the first insulation layer 108 and/or the second insulation layer 110 by preventing crack propagation throughout the insulation volume 105.

[0041] Optionally, the interleaving layer can include a foam layer. The foam layer can be disposed on and/or over the second insulation layer 110 to form a knitline, e.g., a layer of collapsed foam bubbles. Without being bound by theory, the knitline can reduce permeability due to the increase in the foam density, thereby reducing cryogenic pumping and enhancing cryogenic cooling capabilities.

[0042] A conduit 112 extends into the cavity 104 and through each of the inner shell 102, the first insulation layer 108, the second insulation layer 110, and the outer shell 106. The conduit 112 may be a pipe or a tube which extends into the cavity 104 in order to either fill or drain the cavity 104 of liquid hydrogen. The conduit 112 is disposed such that an open end of the conduit 112 is within the cavity 104 while another end of the conduit 112 is connected to a hydrogen source 114 outside of the body of the liquid hydrogen storage container 100. The hydrogen source 114 may include a pump or a condenser as well as one or more feed lines to various other hydrogen sources 114. While only a single conduit is shown, it is to be understood than more than one conduit may be included, such as a conduit for filling, one for withdrawal, one for venting boil-off gas, and optionally other conduits. In some examples, the filling and boil off conduits through the top, while the withdrawal line may be through the top or bottom. Other configurations are also contemplated.

[0043] A support skirt 118 is utilized to support the body of the liquid hydrogen storage container 100. The support skirt 118 may be a concrete skirt outside of the outer surface 126 of the outer shell 106 and then transition to a metal skirt either right outside of the outer surface 126 or as the skirt passes through the outer surface 126 of the outer shell 106. The support skirt 118 may be a plurality of discontinuous columns outside of the outer surface 126 of the outer shell 106 such that the plurality of discontinuous columns provides support to the outer shell 106. The portion of the support skirt 118 which passes through the outer shell 106 and into the insulation volume 105 may include a plurality of hanger rods, such that the support skirt 118 is discontinuous within the insulation volume 105 such that the entirety of each of the first insulation layer 108 and the second insulation layer 110 are still in fluid communication and the insulation spaces are not divided into separate chambers by the support skirt 118.

[0044] Figure 2 illustrates a schematic cross-sectional side view of another liquid hydrogen storage container 200. The liquid hydrogen container 200 includes an intermediate shell 210. The intermediate shell 210 may be an impermeable membrane, such as metallic or non-metallic, depending upon the

embodiment and the types of insulation utilized in one or both of the first insulation layer 108 and the second insulation layer 110. In some examples, when using an impermeable membrane as the intermediate shell, a closed cell foam and/or an open cell foam may be used as the first insulation layer 108.

[0045] The intermediate shell 210 is an impermeable membrane, such that gases or liquid do not pass through the intermediate shell 210, but the intermediate shell 210 is still capable of flexing and bending to maintain contact with both of the first insulation layer 108 and the second insulation layer 110. The intermediate shell 210 may be impermeable at a temperature of about 50 Kelvin to about 100 Kelvin, such as about 60 Kelvin to about 90 Kelvin, such as about 70 Kelvin to about 90 Kelvin, such as about 75 Kelvin to about 85 Kelvin. The intermediate shell 210 is impermeable at least in part because the coefficient of permeability is sufficiently low to provide a predetermined level of impermeability for use of the storage vessel. Without being bound by theory, the coefficient of permeability may be low enough to prevent and/or reduce damage to the first insulation layer when the tank is warmed during maintenance and/or when not in operation of cryogenic cooling.

[0046] In embodiments wherein the intermediate shell 210 is an impermeable membrane, the membrane layer may be one or a combination of epoxy, polyethylene terephthalate (Mylar), aluminized polyethylene terephthalate, polypropylene, polyimide, polyetherimide, polyether ether ketone, or various metal foils. Other materials are also contemplated, but not listed explicitly herein. The membrane may have a modulus of elasticity of greater than 400 kg/mm^2 , such as greater than 500 kg/mm^2 , such as greater than 600 kg/mm^2 , such as greater than 700 kg/mm^2 at a temperature of about 77 Kelvin. The membrane may have a thickness of about 0.1 mm to about 10 mm, e.g., about 0.1 mm to about 8 mm, about 0.5 mm to about 5 mm, or about 1 mm to about 3 mm. Without being bound by theory, a thickness of the membrane of about 0.1 mm to about 10 mm may allow the membrane to flex such that tears and/or cracks are avoided while coating the first insulation layer 108. The modulus of elasticity allows the membrane to flex along with the first insulation layer 108 and the second insulation layer 110 as the first insulation layer 108

and/or the inner shell 102 shrinks and expands during cooling and heating of the first insulation layer 108 and the inner shell 102. The membrane also helps seal the first insulation layer 108 from the second insulation layer 110. Therefore, if there are any gaps or cracks within the first insulation layer 108, the effects of cryopumping may be reduced or eliminated by the presence of the membrane. The use of an intermediate shell 210 which is a flexible membrane may further enable additional materials to be utilized as part of the first insulation layer 108, such as open-cell foam.

[0047] Optionally, there is also a sealant disposed around any opening within the intermediate shell 210, such that there is no fluid communication between the first insulation layer 108 and the second insulation layer 110 even where something passes through the intermediate shell 210, such as the support skirt 118. The sealant can include an epoxy resin such as LOCTITE® Stycast 2850. The sealant can include a diphenol resin, such as epichlorohydrin-4,4'-isopropylidene. The sealant must be capable of providing a seal at a temperature of less than 100 Kelvin.

[0048] Optionally, a collar can be welded to the skirt, piping, and/or supports that penetrate the first insulation layer. The collar can include a membrane chemically bonded to an outer surface of the collar and the first insulation layer. Without being bound by theory, by welding a collar having a membrane to the skirt, piping, and/or supports that penetrate the first insulation layer the cryogenic cooling capability of the cryogenic vessel may be enhanced.

[0049] The intermediate shell 210 may also be referred to as a middle membrane, and is disposed between the first insulation layer 108 and the second insulation layer 110. In such an example, the intermediate shell 210 may be a metal, a polymer, or a combination thereof.

[0050] An intermediate shell 210 may be formed of a material which is not self-supporting, or is otherwise flexible. The first insulation layer 108 may be self-supporting when the intermediate shell 210 is an impermeable membrane. In such an example, the first insulation layer 108 has sufficient structural rigidity

to support pressures exerted by the gas in the second insulation layer 110. Spray-on foam and aerogel blankets may be examples of self-supporting materials which can be used in the first insulation layer 108. The insulation material of the first insulation layer 108 may include a compressive strength of about 14 psi to about 100 psi, e.g., about 14 psi to about 90 psi, about 20 psi to about 80 psi, or about 30 psi to about 70 psi, to support the loads transmitted through the impermeable membrane from both the differential pressure and any forces exerted by granular materials used for insulation in the second insulation layer 110.

[0051] The liquid hydrogen storage container 200 can include one or more gas inputs and one or more pumps or compressors in fluid communication with the first insulation layer 108. In some examples, the one or more gas inputs and one or more pumps are part of or function as a pressure regulator. The one or more pumps or compressors which are fluidly coupled to the first insulation layer 108 assist in maintaining a predetermined pressure within the first insulation layer 108. Liquefaction or freezing of the gases within the first insulation layer 108 create a vacuum (e.g., a pressure below atmospheric pressure), which may vary in absolute value from cell to cell, or be present in a non-linear gradient from one surface to the opposite surface. During operation, pressures within the cells of the foam of the first insulation layer are allowed to reach a predetermined level of vacuum (e.g., sub-atmospheric pressure), providing beneficial thermal conductivity within the cells.

[0052] A second gas source 208 is in fluid communication with the second insulation layer 110 through a conduit 204. The second gas source 208 may be similar to the first gas source 206 in that it may include one or more pumps, compressors, or connections to one or more other fluid delivery systems. The conduit 204 is in fluid communication with the second insulation layer 110, but not the first insulation layer 108. When using a first gas source, the first insulation layer 108 and the second insulation layer 110 receive different gases from different gas sources 206, 208.

[0053] Figures 3A illustrates a close-up view of a portion of the walls forming the liquid hydrogen storage container 100 of Figure 1. Above the portion of the liquid hydrogen storage container 100 is a graph 300 illustrating a schematic of the temperature of the liquid hydrogen storage container 100 at various points within the body of the liquid hydrogen storage container 100. The graph 300 includes a vertical axis 302 which illustrates the temperature (T) and a horizontal axis 304 which illustrates the position within the liquid hydrogen storage container 100 relative to a center of the cavity 104.

[0054] The cavity 104 is maintained at a first temperature T_1 . The first temperature T_1 is at or below the boiling point of the gas within the cavity 104. Therefore, the first temperature T_1 is at or below about 20.3689 Kelvin while storing liquid hydrogen. The temperature rises to a second temperature T_2 within the inner shell 102. The second temperature T_2 may be fairly similar to the first temperature T_1 , such as about 20 Kelvin to about 25 Kelvin, such as about 20 Kelvin to about 22 Kelvin. In some examples, the difference between the first temperature T_1 and the second Temperature T_2 is less than 2 Kelvin, such as less than 1 Kelvin, such as less than 0.5 Kelvin. The second temperature T_2 can be directly related to the first thickness L_1 of the inner shell 102. The first thickness L_1 is about 10 mm to about 100 mm, such as about 10 mm to about 75 mm, such as about 10 mm to about 50 mm, such as about 15 mm to about 45 mm, such as about 20 mm to about 45 mm, such as about 20 mm to about 30 mm.

[0055] The temperature rises through the first insulation layer 108 from the second temperature T_2 to a third temperature T_3 . The third temperature T_3 is above the condensation point of the gases within the second insulation layer 110, such as above the condensation point of nitrogen or argon. The third temperature T_3 may be above the condensation point of the gases within the second insulation layer 110 by less than about 10 degrees, such as by less than about 5 degrees. When the gas within the second insulation layer 110 is nitrogen, the third temperature T_3 is above 77 Kelvin, such as about 78 Kelvin to about 80 Kelvin, such as about 78 Kelvin to about 90 Kelvin, such as about 78 Kelvin to about 100 Kelvin. In other examples, the third temperature T_3 may

be 150K to 170K, to further reduce the likelihood of condensation. In yet other examples, the third temperature T_3 may be ambient temperature.

[0056] To reach a temperature of above 77 Kelvin, the first insulation layer 108 has a thickness L_2 of about 0.1 meters to about 5 meters, such as about 0.55 meters to about 4 meters, such as about 1 meter to about 4 meters, such as about 1.1 meters to about 3.5 meters, such as about 2 meters to about 3 meters. The total thickness of both of the insulation layers 108, 110 combined is within a range of about 0.2 meters to about 5 meters, such as 1 meter to 3 meters, such that construction, transportation, and maintenance are made easier and cheaper. The relative thicknesses of the insulation layers 108, 110 is selected to achieve a predetermined temperature T_3 , while the total thickness (and conductivity) of the first insulation layer 108 and the second insulation layer 110 are selected to provide a predetermined amount (or lack thereof) of leakage/boil off rate.

[0057] As the second insulation layer 110 extends from the outer surface 128 of the first insulation layer 108 to the inside surface 124 of the outer shell 106, the temperature rises until the temperature reaches a fourth temperature T_4 . The fourth temperature is between the third temperature T_3 and an ambient temperature T_6 surrounding the outer surface 126 of the outer shell 106. The fourth temperature T_4 may therefore be about 80 Kelvin to about 320 Kelvin, such as about 100 Kelvin to about 315 Kelvin, such as about 200 Kelvin to about 310 Kelvin, such as about 250 Kelvin to about 310 Kelvin, such as about 273 Kelvin to about 310 Kelvin. In one example, the fourth temperature T_4 is within about 2-5 Kelvin of the ambient temperature T_6 . The second insulation layer has a third thickness L_3 . The third thickness L_3 is as noted above.

[0058] As the outer shell 106 extends from the inner surface 124 to the outer surface 126, the temperature within the outer shell 106 rises from the fourth temperature T_4 to a fifth temperature T_5 . The fifth temperature T_5 is close to an ambient temperature T_6 of the environment surrounding the outer shell 106, such as about 250 Kelvin to about 315 Kelvin, such as about 265 Kelvin to about 310 Kelvin, such as about 273 Kelvin to about 305 Kelvin. The thickness

of the outer shell 106 is a fourth thickness L_4 . The fourth thickness L_4 is less than the first thickness L_1 of the inner shell 102 because the inner shell 102 has the pressurized cavity 104 formed by the inner surface 122. The outer shell 106 enables for general support and protection of the insulation layers 108, 110. However, it is contemplated that the thickness L_4 could be greater in some circumstances, where extra protection of the insulation and/or contents is desired. The fourth thickness L_4 is about 10 mm to about 100 mm, such as about 10 mm to about 10 mm to about 50 mm, such as about 10 mm to about 30 mm, such as about 14 mm to about 25 mm, such as about 15 mm to about 20 mm.

[0059] Figures 3B illustrates a close-up view of a portion of the walls forming the liquid hydrogen storage container 200 of Figure 2. Above the portion of the liquid hydrogen storage container 200 is a graph 350 illustrating a schematic of the temperature of the liquid hydrogen storage container 200 at various points within the body of the liquid hydrogen storage container 200. The graph 350 is similar to the graph 300 of Figure 3A, but further includes a portion which corresponds to the temperature gradient within the intermediate shell 210. The temperature within the intermediate shell 210 is from the third temperature T_3 to a seventh temperature T_7 . The seventh temperature may be substantially the same as the third temperature T_3 or just above the third temperature T_3 , such as about 0 Kelvin to about 3 Kelvin above the third temperature T_3 .

[0060] The intermediate shell 210 has a fifth thickness L_5 of about 10 mm to about 100 mm, such as about 10 mm to about 75 mm, such as about 10 mm to about 50 mm, such as about 15 mm to about 45 mm, such as about 20 mm to about 45 mm, such as about 20 mm to about 30 mm. The fifth thickness L_5 is between the first thickness L_1 and the fourth thickness L_4 . However, other thicknesses and/or relative thickness are also contemplated.

[0061] The embodiments described herein enable a better and more reliable apparatus for insulating liquid gas storage containers, such as liquid hydrogen storage containers. The embodiments described herein are more economic and easier to manufacture. Disclosed embodiments reduce cryopumping within

the first insulation layer 108 by using closed-cells or aerogels with reduced gaseous diffusion through the first insulation layer 108. The second insulation layer 110 can be a thermal insulator than the first insulation layer 108 due to the use of the mixture of glass microspheres and perlite, thereby increasing insulation capabilities compared to conventional insulation devices.

[0062] Some embodiments, which can be combined with other embodiments, utilize an additional intermediate or middle shell 210 (e.g., membrane) between the first insulation layer 108 and the second insulation layer 110. The intermediate shell 210 may be an impermeable membrane which can flex to accommodate changes in dimension of the first insulation layer 108 or a metal/metal alloy shell. The impermeable membrane can further reduce the likelihood for cryopumping.

[0063] While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A liquid gas storage container comprising:
 - an inner shell forming a cavity;
 - an outer shell forming an insulation volume between the inner shell and the outer shell;
 - a first insulation layer disposed within the insulation volume and around the inner shell, the first insulation layer formed of a closed-cell insulation material; and
 - a second insulation layer disposed within the insulation volume between the first insulation layer and the outer shell.
2. The liquid gas storage container of claim 1, wherein the inner shell comprises a cryogenic metal.
3. The liquid gas storage container of claim 2, wherein the cavity comprises a volume of greater than about 3,000 m³.
4. The liquid gas storage container of claim 1, wherein the closed-cell insulation material comprises a first gas, wherein the first gas comprises greater than 50% nitrogen.
5. The liquid gas storage container of claim 1, wherein the second insulation layer comprises a second gas, wherein the second gas comprises greater than 50% argon.
6. The liquid gas storage container of claim 1, wherein the closed-cell insulation material comprises a closed-cell foam.
7. The liquid gas storage container of claim 6, wherein the second insulation layer comprises a bulk fill material.
8. The liquid gas storage container of claim 7, wherein the bulk fill material comprises one or more of perlite, glass microspheres, or silica aerogel, or mixtures thereof.

9. The liquid gas storage container of claim 8, wherein the second insulation layer comprises a mixture of perlite and glass microspheres.

10. The liquid gas storage container of claim 9, wherein the mixture comprises about 60 wt% to about 99 wt% perlite and about 1 wt% to about 40 wt% glass microspheres.

11. A liquid gas storage container comprising:
an inner shell forming a cavity;
an outer shell forming an insulation volume between the inner shell and the outer shell;
a first insulation layer disposed within the insulation volume and around the inner shell formed of a closed-cell insulation material;
a second insulation layer disposed within the insulation volume between the first insulation layer and the outer shell; and
a membrane layer disposed between the first insulation layer and the second insulation layer.

12. The liquid gas storage container of claim 11, wherein the membrane layer comprises one or more of an aluminized Mylar, Mylar, polyuria, epoxy, water glass, or zero-gel.

13. The liquid gas storage container of claim 11, wherein the closed-cell insulation material comprises a closed-cell foam.

14. The liquid gas storage container of claim 11, wherein the second insulation layer comprises a bulk fill material comprising one or more of perlite, glass microspheres, or silica aerogel, or mixtures thereof.

15. The liquid gas storage container of claim 14, wherein the second insulation layer comprises a mixture of perlite and glass microspheres, wherein the mixture comprises about 60 wt% to about 99 wt% perlite and about 1 wt% to about 40 wt% glass microspheres.

16. The liquid gas storage container of claim 11, wherein the first insulation layer has a thickness of about 0.1 meters to about 1.0 meters.

17. The liquid gas storage container of claim 11, further comprising one or more gas inputs and one or more pumps or compressors in fluid communication the second insulation layer.

18. A liquid gas storage container comprising:
an inner shell forming a cavity;
an outer shell forming an insulation volume between the inner shell and the outer shell;
a first insulation layer disposed within the insulation volume and around the inner shell, the first insulation layer formed of a closed-cell insulation material; and
a gas disposed within the insulation volume between the first insulation layer and the outer shell.

19. The liquid gas storage container of claim 18, wherein the gas comprises greater than 50% argon.

20. The liquid gas storage container of claim 18, wherein the gas comprises greater than 50% nitrogen.