Valves on an insulated cryogenic coldbox

Pressure raising vapouriser on a cryogenic liquid delivery tanker

Cryogenic vapourisers and cryogenic air separation unit

Materials selection for cold and very cold cryogenic gases

Liquid CO_2, LNG, liquid oxygen, argon, nitrogen, and hydrogen

By Stephen B. Harrison, sbh4 consulting

Cryogenic liquefied gases are dense and occupy less space than compressed gases. This enables efficient transportation and storage. Taking hydrogen as an example, the payload of a 40 tonne tube-trailer road vehicle with steel compressed gas cylinders is around 300kg of hydrogen. Using cryogenic liquid hydrogen distribution, a road tanker of a similar size can transport about three tonnes of hydrogen, 10 times more than the compressed gas trailer.

When considering the number of vehicles required to deliver hydrogen from a production site to customers, compressed gas deliveries would need ten times the number of driven kilometres. In the worst case, that would also mean ten times as many vehicles and ten times as many qualified heavy goods vehicle drivers. The operating costs of running a cryogenic distribution fleet can be significantly less than using compressed gas tube trailers.

Similar metrics can be built around carbon dioxide (CO_2) distribution, liquefied natural gas (LNG) and the air gases: oxygen, argon and nitrogen. In most cases, these gases are also distributed in bulk using cryogenic tankers, not as compressed gases in tube trailers.

The cryogenic properties of liquid CO_2 are very different to those of LNG and the air gases. And they, differ greatly from hydrogen. Put simply, liquid CO_2 is cold; LNG and liquefied air gases are very cold; and cryogenic liquid hydrogen is extremely cold. These three clusters of products have unique requirements for materials selection to be compatible with each group of cryogens.

Materials selection for liquid CO_2 bulk storage tanks

Liquid CO_2 is generally stored at between 15 and 25 bar. At these pressures, its temperature is between -30°C and – 15°C. This is the temperature range that can be expected during the depths of a Norwegian or Canadian winter. If pressure is lost in the storage vessel, for example due to a pressure relief valve lifting or bursting disk failing, the temperature of the liquid CO_2 will fall to -56°C. The implication is that the storage vessel must be able to withstand a temperature this low.

The most common liquid CO_2 storage tank will have a low-temperature carbon steel liner surrounded by a layer of polyurethane foam insulation then a carbon steel outer jacket. The use of an austenitic stainless steel, such as 304L for the liner is also acceptable, but would increase the cost. Similarly, vacuum insulation between the liner and the outer jacket is possible but more expensive than foam insulation.

A comprehensive explanation of the various materials and modes of construction for bulk liquid CO_2 storage tanks is provided in EIGA Doc 66/22, *Refrigerated Carbon Dioxide Storage at Users' Premises*.

The capture of CO_2 from industrial emissions for climate protection is likely to cause growth in CO_2 liquefaction equipment and bulk liquid CO_2 storage vessels. Many additional liquid CO_2 storage vessels for distribution of cryogenic CO_2 by road, rail and ship will also be required.

LNG and cryogenic liquid air gases

When liquefied, the temperatures of the three main air gases (oxygen, argon, and nitrogen) and LNG are similar. At atmospheric pressure, the temperature of liquid oxygen is -183°C, argon would be -186°C and nitrogen -196°C.

The temperature of LNG is 161.5°C, slightly warmer than the liquefied air gases but within the same cluster when considering the metallurgical properties of steel or aluminium that are used to build cryogenic storage and handling systems.

Martensitic, ferritic, and duplex steels experience a transformation from a ductile state to a brittle state at temperatures between +50°C and -80°C. LNG and the three air gases in cryogenic liquid form are all colder than this. The implication is that these three types of steel are not appropriate and austenitic stainless steel must be used at these low temperatures. Austenitic steels do not have the same sharp transition from ductile to brittle states at these temperatures.

AISI 304 or 316 are grades of stainless-steel that are generally suitable for use with LNG and liquefied air gases. These alloys will contain between 16 and ▸

20% chromium and 8 to 14% nickel. In addition to the composition of the alloy, the crystalline structure of the steel is important in determining its suitability for use at low temperatures. Heat treatment can influence the steel structure and internal stresses.

Aluminium and copper alloys are also suitable for use with cryogenic air gases and LNG. The 6000 series of aluminium alloys is commonly used to make low-pressure finned ambient vaporizers for convert cryogenic liquids to gases at customer sites. 6061 is perhaps the best-known grade of aluminium for this application. In comparison to 2000, 3000 and 5000 series aluminium alloys, 6061 has comparatively high silicon, copper, and iron content but less manganese and magnesium.

For vaporizers that operate at higher pressures, for example to vaporize high pressure pumped liquid oxygen for a medical gases cylinder filling operation, stainless steel or Monel would typically be specified. These materials are more expensive to work with than aluminium and the flow rate through the aluminium vaporizer can be higher, because it has better heat transfer properties. Therefore aluminium is the default choice if it is a good fit for the application.

Aluminium and copper alloys are not as strong as stainless-steel alloys, so their use is generally limited to pipework up to a few inches in diameter. For large diameter vessels used for storage and bulk distribution by road or rail, steel is required. PTFE is the preferred sealing material in these applications.

The EIGA Doc 127/20 *Bulk Liquid Oxygen, Nitrogen and Argon Storage Systems at Production Sites* offers an overview of the materials that are suitable for use with cryogenic liquefied air gases.

The market for air separation units (ASUs) and liquefied air gases storage tanks is in moderate growth. The Covid pandemic created a huge spike in demand of cryogenic bulk liquid oxygen storage tanks to provide additional medical oxygen capacity to hospitals.

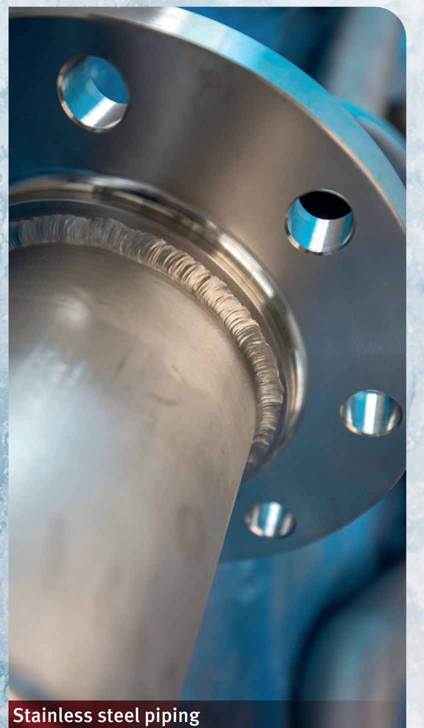
"The Covid pandemic created a huge spike in demand of cryogenic bulk liquid oxygen storage tanks..."

Distributive LNG and the demand for LNG storage tanks and vaporizers is a relatively stable market. However, the surge in LNG imports to Europe since Russian pipeline gas supplies reduced in mid-2022 may see growth in this sector. Also, LNG distribution by rail in the USA has recently been approved and that may open up a new market for cryogenic LNG rail tanks.

Special considerations for liquid hydrogen

When considering metals for use with hydrogen, the issue of embrittlement must always be front of mind. This

LNG fueling station with cryogenic LNG storage tank



Stainless steel piping

CO_2 cryogenic storage

applies equally to cryogenic liquid hydrogen and compressed gaseous hydrogen. Hydrogen is a tiny molecule that can penetrate the smallest of cracks in metallurgical structures. Once it builds up in the metallurgical crystalline structure; it can cause a fracture.

The mechanism of hydrogen embrittlement can be thought of as being like water entering the crack in a rock and then freezing to form ice: the water expands as it freezes to form ice and cracks open the rock.

When considering steel alloys for compressed hydrogen cylinders, the most modern high tensile strength steels used with compressed air gases are not suitable. More traditional, lower strength steels are preferred. The implication is that the cylinder wall must be thicker to withstand the high pressure and hydrogen cylinders are therefore comparatively heavy.

A widely used stainless steel alloy for cryogenic liquid hydrogen is AISI 310. At 25% chrome and 20% nickel, the 310 alloy has an even higher content of these metals than the 304 and 316 alloys, which are commonly used for liquefied air gases.

The AISI 304 alloy has been shown to have a tendency for hydrogen embrittlement. One mitigation that has been proposed, when using 304 stainless steel with liquid hydrogen is that highly stressed parts such as the cold formed heads of bulk liquid storage vessels are solution annealed after cold forming to reduce the residual stresses.

Additionally, it is essential that the inner surfaces of cryogenic liquid hydrogen tanks are free of tool marks and scratches which can be propagation sites for hydrogen embrittlement. This, and other topics related to *Safety in Storage, handling and Distribution of Liquid hydrogen* are covered comprehensively in EIGA Doc 06/19.

Liquid hydrogen vaporizers can either be constructed of a suitable grade of stainless steel, or a 6000 series aluminium alloy, such as 6061. For high pressure vaporizers, for example in pumped liquid cylinder filling operations or hydrogen distribution trailer filling, Monel can be used for the vaporizer.

> “Much of the green hydrogen that will be produced as a clean energy vector will be converted to other e-fuels for distribution”

Growth in liquid hydrogen distribution and storage is inevitable. Much of the green hydrogen that will be produced as a clean energy vector will be converted to other e-fuels for distribution. Hydrogen pipelines will be built to transmit large tonnages over medium distances. Some compressed hydrogen storage and distribution will also exist for shorter distribution journeys. Despite this mix of hydrogen distribution options, there will continue to be growth in hydrogen liquefaction capacity and an increased requirement for cryogenic hydrogen storage vessels and road tankers. gw