$\label{eq:energy} \mbox{ENERGY CARRIERS AND CONVERSION SYSTEMS - Vol. II - Liquid - Hydrogen Storage - Takuji Hanada, Kunihiro Takahashi$

LIQUID-HYDROGEN STORAGE

Takuji Hanada

Air Liquide Japan Co., Ltd., Tokyo, Japan

Kunihiro Takahashi

Center for Supply Control and Disaster Management, Tokyo Gas Co., Ltd., Tokyo, Japan

Keywords: liquid-hydrogen, insulation of liquid hydrogen tank, selection of liquid hydrogen storage, liquid hydrogen storage facilities

Contents

- 1. Introduction
- 2. Insulation of Liquid Hydrogen Tank
- 3. Selection of Liquid Hydrogen Storage Tanks by Purpose
- 4. Type and Shape of Liquid Hydrogen Storage Facilities
- 5. Carriers for Liquid Hydrogen Transportation
- Glossary

Bibliography

Biographical Sketches

Summary

This article describes heat conductivity that affects the storage of liquid hydrogen, illustrating heat insulation methods. The uses and forms are stated regarding liquid hydrogen storage tanks. The article also touches on the reason why vessels used for transporting liquid hydrogen have recently been used as storage tanks.

1. Introduction

The boiling point of liquid hydrogen at atmospheric pressure is as low as 20.4 K. Therefore, to store liquid hydrogen, a heat insulating method having a high adiabatic efficiency is required.

This article describes not only the heat insulation engineering, but also how to select storage tanks according to purpose and type. It also describes dual-use vessels for both storage and transportation purposes as low-temperature vessels of this type become more common.

2. Insulation of Liquid Hydrogen Tank

Heat tends to transfer from high to low if a temperature difference exists between two places. Given that atmospheric temperature is 293 K, there is a temperature difference of 273 K from that of liquid hydrogen.

If liquid hydrogen is stored in an uninsulated tank, it will vaporize very quickly because

such vaporization occurs at a latent heat of 7.56 kcal per liter. Compared with the case of liquid oxygen, whose latent heat of vaporization is 58.1 kcal per liter, as much as 7.68 L liquid hydrogen would vaporize at the calorific value required to vaporize only 1 L liquid oxygen.

When fabricating vessels for storing such super-low temperature substances, an effective insulation method must be adopted to minimize any external heat influx.

The processes of heat transfer may be divided as follows:

- Conduction by permeation through metals or other solids.
- Convection by transmission of gas flow.
- Radiation by transfer in the form of electromagnetic waves, etc.

Therefore, in order to intercept flows of heat transfer, effective measures must be taken separately for each of the three different forms of heat flow:

'Conduction' means the total quantity of heat influx through the connecting materials between the low-temperature inner shell and the atmospheric temperature portion, such as inner shell support, piping, level gauge, thermometer and pressure gauge.

Because the calorific value of such heat conduction is equivalent to the product of the cross-sectional area and heat conductivity and temperature gradient of all the existing materials, heat influx can be minimized by the selective use of materials with a low conductivity for supports or pipes and by minimizing their cross-sectional area with increased length.

Generally, for metallic materials like copper and aluminum, heat conductivity tends to increase at around 20 K to 30 K. Because a material of higher purity conducts heat better, the material and its application method must be selected carefully.

"Convection" can be considered to be a gas flow between the outer and inner shells of the tank and also in the flow of liquid hydrogen packed into the lower part of the inner shell or gaseous hydrogen flowing in the upper section.

Convection of liquid and gaseous hydrogen packed into the tank is inevitable to some extent. The only possible means is to reduce the convection flows of liquid and gas by reducing the temperature difference between the inner and outer shells of the tank.

Heat influx through the main flows of convection can be prevented by purging gas from the space between the tanks and turning it into a complete vacuum. However, although the quantity of heat influx depends on the degree of vacuum, the heat influx remains apparently unchanged at a low vacuum level of 100 KPa to 100 Pa, while the influx decreases greatly at a level of 50 Pa to 1 Pa.

At a level below 0.1 Pa, it decreases further in proportion to the pressure. Because heat influx by convection is proportional to pressure as well as temperature difference, pressure should be kept as low as possible.

In general, the vacuum tank must be closed off by containment. Therefore, to prevent possible deterioration of vacuum due to aging of the metallic materials, namely, by the outgassing effect from the metal surface, adsorbents are provided in direct contact with the inner tank shell, at a lower section of the vacuum tank.

Then, such outgas is adsorbed and removed by the adsorbents which were selected to have the increased adsorbing ability at a low temperature. This process is referred to as the vacuum heat-insulation method.

One such approach is to pack the vacuum tank with a pulverized insulating material of low conductivity; the finely powdered material impedes molecular movement of gas, thus preventing heat transfer to the low temperature side. In recent years, perlite is often used as the powdered material because of its safety, low cost, ease of packing and better performance.

The perlite-packed vacuum insulation method is equally effective in curbing the heat influx, even if the degree of vacuum is higher by one digit.

An older, common method was to cover the exterior of a tank with insulating material of low conductivity, to mitigate the inflow of gas by convection flow, although this approach is rarely used for liquid hydrogen insulation today.

'Radiation' is the phenomenon that occurs in the internal vacuum layer between the inner and outer shells of a tank. Because heat, or thermal energy, transfers through space in the form of electromagnetic waves, from the inner face of the outer tank at high temperature to the outer face of the inner tank at low temperature, it is desirable to minimize the surface area and use a material of small total radiation rate at the working temperature.

The radiation level used to be reduced by applying silver plating having a small radiation rate to the surface of the vacuum tank. This practice is rarely used today since insulating technology has progressed dramatically.

Another approach to reduce heat transfer from the high temperature surface of the outer tank to the low temperature surface is to insert shield plates between the tanks. In this method, thin aluminum or aluminum evaporated films having a high reflection factor are coated perpendicular to the direction of heat transfer, and film spacers having a low thermal conductivity are inserted between the aluminum films and wound up as the insulating material to prevent thermal short circuiting caused by contact of one film with the other.

The thicknesses of the metal reflection film and spacer are about $10 \,\mu\text{m}$ and $100 \,\mu\text{m}$ respectively. This is called the laminated multilayer vacuum insulation method. It is the best-reputed industrial insulation method and is widely used for equipment related to liquid hydrogen.

When a metal reflector and insulating spacer are wound up alternately in multi-layers, a large surface area remains open in the vacuum layer. This would lead to a longer air

exhaust path and hence prolonged exhaust time to make vacuum. This time can be shortened without reducing the insulating effect by drilling one pore of 2 mm or so in diameter every 30×30 mm square over the shield membrane.

The insulating effect may be affected significantly by stratum density of the multi-layers and also by treatment of shield film ends. Therefore, the work requires care and experience.

In addition to the above methods, there are other methods for fluids having a small latent heat like liquid helium or liquid hydrogen, such as the method to prevent heat inflow from parts at atmospheric temperature by using liquid nitrogen shield, or the gas shield method utilizing the sensible heat of a gas for shielding.

As described, various insulating measures are used for processing cryogenic fluids.

3. Selection of Liquid Hydrogen Storage Tanks by Purpose

Storage tanks may be divided into the following four categories by purpose.

- (i) Storage tanks attached and adjacent to the liquefaction plant, which are used as a base for product shipment prior to shipping out liquid hydrogen for delivery to the consuming area. The storage capacity must be determined with due consideration to the liquefying and shipping capacities available and the plant shutdown time for maintenance and inspection of the plant.
- (ii) Similar to the conditions specified in (i), the storage tanks at port which are used to receive liquid hydrogen delivered in bulk by tanker from abroad. The tanks are used as a base for shipping products but are not attached to the liquefaction plant (no tanks of this type have been built yet). The capacity is determined from the volume of delivery by one carrier and adequacy of storage capacity required as the supply base.
- (iii) Storage tanks installed within the consuming sites. Both the capacity and type of tank are determined based on relevant factors such as estimated quantity of consumption, working pressure and conditions of liquid consumption (for instance, such as whether it is consumed as liquid, gas, or both).
- (iv) Storage vessels for small quantities of liquid for laboratory use, which is either hand-carried or transported on a cart with casters.

Ideally, all such tanks or vessels used for whatever purpose should be insulated as best as possible.

In reality, however, for the reasons of technical difficulty, evaporation loss and economic considerations, in general the perlite-packed vacuum insulation type is used for cases (i) and (ii), while the laminated multilayer vacuum insulation type is used for cases (iii) and (iv).

The evaporation loss of the tank for the laminated multilayer vacuum insulation method is far less than that of other methods. However, the maximum capacity to manufacture the tank of this type is around 150 kL.

- -
- -
- -

TO ACCESS ALL THE **11 PAGES** OF THIS CHAPTER, Visit: <u>http://www.eolss.net/Eolss-sampleAllChapter.aspx</u>

Bibliography

Hanada T. Hydrogen storage and transportation by liquefaction. chap.2, p.183-207 in: Ohta T.. et al. editors: Frontier technologies of hydrogen energy systems,. Tokyo; NTS Pub Co. 1995.

Rudiger H, Seifers H, Helzer H, Wolf J. Liquid hydrogen storage system for urban bus. in: Block D. L, Veziroglu T. N. editors. Hydrogen energy progress X, Vol.2, p.967-75.

Biographical Sketches

Takuji Hanada was born 01 January 1935, in Japan; he received his education from the Department of Mechanical Engineering, Hosei University; joined Teikoku Sanso Co., Ltd. (1957–); presently Air Liquide Japan Ltd. Adviser. Previous positions: manager of Plant Designing Department (1970–1975); deputy manager of Plant Equipment Division (1975-1991).

Kunihiro Takahashi was born 28 January 1942 in Japan; he graduated from Chemical System Engineering Department, Faculty of Engineering, the University of Tokyo; completed master course with major in engineering, the University of Tokyo; joined Tokyo Gas Co., Ltd.; presently general manager of the Center for Supply Control and Disaster Management, Tokyo Gas Co., Ltd. Previous positions: appointed as a member of General Research Laboratory of Tokyo Gas Co., Ltd. (1967–1977); appointed as general manager of Technical Development Department, general manager of Engineering Department, and general manager of System Energy Department of The Japan Gas Association (1994–1997); appointed as a member of Sub-task-1-committee of WE-NET committee of New Energy and Industrial Technology Development Organization (1994–1997); has held present position since June 1997; studied research themes: research on production processes and catalysts for hydrogen-rich gas and methane-rich gas.