Guide to Selection of Thermal Properties for Cryogenic Insulation Materials

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1

Overview

1 Overview

Ships, emitting one billion tons of greenhouse gases annually, are subject to regulation by the International Maritime Organization (IMO), a specialized agency of the United Nations, due to the spatial distinction of oceans. The impact of the IMO on the shipbuilding and maritime industries is significant. The organization not only establishes targets for the total amount of pollutants emitted into the oceans but also decides whether to apply specific technologies to achieve pollution reduction goals. As of January 1, 2020, the IMO implemented regulations restricting the sulfur content in fuel oil for all vessels from the previous 3.5% to 0.5%. Due to these IMO regulations, LNG(Liquified Natural Gas) has emerged as an alternative to bunker C oil, with cryogenic insulation materials initially limited to the cargo holds of LNG bulk carriers now being expanded to the fuel tanks of LNG powered ships. While options such as installing scrubbers or using low sulfur fuels are available to comply with the IMO 2020 regulations, the demand for LNG powered vessels, particularly among new vessels, continues to show a sustained upward trend. Some experts believe that the most practical alternative to cope with increasingly stringent environmental regulations is to utilize LNG as a ship fuel. For those reasons, demands for LNG are expected to increase over the next 30 years, the market for cryogenic insulation materials is expected to grow smoothly.

LNG is primarily composed of methane, liquified to -163°C under atmospheric pressure and transported using ships equipped with cryogenic cargo containment system. Compared to its gaseous state, LNG's volume decreases by approximately 600 times, allowing for the transportation of large quantities of natural gas in a single shipment. However, the selection of insulation materials for cargo holds is crucial, especially to minimize heat influx and maintain the extreme low temperature of -163°C. Insufficient thermal insulation performance can increase the amount of boil off gas (BOG), leading to an increased internal pressure and release gas to the external environment. While evaporated LNG can be liquefied again through a reliquefaction process or used onboard Gas Combustion Units (GCUs), minimizing the amount of evaporated gas is crucial from an economic perspective. Therefore, the selection of insulation materials and insulation system technologies that can address this issue is of utmost importance. Since the 1958, the world's first LNG ship, the Methane Pioneer, constructed at a shipyard in Alabama, USA, various types of insulation materials have been utilized to efficiently store and transport LNG. Research for improving the performance of insulation materials applicable to LNG cargo holds has been continuously conducted, and to date, optimized insulation materials are being used. Due to the nature of the ship, both thermal insulation performance and mechanical strength must be considered that minimize heat flux to LNG of -163°C and responding flexibly to the impact load of fluid and thermal stress during operation. It is necessary to fully consider the part that can secure the mechanical strength to bear load condition and lowering the density of insulation material to minimize heat flux, which are in conflict with each other.

Recently, the demand for cryogenic insulation systems has expanded beyond LNG to cover even lower temperature ranges. Although the IMO initially adopted a resolution aiming to reduce greenhouse gas

emissions by 50% by 2050 compared to 2008 levels, with the ultimate goal of achieving zero carbon emissions in the oceans by the end of the century, a more ambitious plan targeting a 100% reduction in greenhouse gas emissions by 2050 was announced during the 80th session of the Marine Environment Protection Committee (2023.07.07). While concerns have been raised about the feasibility of such high targets, there is growing support for the idea that the zero carbon emissions goal should be set for 2050 instead of the end of the century. As a result, the focus is shifting towards longterm utilization of zero carbon fuels such as hydrogen or ammonia. The inclusion of the phrase "development and supply of alternative fuels (zero or low carbon)" in the IMO's longterm greenhouse gas reduction measures suggests an inevitable shift in ship fuel. The mentioned alternative fuels include methanol, hydrogen, ammonia, and biofuels, and the use of liquefied hydrogen should be considered in relation to the demand and application of cryogenic insulation. The liquefaction temperature of hydrogen is -253°C, approximately 90°C lower than that of LNG, demanding advanced insulation technologies for effective insulation. However, given its roughly 800 fold volume reduction compared to its gaseous state, stable storage technology would allow the introduction of inexpensive hydrogen from abroad using ships and its domestic utilization, aligning with the government's roadmap for a hydrogen economy.

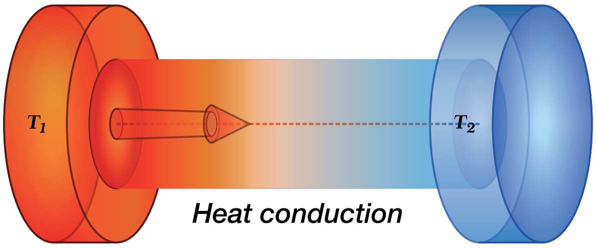
To maximize the efficiency of the storage and transportation of natural gas, insulation materials and technologies applied to LNG at -163°C have been developed for over 60 years. However, for the storage and transportation of hydrogen, which requires an even lower liquefaction temperature compared to natural gas, continuous technological development is necessary. This includes cryogenic structural design to accommodate lower storage temperatures, as well as insulation layer design and production to reduce BOG. Technologies such as vacuum insulation, multilayer insulation, and a vaporcooled radiation shield are being developed to maximize insulation effectiveness for storing liquefied hydrogen at -253°C. Nonetheless, there are still technological limitations on insulation materials, and a complete insulation solution to prevent the evaporation of liquefied hydrogen caused by heat intrusion is currently lacking. Cryogenic insulation materials play a crucial role in realizing low carbon and zero carbon fuel utilization, addressing the environmental pollution issues associated with the use of petroleum or coal. They are considered essential technologies for the utilization of eco friendly fuels. The global trend towards greenhouse gas reduction regulations is preparation for entry into a hydrogen society, where hydrogen, with zero carbon emissions, is utilized as an eco friendly fuel. This highlights the need for new cryogenic insulation systems that facilitate the storage and transportation of hydrogen fuel.

This document describes the insulation systems used in current ships for -163°C LNG and -253°C liquefied hydrogen, and analyzes environmental factors influencing the heat transfer mechanisms and other design elements. Through this analysis, the document serves as a technological guide for material selection during the design of insulation systems in cryogenic environments or the development of innovative insulation systems. Ultimately, it aims to offer information for selecting the thermal properties of insulation materials used in ships, and provide a quantitative database that can be utilized in heat analyses, covering BOG in cargo holds and storage tanks.

2

Heat Transfer Mechanism

2.1 Conduction Heat Transfer
2.2 Convection Heat Transfer
2.3 Radiation Heat Transfer



2 Heat Transfer Mechanism

Heat energy entering to the tank containing cryogenic liquefied gases is transferred through three heat transfer mechanisms: conduction, convection, and radiation. The phenomenon of heat influx from the outside, caused by these heat transfer mechanisms, results in the evaporation of the liquefied gas inside. This process decreases storage efficiency of liquefied gas, which was kept in liquid form to enhance storage efficiency. The Boil off gas, which is either reliquefied or disposed of, results in potential economic losses. Additionally, as the liquid vaporizes, the internal pressure of the tank increases, posing a potential risk to the safety design criteria of cargo holds and causing potential damage to related equipment.
Therefore, the design of the insulation system for cryogenic liquefied gases must take into account these heat transfer mechanisms. For instance, using insulation materials that inhibit heat conduction can reduce conduction heat transfer, and controlling the convection heat transfer is achievable by regulating the convective movements of the internal fluid. In addition, reflective materials can be utilized to reduce radiation heat transfer. An insulation system designed with consideration of these heat transfer mechanisms helps enhance the storage efficiency of cryogenic liquefied gases, minimizing economic losses, potential safety issues, and equipment failure risks. Detailed information on these three heat transfer mechanisms is provided below.

2.1 Conduction Heat Transfer

Conduction heat transfer is a heat transfer mechanism where thermal energy is transmitted through a stationary solid or fluid due to collisions arising from temperature differences among particles within the material. In conduction heat transfer, a high temperature object possesses more thermal energy and transfers energy to adjacent objects with lower thermal energy. Objects in contact with each other transfer thermal energy in this manner, resulting in an equilibrium where they converge to a state of equal thermal energy overall. This mechanism continuously occurs throughout the physically connected objects, with the aim of achieving an equilibrium state by transferring heat from the high temperature region (T_1) to the low temperature region (T_2). While one might commonly associate convection heat transfer with the movement of fluid particles carrying thermal energy, especially in the case of liquid or gaseous states, in reality, adjacent fluid particles continuously transfer energy in the form of conduction heat transfer.

The heat energy through conduction is defined by Fourier's law of conduction[1], which describes the heat transfer rate or thermal conductivity. According to Fourier's Law, the heat transfer rate due to conduction is proportional to the temperature gradient $\frac{dT}{dx}$ across the heat transfer area (A) and the material's thermal conductivity (k) at both ends of the object where thermal energy is being transferred. Mathematically, Fourier's law can be expressed as follows:

Fourier's Law

$$\dot{Q}_{cond} = -kA\frac{dT}{dx} \tag{2.1}$$

Here, $\dot{Q}_{cond}$ represents the heat transfer rate, k is the thermal conductivity of the material[2], A is the area through which heat is transferred, dT is the temperature difference between two objects, and dx represents the length between the two ends of the object where the temperature difference occurs.

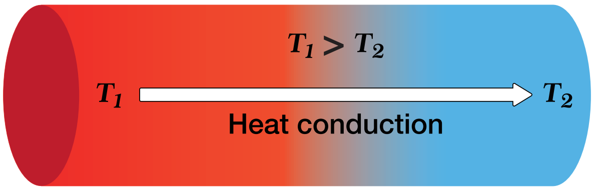


Figure 2.1 Conduction heat transfer

2.2 Convection Heat Transfer

Convection heat transfer is a phenomenon where thermal energy is transferred between a solid surface and a fluid medium, such as gas or liquid, through the movement of fluid particles. When a fluid is heated, its density decreases, causing it to rise, and when it cools, its density increases, causing it to descend. The resulting difference in density causes the fluid to move, facilitating the transfer of thermal energy.

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[1] Fourier's law of conduction states that when heat is transmitted through a medium such as a solid or liquid, the heat transfer rate or heat flux is determined by the temperature gradient and the area through which the heat is transferred.

[2] Thermal conductivity refers to the property of a given material to conduct/transfer heat and can be expressed as follows:. $k = \frac{qL}{A\Delta T}$ Here, q is the heat transfer rate, L is the time over which heat is transferred, A is the heat transfer area, and ΔT is the temperature difference between two objects.

Convection heat transfer involves two types: natural convection, where fluid particles move due to density changes caused by their heating or cooling, and forced convection, where fluid particles are forcibly moved by external forces, transferring thermal energy.

Forced convection is a form of heat transfer that occurs when fluid motion or flow is generated using external power sources such as pumps and fans. The flow induced by external forces increases fluid velocity, leading to an enhanced heat transfer rate and an increase in the convection heat transfer coefficient. Examples of forced convection include using fans in air cooling systems or pumps in liquid cooling systems.

Natural convection is a form of heat transfer that occurs when there is no external power source inducing fluid flow. Fluid motion is generated solely by density changes in the fluid due to temperature differences, i.e., buoyancy. When a fluid is heated, it expands, resulting in a decrease in density and upward movement, while cold fluid becomes denser and sinks. This creates a natural circulation. Examples of natural convection include updrafts generated by heating the air near a relatively high temperature surface and the flow of smoke from a chimney. The convection heat transfer rate can be expressed using Newton's cooling law,[3] as follows:

Newton's cooling law

$$\dot{Q}_{conv} = hA(T - T_{\infty}) \tag{2.2}$$

Here, $\dot{Q}_{conv}$ is the heat transfer rate by convection, h is the convection heat transfer coefficient, A is the area through which heat is transferred, T is the temperature of the object's surface, and T_{∞} is the fluid temperature. According to this law, the rate of heat transfer through convection is driven by the temperature difference between the fluid and the solid surface. The fluid that absorbs the solid's heat energy is effectively limited to some fluid particles in contact with the solid, and the temperature of the fluid in the upper part remains the same as the initial temperature (T_{∞}). The resulting temperature difference within the fluid induces movement of fluid particles due to density changes. This fluid motion increases proportionally to the temperature difference within the fluid (T-T_{∞}). To quantitatively calculate the convection heat transfer rate, which varies depending on the type of fluid, velocity, and size and shape of the solid material, a proportionality constant reflecting these factors, called the convection heat transfer coefficient, is introduced. The convection heat transfer coefficient is mostly determined experimentally, and values for

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[3] Newton's cooling law states that the rate of cooling, i.e., the rate of temperature change, is proportional to the temperature difference between an object and its surroundings. ($T(t)$ is the temperature of the object, T_{env} is the surrounding temperature, and h is the heat transfer coefficient.) $\frac{dT}{dt} = h(T(t) - T_{env})$

various environments are available based on measured convection heat transfer coefficients.

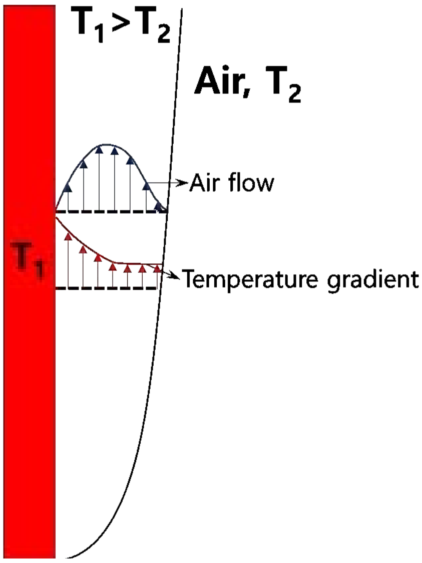

Figure 2.2 Convection heat transfer

2.3 Radiation Heat Transfer

Radiation heat transfer, also known as thermal radiation, specifically refers to the transfer of thermal energy between objects that are separated from each other through the emission and absorption of electromagnetic waves, particularly in the form of infrared radiation. Unlike conduction and convection, which require physical contact or the movement of particles, radiation heat transfer occurs without direct physical contact between objects physically distant from each other. Thermal radiation occurs due to temperature differences between two objects or between an object and its surroundings, and all objects with temperatures above absolute zero (-273.15°C) emit radiant energy. Consequently, radiation heat transfer does not involve the direct emission of thermal energy from higher temperatures to lower temperatures; instead, there is an exchange of thermal energy between the objects. However, the total amount of transferred thermal energy is higher from the surface of the object with a higher temperature, resulting in an overall transfer of thermal energy from the higher temperature object to the lower temperature object.

Radiation heat transfer can be expressed according to the Stefan-Boltzmann Law[4], which quantifies the amount of thermal radiation emitted by an object.

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[4] The Stefan–Boltzmann law is a principle stating that the radiated energy from a black body is proportional to the fourth power of its absolute temperature. Boltzmann theoretically established what Stefan had experimentally observed regarding temperature radiation. The expression for the radiated energy per unit area from a black body at temperature T, per unit time, is given by the following equation (σ is the Stefan–Boltzmann constant, c is the speed of light, h is Planck's constant, and k is the Boltzmann constant).
$E = \sigma T^4 (\sigma = \frac{2\pi^5 k^4}{15c^2 h^3} = 5.6704 \times 10^{-8} Js^{-1} m^{-2} K^{-4})$

Stefan–Boltzmann 법칙

$$\dot{Q}_{rad} = \varepsilon\sigma A T^4 \tag{2.3}$$

$$\dot{Q}_{rad,total} = \sigma A (T_1^4 - T_2^4) \tag{2.4}$$

Here, $\dot{Q}_{rad}$ is the heat transfer rate, ε is the emissivity, σ is the Stefan-Boltzmann constant, A is the area through which heat is transferred, and T is the temperature. However, if there is radiation heat transfer between two objects at different temperatures, Eq. (2.3) is calculated as shown in Eq. (2.4). In Figure 2.3, assuming both objects are black bodies, the emissivity ε is 1, and the net radiative heat transfer is the difference between the radiative heat transfer rates of the higher and lower temperature sides.

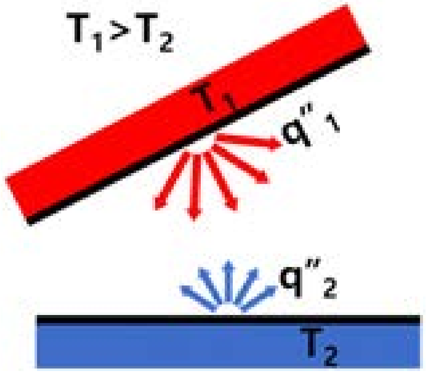
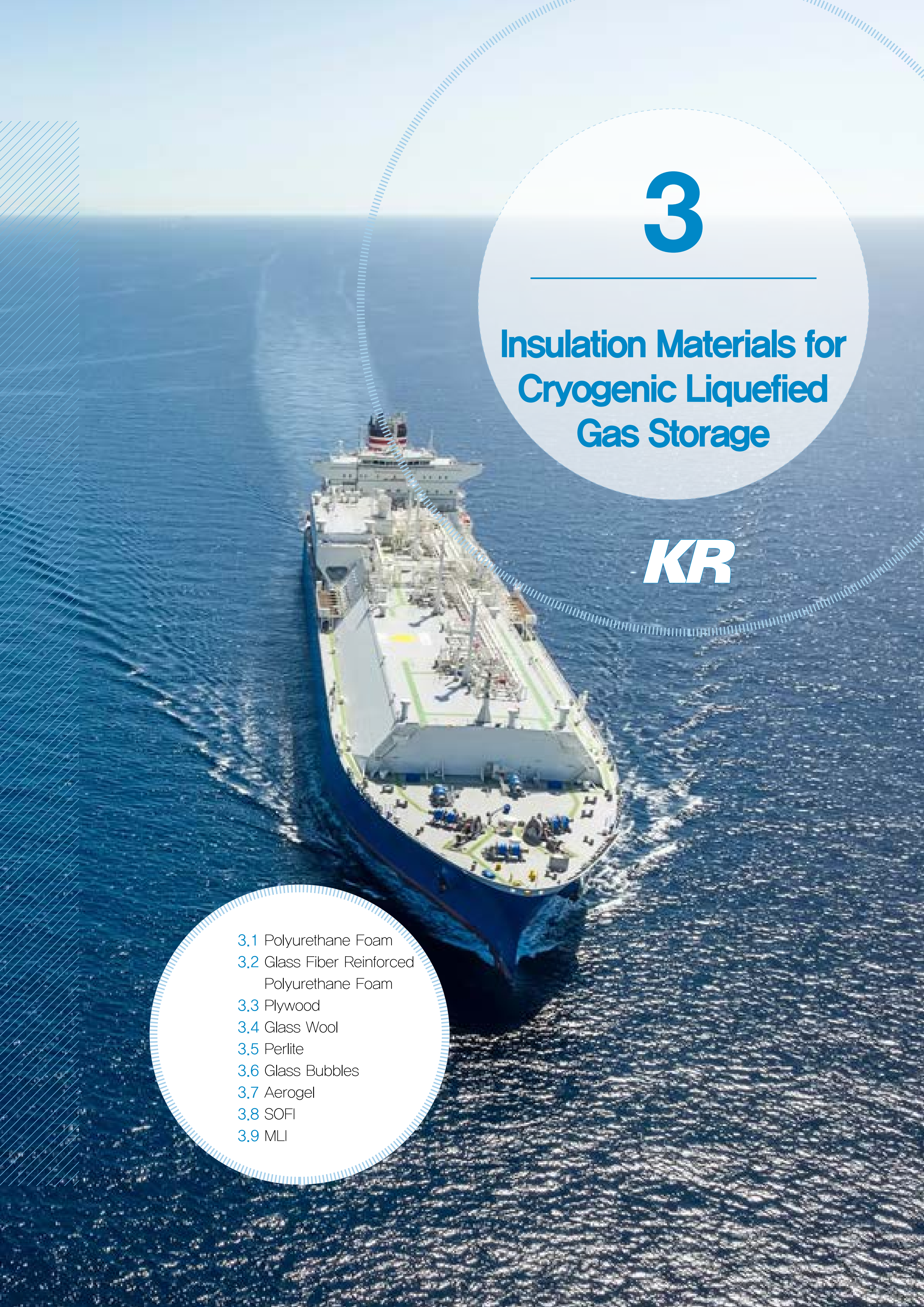


Figure 2.3 Radiation heat transfer

Here, T_1 is the relatively high temperature and T_2 is the relatively low temperature.



3

Insulation Materials for Cryogenic Liquefied Gas Storage

3.1 Polyurethane Foam
3.2 Glass Fiber Reinforced Polyurethane Foam
3.3 Plywood
3.4 Glass Wool
3.5 Perlite
3.6 Glass Bubbles
3.7 Aerogel
3.8 SOFI
3.9 MLI

3 Insulation Materials for Cryogenic Liquefied Gas Storage

Insulating materials used for storage at cryogenic temperatures can be categorized into those designed for -163°C LNG and -253°C liquefied hydrogen. This chapter describes the key characteristics of insulating materials used for LNG and liquefied hydrogen storage in ships. While there has been extensive research on cryogenic insulation properties for LNG storage over the years, information on the properties of materials in a cryogenic environment for liquefied hydrogen is somewhat limited. Therefore, the thermal properties are described within the applicable range. Table 3.1 presents the types and characteristics of insulating materials for cryogenic liquefied gas storage.

Table 3.1 The types and characteristics of insulation applied to cryogenic liquefied gas insulation

Material	Usage	Insulation System	Interference of Heat Transfer	Temperature
Polyurethane Foam	LNG/LH_2	Non–vacuum	Conduction Convection	–200 ~ 150℃
Reinforced Polyurethane Foam	LNG	Non–vacuum	Conduction Convection	–200 ~ 150℃
Plywood	LNG	Non–vacuum	Conduction	–
Glass wool	LNG	Non–vacuum	Conduction Convection	–195 ~ 230℃
Perlite	LNG/LH_2	Non–vacuum / Vacuum	Conduction Convection	–270 ~ 650℃
Glass Bubble	LH_2	Vacuum	Conduction Convection	–
Aerogel	LH_2	Non–vacuum / Vacuum	Conduction Convection	–270 ~ 650℃
SOFI (Spray on Foam Insulation)	LNG/LH_2	Non–vacuum	Conduction Convection	–200 ~ 120℃
MLI (Multi–Layer Insulation)	LH_2	Vacuum	Radiation	–270 ~ 500℃

3.1 Polyurethane Foam

3.1.1 Fabrication Method

Polyurethane is produced through a chemical reaction between polyol and isocyanate. By adding a blowing agent and initiating the polymerization reaction, polyurethane foam with a porous structure is formed.

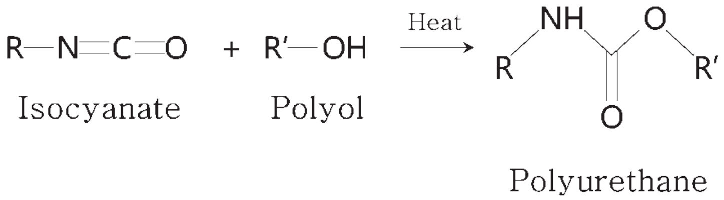


Figure 3.1 Polyurethane formation

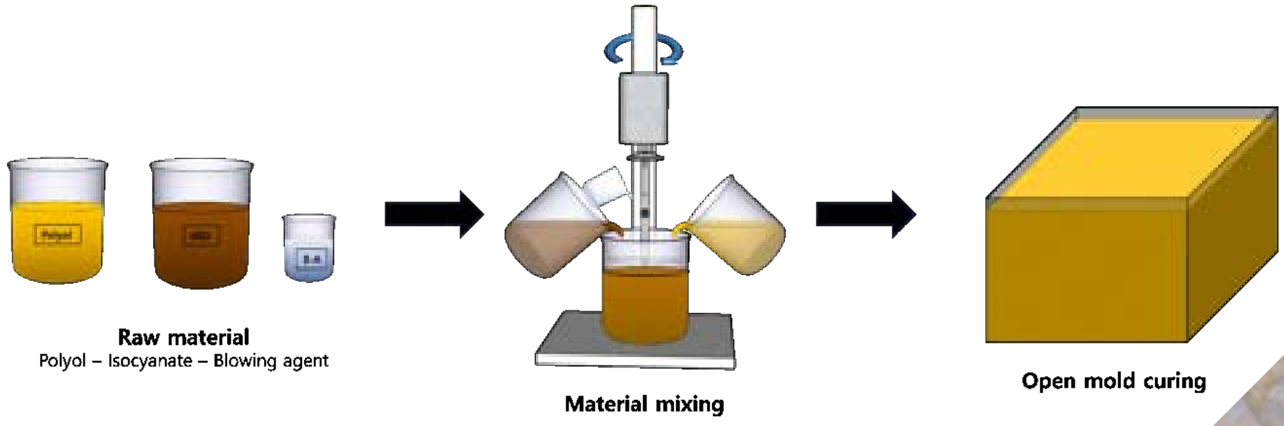


Figure 3.2 Schematic of polyurethane foam fabrication process

3.1.2 Structure

Polyurethane foam has a structure with multiple pores formed by the expansion of gases generated during the foaming process inside the polyurethane. These created pores are called cells, and these cells are enclosed by cell walls. The cell wall consists of struts, which play a role in supporting the load in polyurethane foam, and windows, very thin membrane structures formed when cells meet during the gas expansion process, causing the polyurethane to become extremely thin [1]. As shown in Figure 3.3, struts represent relatively thick and rigid parts that make up the cell wall, while windows depict very thin membrane structures formed when cells meet due to the internal gas expansion during the foaming process of

polyurethane foam. In the case of intact polyurethane foam, it has a closed cell structure through the struts and window structures that make up the cell wall.

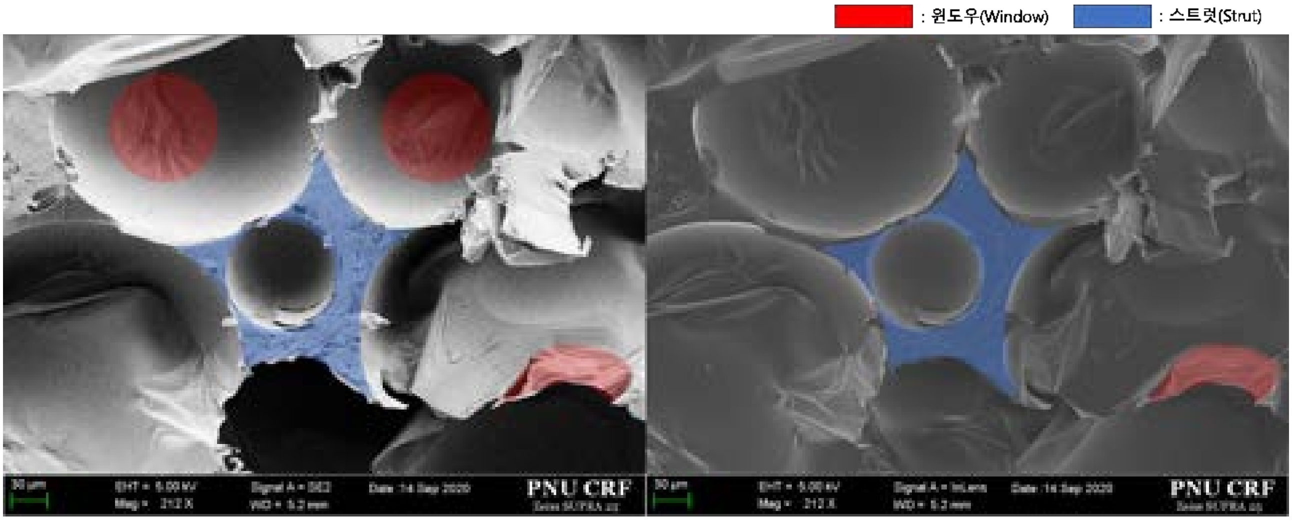


Figure 3.3 Polyurethane foam structure SEM image

3.1.3 Heat Transfer Process

The insulating function of polyurethane foam can be examined by comparing the heat transfer through an empty space, assuming there is an empty space, with the heat transfer when this empty space is filled with polyurethane foam. In the case of an empty space, there is heat transfer through the conduction between air particles and the convection heat transfer caused by the movement of this air. The conduction heat transfer coefficient of air is very low, suggesting excellent insulation performance. However, when air can move freely in the empty space, the convection heat transfer coefficient becomes very large, leading to a significant increase in the over all heat transfer rate. Especially when storing cryogenic cargo such as LNG, the temperature difference at both ends of the insulating space is approximately 188°C (from -163°C to 25°C), resulting in substantial heat transfer through convection. On the other hand, when filling such a space with polyurethane foam, the main heat transfer occurs through the conduction heat transfer and convection heat transfer of the gas inside the polyurethane foam's cell, which is composed of struts and windows. In the case of conduction heat transfer through struts and windows made of polyurethane, the high thermal conductivity of polyurethane itself causes most of the heat energy to be transferred through these cell wall structures. However, the formation of a highly complex heat transfer path with numerous struts and windows, along with a very narrow cross sectional area for the heat transfer path, makes overall heat conduction very challenging. Additionally, convection heat transfer by the gas constituting the cell is hindered due to the small diameter of gas filled cells, approximately 130-180μm, resulting in a low convection heat transfer coefficient and a small temperature gradient contributing to convection heat transfer. Therefore, the heat transfer inside the cell is mostly through conduction involving gas particles. With these characteristics, polyurethane foam ensures outstanding insulation by increasing the length of the heat transfer path by making the path through the cell wall structure more complex while suppressing convection heat transfer in the empty space, and by lowering the convection heat transfer rate based on the thin cell wall structure.

3.1.4 Key Characteristics

Generally, the density of polyurethane foam varies depending on the amount of added blowing agent, and the material shows a decreased thermal conductivity as the temperature in the low temperature range decreases. As the density of polyurethane foam decreases, the size of each cell becomes smaller and denser. This results in longer heat transfer paths, making it more difficult for thermal energy to move through polyurethane foam, leading to lower thermal conductivity[2]. Additionally, as the temperature decreases, the molecules inside the cells of polyurethane foam move less, and the internal gas becomes compressed. These characteristics present challenges for heat transfer through polyurethane foam. However, if the internal foaming gas liquefies, the heat conduction inside the cell increases sharply. Consequently, the thermal conductivity of polyurethane foam may increase in specific low temperature ranges. Therefore, it is essential to consider the operating temperature range and select a nonliquefying blowing agent to prevent this phenomenon. The thermal conductivity based on the type of blowing agent is shown in Figure 3.4. When using CCl3F (trichlorofluoromethane) as the blowing agent, the thermal conductivity of polyurethane foam increases as the temperature decreases due to the liquefaction of the foaming gas inside the cells at -3°C, shifting from gas conduction to liquid conduction[3]. A similar trend is observed with HCFC-R141b blowing agent[4]. However, in the case of recently used HFC blowing agents, there is no occurrence of liquefaction of the internal foaming gas even at -163°C, preventing a reversal of thermal conductivity[5].

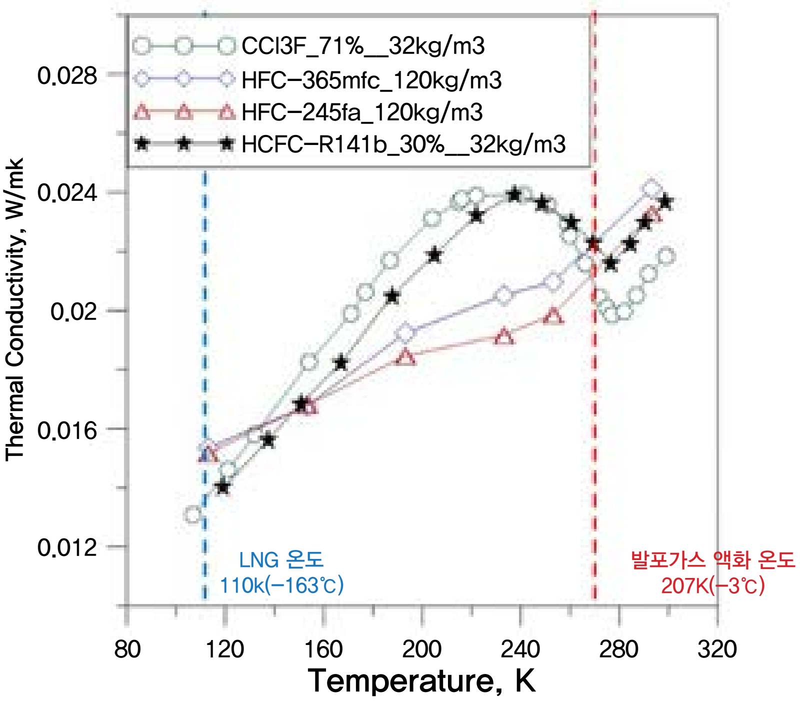


Figure 3.4 Thermal conductivity of polyurethane foam according to the blowing agent

Figure 3.5 Polyurethane foam insulation

Table 3.2 Thermal conductivity of polyurethane foam

Material	Density	Temperature	Thermal conductivity	Specific heat	Reference
	kg/m^3	K	W/m · K	KJ/kg · K	
Polyurethane foam	33	20	0.001	–	[3]
		110	0.004	–	[3]
		300	0.023	–	[3]
	96	100	0.0163	1500	[6]
		230	0.0248	1500	[6]
	120	110	0.01517	920	[5]
		190	0.01846	920	[5]
		300	0.029	920	[7]
	150	300	0.02988	–	[8]
	170	250	0.0300	–	[9]
		290	0.0277	–	[9]
	210	300	0.03362	–	[10]

3.2 Glass Fiber Reinforced Polyurethane Foam

3.2.1 Fabrication Method

Glass fiber reinforced polyurethane foam is produced by spraying a mixture of polyol and isocyanate onto a long, stretched continuous strand mat (CSM) of glass fiber. The glass fiber mat impregnated with the mixed polyurethane solution expands uniformly throughout the entire area as the polyurethane solution undergoes polymerization, resulting in the simultaneous expansion and curing of the mat with the polyurethane foam.

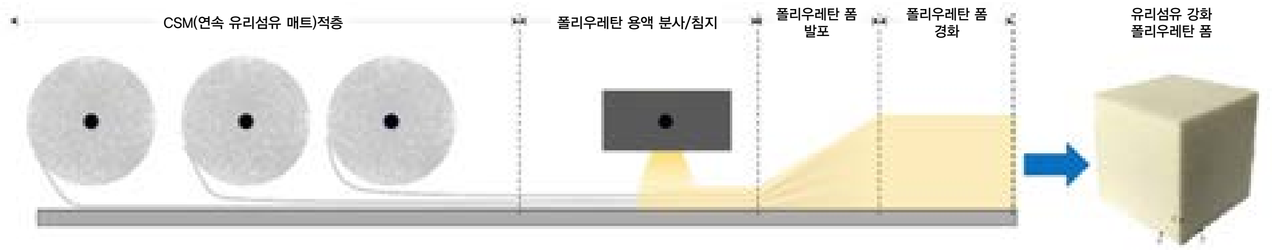


Figure 3.6 CSM reinforced polyurethane foam fabrication process

3.2.2 Structure

Glass fiber reinforced polyurethane foam consists of glass fibers uniformly distributed within the polyurethane foam. The glass fibers typically take the form of continuous filaments, evenly distributed throughout the foam, as shown in Figure 3.7. The polyurethane adheres to the glass fibers, enhancing the material's mechanical strength. The high tensile strength of the glass fibers significantly contributes to reinforcing the tensile strength of the material. This reinforcement is particularly beneficial for withstanding tensile loads due to thermal contraction in insulating materials applied in cryogenic environments.

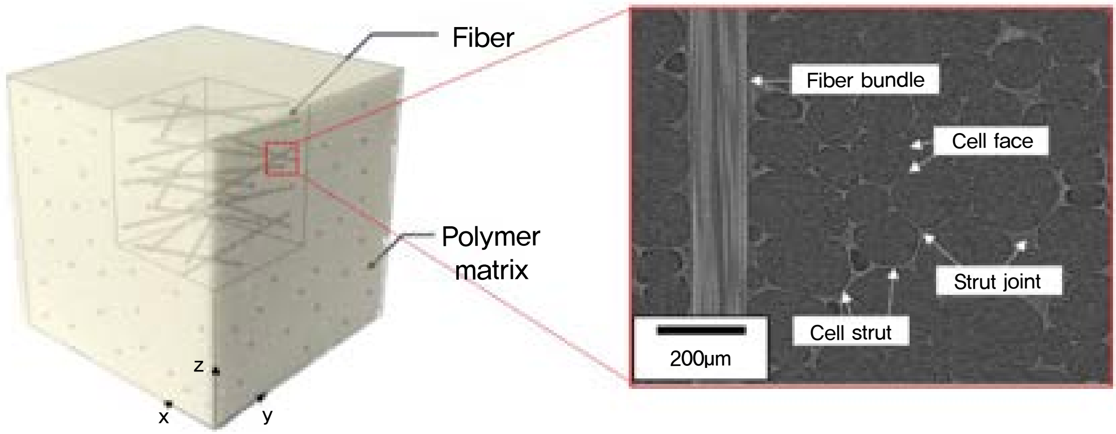


Figure 3.7 Global and micro structure of glass fiber reinforced polyurethane foam[11]

3.2.3 Heat Transfer Process

When glass fiber reinforced polyurethane foam is used as insulation, it can block convection heat transfer and minimize conduction heat transfer through the same mechanism as polyurethane foam alone. However, the presence of glass fibers within the glass fiber reinforced polyurethane foam introduces additional conductive paths for heat transfer. Since glass fibers are conductive materials, they create paths that allow heat to transfer more easily through the material. While this can increase the thermal conductivity compared to conventional polyurethane foam, the insulation properties are not significantly compromised, as long as the glass fibers are oriented horizontally rather than penetrating the material vertically. This orientation helps to prevent the weakening of insulation properties by not providing a direct thermal bridge between room temperature and cryogenic temperature areas.

3.2.4 Key Characteristics

Glass fiber reinforced polyurethane foam is a composite material that combines the advantages of both glass fiber and polyurethane foam. The glass fiber reinforces the polyurethane foam, enhancing mechanical properties such as strength, stiffness, and durability. Meanwhile, the polyurethane foam allows for a lightweight material with excellent insulation properties.

Figure 3.8 Reinforced polyurethane foam insulation

Table 3.3 Thermal conductivity of reinforced polyurethane foam

Material	Density	Temperature	Thermal conductivity	Reference
	kg/m^3	K	W/m · K	
Reinforced polyurethane foam	120	300	0.0272	[12]
	128	300	0.0286	[12]
	118	300	0.0279	[12]

3.3 Plywood

3.3.1 Fabrication Method

Plywood is mainly made from dense birch wood. First, birch wood logs are finely peeled using precision lathe machinery to create thin veneers. These veneers are then stacked in a way that the wood grains intersect perpendicularly. The birch wood veneers, arranged perpendicular to each other, are bonded using resin adhesive.

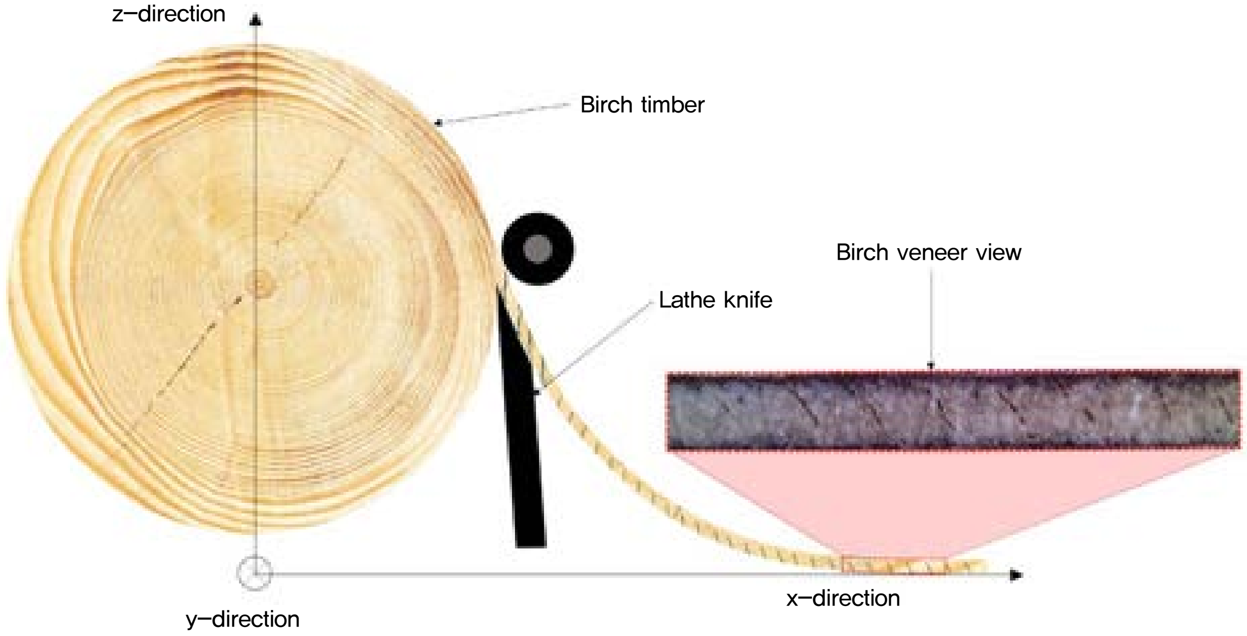
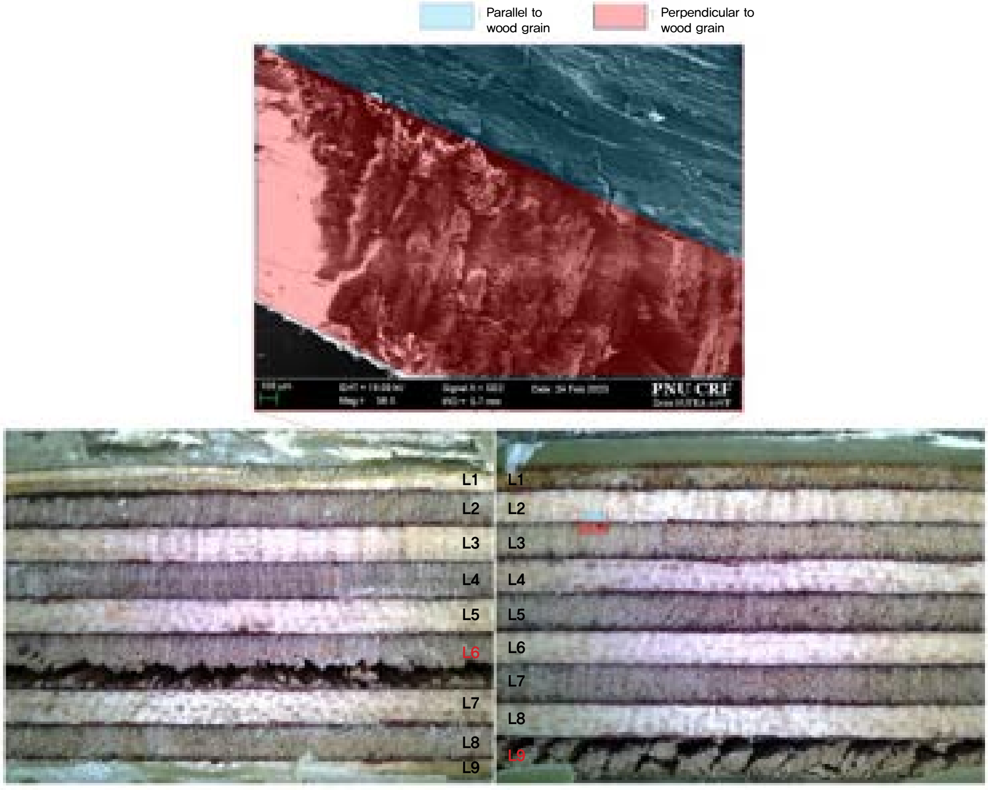


Figure 3.9 Schematic view of plywood fabrication from birch wood

3.3.2 Structure

Plywood has a structure where veneers and resin adhesives are alternately stacked, typically having an odd number of layers. This is done to address concerns that arise when applying veneers in an even number of layers. In such cases, the upper and lower sides of the plywood have wood grains in different directions, creating challenges in the manufacturing process, especially when considering the aesthetics of furniture or structures. Additionally, for structures that experience adhesive or shear loads on the plywood surface, having different wood grain directions in the upper and lower parts of the plywood can significantly weaken the shear strength. This vulnerability occurs due to inherent defects in the plywood manufacturing process, specifically during the lathe machining process where cylindrical logs are planed into flat shapes. In this process, the birch wood veneers, once planed from a cylindrical shape to a flat form, may develop fine cracks, referred to as lathe checks. These checks contribute significantly to the failure mechanism under shear loads in plywood. Therefore, it is essential to consider this vulnerability in the application of plywood in actual structures. Specifically, the odd number of layers in plywood is designed to ensure equal shear strength in the upper and lower parts. This is achieved by installing the plywood in a way that the wood grain direction in the upper and lower parts is parallel to the direction of shear loads, providing sufficient inplane shear strength.



(a) (b)

Figure 3.10 Nine(odd) layer plywood in plain shear failure mode with different outermost side wood grain direction, (a) parallel to wood grain and (b) perpendicular to wood grain

3.3.3 Heat Transfer Process

Generally, the material known as plywood may not be considered an insulating material compared to insulators such as polyurethane foam, perlite, and glass bubbles, as it has a relatively high thermal conductivity. In reality, plywood is applied in the insulation system of LNG bulk carriers to ensure the structural strength of insulation panels composed of glass fiber reinforced polyurethane foam. While Glass Mat Reinforced Thermoplastic (GMT) panels or epoxy resin with added glass fibers (G-10 material) can serve a similar purpose, they may face challenges such as exposure to high temperatures during welding, deformation, combustion issues, and adhesive problems due to the smooth surface of these polymerbased materials, which have a low surface area compared to glass fiber reinforced polyurethane foam. For these reasons, plywood is chosen, especially in applications such as support structures for cryogenic cargo windows, where G-10 material, despite its excellent insulation performance with a thermal conductivity of about 0.3 W/m·K, has adhesive issues with glass fiber reinforced polyurethane foam, which has a low thermal conductivity ranging from 0.06 to 0.17 W/m·K.

The reason plywood exhibits lower thermal conductivity than other polymer materials lies in the structural characteristics of the wood that makes up plywood. Figure 3.11 shows a crosssection of plywood captured using a Scanning Electron Microscope (SEM). The SEM image depicts crosssections where the lower and upper layers reveal the fiber structures of wood cut perpendicular and parallel to the length direction, respectively. As seen in the image, wood is composed of very thin fiber structures, each forming a closed cell structure. This closed cell structure is similar to the cell structure of polyurethane foam, creating a complex thermal conduction path with internal voids and very thin cell walls made of cellulose and lignin. This complexity enhances the insulation performance and contributes to superior insulation performance compared to polymer materials without internal voids (e.g. GMT, G-10).

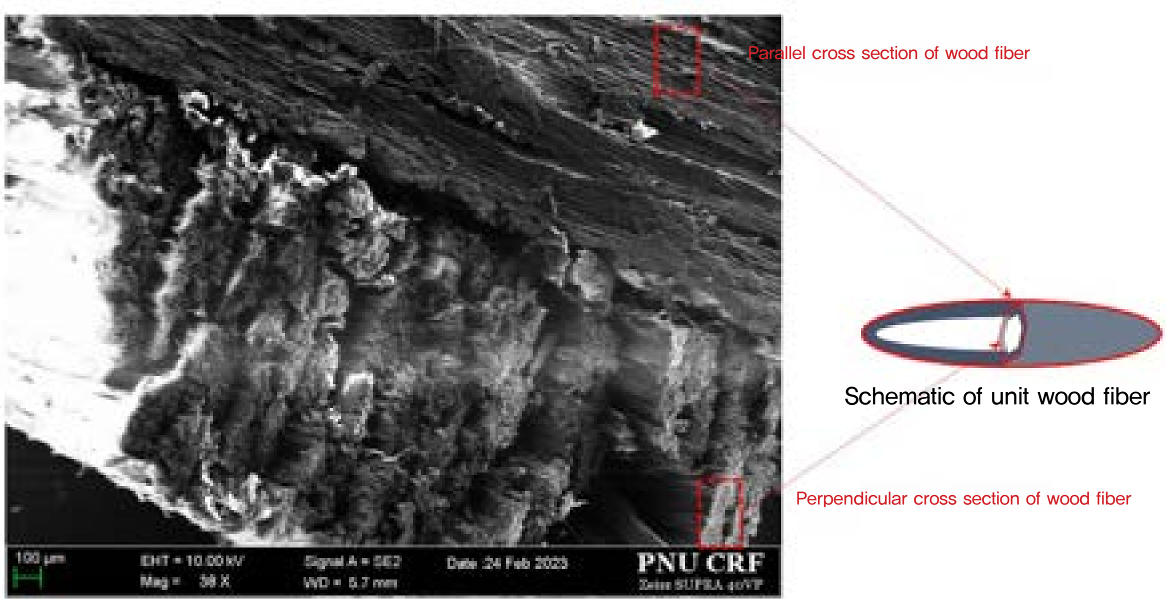


Figure 3.11 Plywood structure SEM image and schematic of unit wood fiber

3.3.4 Key Characteristics

Plywood reaches an equilibrium moisture content depending on the ambient temperature and relative humidity, which significantly influences the mechanical properties and insulation performance of the wood. Moreover, moisture within plywood accelerates the conduction heat transfer through water, leading to a substantial increase in the thermal conductivity of wood [13]. Therefore, it is desirable to apply plywood in insulation systems after ensuring that it has been adequately dried, maintaining the wood's moisture content in a dry state. Due to the moisture absorption characteristics of the wood composing plywood, gradually releasing moisture in a vacuum environment to break the vacuum is not advisable for plywood.

Figure 3.12 Plywood insulation

Table 3.4 Thermal conductivity of plywood

Material	Density	Temperature	Thermal conductivity	Specific heat	Reference
	kg/m^3	K	W/m · K	J/kg · K	
Plywood	550	110	0.062	1210	[13]
		300	0.118	1210	[13]
	680	110	0.062	–	[14]
		200	0.095	–	[14]
		280	0.118	–	[14]
	710	300	0.17	1088	[7]
	880	300	0.13	1260	[6]

3.4 Glass Wool

3.4.1 Fabrication Method

The fabrication process of glass wool is depicted in Figure 3.13. First, glass powder is introduced into ① and melted at a temperature of 1300℃. The molten glass is then stabilized evenly in ② and allowed to flow through a funnel (③). The hot molten glass, flowing through the funnel, is attenuated and solidifies when it meets the high speed rotating device (④). This process is similar to the production principle of cotton candy, where the high viscosity liquid, when flowing over a high speed rotating device, attenuates due to the viscosity, and solidifies into fibrous solid as it cools. The formed glass fibers fall downward, and in ⑤, a polymer binder is sprayed, and the fibers are collected on a conveyor with an intake device (⑥) underneath. The collected glass fiber mass is heated to 250℃ in the space of ⑦, melting the polymer binder to bond the glass fiber masses together, coating individual fiber strands for waterproofing and oil resistance. Subsequently, the material is cooled through the in take device (⑧), resulting in the final production of glass wool[15].

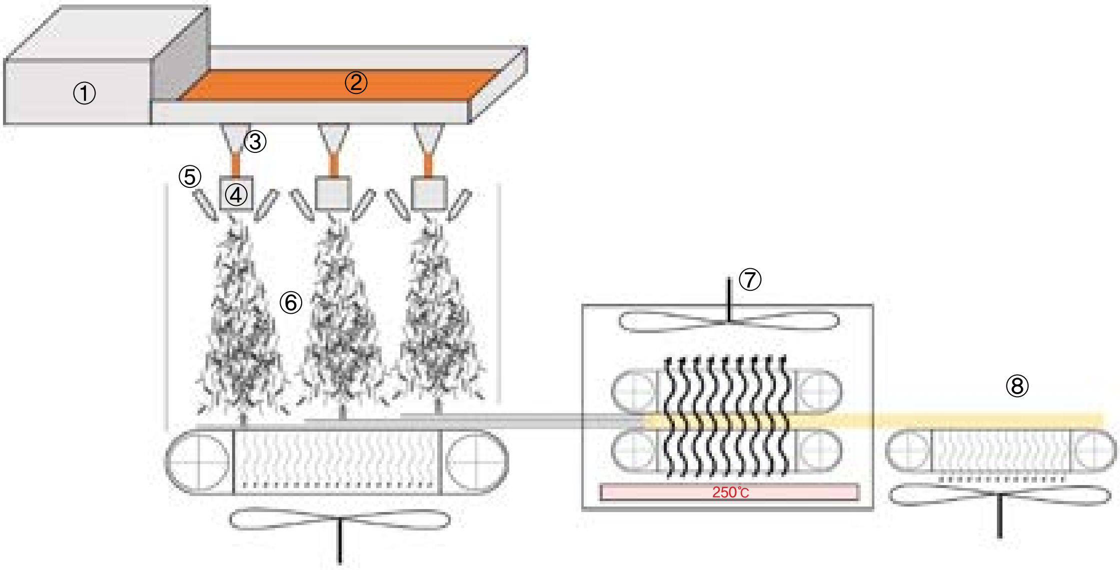


Figure 3.13 Schematic of glass wool fabrication process

3.4.2 Structure

Glass wool is an inorganic fiber obtained by spinning molten glass in a high speed rotating device, attenuating it into extremely fine solidified glass fibers, and randomly arranging them into a mat like insulation using a polymer binder. The structure of glass wool appears similar to cotton when viewed externally, as shown in Figure 3.14. As seen in scanning electron microscope images, it consists of very thin glass fiber strands layered randomly. This structure resembles materials like paper or masks, where fiber strands are layered. While it is challenging for air to pass through this structure in a natural convection state, in a forced convection environment, such as with breathing or applied air pressure, air can flow through the glass wool.

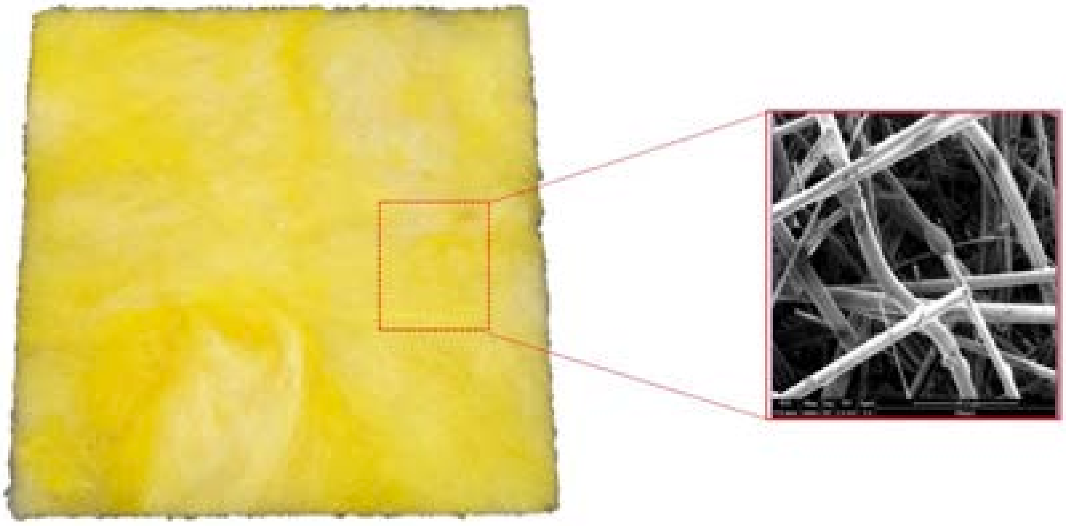


Figure 3.14 Macroscopic and microscopic structure of glass wool[16]

3.4.3 Heat Transfer Process

The heat transfer mechanism of glass wool differs from that of plywood or polyurethane foam due to its internal structure lacking sealed cell formations. Glass wool consists of very thin glass fibers layered randomly, allowing gas to pass through the structure. However, unless an external force, such as pressure, compels the movement of gas, there is no spontaneous airflow. Therefore, when glass wool is installed in a sealed environment, it obstructs the flow of air, suppressing convection heat transfer. The air inside the glass wool primarily conducts heat energy in the form of conduction through air, allowing convective effects to be ignored. This insulation mechanism is similar to the structure of bird feathers, where convection heat transfer is minimized, preventing heat loss by trapping warm air without being influenced by external convection.

In experiments conducted to verify the insulation mechanism of glass wool, the effective thermal conductivity for each material composing glass wool was examined, and the results are shown in Figure 3.15. The effective thermal conductivity considers the conduction heat transfer through the gas, taking into account the average distance between glass fibers, conduction heat transfer through the glass fibers, and radiation heat transfer. The experiments were performed considering the geometric characteristics of the microstructure of glass wool, specifically the heat transfer pathways[17].

The theoretical equation for the conduction heat transfer through the gas utilizes the theory of thermal conductivity for air in the ideal gas state. The internal gas thermal conductivity within glass wool is calculated considering the distance the internal gas can move, taking into account the pressure of the gas and the distance between fiber particles in a free state ideal gas.

$$\lambda_{ge} = \lambda_g \times \frac{pL_0}{pL_0 + E \cdot T} \tag{3.1}$$

Here, λ_g is the thermal conductivity of air in a free ideal gas state, p is atmospheric pressure, L_0 is the distance between fibers, and E is the specific gas constant for air, which is 2.332X10^{-5}N/m^2 T is the average temperature of the gas.

For the conduction heat transfer through glass fibers, the thermal conductivity coefficient of the glass fibers themselves and the geometric characteristics of the microstructure of glass wool are taken into account.

$$\lambda_F = \frac{32(1-\varepsilon)^2 \cdot \lambda_s}{\pi\left(3 + \frac{\pi}{4(1-\varepsilon)}\right)} \tag{3.2}$$

Here, λ_s is the thermal conductivity coefficient of a single glass fiber strand and ε is the empty space per unit area of glass wool, that is, the porosity. Therefore, 1-ε can be considered as the region within the glass wool where conduction heat transfer through glass fibers occurs.

For radiation heat transfer, each glass fiber passing through the glass wool undergoes radiation heat transfer, involving absorption, transmission, reflection, and diffusion.

$$q = \frac{\sigma_s(T_0^4 - T_1^4)}{\frac{1}{\varepsilon_0} + \frac{1}{\varepsilon} - 1} = \frac{\sigma_s(T_1^4 - T_2^4)}{\frac{2}{\varepsilon} - 1} = \cdots = \frac{\sigma_s(T_{n-1}^4 - T_n^4)}{\frac{1}{\varepsilon_0} + \frac{1}{\varepsilon} - 1} \tag{3.3}$$

Here, q is the radiative heat flux, σ_s is the Stefan-Boltzmann constant ($5.7 \cdot 10^{-8}$W/m^2K^4), T_0, T_n are the temperatures of the two ends of the wall, ε_0 is the emissivity of this wall, T_1, T_2, $\cdots$, T_{n-1} epresent the temperatures of each glass fiber where radiative heat transfer occurs, and ε denotes the emissivity of the glass fiber.

The effective thermal conductivity of glass wool is expressed as the sum of various heat transfer paths.

$$\lambda = \lambda_G + \lambda_F + \lambda_R \tag{3.4}$$

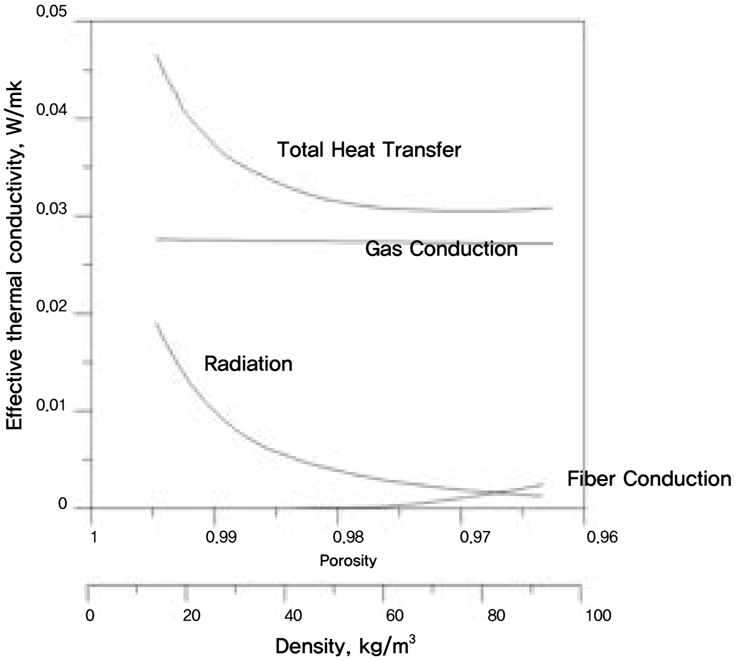


Figure 3.15 Glass wool heat transfer mechanism with density variation[17]

3.4.4 Key Characteristics

Due to the manufacturing process, glass wool is composed of very small diameter glass fibers, forming a structure where heat transfer through glass fiber conduction is challenging. The majority of thermal energy transfer in glass wool occurs through the conduction of air inside. In cases where the internal structure is not a trapped cell structure, like in glass wool, radiation heat transfer is significantly influenced by the spacing between glass fibers. Consequently, unlike polyurethane foam, the effective thermal conductivity tends to increase as density decreases. Therefore, in vacuum environments, high density glass wool may be advantageous for insulation. In atmospheric pressure conditions, glass wool, unlike polyurethane foam, can easily absorb moisture from the air. It is essential to monitor humidity conditions during storage, as increased moisture absorption leads to a significant rise in the conduction heat transfer coefficient of the internal gas.

Figure 3.16 Glass wool insulation

Table 3.4 Thermal conductivity of plywood

Material	Density	Temperature	Thermal con–ductivity	Specific heat	Reference
	kg/m^3	K	W/m · K	KJ/kg · K	
Glass wool	24	110	0.032	700	[14]
		300	0.036	700	[14]
	40	300	0.032	700	[18]
	80	300	0.033	700	[18]
	140	300	0.0335	700	[18]

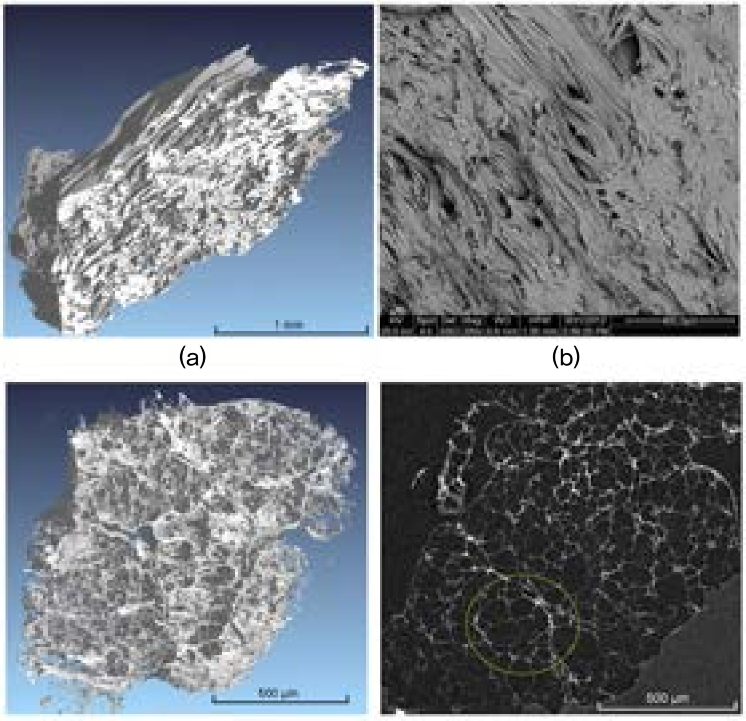
3.5 Perlite

3.5.1 Fabrication Method

Perlite is produced by finely grinding minerals such as pumice stone, obsidian, and trachyte, extracted from volcanic rocks. After grinding, the minerals undergo a process of expansion through heating. In this process, the volume of the ore increases by 10 to 20 times, as volatile components (moisture) present in the perlite ore vaporize and expand within the ore, creating pores during heating at temperatures ranging from 900 to 1200°C. The resulting perlite has a porous structure, possessing excellent insulation performance due to the presence of internal gas layers.

3.5.2 Structure

The perlite ore, as shown in Figure 3.17, has fine pores within its structure, containing volatile substances such as moisture that can expand in high temperature environments. When the perlite ore is heated to a range of 900 to 1200°C, the minerals become molten, and the moisture trapped within the pores of the minerals expands, causing the perlite ore to expand into a porous cellular structure. While expanded perlite at the ore stage already has small pores, the pore size is very small, resulting in a low porosity and decreased insulation performance. However, through the heating and expansion process, the existing small pores expand, and the perlite undergoes a melting and expansion process that significantly reduces the wall thickness.



(a) (b)

(c) (d)

Figure 3.17 Micro structure of perlite raw material with CT (a), SEM (b) and expanded perlite with CT (c), SEM (d)[19]

3.5.3 Heat Transfer Mechanism

Perlite, as depicted in Figure 3.17, develops a cell structure similar to that of polyurethane foam, and its actual heat transfer mechanism is also akin to polyurethane foam. The heat transfer within the cell consists of the conduction heat transfer through the air trapped inside the cell, moisture, and volatile components, as well as the conduction heat transfer along the perlite cell walls. However, unlike polyurethane foam, perlite exists in the form of very small particles, resembling a powder, rather than being connected like polyurethane foam, which forms a continuous structure. When existing as independent powder particles, air layers are inevitably included at the interfaces where the particles come into contact. In an atmospheric pressure environment, where air is present, the area where heat transfer occurs through the air is larger than in polyurethane foam. In the case of installation in a cryogenic environment, polyurethane foam allows design at the material level to prevent gas condensation within the cells by altering the blowing agent composition. However, for perlite, moisture or other volatile components infiltrated into the mineral act as the blowing agent, making material level modifications difficult. Consequently, the insulation performance of perlite is relatively lower than that of polyurethane foam.

3.5.4 Key Characteristics

Perlite has a unique structure that can create an effective barrier against heat transfer. Characterized by its small and lightweight particles, perlite features high porosity, creating numerous small spaces where air or gas can be trapped. The trapped air or gas plays the role of an insulating layer, significantly reducing the heat transfer rate through convection. Additionally, the thin walls of perlite particles provide more heat transfer paths, reducing heat transfer through conduction. However, due to the nature of the minerals constituting perlite, the cell wall structure is fragile and prone to breakage, which may lead to a decrease in insulation performance under physical forces such as external impacts. Therefore, designs should be implemented to avoid applying unnecessary loads.

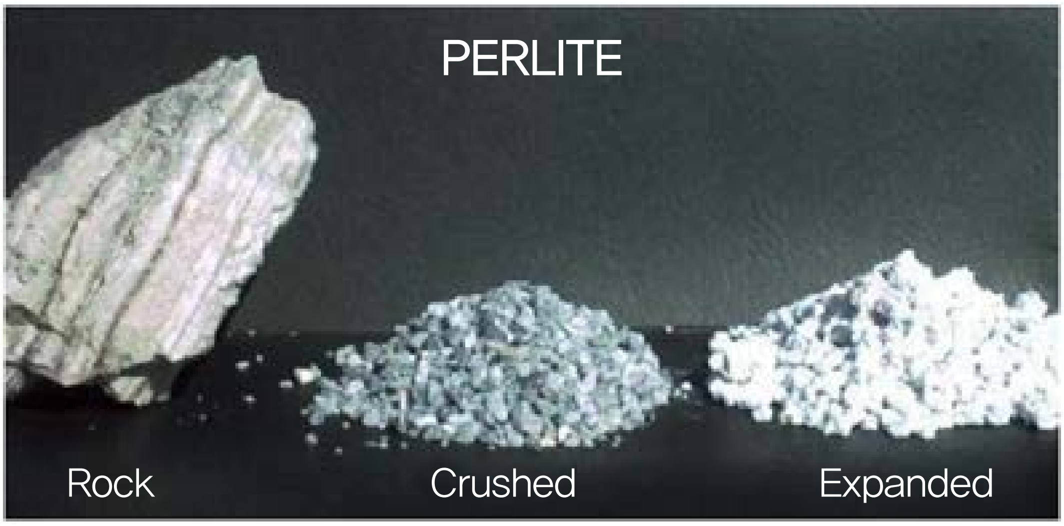


Figure 3.18 Perlite insulation

Table 3.6 Thermal conductivity of perlite

Material	Density	Temperature	Thermal conductivity	Specific heat	Reference
	kg/m^3	K	W/m · K	KJ/kg · K	
Perlite	387	110	0.018	700	[14]
		140	0.024	700	[14]
		200	0.036	700	[14]
		243	0.044	700	[14]
		283	0.052	700	[14]

Table 3.7 The effective thermal conductivity of perlite[20]

Material	Cold vacuum pressure	Density	Temperature	Thermal conductivity
	mTorr	kg/m^3	K	mW/m · K
Perlite	0.1	132	20	0.96
	1			1.00
	10			1.31
	100			3.82
	1×10^3			14.02
	1×10^4			27.87
	1×10^5			33.75
	7.6×10^5			35.03

3.6 Glass Bubbles

3.6.1 Fabrication Method

Glass bubbles are glass beads with internal voids, essentially a glass powder containing a blowing agent, such as crushed silica (SiO2), exposed to high temperature and vacuum conditions. The blowing agent, typically a compound of sulfur or a combination of sulfur and oxygen, is added in an amount of about 0.12% by weight based on the weight of the glass bubbles. The glass powder with the blowing agent is heated to temperatures exceeding 1300°C, while maintaining a vacuum of 6,773 Pa (50.8 torr) inside the heating system. In this process, the foaming gas within the molten glass in the high temperature environment reaches equilibrium with the vacuum condition of 6,773 Pa at a temperature of 1300°C. As a result, glass bubbles produced in this way have an internal vacuum state of approximately 1279 Pa (9.6 torr), which is considered a partial vacuum, under room temperature conditions when applying the ideal gas law. This internal partial vacuum allows glass bubbles to maintain excellent insulation performance even in atmospheric pressure environments.

3.6.2 Structure

Glass bubbles typically have a diameter ranging from 10 to 300 μm and are made of glass, forming small hollow spheres. Due to the manufacturing characteristics of glass bubbles, the empty space is maintained in a partial vacuum state, and the thickness of glass bubbles varies depending on the production temperature. While a similar manufacturing process to perlite is applied when excluding the vacuum environment, there are structural differences. Perlite has a relatively irregular shape, and a porous structure is formed within individual particles. In contrast, glass bubbles have a complete spherical shape for each individual particle, and each particle contains a single cell. This structural difference arises because the process for glass bubbles operates at a temperature where glass is fully molten, allowing glass particles to form liquid droplets. In contrast, the perlite process does not occur at the melting temperature, preventing the formation of liquid droplets within the particles.

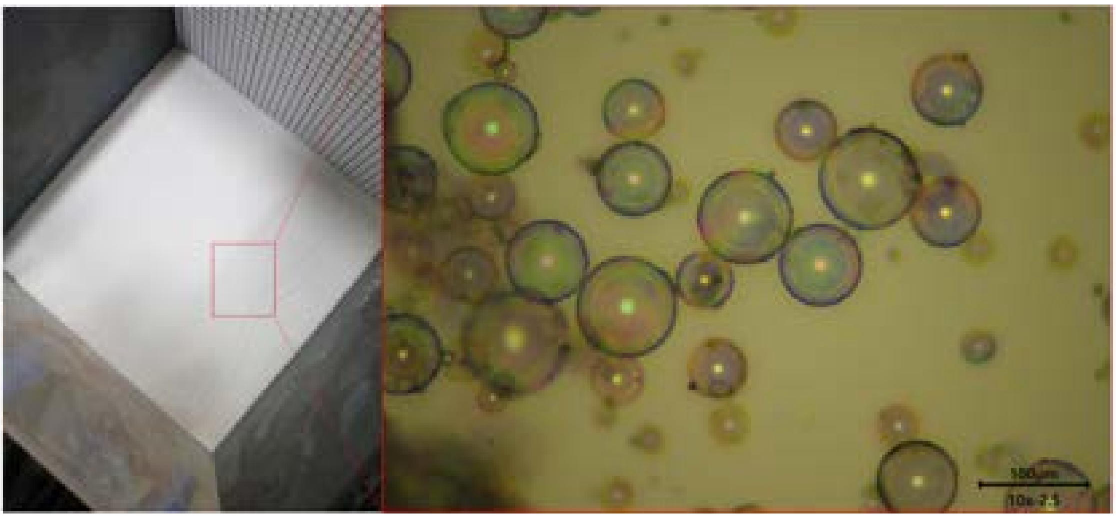


Figure 3.19 Microstructure of glass bubble (3M, K1 type glass bubble)

3.6.3 Heat Transfer Process

The heat transfer process in glass bubbles is similar to that of perlite and polyurethane foam, but there are slight differences. The conduction heat transfer along the cell walls, the conduction heat transfer of the gas inside the cell, and the conduction heat transfer due to the gas in the voids created when particles meet can be compared to perlite, which is an insulating material of the same powder type as glass bubbles. First, considering the conduction heat transfer along the cell walls, there is a difference in the thermal conductivity of the mineral materials that glass and perlite comprise. However, when considering the crosssection of a single particle, the area of the gas space inside the cell is much larger than that of the cell wall. Therefore, it does not significantly contribute to the overall thermal conductivity. Next, looking at the conduction heat transfer of the gas inside the cell, perlite has atmospheric pressure gas inside due to the evaporation of moisture or volatile substances. In contrast, glass bubbles maintain a vacuum inside the cell, resulting in a relatively low thermal conductivity coefficient, providing superior insulation performance compared to perlite. Lastly, the conduction heat transfer of the gas in the voids created when particles meet is almost the same for perlite and glass bubbles. In cases with small average particle sizes and particle distribution, reducing the volume of the void spaces can be advantageous for securing thermal insulation performance.

3.6.4 Key Characteristics

Glass bubbles form point contacts between adjacent spheres, and the thermal conductivity is lower compared to cases where faces meet. When heat energy is applied to glass bubbles from an external heat source, the point contacts between the glass bubble spheres increase thermal resistance, hindering the conduction heat transfer more than when faces meet. Unlike other powder type vacuum insulating materials, glass bubbles have a vacuum state inside the material, providing superior insulation performance in a partial vacuum environment. Due to these characteristics, NASA is replacing traditional perlite insulation with glass bubbles for terrestrial insulation materials, and glass bubbles are being applied to the vacuum insulation of large capacity terrestrial liquefied hydrogen storage tanks currently under construction[21].

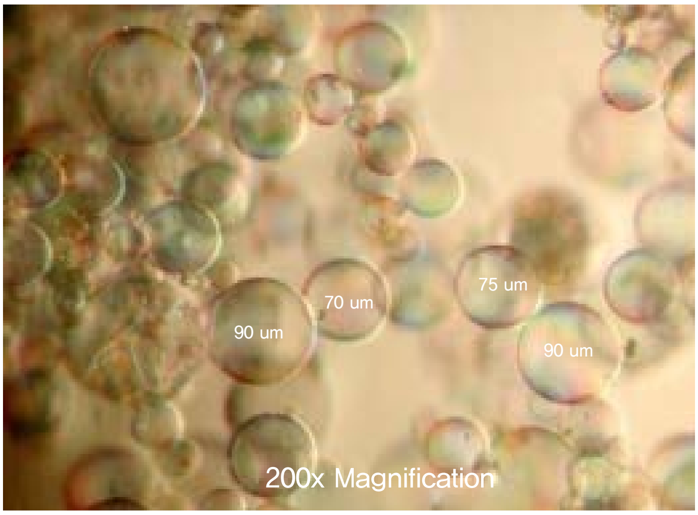


Figure 3.20 Glass bubbles

Table 3.8 The effective thermal conductivity of glass bubble[20]

Material	Cold vacuum pressure	Density	Temperature	Thermal conductivity
	mTorr	kg/m^3	K	mW/m · K
Glass bubble	0.1	65	20	0.7
	1			0.71
	10			0.82
	100			1.71
	1×10^3			7.8
	1×10^4			19.88
	1×10^5			25.14
	7.6×10^5			25.66

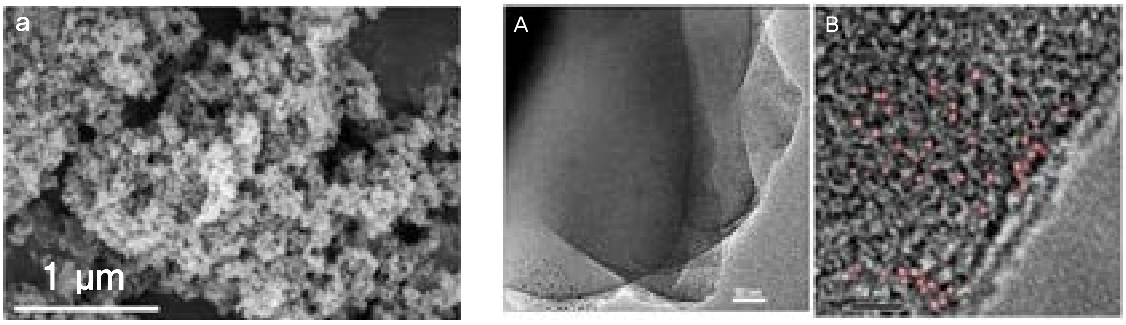
3.7 Aerogel

3.7.1 Fabrication Method

Aerogel is produced by dissolving silicon alkoxide (Si(OR)4) in water, which reacts with the silicon alkoxide group (Si-OR) to form silanol groups (Si-OH). These silanol groups then react with each other or with silicon alkoxide groups to form siloxane bonds (Si-O-Si), creating larger molecules. Nanoparticles wherein these siloxane bonds have sufficiently progressed will coalesce with other nanoparticles once they reach a critical size, forming a unique structure. This structure captures the initial water content, resulting in the formation of a gel like silica hydrogel. The aerogel is produced by replacing the water, or moisture, inside this silica hydrogel with air. The process involves immersing the silica hydrogel in a methanol solution to thoroughly evaporate the internal moisture, transforming it into a silica alcogel. The silica alcogel is then placed in a pressure resistant container that can withstand supercritical substitution. After sealing the supercritical substitution container, liquefied carbon dioxide is introduced to initiate methanol carbon dioxide substitution under high pressure. The substituted methanol is then vented, and liquefied carbon dioxide is supplied again to completely substitute the methanol inside the silica gel. Gradually releasing the pressure causes the liquefied carbon dioxide to vaporize and evaporate, and the space vacated by the evaporated carbon dioxide is filled with ambient air. This method traps air within the fine structure composed of silica nanoparticles, preventing the movement of air and perfectly inhibiting convection heat transfer, resulting in an insulating material with enhanced performance known as silica aerogel.

3.7.2 Structure

Aerogel has a network structure composed of interconnected nanoparticles, and this structure perfectly inhibits the convection phenomenon of air. Due to its solid state structure, it allows conduction heat transfer through air, resulting in excellent insulation performance. In typical scanning electron microscope (SEM) analysis images, it can be observed that the size of silica aerogel particles is much smaller compared to the particles of other insulating materials. Further analysis at the nanometer (nm) scale using Transmission Electron Microscopy (TEM) reveals interconnected silica nanoparticles smaller than 3 nm, with empty spaces between them.



(a) (b)

Figure 3.21 Microstructure of silica aerogel with (a) SEM[22] and (b) TEM[23]

3.7.3 Heat Transfer Process

The heat transfer mechanism of aerogel is similar to that of powder type insulation materials such as perlite and glass bubbles among the mentioned insulating materials. However, aerogel particles are extremely fragile, much smaller in size compared to perlite or glass bubbles, and contain an air layer similar to glass wool rather than cell shaped voids. In such cases, the heat transfer mechanism mostly occurs in the form of conduction heat transfer, where the conductivity coefficient of 3nm diameter silica nanoparticles is the largest. However, the actual proportion of silica nanoparticles within the aerogel is very small, and thus the conduction heat transfer through air predominates. In this context, the difference between the conduction heat transfer of air inside silica aerogel and air inside glass bubble or perlite lies in the presence of space for air movement. Glass bubbles or perlite have sufficient space inside the cell for gas molecules to move, causing minimal convection. On the other hand, in the case of aerogel, the diameter of the void space is 50 to 60nm. For comparison, the collision distance for nitrogen molecules with a diameter of 0.36nm is 59nm under atmospheric pressure, allowing significant suppression of gas molecule movement. Therefore, aerogel achieves excellent insulation performance in atmospheric pressure conditions due to the almost complete exclusion of gas molecule movement through solid air.

3.7.4 Key Characteristics

Aerogel is fabricated and utilized in various forms such as beads or blankets. Aerogel beads consist of small spherical particles and are used as the core insulation material in vacuum insulation technology. By placing these beads in a sealed container and removing the air, a vacuum can be created, further reducing heat transfer in vacuum insulation. Aerogel blankets are flexible sheets applied as internal and external insulation layers in vacuum insulation technology. They can be applied to various surfaces such as pipes and tanks, making them particularly useful in limited spaces where the thickness of insulation material has to be minimized.

(a) (b)

Figure 3.22 Aerogel particle(a) and blanket(b) insulation

Table 3.9 The effective thermal conductivity of aerogel beads and blanket[20]

Material	CVP	Density	Temperature	Thermal conductivity
	mTorr	kg/m^3	K	mW/m · K
Aerogel beads	0.1	80	78	1.82
	1			1.93
	10			2.65
	100			4.42
	1×10^3			7.64
	1×10^4			8.97
	1×10^5			11.3
	7.6×10^5			15.8
Aerogel Blanket	0.1	133	78	1.47
	1			1.64
	10			2.06
	100			2.91
	1×10^3			4.26
	1×10^4			5.60
	1×10^5			6.75
	7.6×10^5			11.24

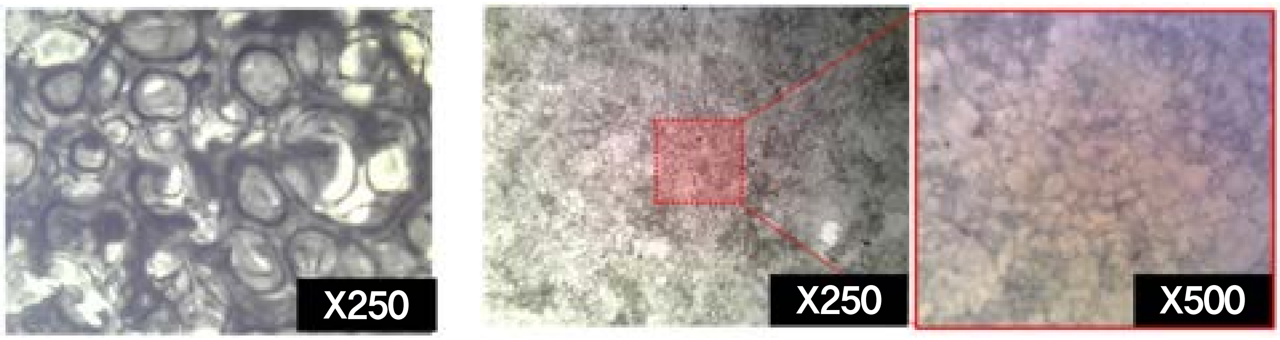
3.8 SOFI

3.8.1 Fabrication Method

SOFI (Spray On Foam Insulation) is produced using the same bonding method as polyurethane foam, but it differs in the foaming process of polyurethane foam. In the manufacturing process of polyurethane foam, more foaming agents are dissolved, and through the agitation section, polyurethane foam is pressurized and expanded using a nozzle structure that allows diffusion from a very narrow tube. This results in the production of low density polyurethane foam sprayed over a wide area.

3.8.2 Structure

As shown in Figure 3.23, SOFI is similar in structure to polyurethane foam; however, to reduce density, the size of cell voids in the structure of polyurethane foam is minimized within the same volume to incorporate as many voids as possible. Consequently, the thickness of struts and windows that make up the cell walls is reduced, leading to an overall structural strength lower than that of polyurethane foam.



(a)

(b)

Figure 3.23 Microstructure of polyurethane foam density (a) 120kg/m^3 and (b) 37.5kg/m^3

3.8.3 Heat Transfer Process

The thermal conductivity of SOFI is similar to polyurethane foam; however, in the case of SOFI, the size of cell voids decreases along with the thickness of cell walls. As a result, the area of the polyurethane section with relatively high thermal conductivity values is reduced, and the decreased size of cell voids reduces the impact of natural convection caused by the airflow within the voids. Therefore, the insulation performance of SOFI is relatively superior to that of polyurethane foam.

3.8.4 Key Characteristics

Unlike polyurethane foam, which is produced in panel units and transported to the site, SOFI is applied directly to metal surfaces onsite without the need for separate adhesives in the insulation system. This saves space, time, and costs during installation of insulation. When sprayed onto the surface of cryogenic liquid gas cargo tanks, SOFI is initially evenly applied in liquid form to the metal surface. It quickly reacts and expands to form an insulation layer consisting of polyurethane foam and a fine porous layer. As a result, SOFI can be applied to almost any surface, allowing for installation of the insulation system without spatial constraints, even on irregular or complex shapes and curves. However, due to SOFI's low mechanical properties, it is vulnerable to tensile and compressive loads. In cryogenic applications, glass fiber is added to reinforce it against tensile loads, and it is used in areas that do not support structural loads.

Figure 3.24 SOFI insulation

Table 3.10 The effective thermal conductivity of SOFI[20]

Material	CVP	Density	Temperature	Thermal conductivity
	mTorr	kg/m^3	K	mW/m · K
Glass bubble	0.1	42	78	7.75
	1			8.68
	10			14.46
	100			18.41
	1×10^3			19.69
	1×10^4			19.85
	1×10^5			19.97
	7.6×10^5			21.17

3.9 MLI

3.9.1 Fabrication Method

Multi-Layer Insulation (MLI) can be broadly divided into two layers. First, it consists of an aluminum deposited polyester film that shields against radiation heat transfer, and a breathable layer of fibrous material called a spacer. This spacer ensures that there is no conductive heat transfer between the aluminum deposited films. The aluminum deposited polyester film is produced through vacuum deposition. By placing a polyester film on top and melting aluminum underneath, evaporated aluminum atoms condense upon hitting the polyester film, forming an extremely thin aluminum film. The resulting aluminum deposited polyester film is then combined with a spacer through adhesion or stitching. This combined aluminum deposited polyester film and spacer constitute one layer, and multiple layers are stacked to form the MLI insulation material.

3.9.2 Structure

MLI has a structure composed alternately of reflective layers and spacer layers. The reflective layers are typically made of thin films, such as mylar or foil, coated with reflective materials including aluminum or silver. Spacer layers are constructed using low thermal conductivity insulating materials such as glass fiber, nylon, silk net, and similar substances. Table 3.11 indicates the materials used for the reflective and spacer layers.

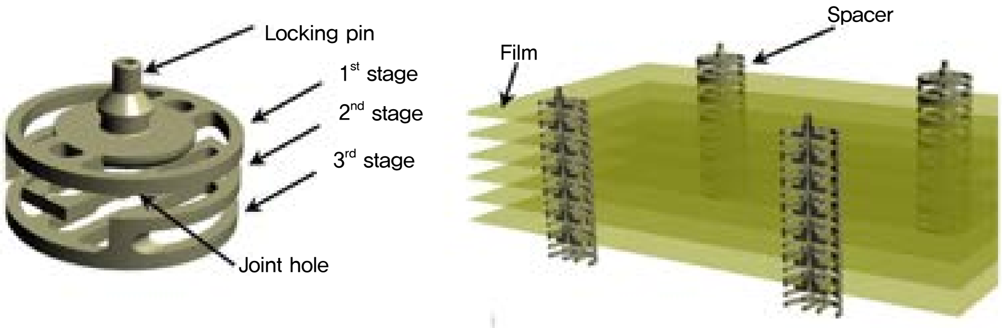


Figure 3.25 Schematic of MLI insulation system[24]

3.9.3 Heat Transfer Process

MLI heat transfer consists of radiation heat transfer emitted from the aluminum deposited polyester film, convection and conduction heat transfer from the air present in the layer with a spacer, and conduction heat transfer through the spacer material. First, radiation heat transfer is defined by the following equation, which is similar to the radiative heat transfer mechanism described earlier for glass wool.

$$q_{rad} = \frac{1}{(N-1)} \frac{1}{\left(\frac{2}{\varepsilon_S} - 1\right)} \sigma \left(T_H{}^4 - T_C{}^4\right) \tag{3.9}$$

Here, $N-1$ is the number of layers in MLI and ε_S is the emissivity of the aluminum deposited film.

Additionally, the conductive heat transfer rate due to the contact between the aluminum deposited film and the spacer material is calculated as follows:

$$q_{cond} = \frac{1}{(N-1)}\frac{1}{Rl_p^2}(T_H - T_C) \tag{3.10}$$

Here, R is the thermal resistance of the spacer material and l_p is defined as the distance between spacers. Finally, for convection and conduction heat transfer from the spacer layer to the air, convection heat transfer is almost negligible due to the extremely low thickness of the spacer, and under normal atmospheric pressure conditions, heat transfer mostly occurs through air conduction. The thermal conductivity is approximately 0.0275 under normal atmospheric pressure conditions, but in high vacuum environments, the contribution of air layer conduction can be neglected as it is significantly reduced. Therefore, in atmospheric pressure conditions, the heat transfer rate can be expressed as follows:

$$q_{total} = \frac{1}{(N-1)}\frac{1}{Rl_p^2}(T_H - T_C) + \frac{1}{(N-1)}\frac{1}{(\frac{2}{\varepsilon_S} - 1)}\sigma(T_H^4 - T_C^4) + 0.0275d(T_H - T_C) \tag{3.11}$$

Since the conduction heat transfer term can be neglected in high vacuum environments, the equation can be written as follows:

$$q_{total} = \frac{1}{(N-1)}\frac{1}{Rl_p^2}(T_H - T_C) + \frac{1}{(N-1)}\frac{1}{(\frac{2}{\varepsilon_S} - 1)}\sigma(T_H^4 - T_C^4) \tag{3.12}$$

3.9.4 Key Characteristics

The reflective layers of MLI reflect a significant portion of the heat radiation that reaches the low emissivity, aluminum coated polyester film, reducing the amount of heat energy transmitted through radiation. The spacer layer helps minimize heat transfer through conduction and convection by creating small air gaps between the layers of aluminum coated polyester film, minimizing physical contact and air movement. This is particularly effective in high vacuum environments, where it eliminates heat transfer through air conduction and radiation via MLI, resulting in excellent insulation performance.

Figure 3.26 MLI insulation material

Table 3.11 Typical spacer and reflector materials used in MLI systems[25]]

Category	Material	Description	Thickness (mm)
Reflector	Mylar	Double–aluminized Mylar; 400 angstroms aluminum	0.006
	Foil	Aluminum foil; type 1145–0; 99.45% purity	0.007
Reflector	Paper	Micro–fiberglass paper; lydall Cryotherm243	0.025
	Fabric	Polyester non–woven fabric	0.08
	Net	Polyester netting; Dacron B4A & B2A	0.02
	Silk Net	Silk netting	0.02

Table 3.10 MLI systems thermal performance data[25]

Material	CVP	Density	Temperature	Thermal conductivity
	mTorr	Layers/mm	K	mW/m · K
Mylar/Paper blankets	5×10^{-3}	2.1	78	0.033
	0.1			0.044
	1			0107
	10			0.467
	100			2.63
	1.02×10^{3}			10.1
	1.01×10^{4}			14.8
	1.00×10^{5}			15.2
	7.69×10^{5}			16.4

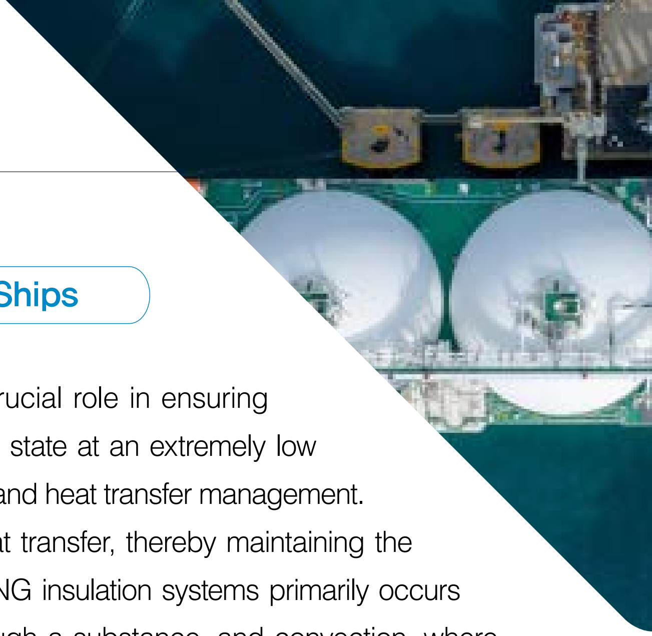
Material	CVP	Density	Temperature	Thermal conductivity
	mTorr	Layers/mm	K	mW/m · K
Foil/Paper rolled	1×10^{-3}	3.6	78	0.03
	4×10^{-3}			0.033
	5×10^{-3}			0.038
	0.2			0.04
	1			0.056
	3			0.09
	10			0.227
	30			0.492
	956			5.67
	1.01×10^{4}			10.1
	1.00×10^{5}			13.3
	7.40×10^{5}			15.8
Mylar/net	1×10^{-3}	2.6	78	0.029
	2×10^{-2}			0.031
	0.1			0.04
	1			0.072
	10			0.469
	100			3.24
	1.04×10^{3}			8.08
	1.00×10^{4}			10.2
	9.9×10^{4}			14.7
	7.69×10^{5}			17.5

Material	CVP	Density	Temperature	Thermal conductivity
	mTorr	Layers/mm	K	mW/m · K
Mylar/Fabric	6×10^{-3}	1.6	78	0.026
	0.1			0.057
	0.3			0.066
	1			0.108
	10			0.568
	99			3
Mylar/Silk net	6×10^{-3}	0.85	78	0.038
	0.1			0.077
	1			0.191
	7.6×10^{5}			22.8
Single LBMLI	1×10^{-3}	0.5	78	0.096
	0.1			0.103
	1			0.266
	10			0.483
	100			2.33
	994			10.2
	1.00×104			16.1
	9.99×104			16.4
	7.6×105			17.1

4

Insulation System for LNG Cargo Holds In Ships

4.1 Mark–III (GTT)
4.2 NO96 (GTT)



4 Insulation System for LNG Cargo Holds In Ships

The insulation system for LNG cargo holds in ships plays a crucial role in ensuring safe and efficient transportation. LNG, transported in a liquefied state at an extremely low temperature of -163°C, requires careful temperature maintenance and heat transfer management. The primary purpose of the insulation system is to minimize heat transfer, thereby maintaining the temperature of LNG and ensuring ship safety. Heat transfer in LNG insulation systems primarily occurs in two ways: conduction, where heat is directly transferred through a substance, and convection, where heat is transferred through the movement of fluids. To reduce convection heat transfer, it is essential to place insulation materials in empty spaces. Insulation materials disrupt the movement of fluids in empty spaces, reducing convection heat transfer. By doing so, temperature loss around LNG can be minimized, ensuring safe transportation. Additionally, to decrease conduction heat transfer, the thickness of the insulation material can be increased. As the thickness of the insulation material increases, the rate of heat transfer decreases, allowing the use of thick insulation to minimize heat loss and achieve stable temperature maintenance. However, when determining the thickness of insulation material, the available space within the ship design should be considered. As such, the appropriate selection and placement of insulation materials play a crucial role in regulating heat transfer and constructing an efficient insulation system.

The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code)[5] provides guidelines for the characteristics and testing factors to be considered for insulation materials, as follows:

❶ The insulation materials should be suitable for design loads.
❷ The insulation materials should have the following properties, and tests should be conducted to ensure suitability for operation:

- Compatibility with LNG fuel
- Solubility in LNG fuel
- Absorption of LNG fuel
- Shrinkage
- Ageing
- Closed cell content
- Density
- Mechanical properties affected by LNG and other loads, Thermal expansion and contraction
- Abrasion
- Bonding
- Thermal conductivity
- Resistance to vibrations
- Resistance to fire and flame spread
- Resistance to fatigue and crack propagation

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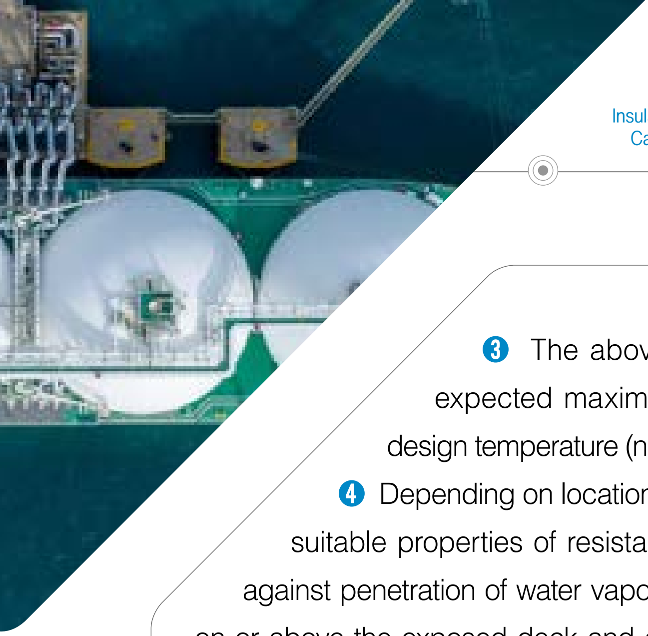
[5] IGC Code (The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk)



❸ The above properties should be tested for the range between the expected maximum temperature in operation and 5°C below the minimum design temperature (not lower than -196°C).

❹ Depending on location or environmental conditions, insulation materials should have suitable properties of resistance to fire and flame spread, and be adequately protected against penetration of water vapor and mechanical damage. If insulation materials are located on or above the exposed deck and close to the tank cover penetration area, they should be fire-resistant or have slow flame propagation, and protected with an approved vapor sealant.

❺ Insulation materials that do not meet the criteria for fire resistance should be applied in permanently inert storage tank areas, and their surfaces should be covered with a slow-diffusing material to form an approved vapor seal.

❻ Thermal conductivity tests should be conducted using appropriately aged samples.

❼ Where powder or granulated insulation is used, the necessary measures should be taken to prevent compacting of the material during operation, maintain the required thermal conductivity, and prevent undue increase of pressure on the cargo containment system.

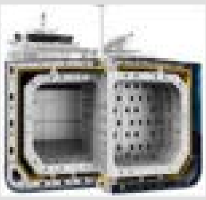
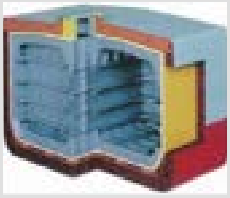
Type	Independent Type A	Independent Type B	Independent Type C	Membrane
Shape				
Design pressure	〈 0.07 Mpa (=0.7 bar)	〈 0.07 MPa (=0.7 bar)	0.3~0.5 MPa (=3~5 bar)	〈 0.0025 MPa (=0.25 bar)
Cargo hold for LNG carrier	LNT–A tank	Moss tank, SPB tank	Cylindrical tank, Bilobe tank	MARK–III, No. 96
Secondary membrane	Full secondary membrane	Partial secondary membrane	Not required	Full secondary membrane
Insulation material	Polyurethane foam	Polyurethane foam	Polyurethane foam	• Reinforced polyurethane foam
Volumetric efficiency	Perlite/glass wool insulation box	Spherical: Good Rectangular: Bad	Bad	Good
Remarks	Expensive	High reliability	High reliability	Sloshing issue

Figure 4.1 Typical types of LNG cargo containment system

Insulation materials for LNG ship cargo holds are manufactured considering the above characteristics. The cargo holds where such insulation materials are used are classified into two types according to the IGC Code: independent cargo holds and membrane cargo holds. Each type of cargo hold is equipped with an insulation system tailored to its unique characteristics such as storage capacity and shape. Figure 4.1 illustrates the types of LNG bulk carriers' cargo holds classified by the IGC Code.

The independent type LNG cargo hold, as per the IGC Code, employs a configuration where the external and internal tank walls are installed separately. In this type, an insulation system is placed between the internal and external tanks. Polyurethane foam is commonly used as the insulation material, either in the form of panels that are sprayed or directly applied in a spray form onto the surface of the cargo hold. The insulation material is typically applied with a density in the range of 40 to 60 kg/m^3.

For the membrane type LNG cargo hold, the insulation system is directly installed within the external wall. This method integrates the insulation system into the structure of the cargo hold itself, requiring materials with sufficient strength and durability to withstand internal and external loads. Accordingly, suitable materials should be chosen and applied, considering the characteristics of the insulation material. Representative membrane type LNG cargo hold insulation systems include Mark-III, NO96, and KC-1, generally composed of a primary membrane, primary insulation panel, secondary membrane, and secondary insulation panel. The primary membrane directly contacts LNG, serving as a watertight seal, while the primary and secondary insulation panels are applied as insulating components to maintain a temperature of -163°C. The secondary membrane prevents LNG penetration into the hull in case the primary membrane is damaged or fractured. Detailed configurations of each Mark-III and NO96 insulation system are explained in sections 4.1 and 4.2, respectively.

4.1 Mark-III (GTT)

4.1.1 Insulation System Components

The insulation material of the Mark-III insulation system consists of glass fiber reinforced polyurethane foam and plywood. The plywood is adhered in a sandwich form to the polyurethane foam.

4.1.2 Key Characteristics

The Mark-III system uses 304L stainless steel as the primary membrane material that directly contacts LNG to prevent LNG leakage. To reduce thermal stress due to cryogenic thermal contraction of 304L stainless steel, it is applied in a corrugated structure. The corrugated portion expands during thermal contraction at low temperatures, relieving thermal stress. This structure allows for contraction during LNG loading at cryogenic temperatures and expansion during LNG unloading at relatively higher temperatures, thus alleviating thermal stress. The first and second insulation panels are applied in a form where glass fiber reinforced polyurethane foam is bonded to plywood. The polyurethane foam, reinforced with glass fibers, must have sufficient strength to withstand fluid induced sloshing loads, which are caused by the relative motion between the ship's 6-DOF (degrees of freedom) motion during navigation and the free surface motion of LNG cargo. For this purpose, glass fiber reinforced polyurethane foam with a density of around 130 kg/m^3 is used. Moreover, glass fiber reinforced polyurethane foam has a low thermal conductivity, offering high resistance to heat. The plywood serves to distribute the weight of LNG cargo and prevent damage to the cargo hold. Additionally, it prevents damage to the polyurethane foam by absorbing the heat generated during welding. While polyurethane foam may melt or deform when exposed to welding heat, plywood has high heat resistance, withstanding high temperature welding without deformation or melting. These properties contribute to maintaining the integrity of the insulation system.

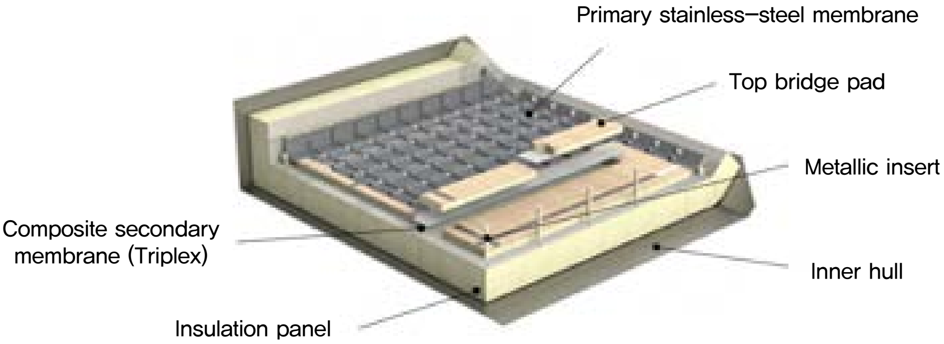


Figure 4.2 Mark–III LNG insulation system[26]

4.2 NO96 (GTT)

4.2.1 Insulation System Components

The insulation material of the NO96 insulation system consists of perlite, glass wool, and plywood. Perlite or glass wool is filled inside the plywood boxes.

4.2.2 Key Characteristics

The NO96 system uses a 36% nickel alloy with almost no thermal contraction in cryogenic environments to prevent LNG leakage. This alloy, known as Invar due to its minimal temperature induced deformation, is applied in plate form. The primary and secondary insulation panels are arranged by filling perlite or glass wool into the plywood boxes that support the load of the LNG cargo. Initially, perlite was mainly used, but recently, glass wool has been preferred because of its lower thermal conductivity, providing more effective insulation. The plywood boxes distribute the weight of the LNG cargo, ensuring safety, and serve to protect the insulation material. They support the insulation panels, prevent compression of the insulation material to maintain insulation effectiveness, and absorb shocks and vibrations that may occur during cargo transport. Like the primary membrane, the secondary membrane also utilizes Invar, a 36% nickel alloy, for its resistance to temperature induced deformations.

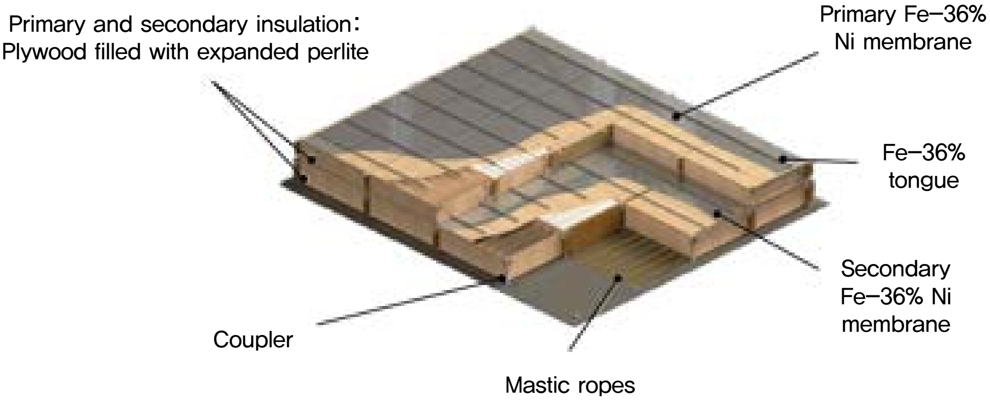


Figure 4.3 NO96 LNG insulation system[27]

5

Insulation System for Liquefied Hydrogen Cargo Holds in Ships

5.1 Suiso Frontier
(Kawasaki Heavy Industries)
5.2 Kobe LH2 Terminal Liquefied Hydrogen Cargo Hold
(Kawasaki Heavy Industries)
5.3 Cylindrical Liquefied Hydrogen Cargo Hold
(Kawasaki Heavy Industries)
5.4 MOSS MARITIME

5 Insulation System for Liquefied Hydrogen Cargo Holds in Ships

The insulation system for liquefied hydrogen cargo holds requires high insulation performance due to the temperature being approximately 90°C lower (-253°C) compared to LNG at -163°C. In environments using liquefied hydrogen, vacuum insulation systems are primarily applied to minimize heat transfer, with nonvacuum insulation systems also being used.

The vacuum insulation system reduces heat transfer by creating a vacuum in the space, minimizing conduction or convection heat transfer. In a vacuum state, there is no medium for heat conduction, and the sparse gas molecules make convection heat transfer difficult, mainly causing heat transfer through radiation. Therefore, special insulation materials that block radiation heat transfer are used. A point of caution in vacuum insulation systems is the potential loss of vacuum over time, which can occur due to factors such as gas penetration, gas molecule diffusion, and gas discharge. These factors gradually increase the number of gas molecules in the vacuum space, leading to an increase in convection heat transfer. Therefore, periodic maintenance and monitoring are necessary to maintain the vacuum pressure level within the system.

Nonvacuum insulation systems, on the other hand, reduce heat transfer without using a vacuum. Similar to LNG cargo hold insulation systems, conduction and convection heat transfer dominate. Placing insulation material in the empty space inhibits convection heat transfer and controls direct conduction heat transfer through the material. Nonvacuum insulation systems do not use complex vacuum systems, making maintenance and operation relatively straightforward. However, one drawback is the increased insulation material thickness. As such, it is important to consider insulation characteristics when selecting and applying appropriate materials.

Safety in the transportation of liquefied hydrogen is a critical issue, and related regulations and recommendations continue to develop. Before 2016, liquefied hydrogen was not considered a general bulk cargo transported at sea and was not included in the IGC Code. However, after 2016, the IMO revised the guidelines for liquefied hydrogen carriers, adopting Resolution MSC.420(97))[6] during the 97th session of the Maritime Safety Committee (MSC)[7]. These interim guidelines are based on safety accident scenarios for ensuring the safety of transporting liquefied hydrogen and provide more specific requirements for each item. Moreover, they serve as the first official document recognizing liquefied hydrogen as a cargo. The key content of the interim guidelines is structured as shown in Table 5.1, and Table 5.2 presents the main content related to insulation materials[28].

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[6] MSC.420(97), one of the guidelines published by IMO, contains interim recommendations for carriage of liquefied hydrogen in bulk

[7] The MSC (Maritime Safety Committee), a technical body of IMO, is a committee composed of member states with interests in maritime safety.

Table 5.1 Interim recommendations for carriage of liquefied hydrogen in bulk.

No.	Contents
1	Introduction
2	Interim Recommendations for Carriage of Liquefied Hydrogen in Bulk
3	Explanation on General Requirements
	3.1 Properties of Liquefied Hydrogen
	3.2 Explanation on Respective Requirements
4	Special Requirements Against Hazards of Liquefied Hydrogen
	4.1 Hazards of Liquefied Hydrogen to Be Considered
	4.2 Low temperature hazard
	4.3 Hydrogen Embrittlement
	4.4 Permeability
	4.5 Low Density and High Diffusivity
	4.6 Ignitability
	4.7 Fire Hazard
	4.8 High Pressure Hazard
	4.9 Health Hazard
	4.10 Wide Range of Flammable Limit

Table 5.2 Special Requirements for carriage of liquefied hydrogen in bulk

No.	Special Requirement	Related Hazard
1	When vacuum insulation is used for a cargo containment system, the insulation performance should be evaluated to the satisfaction of the Administration based on experiments, as necessary.	4.1
2	Requirements for materials whose design temperature is lower than −165˚C should be agreed with the Administration, paying attention to appropriate standards. Where minimum design temperature is lower than −196˚C, property testing for insulation materials should be carried out with the appropriate medium, over a range of temperatures expected in service.	4.2
3	Materials of construction and ancillary equipment such as insulation should be resistant to the effects of high oxygen concentrations caused by condensation and enrichment at the low temperatures attained in parts of the cargo system (refer to the requirement for nitrogen).	4.2
4	For cargo pipes containing liquid hydrogen and cold hydrogen vapour, measures should be taken to prevent the exposed surfaces from reaching −183˚C. For places where preventive measures against low temperature are not sufficiently effective, such as cargo manifolds, other appropriate measures such as ventilation which avoids the formation of highly enriched oxygen and the installation of trays recovering liquid air may be permitted in lieu of the preventive measures. Insulation on liquid hydrogen piping systems exposing to air should be of non−combustible material and should be designed to have a seal in the outer covering to prevent the condensation of air and subsequent oxygen enrichment within the insulation.	4.2
5	When deterioration of insulation capability by single damage is possible, appropriate safety measures should be adopted taking into account the deterioration.	4.8

(4.1) Hazards of liquefied hydrogen to be considered

- When using vacuum insulation, the potential weakening of insulation properties at the expected carriage temperature of liquefied hydrogen (loss of vacuum; gas influx due to cracks in valves or welds, virtual leakage resulting from dust, moisture, and gas particles adsorbed by insulation material, etc.) must be considered. The evaluation of vacuum insulation should be specified for the normal range or the upper limit of the Cold Vacuum Pressure (CVP), and vacuum loss should be defined based on this value. Therefore, when designing and testing cargo containment systems and pipelines, the effect of vacuum pressure should be taken into account. Additionally, supporting structures and adjacent hull structures should be designed considering the cooling effect due to loss of vacuum insulation.

(4.2) Low temperature hazard

- Requirements for materials with a design temperature lower than -165°C must be discussed with regulatory authorities and comply with appropriate standards. If the design minimum temperature is lower than -196°C, tests must be conducted to obtain relevant thermal properties for the expected design temperature.
- Construction material and ancillary equipment such as insulation should be resistant to the effect of high oxygen concentration caused by condensation and concentration at low temperatures occurring in parts of the cargo system.

- For cargo pipes containing liquefied hydrogen and cold hydrogen vapor, measures should be taken to prevent exposed surfaces from reaching -183°C. The insulation material for liquefied hydrogen piping systems exposed to air must be non-combustible, and the design should include sealing on external covers to prevent air condensation and resulting oxygen concentration.

(4.8) High pressure hazard

- Safety measures are necessary for vacuum insulation systems used for the preservation of liquefied hydrogen to prevent insulation deterioration that may lead to rapid temperature rise or excessive vaporization.

Regarding the MSC.420(97) interim recommendations, the Suiso Frontier built by Kawasaki Heavy Industries in Japan is the only case where a liquefied hydrogen cargo containment system has been applied to an actual ship. Detailed information on this is provided in section 5.1. Additionally, research and development are ongoing for liquefied hydrogen storage tanks, and details can be found in sections 5.2 to 5.4.

5.1 Suiso Frontier (Kawasaki Heavy Industries)

5.1.1 Insulation System Components

The insulation system of the Suiso Frontier applies MLI within the vacuum space, providing insulation performance approximately 10 times higher than the insulation system applied to conventional LNG cargo containment systems.

5.1.2 Key Characteristics

The insulation system of the Suiso Frontier incorporates a Type C liquefied hydrogen cargo containment structure with a double wall design for hydrogen storage. The double wall consists of an inner tank and an outer shell, both constructed from stainless steel. The inner tank serves as the actual storage space for liquefied hydrogen, while the outer shell surrounds the inner tank, providing a protective layer.

The space between these two walls is maintained in a high vacuum state, minimizing heat transfer and preserving the temperature of the internal liquefied hydrogen. Within the vacuum insulation system, a highly reflective metal coating film known as MLI is applied. MLI reduces radiation heat transfer, and prevents external heat from reaching the interior. Additionally, the support structure is made of Glass Fiber Reinforced Plastic (GFRP). GFRP is a lightweight yet strong material, offering structural stability to the tank while providing insulation effects. This structural design ensures the safe storage of internal liquefied hydrogen while protecting it from external temperature fluctuations.

Figure 5.1 Structure of HYDROGEN FRONTIER liquid hydrogen storage tank[29]

5.2 Kobe LH2 Terminal Liquefied Hydrogen Cargo Hold (Kawasaki Heavy Industries)

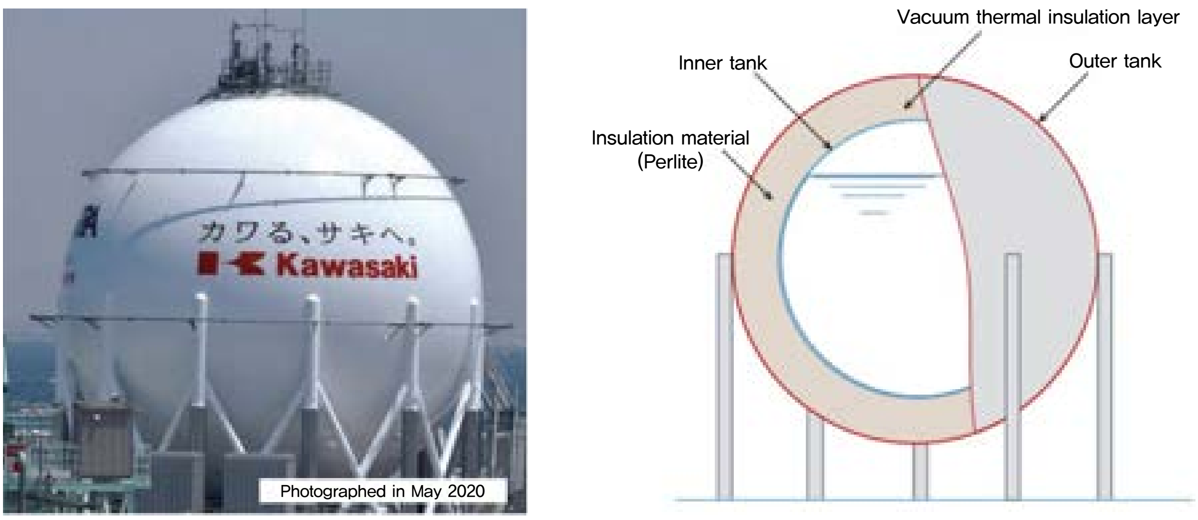
5.2.1 Insulation System Components

The MOSS type liquefied hydrogen cargo hold at the Kobe LH2 Terminal is equipped with a vacuum insulation system using perlite as the filling material.

5.2.2 Key Characteristics

The insulation system of the Kobe LH2 Terminal's liquefied hydrogen cargo hold is designed as a double walled tank with perlite vacuum insulation to store liquefied hydrogen in a spherical shell. The double wall configuration consists of an internal tank and an external tank. The internal tank plays a role in preventing leakage or loss of liquefied hydrogen, while the external tank protects the internal tank and provides structural support.

The space between the internal tank and external tank is equipped with a vacuum insulation system filled with perlite. Perlite is known as a lightweight insulation material that hinders heat transfer, minimizing thermal conductivity. In a vacuum, heat transfer primarily occurs through radiation. However, when filled with perlite, the porous structure and properties of perlite disrupt the radiation heat transfer path, preventing efficient heat transfer. As a result, the predominant heat transfer mechanism within the vacuum space shifts from radiation to conduction. Conduction heat transfer involves the transfer of heat between materials in direct contact, and through this heat transfer path, the perlite filling hinders internal heat transfer and enhances the insulation effect.



Photographed in May 2020

(a)

(b)

Figure 5.2 Kobe LH2 terminal Liquefied hydrogen storage tank(a) and conceptual diagram of vacuum thermal insulation structure(b)[29]

5.3 Cylindrical Liquefied Hydrogen Cargo Hold (Kawasaki Heavy Industries)

5.3.1 Insulation System Components

The cylindrical liquefied hydrogen cargo hold under development by Kawasaki Heavy Industries employs a nonvacuum insulation structure for the insulation system. This structure incorporates foam type insulation material, and adopts a nonvacuum structure with atmospheric pressure hydrogen gas between the internal tank and external tank.

5.3.2 Key Characteristics

The cylindrical liquefied hydrogen cargo tank features a cylinder shape with a flat bottom, providing higher volumetric efficiency compared to traditional spherical cargo tanks. This cargo tank adopts a double wall structure composed of an internal tank and an external tank. The internal tank serves as the actual storage space for liquefied hydrogen, while the external tank protects the internal tank and acts as a barrier against external elements. A nonvacuum structure with atmospheric pressure hydrogen gas exists between the internal tank and the external tank. This structure prevents the buckling phenomenon caused by vacuum pressure, enhancing the safety of the storage tank. However, as it involves the use of flammable hydrogen gas between the internal and external tanks, additional considerations for safety design criteria of conventional cargo tanks are necessary.

Inside the internal tank, polymer foam insulation, including polyurethane foam, is applied to prevent heat transfer and maintain the temperature stability of the internal liquefied hydrogen. However, there may be an issue where hydrogen gas permeates the surface of polymer foam insulation, leading to a degradation in insulation performance. To address this, the development project includes an assessment of gas barrier methods. The objective of this method is to maintain insulation performance by applying a gas barrier material to the surface of the insulation, preventing the penetration of hydrogen gas.

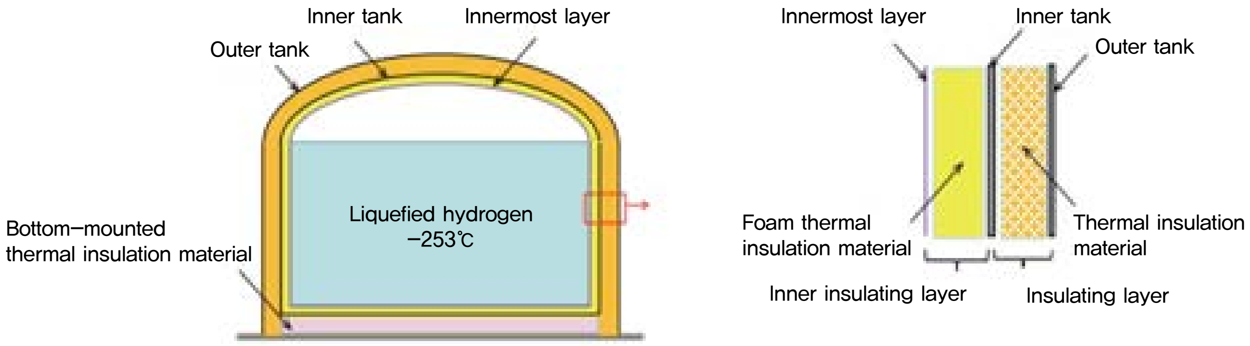


Figure 5.3 Design structure of cylindrical liquid hydrogen storage tank[29]

5.4 MOSS MARITIME

5.4.1 Insulation System Components

The insulation system in MOSS MARITIME design forms a vacuum space between the internal tank and the external tank. Inside this vacuum space, MLI is applied. At the same time, polyurethane foam insulation is used on the surface of the external tank.

5.4.2 Key Characteristics

The MOSS MARITIME design features tanks designed with a double wall structure using stainless steel. This design serves to prevent leakage or loss of liquefied hydrogen, with the external tank protecting the internal tank and providing structural support. MLI is installed in the vacuum space between the internal and external tanks. It reflects radiant heat, minimizing heat transfer between the internal and external tanks. This prevents the internal liquefied hydrogen from reacting sensitively to external temperature changes, helping to maintain a stable temperature. Additionally, a 300mm layer of polyurethane foam insulation is applied to the outer surface of the external tank. This insulation enhances the performance of the insulation system and acts as a protective device that prevents rapid evaporation of the internal liquefied hydrogen due to vacuum space losses.

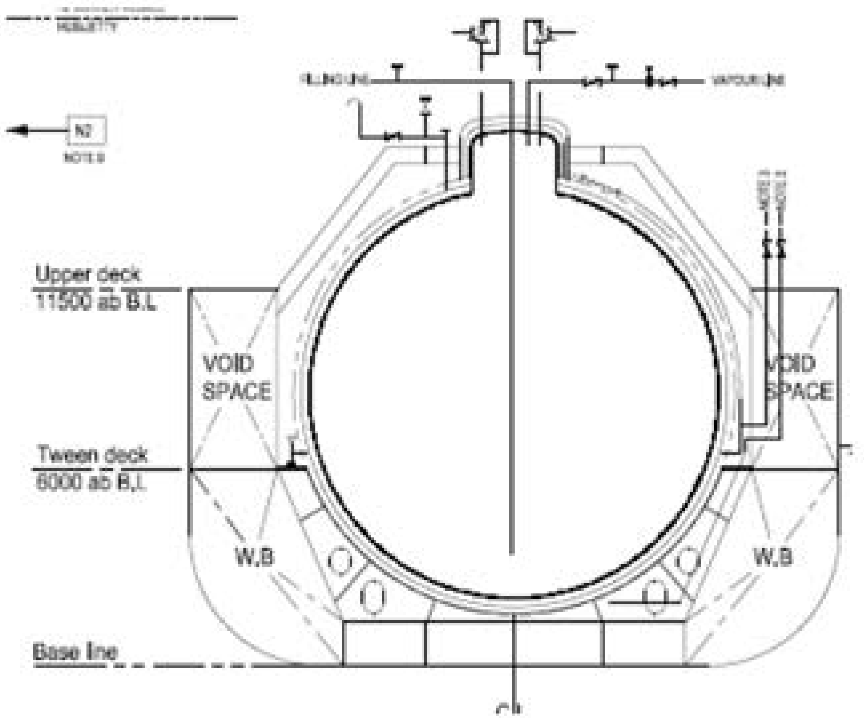


Figure 5.4 Structure of MOSS MARITIME liquid hydrogen storage tank[30]

6

Insulation Performance Evaluation Methods

6.1 Insulation Performance Evaluation Standards (Insulation Performance Evaluation Equipment)
6.2 ASTM C1774 (Cryogenic Insulation Performance Testing Method)
6.3 ASTM C518 (Heat Flow Meter Method)
6.4 ASTM C177 (Guarded Hot Plate Method)

6 Insulation Performance Evaluation Methods

6.1 Insulation Performance Evaluation Standards (Insulation Performance Evaluation Equipment)

This chapter presents information on the heat flow meter method and guarded hot plate method, widely used to measure thermal conductivity in the low temperature and cryogenic temperature range, and methods and principles of cryogenic insulation performance measurement using cryostat equipment, introduced in recent research, especially in studies involving liquefied hydrogen. Figure 6.1 schematically illustrates the thermal conductivity measurement methods provided by the German company Netzsch and the materials that can be measured by each method

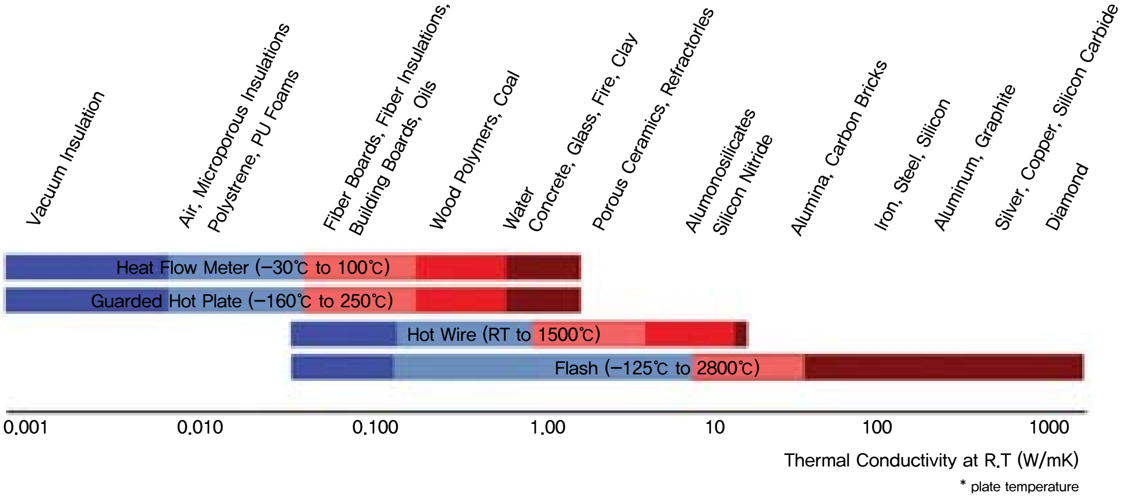


Figure 6.1 Comparison of measurement methods and material type for the ranges of thermal conductivity (Courtesy of Netzsch)[31]

Cryogenic insulation systems commonly applied to ships are typically composed in a stacked or combined form with two or more materials. Since to evaluate the insulation performance of each material, standardized specimens and equipment should be used to quantitatively measure thermal conductivity. Some methods for measuring the thermal conductivity of insulation materials are the heat flow meter method, guarded hot plate method, and cryogenic insulation thermal performance testing method. The appropriate method should be chosen based on the applicable temperature range and measurement method described in each section. Table 6.1 summarizes the ASTM insulation performance evaluation standards. Based on this summarized information, Chapter 6 describes the insulation performance evaluation standards.

Table 3.8 The effective thermal conductivity of glass bubble[20]

Method (ASTM)	Type	Sample	Delta Temp	Boundary Temp Range(K)	k–value Range (mW/m–K)	Heat Flux Range (W/m^2)	Reference Test Material
Astm1774 (Annex A1) Cryostat 100	• Absolute • Boiloff • Calorimeter	• Cyl.	Small	77 to 300	0.01 to 60	0.1 to 500	• Blanket • Molded • bulk fill
Astm1774 (Annex A2) Cryostat–2	• Comparative • Boiloff • Calorimeter	• Cyl.	Small	77 to 300	0.1 to 60	1 to 500	
Astm1774 (Annex A3) Cryostat 500	• Absolute • Boiloff • Calorimeter	• Flat • Disk	Large	77 to 300 (5X10^{-5}) torr	0.05 to 100	1 to 1000	• MLI • Foam • Aerogel
Astm1774 (Annex A4) Cryostat 400	• Comparative, • Boiloff • Calorimeter	• Flat • Disk	Large	77 to 300	0.5 to 100	10 to 1000	• Rigid materials • Soft materials
Astm1774 (Annex A4) Macro flash	• Comparative, • Boiloff • Calorimeter	• Flat • Disk	Large	77 to 403	10 to 1000		• Foam • Powder • Aerogel • Carbon • Wood • Glass • Ceramic • Metal • MLI
Astm1774 (Annex A5) Electrical Power Cryostat	• Cryogen	• Flat	Large				
Astm1774 (Annex A6) Electrical Power Cryostat	• Cryocooler	• Flat • Disk	Large				
C518	• Comparative, • Heat Flow Meter	• Flat, • square	Large	273 to 383	5 to 500	–	• Blanket, • Batt type, • Loose fill
C177	• Absolute, • Guarded Hot Plate	• Flat, • disk	Large	93 to 773	14 to 2000	–	
C745	• Absolute, • Boiloff • Calorimeter	• Flat, • disk	Large	250/670 and 20/300	–	0.3 to 30	

6.2 ASTM C1774 (Cryogenic Insulation Performance Testing Method)[32]

This test method is a procedure for measuring the heat flux and steady state thermal properties of insulation systems under cryogenic conditions. Insulation systems may consist of homogeneous or nonhomogeneous materials, composed of one or more materials. These insulation systems can take the form of flat plates, cylinders, or spherical shapes and may be exposed to conditions ranging from absolute temperatures of 0 K or 4 K to 400 K and from high vacuum to atmospheric pressure. The functionality of most cryogenic insulation systems requires a high level of insulation performance to maintain significant temperature differences. To evaluate the performance of such insulation systems, tests are conducted according to the procedures defined in ASTM C1774 (Standard Guide for Thermal Performance Testing of Cryogenic Insulation Systems). The test equipment in ASTM C1774 is classified into the boiloff calorimeter method and electrical power method. The boiloff calorimeter method is further classified into absolute and comparative methods.

6.2.1 Boiloff Calorimeter

The boiloff calorimeter is a method for measuring the thermal conductivity of a specimen using cryogenic fluids. By bringing the insulation system into contact with cryogenic fluid at a constant temperature and pressure, the heat generated during the fluid's evaporation is measured to calculate the thermal conductivity. The test equipment consists of a vacuum chamber, a cryogenic fluid storage and supply system, and a temperature control and data collection system. The mass of the cryogenic liquid in the boiloff calorimeter is measured using a scale, and the changes in mass are recorded in realtime. During the test, cryogenic fluid must be injected to maintain the evaporation rate, and the evaporation rate must be accurately measured to determine the thermal characteristics of the specimen.

Cryogenic boiloff calorimeters are used to determine the effective thermal conductivity and heat flux of the specimen. In this case, the specimen is set under specific environmental conditions, such as boundary temperatures, cold vacuum pressure[8], and the composition of residual gases. As part of the test preparation, temperature sensors are installed on the insulation material, and vacuum pumping and heat cycling or nitrogen purging are performed. The test defines the steady state heat leak rate (watts) for the specimen under the planned test conditions, utilizing equipment that includes stable warm boundary temperature (WBT) and cold boundary temperature (CBT), as well as cold vacuum pressure.

For example, the cold mass of liquid nitrogen maintains a CBT of approximately 78K. The WBT is maintained at about 293K using an external heater.

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[8] Cold vacuum pressure : Steady state pressure reached inside the insulation system after cooldown

The vacuum range includes high vacuum (HV), soft vacuum (SV), and no vacuum (NV). The residual gas is typically nitrogen, but different gases can be used depending on the environmental conditions required for the experiment.

HV(High Vacuum) : 10^{-6} torr〈 Pressure 〈10^{-3} torr
SV(Soft Vacuum) : 10^{-2} torr〈 Pressure 〈10 torr
NV(No Vacuum) : 100 torr〈 Pressure 〈1000 torr

Here, the rate of heat transfer (Q) of the insulation system is directly proportional to the flow rate of the liquid nitrogen boiloff gas, and the flow rate is measured by a precision scale or a mass flow meter connected to the data acquisition system. During flow rate measurement, the back pressure from the tube connected to the flow meter is approximately 0.1 psig. This pressure corresponds to the saturation pressure of the cryogenic fluid, which is 198.6 J/g, equivalent to the latent heat of vaporization of liquefied hydrogen. As in the example test described above, the apparent thermal conductivity (k-value) of the insulation system is determined by Fourier's law of heat conduction for cylindrical or flat specimens, and the average heat flux is calculated by dividing the effective area of heat transfer by the total heat transfer rate. The boiloff calorimeter method, as shown in Table 6.2, is divided into cylindrical/flat specimen testing equipment based on the shape of the specimen. Depending on the insulation system performance test method, it is classified as an absolute method or a comparative method.

Table 6.2 Typical Characteristics of Boiloff Calorimeter Apparatuses

Geometry	Type	Heat Flux Range (W/m2)	K_e Range (mW/mK)	Typical Specific Size
Cylindrical	Absolute	0.1 to 500	0.01 to 60	1m length; up to 50mm thickness
Cylindrical	Comparative	1 to 500	0.1 to 60	0.5m length; up to 30mm thickness
Flat Plate	Absolute	1 to 1,000	0.05 to 100	200mm diameter; up to 30mm thickness
Flat Plate	Comparative	10 to 1,000	0.5 to 100	75mm or 200mm diameter; up to 30mm thickness

6.2.1.1 Cylindrical Boiloff Calorimeter

Depending on the shape of the specimen, the cylindrical boiloff calorimeter evaluates specimens surrounded by a cylindrical cryogenic chamber. The cylindrical specimen, as shown in Figure 6.2 (Cryostat-100), consists of upper and lower guard chambers and an intermediate test chamber. To minimize heat influx, each of the three chambers is partially filled with cryogenic fluid through feedthroughs, allowing vaporized gas to be discharged. The nitrogen gas pumping system is directly connected to a turbo pump, and the vacuum level can be adjusted to below 5X10-5 by nitrogen gas purging and residual gas pressure control in the nitrogen gas supply system. As shown in Figure 6.2, the cryogenic calorimeter is surrounded by an MLI layer at its center. The outer container is surrounded by a high vacuum pumping system and a heating sheet to control the warm boundary temperature.

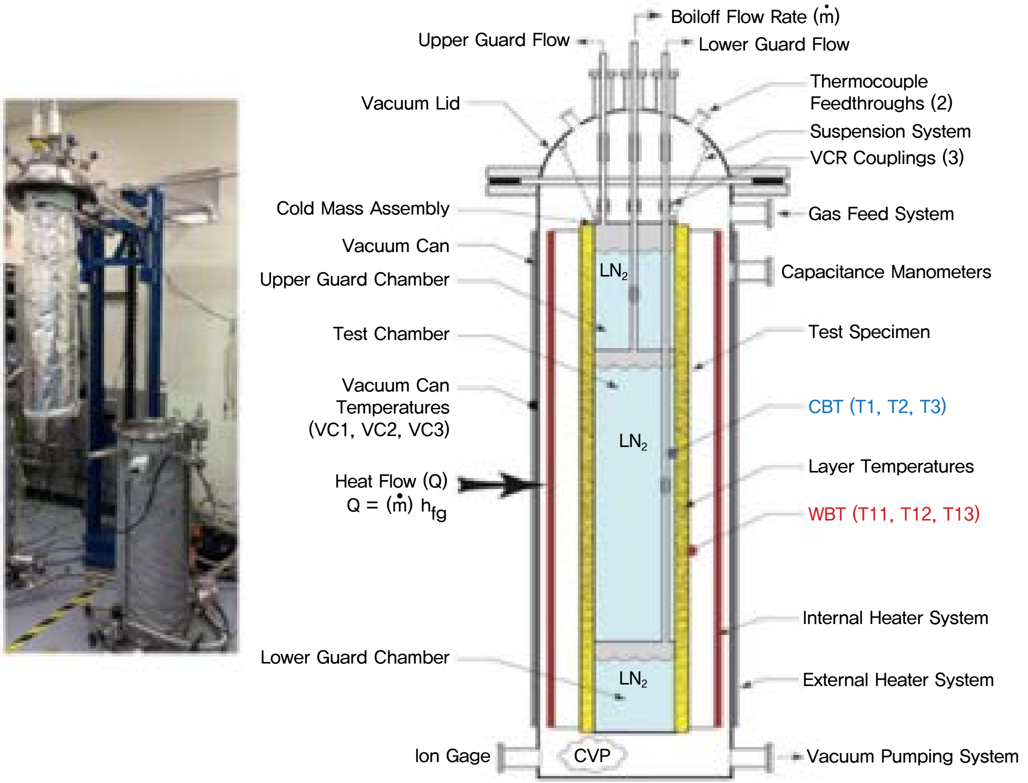


Figure 6.2 ASTM C1774, Annex A1: Cylindrical boiloff calorimeter (Cryostat-100)

The thickness of the specimens evaluated using the above equipment is highly sensitive, and specimens with a maximum thickness of approximately 50mm need to be assessed. Blanket, clamshell, molded, or bulkfill materials can be evaluated. A blanket can be composed of individual layers or various combinations of layers. Multilayer insulation specimens can be applied in the form of a blanket, layer by layer, or in a rolled form.

The cylindrical equipment also allows for the evaluation of insulation systems applied in the form of tanks and pipes. Additionally, it has the advantage of minimizing end effects or unwanted lateral heat transfer during testing. The rate of heat transfer Q through the insulation specimen to the cryogenic fluid chamber is directly proportional to the natural boiloff rate V of the cryogenic fluid, as seen in the equation below.

$$Q = V_{stp}\rho_{stp}h_{fe}(\rho_{f}/\rho_{fe}) \tag{6.1}$$

Here, stp represents standard temperature and pressure and (ρ_{f}/ρ_{fe}) is the density correction factor (between liquid and saturated liquid). The effective thermal conductivity(K_e) is calculated from Fourier's law of heat conduction through the cylinder wall..

$$K_e = (Q/\Delta T)(A_e/x) = [Qln(d_0/d_i)]/1\pi L_e\Delta T \tag{6.2}$$

$$A_e = (2\pi xL_e)/ln(d_0/d_i) \tag{6.3}$$

The heat flux(q) is calculated by dividing the total heat transfer rate by the effective heat transfer area, as shown in the following equation.

$$q = Q/A_e \tag{6.4}$$

6.2.1.2 Flat Boiloff Calorimeter

The cylindrical flat plate boiloff calorimeter and heat flow meter enable the evaluation of the insulation performance of flat plate shaped specimens. The advantages include (1) suitability for small specimens, (2) compressibility, (3) testing with different purge gases at atmospheric pressure, and (4) ease of applying the results. Powder type insulation tests are more challenging than flat plate type tests but have been successfully conducted. For example, as shown in Figure 6.3, Cryostat-500 uses a liquefied nitrogen evaporator as an energy meter. The low thermal conductivity buffer device adjusts the specimen's thickness and compressive force. The equipment in Figure 6.3 evaluates specimens with a diameter of 203 mm, and it can measure the absolute thermal performance by blocking the top and circumference around the specimen. The adjustable guard ring can be calibrated with known materials. The cryogenic fluid chamber (cold mass assembly), consisting of the test chamber and guard chamber, is fixed to the upper lid. The low thermal conductivity buffer system allows for adjusting the specimen thickness to approximately 30 to 40 mm during testing.

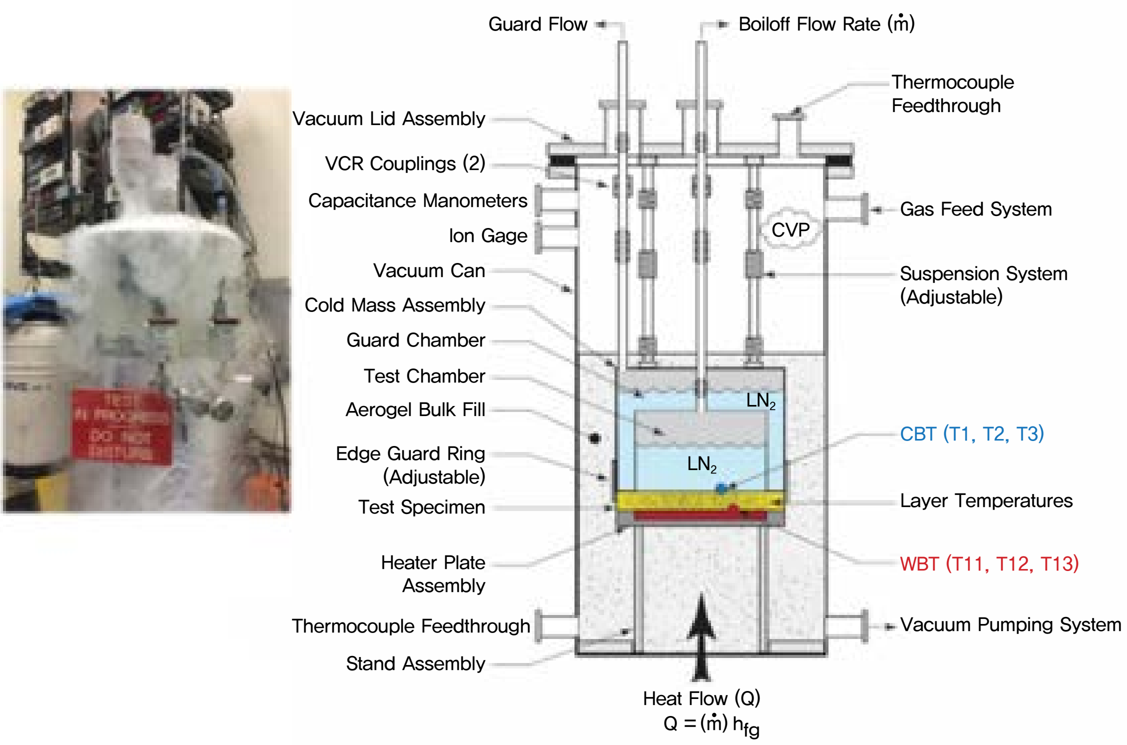


Figure 6.3 ASTM C1774, Annex A3: Flat Plate boiloff calorimeter (Cryostat–500)

Moreover, there is a heating plate system for controlling the warm boundary temperature, and a vacuum level is created in an environment below 5X10-5. The steady state condition is reached when the boiloff rates stabilize in both chambers and the temperature distribution stabilizes according to the thickness. The mass flow meter automatically compensates for gas density in the range of 273K to 323K. The heat transfer rate Q of the insulation specimen is directly proportional to the boiloff gas rate data V of the cryogenic fluid, as described in the aforementioned cylinder boiloff calorimeter. K_e determined through the plate specimen is expressed as shown in the equation below (where heat flux is $q = Q/A_e$)

$$K_e = Qx/A_e\Delta T = 4Qx/\pi(d_e)^2\Delta T \tag{6.5}$$

6.2.1.3 Absolute/Comparative Methods for Insulation Performance Evaluation

The absolute method involves evaluating the performance of insulation systems using equipment that is thermally fully guarded. As shown in Figure 6.4, both the top and bottom have cryogenic chambers, ensuring complete thermal isolation and eliminating end effects. That is, with the absolute method, the test chamber is fully sealed off from ambient heat loss when measuring the properties of the insulation system.

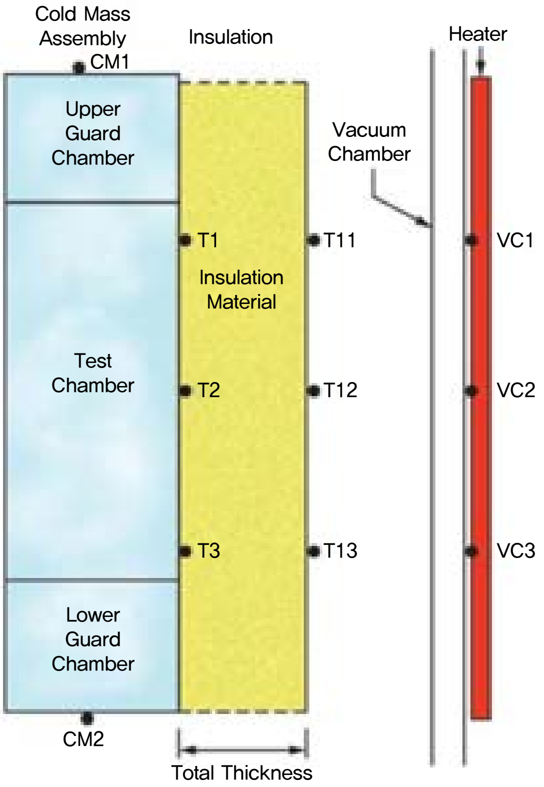


Figure 6.4 (ASTM C1774 Annex A1): Simplified schematic of a cylindrical boiloff calorimeter (Absolute)

On the other hand, the relative comparison method involves partially guarding the test chamber from heat leakage. In contrast to the absolute method, the relative comparison method simplifies the structure by using a low thermal conductivity insulation material as the guard stack instead of a thermally fully guarded cryogenic guard chamber. This allows for comparison of insulation system characteristics based on a simplified design.

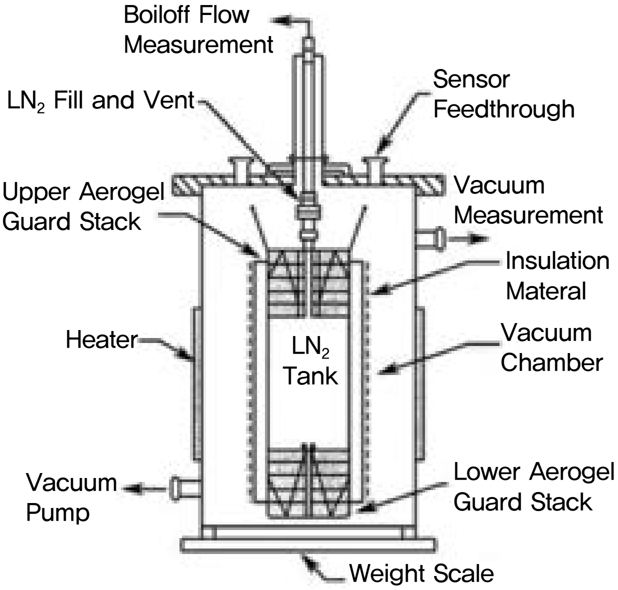


Figure 6.5 (ASTM C1774 Annex A3): Simplified schematic of a cylindrical boiloff calorimeter (Comparative)

6.2.2 Electrical Power Test

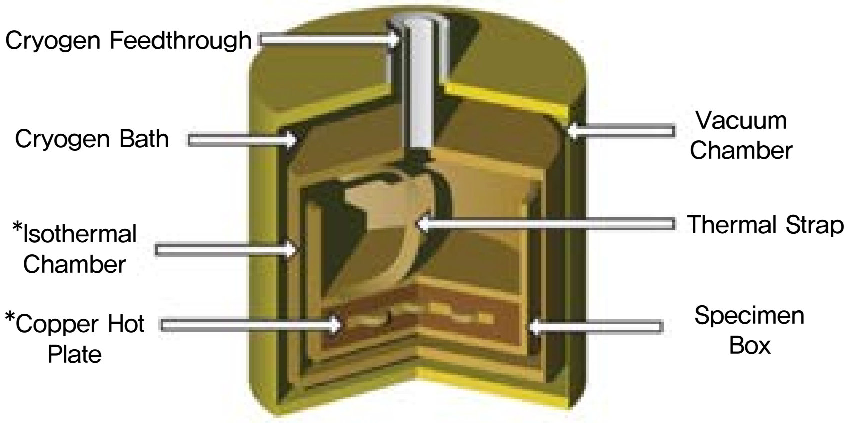
The electrical power test is a method used to measure the thermal conductivity of a specimen using embedded heaters and temperature sensors. In this method, the specimen is heated to a constant temperature, and the heat flux and temperature gradient are measured to calculate the thermal conductivity. An isothermal specimen box made of materials with high thermal conductivity, such as copper, is used. This box, located inside a vacuum chamber, serves the purpose of maintaining a constant temperature during the test, while the vacuum chamber acts as auxiliary protection against heat leakage. The heat flux Q transmitted through the test specimen in the power test is calculated as follows.

$$Q = UI\eta_{heater} - Q_{loss} \tag{6.6}$$

Here, U is the voltage, I is the power, η_{heater} is the heater power constant, and $Q_{loss}$is the heater power loss. The effective thermal conductivity(K_e) is calculated as follows. Based on the concepts mentioned above, the cryostat equipment can be classified into cryogen based and cryocooler based power test apparatuses.

6.2.2.1 Cryogen based electrical power

The cryogen based electrical power cryostat equipment, as shown in Figure 6.6, includes an isothermal specimen box made of copper. Flexible copper straps are connected to the top of the isothermal chamber to ensure thermal equilibrium. The hot plate is installed with two temperature sensors and an electrical heater. The specimen box is installed with a silicon diode thermocouple and an electrical heater. The hot plate heater is used to apply heat for thermal conductivity measurements (generally assisting in heating the specimen box as the temperature increases). The specimen box is thermally connected to an isothermal vacuum sealed chamber. This chamber will later be placed in a vacuum and is equipped with suitable temperature sensors and heaters. Specimens with heights of 20mm and diameters of 152 or 203mm are both permissible.



*Includes electric heater and temperature sensor

Figure 6.6 (ASTM C1774 Annex A5): Electrical power cryostat apparatus (cryogen based)

6.2.2.2 Cryocooler Based Electrical Power

This equipment includes an appropriate cryocooler refrigerant system and a thermally connected test chamber. The design can accommodate either a flat plate or a cylinder. The specimen used to test a 204mm diameter circular disk is shown in Figure 6.7. The cooling plate and the heating plate are positioned inside the isothermal specimen box. The cooling plate, incorporating a copper plate, provides uniform temperature and is attached to a cryogenic cooler that can be applied to 20K and up to required temperatures. The heating plate is composed of copper plates fixed on both sides of a foil heater with bolts, and a stainless steel compression spring provides pressure to maintain surface contact. The heating plate plays a role in applying a constant heat flux to the specimen. When a heat flux is generated, a temperature gradient forms within the insulation system. When the system reaches a steady state, temperatures are measured on each face of the specimen. Temperature sensors, embedded in the center and at the edges of the specimen, are typically silicon diodes or platinum resistance sensors. They are used to measure the specimen's temperature gradient.

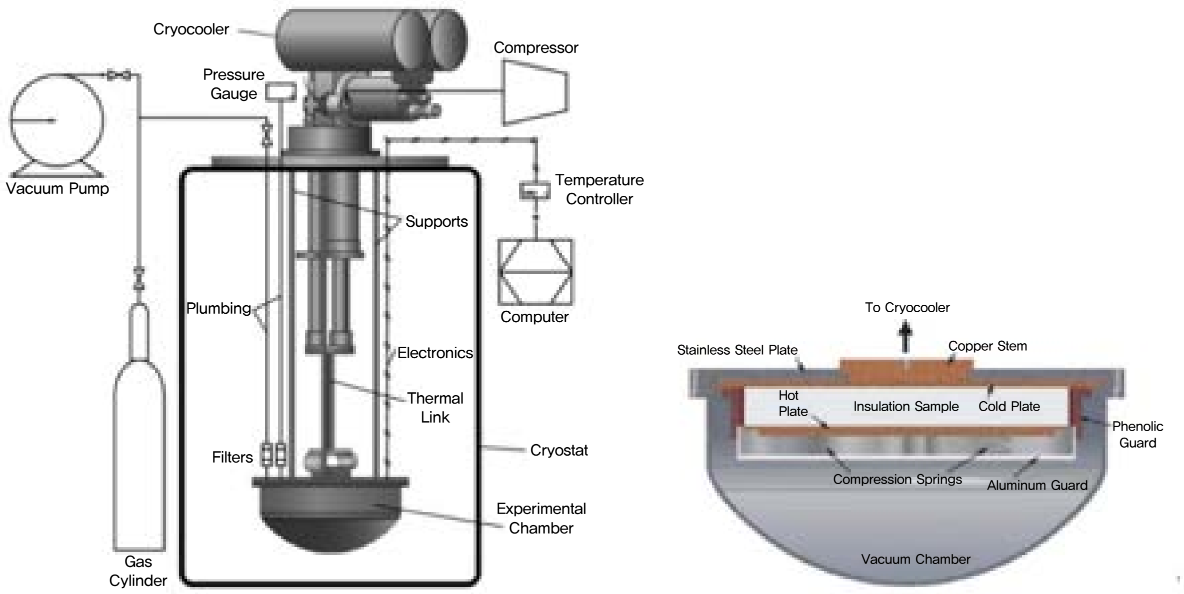


Figure 6.7 (ASTM C1774 Annex A6): Electrical power cryostat apparatus (cryocooler based)

In this test, the specimen must maintain a constant thickness and have a flat surface to ensure contact between the heating plate and the cooling plate. Therefore, if the insulation material is porous or the surface is not sufficiently flat, as in the case of silica aerogel (SOFI), the contact surface may pose a problem. When using powder form insulation materials such as aerogel beads or perlite, they can be employed as specimens, but equipment is needed to maintain rigidity. In addition, a consistent distance should be maintained between the cooling plate and the heating plate.

6.3 ASTM C518 (Heat Flow Meter Method)[33]

The heat flow meter method is a technique used to measure the thermal conductivity and thermal resistance of insulation systems under steady state conditions. This testing method, employing a comparative approach, is used to quickly determine the steady state heat transfer characteristics of insulation when the equipment is calibrated. Insulation systems typically take on a square shape with dimensions ranging from 150mm to 300mm, and both the upper and lower surfaces should be flat. The thickness should not exceed 250mm and must be either the actual thickness of the material or a size sufficient to adequately reflect its thermal properties. The test is conducted with ambient temperatures within the range of 10°C to 40°C, and, generally, measurements are obtained under temperature conditions ranging from -20°C to 70°C. The temperature difference between specimens in all tests should be within 10°C. To evaluate the performance of such insulation systems, tests are carried out following the procedures defined by ASTM C518 (Standard Test Method for Steady State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus). In preparation for the test, the equipment is calibrated using specimens measured by the absolute method. The test, utilizing equipment including cooling and heating plates and heat flux sensors, measures the thermal conductivity of the specimen under steady state conditions in the planned test environment. Figures 6.8 and 6.9 schematically illustrate the heat flow meter method and the apparatus, respectively.

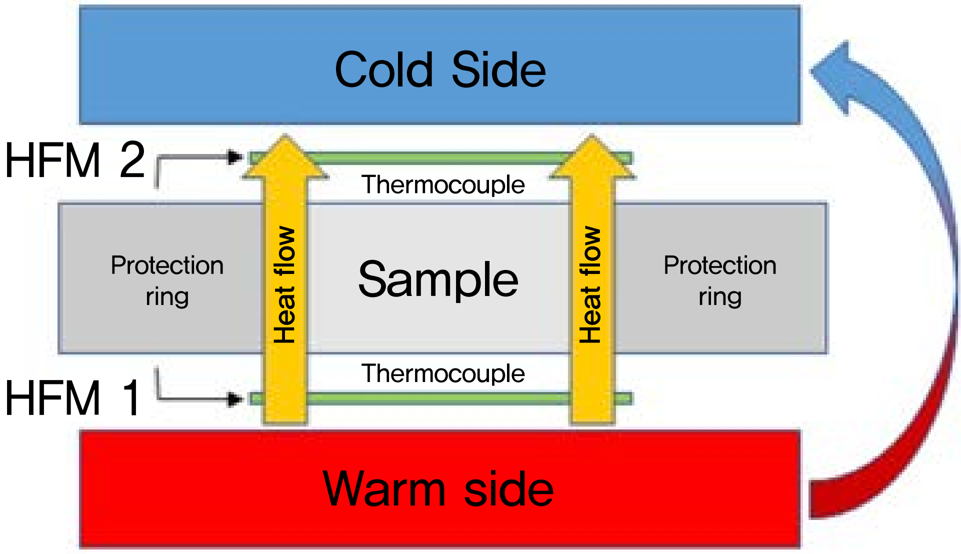


Figure 6.8 Schematic diagram of heat flow meter method (C518)

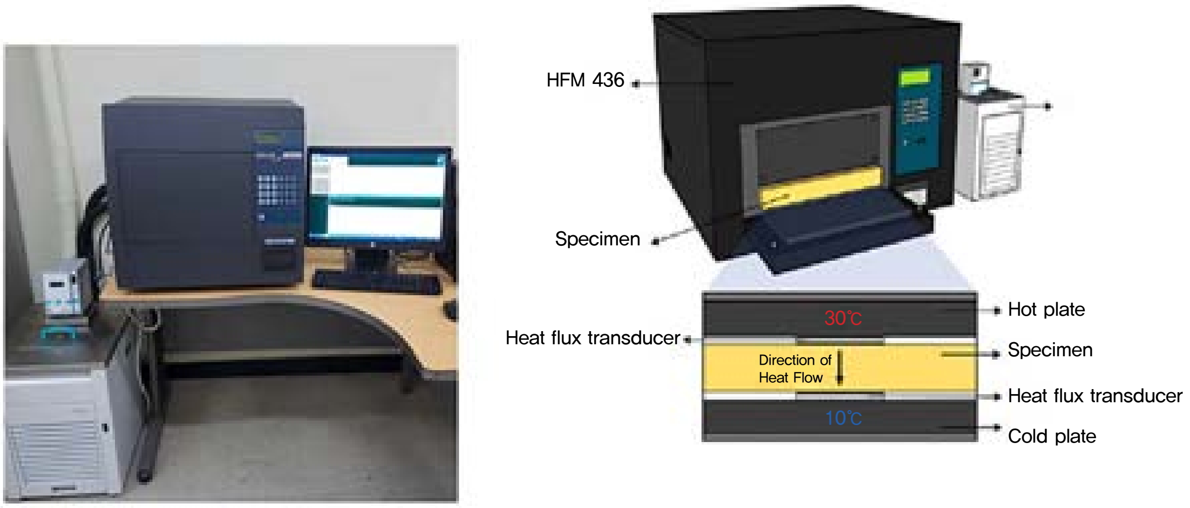


Figure 6.9 Heat flow meter apparatus (HFM 436, Netzsch社, Germany) (C518)

According to the aforementioned test, the thermal conductivity, thermal resistance, or a combination of both for the insulation system is calculated using Fourier's law of heat conduction. When measuring the thermal conductivity of a single test specimen, the thermal conductivity and thermal resistance of the target specimen are as follows:

$$C = S \cdot E/\Delta T \qquad (6.7)$$

$$\lambda = S \cdot E \cdot (L/\Delta T) \qquad (6.8)$$

Here, C represents the thermal conductivity per unit thickness, S is the correction factor, E is the heat flux transducer output, ΔT is the temperature difference across the specimen, and L denotes the distance between the cooling and heating plates. When measuring the thermal conductivity with two specimens, the thermal conductivity of each specimen can be added to calculate the overall thermal conductivity of all specimens. Additionally, the average thermal conductivity of specimens can be calculated using the average of the thermal conductivity values for each specimen. The sum of thermal conductivities and the average thermal conductivity of specimens are calculated using the following equations:

$$C = S \cdot E/(\Delta T_a + \Delta T_b) \qquad (6.9)$$

$$\lambda_{ave} = (S \cdot E/2) \cdot (L_a + L_b)/(\Delta T_a + \Delta T_b) \qquad (6.10)$$

Here, L_a is the thickness of insulation material a, L_b is the thickness of insulation material b, ΔT_a is the temperature difference across insulation material a, and ΔT_b is the temperature difference across insulation material b.

6.4 ASTM C177 (Guarded Hot Plate Method)[34]

The guarded hot plate method is a method used to measure the heat flux of insulation systems by measuring the steady state heat flow through materials with low thermal conductivity. This test can measure a variety of samples ranging from opaque solids to porous or transparent materials. Additionally, it is an absolute method that places guarded hot plates around the specimen to focus on the heat transfer of the specimen itself and minimize heat loss from the sides of the specimen. This method is utilized to accurately assess the heat transfer characteristics of insulation systems. Insulation systems are typically square or circular, ranging from 100mm to 300mm, with flat upper and lower surfaces. The thickness is usually 25mm.

This performance evaluation test can measure thermal conductivity at very low temperatures, using a cryogenic refrigerant such as liquid nitrogen with a boiling temperature of -196°C. It operates on the principle of injecting liquid nitrogen between the specimen and the hot plate to cool the specimen temperature. This is commonly employed in industrial applications to measure the insulation performance in environments as low as -163°C, typical for LNG temperature conditions. It is crucial to keep the temperature difference within 10 to 20°C during this test. The test, suitable for measuring one or two specimens, is conducted following the procedures defined by ASTM C177 (Standard Test Method for Steady State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded Hot Plate Apparatus) to evaluate the performance of such insulation systems.

For test preparation, when measuring two specimens, it is important to ensure they have similar thickness, area, and density. The test utilizes equipment including heating plates and guarded hot plates to measure the heat flow and thermal conductivity through each specimen. Figure 6.10 presents a schematic illustration of the guarded hot plate method and Figure 6.11 shows the domestic test apparatus.

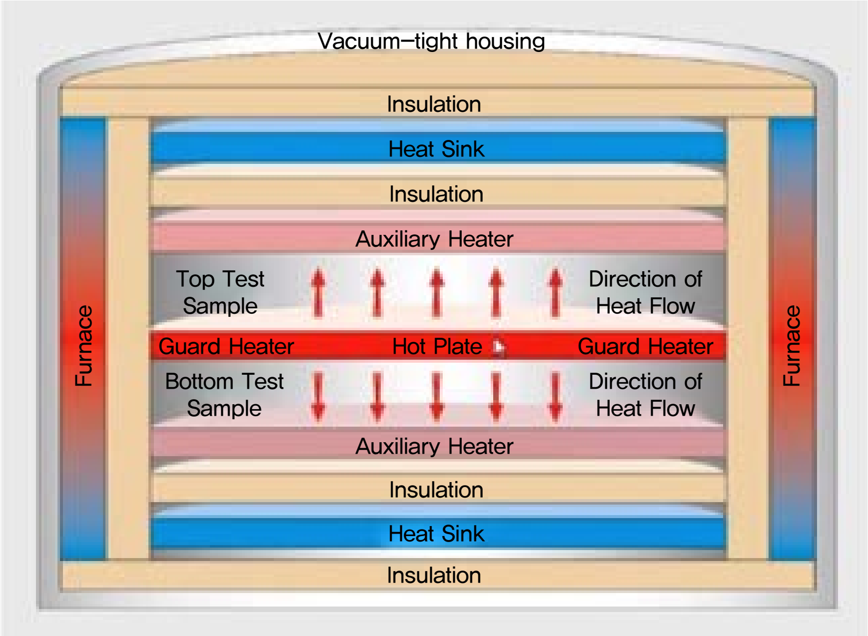


Figure 6.10 Schematic diagram of guarded hot plate method (C177)

Figure 6.11 Commercial guarded hot plate method apparatus (C177)

According to the above test, the heat flux applied to the wires of the hot plate is assumed to be the heat flow, and the power per unit time can be measured. Through Fourier's law, the thermal conductivity is then calculated.

$$Q = E \cdot I = -\lambda \cdot 2 \cdot A\frac{\Delta T}{d} \tag{6.11}$$

$$= \frac{E \cdot I}{A} \cdot \frac{1}{2\frac{\Delta T}{d}} \tag{6.12}$$

Here, Q represents the heat flux, E is the heating output, λ is the thermal conductivity of the material, A is the cross sectional area of the material, d is the thickness of the measured specimen, and ΔT denotes the temperature difference across the specimen.

7

Conclusion and Discussion

7 Conclusion and Discussion

This technical document began with an understanding of the heat transfer mechanisms in insulating materials applied in cryogenic environments, followed by an introduction of the characteristics of cryogenic storage systems represented by LNG and liquefied hydrogen, and methods for evaluating the insulation performance of materials. By organizing the thermal properties of insulating materials applied in LNG and liquefied hydrogen storage systems, the document is aimed at enhancing their future applicability.

Some examples of insulating materials applied in the LNG field are polyurethane foam, plywood, glass wool, and perlite.

❶ Polyurethane foam has a cellular structure that forms very small air layers within the cells. The struts and windows forming the cell structure consist of polyurethane, which has a very high thermal conductivity. However, these structures are very thin compared to the air layers, creating a complex path that hinders conductive heat transfer. The small air layers mitigate temperature differences occurring in each layer, disrupting convection heat transfer.

❷ Plywood is composed of cellulose due to the characteristics of wood. Cellulose forms the walls of xylem, which consists of elongated cells. While the wood is filled with water in these xylem vessels, after harvesting, they transform into air layers. This characteristic complicates the conduction heat transfer path, resulting in relatively good insulation performance.

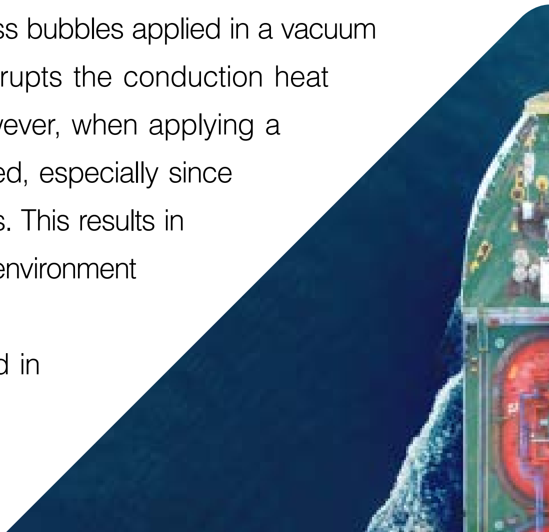
❸ Glass wool has very thin glass fibers clustered similar to cotton, increasing the thermal resistance and disrupting conduction heat transfer paths. The complex entanglement of thin glass fibers hinders convection heat transfer by impeding the movement of air trapped in the glass fiber layer.

❹ Perlite has thin ceramic walls with air layers generated within the rock layers. This structure increases the thermal resistance and disrupts conduction heat transfer by enhancing the contact resistance between ceramic particles. Perlite causes the internal air layers to split into smaller ones, hindering convection heat transfer.

For liquefied hydrogen insulation, materials such as perlite, glass bubbles, SOFI, and MLI are used.

❶ In the case of powder form insulation materials such as perlite and glass bubbles applied in a vacuum environment, the increase in the conduction heat transfer path disrupts the conduction heat transfer, similar to the case of the LNG field mentioned above. However, when applying a vacuum environment, convection heat transfer is almost fully eliminated, especially since the conventional conductive heat transfer through air layers disappears. This results in a lower effective thermal conductivity in comparison to the insulation environment of existing LNG storage systems.

❷ SOFI, made of low density polyurethane foam, has been widely used in



C-type LNG storage tanks. However, it is also applied in the environment of liquefied hydrogen. While it has a relatively high thermal conductivity among vacuum insulating materials, it exhibits superior insulation performance compared to a simple vacuum insulation layer. Due to the structural characteristics of polyurethane foam, it contains internal air layers even in a vacuum environment. Conduction heat transfer and convection heat transfer become difficult since SOFI inhibits convection heat transfer occurring in the simple vacuum layer and partially absorbs radiation heat transfer in the vacuum environment for conduction heat transfer.

③ Through a metallic film layer, MLI shields and reflects the dominant heat transfer mechanism in a vacuum environment, that is, radiation heat transfer. This action redirects thermal energy towards the outer direction of the insulation system for liquefied hydrogen cargo holds. As such, MLI demonstrates excellent performance in preventing radiation heat transfer.

Tanks storing cryogenic liquefied gases experience the transfer of thermal energy from the high temperature external environment to the low temperature internal state through three heat transfer mechanisms: conduction, convection, and radiation. The internal cryogenic fuel vaporizes due to the transferred heat, leading to an increase in internal tank pressure. Traditional LNG storage systems employ vacuum insulation to block conduction and convection heat transfer. However, the development of liquefied hydrogen storage systems is more focused on insulation that blocks radiation heat transfer.

The principles of devices measuring cryogenic insulation performance include the heat flow meter method, guarded hot plate method, and BOG measurement method. The use of standardized specimens and equipment based on these principles is recommended for quantitative measurement of heat transfer. Generally, as the temperature decreases, the thermal conductivity of materials decreases. Therefore, to improve the performance of insulation materials or develop new materials, it is considered economically viable to first confirm performance enhancement at room temperature or -30°C using the heat flow meter method and then consider the guarded hot plate method to measure cryogenic properties.

Following the development of the world's first dry LNG cargo containment system, insulation materials for efficient LNG storage have undergone significant developments through various methods over the past 60 years. As the market competition intensifies for the most efficient storage technology for LNG and carbon neutral hydrogen, which are expected to see continuous demand growth, the demand for the development of cryogenic insulation technology is expected to increase.

① In terms of trends in products related to hydrogen liquefaction storage systems, the global market size for liquefied hydrogen storage is expected to reach $75.93 billion by 2025, marking an average annual growth rate of 8.4% from $46.80 billion in 2019. Additionally, the domestic market size is forecasted to reach 3.501 trillion won by 2025, growing at an average annual rate of 8.8% from 2.110 trillion won in 2019.

The field of hydrogen liquefaction storage systems is expected to continue growing steadily by more than 8% both domestically and internationally.[35]

❷ In South Korea, technological development is underway to supply liquefied hydrogen produced at hydrogen liquefaction plants to terrestrial filling stations starting from 2023. Research and development are being conducted on liquefied hydrogen cargo holds, which involve the production of pressure vessels made of stainless steel and metal containers for vacuum and insulation. The Korea Gas Safety Corporation is establishing safety standards for liquefied hydrogen cargo holds and focusing on the commercialization of liquefied hydrogen.[36]

❸ Liquefied hydrogen storage technology is expected to play a significant role as an environmentally friendly energy solution in the ship industry. The shipping industry handles almost 90% of global trade and currently relies mostly on fossil fuels as ship fuels, making energy efficiency and reduction of carbon emissions critical challenges. The International Maritime Organization (IMO) has set a target to achieve net zero greenhouse gas emissions from the shipping industry by 2050. To achieve this goal, the development of technologies related to zero carbon fuels (such as hydrogen and ammonia) for propulsion and transportation vessels is essential.

For cryogenic (-253°C) and vacuum environments, constraints such as adhesion and welding should be minimized for most cryogenic insulation materials to consider thermal contraction due to exposure to low temperature environments. In the case of SOFI, glass fiber mesh is added to prevent cracks, and except for SOFI, the remaining insulation materials are applied in a nonadhesive form in vacuum environments. For MLI, which requires adhesion, Velcro is used to prevent thermal contraction stress. These cryogenic vacuum insulation materials are dominated by conduction and convection heat transfer through gas in normal atmospheric pressure environments. However, in high vacuum environments, as the gas density decreases, most heat energy is transferred through radiation since it is difficult to do so through conduction and convection. As such, MLI, which has excellent performance in shielding radiation heat transfer, has the best insulation performance. The space shuttles of the National Aeronautics and Space Administration (NASA), which primarily utilize liquefied hydrogen, use the SOFI MLI system for their liquefied hydrogen fuel tanks. While SOFI has relatively poor insulation performance in vacuum environments, spacecraft do not take the form of storage containers with double walls, unlike terrestrial storage tanks, due to weight issues. Therefore, SOFI is applied during the initial takeoff preparation under atmospheric pressure to secure short term insulation performance. Once exposed to the space environments, the high vacuum environment allows MLI to effectively shield most of the radiant heat energy from the sun, ensuring excellent insulation performance.

However, MLI is not applied to terrestrial liquefied hydrogen storage tanks. Terrestrial liquefied hydrogen storage tanks mostly store large amounts of liquefied hydrogen, resulting in a very large volume of insulation space. The maximum vacuum achievable in such spaces is different from the high vacuum space environment, making it difficult to compose and maintain the insulation performance of MLI.

Therefore, powder type insulation systems, rather than MLI, are applied. Previously, perlite was used for such powder type insulation, but the irregularity of perlite particles and the relatively thick walls composing perlite facilitated conduction heat transfer. This was resolved by using spherical glass bubbles, which ensure uniformity and have much thinner walls compared to perlite.

The insulation materials selected for liquefied hydrogen storage tanks can be classified based on the volume of the storage tank. In the case of smaller volumes, the volume of the available space to create a vacuum environment is relatively small, making it easier to create and maintain a high vacuum environment. However, the capacity for storing liquefied hydrogen is small, and thus even a small amount of heat energy transfer can significantly increase the BOR. Therefore, applying MLI can ensure the efficiency of the insulation material in a high vacuum environment and contribute to reducing the BOR. Conversely, for larger capacity liquefied hydrogen storage tanks, creating and maintaining a high vacuum environment in the insulation space is relatively difficult due to the large volume. In fact, applying MLI, which has excellent insulation performance in a high vacuum environment, can actually decrease insulation performance. Therefore, powder type insulation materials with excellent insulation performance in a medium vacuum environment are more efficient. The appropriate vacuum level should be determined based on the capacity of the liquefied hydrogen storage tank, and insulation materials with excellent insulation performance should be selected based on this vacuum level.

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