

HYDROGEN STORAGE

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Fourth article in a series of five works devoted to cryogenic technologies of hydrogen energy. The article discusses the main methods of hydrogen storage, their advantages and disadvantages, as well as the difficulties associated with it. Advanced and promising storage methods and devices, aimed at reducing the hydrogen losses during storage and transportation, are shown.

Keywords: hydrogen storage, liquid hydrogen tanks, chemically bonded hydrogen, low-temperature thermal insulation.

Hydrogen storage is a rather complicated and therefore expensive process due to the very low density of hydrogen (in all phase states), which can lead to hydrogen leaks in case of equipment faulty sealing. Strict requirements are imposed on hydrogen storage: storage systems should withstand either cryogenic temperatures or high pressures, or contain active materials that interact with water or air. Therefore, when storing hydrogen, it is necessary to ensure high reliability and safety [1].

The main methods of hydrogen storage are:

physical: in a compressed or liquefied state;

physico-chemical: primarily in the bound state in metal-hydrides;

chemical: in chemical compounds of hydrogen, for example, in ammonia.

The simplest method of hydrogen storage is in a gaseous state (in a cylinder), but since the gaseous hydrogen density under normal conditions is only 90 g/m^3 , an 11.2 m^3 cylinder is required to store 1 kg of hydrogen. Hydrogen is stored in regular steel cylinders at a pressure of up to 200 atm; at this pressure, approximately 16 kg of hydrogen is stored in a 1 m^3 tank, i.e. to store 1 kg of hydrogen at a pressure of 200 atm, a tank with a volume of approximately 62 l is required. In a tank of this volume (but at normal pressure), 50 kg of gasoline can be stored. For comparison, the lower calorific value of hydrogen is 120 MJ/kg, which is more than 4 times higher than that of gasoline (approximately 25 MJ/kg), i.e., 1 kg of hydrogen is equivalent to nearly 4.5 kg of gasoline.

Thus, the energy capacity of hydrogen compressed to a pressure of 20 MPa is 17.3 times less than the energy capacity of liquid hydrocarbon fuel (when stored in a tank of the same volume).

The density of liquid hydrogen is $\sim 70 \text{ kg/m}^3$, which is 1.67 times higher than the density of gaseous hydrogen (42 kg/m^3) at a pressure of 70 MPa. Therefore, the volumetric energy density of liquid hydrogen at normal pressure is 8.5 MJ/l, which is 2.45 times less than the volumetric energy density of liquid methane (20.8 MJ/l).

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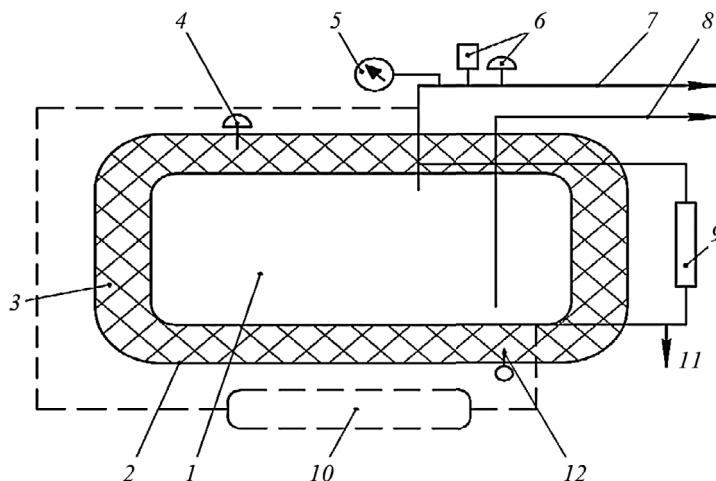


Fig. 1. Diagram of a typical tank for liquid hydrogen: (1) inner vessel (tank) for liquid hydrogen; (2) outer vessel (casing); (3) thermal insulation; (4) casing safety diaphragm; (5) pressure gauge; (6) safety devices (valve and diaphragm) of the inner vessel; (7) pipe for gas discharge; (8) drain and fill pipe; (9) level indicator; (10) evaporator (or receiver with compressed gaseous hydrogen or helium); (11) branch pipe for sampling liquid hydrogen; (12) vacuum control in the insulating space.

The boiling point of hydrogen is 20 K; therefore, the process of hydrogen liquefaction is quite energy-intensive: 25–45% of the energy of hydrogen being liquefied is spent on the liquefaction process.

For the storage and transportation of liquid hydrogen, special tanks are used. These tanks are similar in design to tanks for liquid oxygen and nitrogen, but differ in material, enhanced thermal insulation and leak-tightness, as well as the presence of special equipment stipulated by safety regulations.

Tanks for liquid hydrogen usually consist of two or more metal vessels arranged concentrically with respect to each other (Fig. 1) [1].

The central (inner) vessel is intended for liquid hydrogen. A vacuum is maintained between the inner and outer vessels (to reduce the heat flow to the inner vessel) or vacuum-powder or multilayer thermal insulation is arranged. In the insulating space, screens in the form of coils or sheets cooled with liquid nitrogen (or hydrogen vapour evaporating from the inner vessel due to heat losses) are sometimes installed. A combination of several types of insulation is possible. Tanks are designed taking into account the exclusion of air ingress into the hydrogen environment during the tank operation.

The inner vessel is usually made of corrosion-resistant steel, aluminium, titanium or copper, the outer vessel (casing) is usually made of carbon steel.

The most important property of a tank for liquid hydrogen is the amount of losses from evaporation per time unit (usually per day), expressed as a percentage of the internal tank volume.

Tanks for storage and transportation of liquid hydrogen are equipped with safety devices: valves and burst diaphragms (designed for 1.1 and 1.2 operating pressure, respectively) to release part of the gaseous hydrogen in the event of a sudden liquid evaporation. Safety devices are installed on the pipeline for discharging hydrogen vapour from the internal tank (on the gas discharge line).

Liquid hydrogen storage can be short-term and long-term. The constant product evaporation due to heat gains through the thermal insulation leads not only to liquid losses, but also to an increase in the concentration of impurities in the liquid. With each filling of the tank, the oxygen or air crystals accumulation in the tank from the incoming liquid hydrogen is possible. Spontaneous cracking of shock-sensitive oxygen crystals releases energy sufficient to start a combustion reaction. Therefore, to ensure normal trouble-free operation of tanks (transportation and stationary), they are periodically (at intervals of 1–2 years) emptied and warmed up in order

to sublimate oxygen crystals and other impurities. The content of impurities in the remaining gas is a criterion for assessing the storage life and the need to defrost the tanks.

The specific heat of vaporization of a liquid is the lower, the lower its boiling point. Therefore, the supply of a small amount of heat causes the evaporation of a significant amount of liquid hydrogen (one of the lowest boiling liquids). Due to the low heat of vaporization, the volume of liquid hydrogen decreases 7.7 times faster than the volume of liquid oxygen, with an equal amount of heat supplied.

To reduce the liquid hydrogen losses during long-term storage of large volumes of hydrogen, either reverse condensation of evaporated hydrogen is used (using cryogenic refrigerators), or the liquid hydrogen temperature is maintained below the equilibrium boiling point (due to preliminary liquid hydrogen supercooling), or the vessel with liquid hydrogen is preliminary evacuated.

Condensation of hydrogen vapour is carried out by a colder cryoagent, usually gaseous helium, circulating in the coil of a helium refrigerator located in the vapour space of the tank above the liquid surface. Liquefaction plants with the use of evaporating hydrogen as a working fluid and the return of this hydrogen in a supercooled state to a cryogenic tank are also used. Cryostatting can also be carried out by placing a coil, in which a cooling agent circulates, in the liquid [2].

Liquid hydrogen (like any cryogenic liquid) can separate into temperature levels during long-term storage in a tank that has no vapour discharge from it. At that, the temperature of the liquid on the surface rises faster than the temperature of the rest liquid mass. The warmest liquid (with the lowest density) goes up, while the colder liquid goes down. The pressure in the tank depends on the liquid temperature at the interface between the gaseous and liquid phases and, in case of separation, is determined by the temperature of the warmer surface layer. Thus, the liquid hydrogen layering is accompanied by a dangerous increase in pressure in the tank, and the permissible duration of liquid hydrogen storage without the possibility of discharging gaseous hydrogen is reduced. To eliminate such layering, mixing of liquid hydrogen in a cryogenic tank is used.

Transportation of liquid hydrogen over considerable distances is carried out by rail or road transport in special tanks on car trailers and semi-trailers with a volume of 25–55 m³ of liquid hydrogen at a pressure slightly higher than atmospheric one (to prevent air from entering the hydrogen environment). The design of hydrogen transportation tanks is similar to the means of transporting liquid oxygen and nitrogen.

The following types of low-temperature thermal insulation of equipment for liquid hydrogen are used [3]:

- high vacuum (effective thermal conductivity coefficient of 0.9–3.0 mW/(m·K));
- vacuum-powder (effective thermal conductivity coefficient of 0.3–0.8 mW/(m·K));
- multilayer: vacuum-multilayer, screen-vacuum (effective thermal conductivity coefficient of 0.02–0.10 mW/(m·K)).

Based on the combination of these types, combined insulation options have been developed: vacuum-powder insulation with a nitrogen screen, multilayer-powder insulation, and other.

The use of high vacuum is the possibility of providing effective thermal insulation, excluding two essential heat transfer methods: convection and heat transfer due to thermal conductivity. Heat transfer through a space with a high vacuum is determined mainly by radiation, heat transfer by residual gases and thermal conductivity of the structural support elements. High vacuum insulation is used in pipelines and laboratory vessels for storing liquid hydrogen [4].

To reduce heat transfer by radiation, screening is most effective; however, the installation of rigid metal screens in the insulating space is associated with structural difficulties, and the supporting elements between the screens are thermal bridges that reduce the screening efficiency. In this regard, it is advisable to use “floating”

pendent screens that are in poor contact with adjacent walls. In hydrogen and helium liquefaction plants and in tanks for their storage, a significant reduction in heat flow to these liquids is ensured by cooling the screen with liquid nitrogen, which is equivalent to using 150–200 uncooled screens. The screen surface material is selected taking into account high reflectivity [5].

The main advantage of high vacuum thermal insulation is a significant reduction in the heat transfer coefficient. The amount of heat transferred through the residual gas decreases with increasing the vacuum depth and at a pressure of 10^{-5} mm Hg becomes very low. According to calculations, the conductivity of the residual gas at pressures in an evacuated space of the order of $3 \cdot 10^{-6}$ mm Hg is less than 0.05% of the total heat flow for surfaces with an emissivity of 0.74 or less than 1% for the aluminium foil surface. In addition, high vacuum insulation does not require the use of additional materials.

The total heat gain in the case of using high vacuum thermal insulation is determined by the formula

$$Q_h = Q_r + Q_g + Q_{hm},$$

where Q_r is the heat transfer by radiation (the main part of heat transfer); Q_g is the heat transfer by the residual gas; Q_{hm} is the heat transfer over the “hard skeleton” of the heat-insulating material [6].

The disadvantages of high vacuum insulation include: the need for a sealed casing with sufficiently thick walls or reinforcing elements to maintain mechanical stability under external pressure impact; difficulties in creating and maintaining a high vacuum for a long time (therefore, the use of high vacuum pumps and sealing of the insulating space are required); the need for careful polishing of the walls (limiting the evacuated space), as well as the use of various metals with a low blackness degree.

Vacuum-powder thermal insulation is a powdery or fibrous material with a low density (perlite, aerogel, glass wool) located in a vacuum space. With this type of insulation, the heat transfer process includes three simultaneously operating heat transfer mechanisms: gas thermal conductivity, solid particles thermal conductivity, radiation. To increase the effectiveness of thermal insulation, it is necessary to minimize the action of all three mechanisms. It was noted that heat transfer through coarse perlite powders is carried out by 70% by means of thermal conductivity and only by 30% by means of radiation.

Powders are good adsorbents; therefore, gases desorbed from surfaces and penetrating through micro-holes are absorbed, and the required vacuum is maintained for a long time without re-pumping. However, many powders are hygroscopic and require special treatment to remove moisture from them. With vacuum-powder insulation, the heat capacity of the equipment increases significantly, as a result of which the stationary modes (especially when filling large vessels with liquefied gases) are established very slowly: after a few days or weeks.

Advantages of vacuum-powder insulation include: absence of high vacuum, which allows using regular mechanical pumps; no polishing of boundary surfaces is required; the possibility of using relatively inexpensive powdery and layered heat-insulating materials; ease of installing the thermal insulation.

Disadvantages of vacuum-powder insulation include: the difficulty of evacuation due to the high pumping resistance created by the powder layer, as well as due to gas releases from the powder; increase in the amount of heat (which should be removed during the cooling process) due to the high heat capacity of the insulating material.

The effective thermal conductivity coefficient of vacuum-powder insulation consists of the following parts:

$$\lambda_{ef} = \lambda_t + \lambda_g + \lambda_r,$$

where λ_t is the thermal conductivity of powders and fibres; λ_g is the thermal conductivity of the residual gas; λ_r is the conditional thermal conductivity during heat transfer by radiation.

The thermal conductivity of evacuated powders and fibres λ_t is determined from reference materials [7].

Due to the need for long-term storage and transportation of large amounts of liquid hydrogen and the reduction of heat transfer to liquid hydrogen, a multilayer insulation, consisting of alternating layers of insulating and screening materials, has been developed. Reflective screens of multilayer insulation are designed to reduce radiant heat transfer between surfaces with different temperatures.

The advantages of multilayer insulation over other types of insulation include: the possibility of a significant reduction in heat transfer (achievable thermal conductivity coefficients are approximately an order of magnitude lower than for the best samples of vacuum-powder insulation); significantly less weight of insulation per unit volume than for other types of insulation (except for high vacuum); absence of shrinkage, which often occurs when using various types of vacuum-powder insulation; lower consumption of materials in the manufacture of the insulation layer with the required efficiency; shorter duration of insulation cooling time compared to vacuum-powder insulation.

Disadvantages of multilayer insulation include: the need to create and maintain a high vacuum (up to 10^{-5} mm Hg); complexity of installation on the equipment due to the need to place supports, hangers and pipelines in the insulating space; high specific cost per unit volume.

However, the cost of an insulating structure with multilayer insulation is less than the cost of a vacuum-powder insulation equivalent in terms of efficiency. Nevertheless, taking into account the noted disadvantages, it is believed that multilayer insulation is not cost-effective in all cases.

None of the considered types of low-temperature thermal insulation can be optimal for all possible designs of tanks for liquid hydrogen. The choice of the thermal insulation type significantly affects the design of cryogenic equipment, is determined by the requirements for the quality of insulation and such factors as overall dimensions, strength and weight characteristics of insulated objects, cost, operation conditions, etc. For example, high-quality multilayer insulation is not always economically justified due to the complexity of manufacturing and installation, as well as the high cost of materials.

All materials for storing hydrogen in a bound state can be conventionally divided into two groups: the *first group* includes substances containing hydrogen, which is released under certain conditions, for example, with an increase in temperature, a catalyst action (examples are the catalytic reactions of ammonia decomposition at 800–900 °C and hydrogenation-dehydrogenation reactions of unsaturated hydrocarbons); the *second group* includes energy-accumulating substances that absorb and release hydrogen when the temperature changes due to the processes of sorption or binding of hydrogen molecules when they penetrate into the metal thickness through micro-pores (due to the small size of hydrogen molecules) with the generation of so-called metal-hydrides [8].

The beginning of the study of hydrides is the work of William Graham, who discovered in 1866 the effect of the absorption of a significant amount of hydrogen by palladium (Pd) with the generation of the $\text{PdH}_{0.6}$ compound. Since then, the Pd-H system has been an object of study for experts in metallurgy, physics and chemistry of solid bodies [9].

The use of hydride-generating metals as a hydrogen storage medium is quite simple: when cooled, the metal absorbs hydrogen, and when heated, hydrogen is released and supplied to the consumer. Palladium is not currently considered for hydrogen storage due to its high cost; in addition, after 20–30 operation cycles, palladium is destroyed and becomes unsuitable for the generation of a metal-hydride compound. However, palladium and its compounds are of interest in other areas of hydrogen power engineering, for example, as catalysts for various chemical reactions, as a membrane material for fine hydrogen purification (to ensure stable operation of fuel cells). Russia has 50% of the world's palladium production, which is used to implement a number of hydrogen technologies.

At present, in addition to palladium, many materials are known that absorb hydrogen, including 48 metals. For example, magnesium absorbs 0.076 mass fractions of hydrogen. However, due to the high temperature of hydrogen desorption, the use of magnesium in devices is not rational [9].

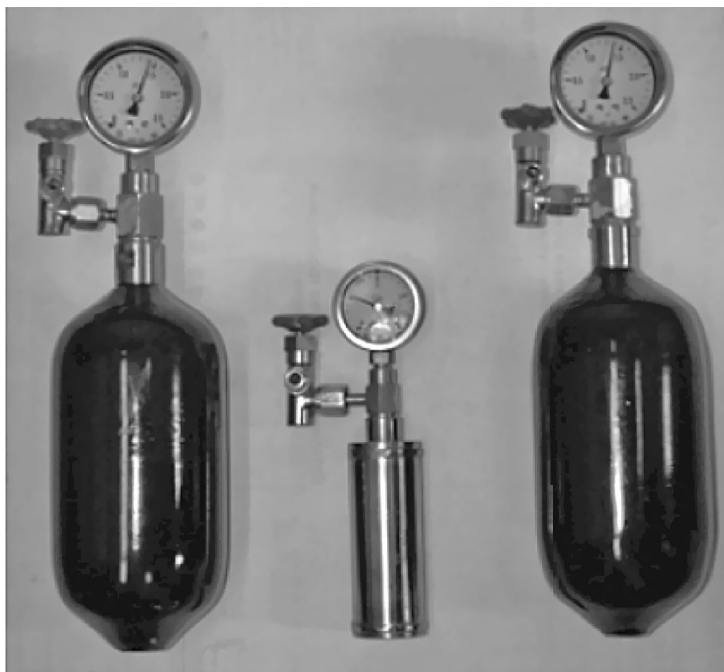


Fig. 2. Metal-hydride hydrogen accumulators developed at the Institute of Problems of Chemical Physics of Russian Academy of Sciences (IPCP RAS).

The metal-hydride method of hydrogen storage provides the maximum compactness of the equipment (compared to the use of cryogenic tanks). However, the mass of the hydrogen storage system based on metal-hydrides is much larger, which complicates the use of metal-hydrides in road vehicles, as potentially the main consumer of hydrogen storage systems for the operation of a propulsion device.

Another important advantage of the metal-hydride method of hydrogen storage is high safety: at room temperature, the pressure of gaseous hydrogen in metal-hydrides is several atmospheres.

Commercial hydrogen accumulators based on metal-hydrides in the form of tanks are primarily intended for laboratory use (Fig. 2).

The metal-hydride tank is usually a tubular body, inside of which a heat exchanger is located to intensify heat transfer in powdered metal-hydride placed outside of tubes. The need for a heat exchanger is associated with the low thermal conductivity of metal-hydride materials powders and the limitation of the dynamics of hydrogen absorption/desorption processes due to heat transfer. To increase the rate of hydrogenation/dehydrogenation processes with a characteristic time of less than 10–15 minutes, the characteristic size of the cavity for filling the metal-hydride powder should be no more than 5–6 mm. Usually, there are fittings on the end flange of the tank for receiving and discharging gaseous hydrogen and for loading metal-hydride powder [10].

Among the large metal-hydride hydrogen storage systems built to date, the largest was built by Laborsysteme GmbH (division of HERA Hydrogen Storage Systems, Germany) for the U-212 submarine. The system is designed to store 15,000 m³ of hydrogen (100 tons of hydride-generating material was required) and provides power to the fuel cell propulsion device for 30 days of underwater navigation [8].

The most appropriate way of storing and delivering hydrogen is selected based on the specific task. A small amount of hydrogen (up to 100 g) is best stored in a bound state in metal-hydride devices, an average amount (up to 10 kg) — in a compressed state in cylinders; for large amounts of hydrogen, there are currently no alternatives to cryogenic storage of liquefied hydrogen.

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