PRESSURIZED HYDROGEN STORAGE

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Summary

Hydrogen has been stored as a pressurized gas in high-pressure gas vessels since the beginning of the 20th century. The main reason for pressurizing hydrogen is that when it is pressurized its apparent volume becomes smaller, making storage and transportation more convenient. Another important reason for storing pressurized hydrogen is that there is no need for systems to increase the gas pressure, such as a compressor or gas blasting system, when the hydrogen is used. This paper is concerned with pressurization and storage of hydrogen. It covers matters requiring special care from the viewpoint of safety when using pressurized hydrogen, technical developments affecting storage vessels, and actual examples of pressurized hydrogen storage.

1. Pressurized Hydrogen Storage

Generally speaking, the following four main components are needed to pressurize and store hydrogen.

(i) *Hydrogen generator:* Reformer for petroleum and natural gas, electrolyzer for water, etc.
(ii) *Hydrogen compressor:* A mechanical compressor is generally used, although a high-pressure water electrolyzer can compress hydrogen.

(iii) *Hydrogen refiner:* Oxygen and water impurities must always be removed; other impurities should also be removed.
(iv) *Pressure vessel:* Gas cylinder, storage tank, or similar vessel.

When hydrogen is compressed and stored, mechanical work is done and energy is stored. It is important to note that the energy storage efficiency differs depending on the variety of gas. When gases are compressed to the same pressure, the energy needed for compression varies according to the specific heat ratio γ and the isopiestic specific heat Cp and so on, of each gas. When hydrogen is handled as an ideal gas, the work W_{ad} needed for adiabatic compression of one mole of hydrogen is obtained as shown below.

- Hydrogen pressure before compression: P_1
- Volume before compression: V_1
- Temperature before compression: T_1
- Hydrogen pressure after compression: P_2
- Volume after compression: V_2
- Temperature after compression: T_2
- Isopiestic specific heat: Cp
- Isovolumic specific heat: Cv

The following formulas lead to the work W_{ad}:

$$P_1V_1\gamma = P_2V_2\cdot\gamma,$$

$$P_1V_1 = RT_1,$$

$$P_2V_2 = RT_2,$$

$$\gamma = C_p\cdot C_v^{-1}$$

$$(P_1V_1 - P_2V_2)(\gamma - 1)^{-1}$$

$$W_{ad} = \int_{p_2}^{p_1} PdV = (p_1v_1 - p_2v_2)(r-1)^{-1} = R(T_1 - T_2)\cdot(\gamma - 1)^{-1}$$

Here, R is the gas constant.

Because compressor efficiency actually exists, the work needed for hydrogen compression can be expressed as W_{ad}^{-1}.

Another important character of compressed hydrogen is that it can be stored as energy. For instance, when hydrogen under pressure is applied to a metal hydride, the hydrogen reacts exothermically with the metal hydride, and heat energy can be taken out, whereas compressed air can be converted only to mechanical energy.

Energy storage is explained here using hydrogen as an ideal gas; in reality, however, the compression of hydrogen is a somewhat more complicated phenomenon, and we must handle hydrogen as a real gas. For instance, if hydrogen is an ideal gas, and has been compressed to 30 MPa, and this compressed hydrogen is then released to atmospheric pressure, the volume of hydrogen will be 300 times the volume of compressed hydrogen. But in fact, the volume is only about 254 times. This discrepancy between the volume of real gas and the volume of ideal gas is generally explained using the concept of the compressibility factor Z. For an ideal gas, Boyle-Charles' law is expressed as $PV = nRT$, where P, V, n, T, and R represent the pressure, volume, molecule number of hydrogen, temperature, and gas constant respectively.

When hydrogen is handled as a real gas by introducing the concept of the compressibility factor Z, Boyle-Charles' equation is expressed as $PV = nZRT$.

As the temperature of the hydrogen becomes lower, and the pressure of the hydrogen increases, the influence of the compressibility factor will be greater.

The compressibility factor Z of hydrogen here is obtained from the following approximate equation.
$Z = 1 + p(A + BT^{-1} + CT^{-2} + DT^{-3} + ET^{-4})$

Here, p is pressure, T is temperature, $A = 4.93482 \times 10^{-5}$, $B = 2.04036$, $C = 8.15334 \times 10$,
$D = -65561 \times 10^{4}$, $E = 4.56516 \cdot \times 10^{6}$

Table 1 shows the compressibility factor Z of hydrogen, obtained using the approximate expression.

T (K)	P (MPa)	Z	T (K)	P (MPa)	Z
250	0.1013	1.0007	400	0.1013	1.0005
250	5	1.0324	400	5	1.0241
250	10	1.0649	400	10	1.0481
250	20	1.1298	400	20	1.0963
250	30	1.1946	400	30	1.1444
300	0.1013	1.0006	450	0.1013	1.0004
300	5	1.0295	450	5	1.0219
300	10	1.0589	450	10	1.0438
300	20	1.1178	450	20	1.0876
300	30	1.1768	450	30	1.1313
350	0.1013	1.0005	500	0.1013	1.0004
350	5	1.0266	500	5	1.0200
350	10	1.0532	500	10	1.0400
350	20	1.1064	500	20	1.0801
350	30	1.1596	500	30	1.1201

Table 1. The value of the compressibility factor Z of hydrogen calculated by the approximate expression

2. Safety Points

Until recently, separate guidelines for the safe handling of compressed hydrogen were stipulated by each nation. In the USA, DOT stipulated the standards for high-pressure gas vessels, etc., from the viewpoint of maintaining safety during the transportation of compressed hydrogen. Other guidelines in the US for the safe handling of hydrogen are issued by DOE, NFPA and CGA. In Japan the High-Pressure Gas Safety Law under the jurisdiction of the Ministry of International Trade and Industry provides similar standards and guidelines and is known worldwide.

Other similar standards and guidelines in Japan are the Ministry of Labor's Labor Safety and Sanitation Law and the Ministry of Home Affairs' Standards for the handling of dangerous substances. In Germany, TUV has provided guidelines on safety standards for compressed hydrogen vessels and accessories including valves. Hydrogen has recently been attracting attention as an energy source, and as the scope of its use has expanded, uniform international guidelines concerning methods of handling hydrogen safely have become necessary.

One example is the ICSC (International Chemical Safety Card) developed by IPCS (International Program for Chemical Safety), a joint project by WHO (World Health Organization), UNEP (United Nations Environment Program), and ILO (International Labor Organization), with the cooperation of the EU; ICSC has been collecting safety data on hydrogen, and has been translating them into various national languages. ISO (International Standardization Organization) has also drawn up international standards for hydrogen-related machines and equipment including those used for compressed hydrogen and liquid hydrogen. In 1998, the Hydrogen Research Institute and National Renewable Energy Laboratory published comprehensive guidelines, a collection of standards for hydrogen in the US and Canada, as the Sourcebook for Hydrogen Applications, published on a CD-ROM.

The physical properties and chemical characteristics of hydrogen will be described separately, so will not be mentioned in detail here. However, this article will mention matters requiring special attention in order to ensure safety when compressing hydrogen. The explosive combustion composition range of hydrogen and air is very wide; when air contains 4% to 75% hydrogen, explosive combustion of hydrogen occurs. Also, there is the danger that in explosive combustion composition, hydrogen can be ignited by the existence of a catalyst, or by a spark with very small energy, such as static electricity. The minimum ignition temperatures of hydrogen in combustion composition range from 763 K to 853 K; therefore, even the compression heat that is generated when hydrogen is compressed can cause ignition and explosion.

Therefore it is very dangerous to compress mixed gas consisting of hydrogen and a combustion-improving gas such as air, oxygen or chlorine without due care. In Japan, for instance, the act of compressing hydrogen in a composition likely to explode is prohibited by the High Pressure Gas Safety Law. On the other hand, the utilization of compressed hydrogen and oxygen gas in a detonation composition has been studied accompanying advances in technological development, because the explosive power of hydrogen in a detonation composition is equivalent to that of explosives such as TNT, and in addition the final product of the explosion combustion is clean, being only water.

When hydrogen in a combustible and explosive composition is compressed and stored for such technological development, the process must be well controlled to eliminate compression heat, static electricity, and catalytic substances, and at the same time the process should be done after substantiation and verification of sufficient safety.

The next matter in the storage of compressed hydrogen requiring special caution is the problem of hydrogen embrittlement of carbon steel. It is understood that hydrogen embrittlement of carbon steel occurs because carbon in the steel reacts with hydrogen that has penetrated into the steel under high pressure and high temperature conditions, and that when the carbon and hydrogen have formed methane gas, the volume of the methane gas expands, causing cracking of the steel. As a method of preventing hydrogen embrittlement, steel to which Cr, Mo, W, Ti, V, or Nb has been added is often used. These added elements are effective in preventing hydrogen embrittlement because they form carbides far more stable than steel, so that these elements fix the carbon in the steel, which would otherwise react with the hydrogen to form methane. The steel used for ordinary high-pressure gas cylinders can develop hydrogen embrittlement; therefore such cylinders must not be kept under high temperature conditions. When a high-pressure cylinder has developed hydrogen embrittlement, the cylinder cannot withstand the inner pressure, and explodes like a giant grenade, scattering pieces of the shattered cylinder; this is very dangerous.

Ordinarily the prevention mechanism of a cylinder is designed to protect against irregular increases in inner pressure when the cylinder has sufficient strength, but if the strength of the steel of the cylinder has fallen due to hydrogen embrittlement, the cylinder may break down at any time. G.A. Nelson shows the applicable pressure and temperature limitations for various steels, in consideration of hydrogen embrittlement.

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Biographical Sketches

Jo Suzuki was born 16 April 1950, in Japan; he received his education from the Department of Chemistry, Tokyo Scientific University; engages for metal hydrides system development work, Suzukishokan Co., Ltd. (1973–); has been appointed to the Commissioner of the Hydrogen Energy Systems Society of Japan (1987–); has been appointed Manager of the Research Association for the Development and Application of Metals-Hydrogen System, Japan (1989–99); has been appointed to member of the HTTR Technology Development Committee, Japan Atomic Energy Research Institute (1999–).

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