NEW CHINA NATIONAL STANDARD ON SAFETY OF HYDROGEN SYSTEMS: KEYS FOR UNDERSTANDING AND USE

ABSTRACT

Development of regulations, codes and standards on hydrogen safety is a primary ingredient in overcoming barriers to widespread use of hydrogen energy. Key points of the new China National Standard *Essential safety requirements for hydrogen systems*, metal hydrogen compatibility and risk control of flammability and explosion are discussed. Features of the new standard such as safety requirements for slush hydrogen systems and solid state hydrogen storage systems, and introductions for hydrogen production by renewable energy are analyzed in this paper.

1.0 INTRODUCTION

Hydrogen is considered as one of the most promising energy carriers in the 21st century for its characteristics of unlimited supply, inherent pollution free nature and high energy efficiency [1]. However, implementation of hydrogen economy demands a transition due to the challenges of technology and infrastructure development and cost reduction [2-3]. Demonstration projects continue to validate and disseminate hydrogen technology in P.R. China such as in 2008 Beijing Olympic Game and 2010 Shanghai Expo. Nevertheless, as in many other countries, extension and accessibility still need continual improvement. Safety issue is one of the stumbling blocks on the way towards commercialization of the new technology.

Development of regulations, codes and standards on hydrogen safety is a primary ingredient in overcoming commercialization barriers and realizing hydrogen economy. Standardization organizations on hydrogen energy such as ISO/TC 197 constantly strive to carry out the standardization of hydrogen safety, which will contribute to overcome the challenges [4]. There have been some standards on hydrogen safety used in hydrogen production, storage and application. Guidelines for the use of gaseous and liquid hydrogen are provided by NASA–NSS1740.16: 1997 [5], AIAA G-095: 2004 [6] and the widely used Technical Report ISO/TR 15916: 2004 [7]. Furthermore, guidelines for the use of slush hydrogen are also included in NASA–NSS1740.16: 1997 and AIAA G-095: 2004.

As the first and most essential China National Standard on safety of hydrogen systems, *Essential safety requirements for hydrogen systems* [8] has its own characteristics. Hence, key points of the new standard, metal hydrogen compatibility and risk control of flammability and explosion are discussed. Features of the new standard such as basic safety requirements and guidelines for the design and use of slush hydrogen systems and solid state hydrogen storage systems, and introductions for hydrogen production by renewable energy are also analyzed in this paper.

2.0 KEY POINTS OF THE STANDARD

It is peculiar properties of hydrogen that make it valuable as a fuel also can be those that make it dangerous [2]. The primary hazards related to hydrogen systems can be categorized in:

- Hydrogen embrittlement (HE);
- Leakage and permeation;
- Flammability and explosion;
- Overpressure;
- Low temperature;
- Solid state hydrogen storage hazards;
- Physiological hazards.

Control of the above hazards is the key ingredient for insuring the safety of hydrogen systems and thus becomes the main content of the standard. Given risk control difficulty and catastrophic consequence, key points of the standard are focused on metal hydrogen compatibility and risk control of flammability and explosion.

2.1 Metal Hydrogen Compatibility

Metal hydrogen compatibility is a basic requirement for those materials in contact with hydrogen. High-purity hydrogen under high-pressure at or below ambient temperature is considered to have seriously adverse impact on mechanical properties of most metals [9]. The harmful effects of high-pressure hydrogen on metals are usually reflected in remarkable decrease of percentage reduction of area after fracture. Invasion of hydrogen atoms promotes localized plastic process, accelerates crack propagation rate and eventually leads to loss of structural strength of metals [10-11]. Due to HE, lots of metallic materials commonly used in pressure vessels and pipes can not be used in hydrogen systems directly.

HE can be categorized in environmental and internal HE which always happen at the same time and have interactions. Environmental HE is generally observed in metals and alloys used in the gaseous hydrogen environment, which may lead to increase in surface cracks and loss in ductility. Internal HE is caused by metals and alloys absorbed hydrogen. Small amounts of hydrogen may cause premature failures which always occur with little and even no warning. Consequently, material deterioration caused by hydrogen greatly increases the risk of sudden failure of hydrogen systems.

Although the mechanism of HE is still impenetrable, extensive study has been made by researchers from the United States, Japan, Canada, etc. Work on modeling, simulation, prediction of hydrogen-induced crack initiation and growth, and HE test has been done so much [12-15]. HE susceptibility varies with different metallic materials [16]. Furthermore, HE of stainless steels increases with temperature decrease, reaches a maximum between 200 and 300 K, and then decreases with further temperature decrease [17]. However, HE will not occur when nickel equivalent is above 27%, regardless of temperature change [17]. Based on the existing study work, the standard provides essential requirements for metallic materials and engineering control methods of HE.

Selecting metallic materials resistant to HE is the best way to mitigate the risk. Essential requirement of metallic material selection is that in all applications where metals come in contact with hydrogen, metal hydrogen compatibility shall be demonstrated.

Guidelines for risk control of HE include:

- Use specified test methods to select metallic materials;
- Restrict hardness and strength of metals;
- Consider HE susceptibility of metallic materials affected by temperature change;
- Minimize residual stress;
- Avoid or minimize cold plastic deformation from fabrication;

Etc.

Useful material data are also offered in the standard as an informative annex, such as metallic materials commonly used in hydrogen environment. In the standard, the following metals are recommended for use in contact with hydrogen: S31603 (UNS S31603), S31608 (UNS S31608), 6061 (UNS A6061), etc. S31603 and S31608 have been successfully used in high pressure hydrogen storage vessels with maximum pressure 77 MPa in P.R. China.

2.2 Risk Control of Flammability and Explosion

Hydrogen-oxidizer mixtures can combust either as fire, deflagration or detonation. The ample range of flammability (4~75% by volume) and detonation (18.3~59% by volume) and tiny ignition energy (0.017mJ) of hydrogen tend to result in combustion and explosion in hydrogen systems.

Hydrogen can pass through small leak paths and even permeate through materials. The accidentally released hydrogen can result in vapor cloud explosion, if confined and ignited. Continuously released hydrogen can form a jet fire whose thermal radiation may impinge on other devices and lead to physiological hazards, if ignited. Explosion of hydrogen systems may occur due to the sharp rise of interior temperature or pressure and degradation of material properties caused by fire, e.g. explosion of a compressed hydrogen storage system in a Sports Utility Vehicle (SUV) was extremely terrible [18]. Blast pressure was still greater than 12 kPa at a distance of 15 m, the maximum fireball diameter was 24 m, and fragment projectiles from SUV were found at distance up to 107 m from the original SUV location [18]. Detonation can move rapidly throughout the combustible region, and its shock wave can even impact the un-combusted region. In addition, if liquid and slush hydrogen transfer lines are not sufficiently thermally insulated, oxygen-enriched condensate outside the lines can enhance the flammability of materials.

As many other cases, to be familiar with and master combustion properties of hydrogen is prerequisite and foundation to mitigate and control the risks. In the standard, users can find complete tables of combustion properties of hydrogen, ignition and combustion property comparison of hydrogen with other common fuels, etc. Although it is still difficult to establish a precise prediction method of hydrogen flammability and explosion risks [19], engineering control methods have been proved to be effective and thus are presented in the standard.

Preventing formation of unwanted hydrogen/oxidizer mixture is one of the key ingredients of risk control of flammability and explosion. The goal can be achieved by keeping hydrogen and oxidizer separate, e.g. purging hydrogen systems before filling, ventilating confined space, disposing vent hydrogen, maintaining positive pressure and periodically warming up liquid and slush hydrogen systems, etc.

Another key is to eliminate ignition sources. Designers, users and safety evaluators should pay attention to the ignition source around hydrogen systems all the time. All kinds of electrical, thermal and mechanical ignition sources should be eliminated, e.g. ensuring inherent safety of selected electrical equipment used in hydrogen environment, preventing spark induced by mechanical impact and friction, eliminating open flames, etc.

Other means are needed to detect hydrogen because of the limitations of human senses. Hydrogen or hydrogen flame detectors are recommended to use where hydrogen tends to leak or accumulate. Keeping safety distances of hydrogen systems and stations can also mitigate the risks. Furthermore, it is also important to ensure liquid and slush hydrogen transfer lines sufficiently thermally insulated and to eliminate combustible materials outside the lines.

Optimizing hydrogen storage vessel structure to improve its inherent safety is an innovative way to control flammability and explosion risks. A kind of multifunctional layered stationary high-pressure hydrogen storage vessel shown in Fig.1 was developed by the Institute of Process Equipment, Zhejiang University, P.R. China [20-22]. This developed pressure vessel type is flexible in design, convenient in fabrication, safe in use, wide in feasibility and easy in on-line safety monitoring [23]. Compared with traditional seamless hydrogen storage vessel, it has less leakage sources and completely does away with unexpected disastrous whole brittle fracture.

Besides, the problem of metal high-pressure hydrogen compatibility may be solved by using this pressure vessel type, since the inner shell can be manufactured with metallic materials resistant to HE. Three such vessels with maximum volume of 5 m^3, maximum design pressure of 77 MPa have already been used in a hydrogen refueling station in Beijing, P.R. China, and the design standard [24] has been promulgated.

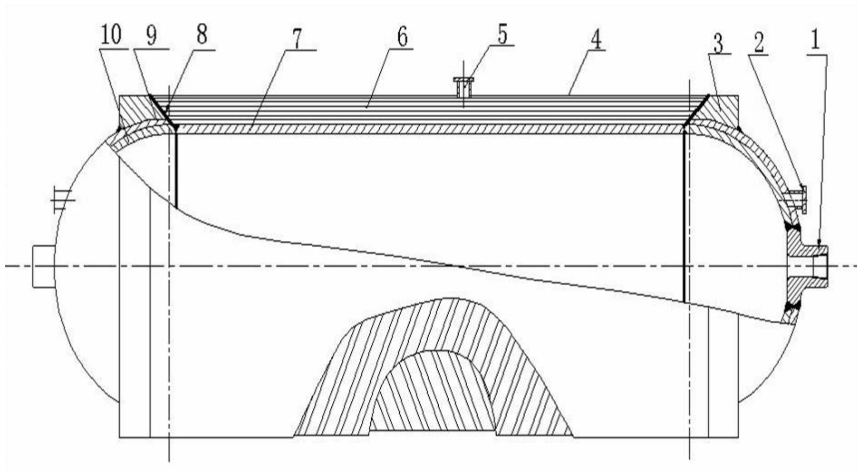

Figure 1. Construction of multifunctional layered stationary high-pressure hydrogen storage vessel. 1 – End nozzle; 2 – Head nozzle; 3 – Reinforcing ring; 4 – Protective shell; 5 – Cylinder nozzle; 6 – Flat steel ribbon wound cylindrical shell; 7 – Inner shell; 8 – Slant weld; 9 – Outer hemispherical head; 10 – Inner hemispherical head.

3.0 FEATURES OF THE STANDARD

Formulation of the new standard was started in 2008 and finished in 2010. Considering the technology and industry development, the standard covers new key safety issues of hydrogen systems and latest hydrogen technology. For example, considerations for the temperature rise when fast filling operations, safety requirements for large stationary high-pressure hydrogen storage vessels, type selection requirements for compressor, etc. are included in the standard. The main features of the standard are as follows.

3.1 Slush Hydrogen Systems

Slush hydrogen is of great interest for space program because of its high density. Using slush hydrogen can reduce physical size and weight of the storage systems, and can also eliminate or reduce some of the problems related to liquid hydrogen storage such as low density, short holding time due to its low latent heat, hazards associated with high vent rates, etc [25]. Considering the technology development tendency, the standard provides essential safety requirements and guidelines for slush hydrogen systems.

Safety-related thermophysical properties of slush hydrogen are provided in the standard, such as vapor pressure, volume change, thermal stratification, aging, etc. Some hazards that exist with gaseous hydrogen and liquid hydrogen also exist with slush hydrogen. However, there are also unique hazards involved in slush hydrogen systems. Air leakage into slush hydrogen systems can easily happen since the vapor pressure of slush hydrogen is lower than atmospheric pressure. Sharp volume increase can occur when the solid phase of slush hydrogen melts. Aging of solid hydrogen particles in slush hydrogen could result in particle settling and even overpressurization of slush hydrogen flow.

Main risk control methods of slush hydrogen systems are in common with those of liquid hydrogen systems. Nevertheless, the special properties of slush hydrogen call for additional safety requirements and guidelines. Since the operating temperature of slush hydrogen is lower, operations of slush hydrogen require greater care. Accumulation of solid particles that could block valve seats, instrumentation ports or relief valve openings should be precluded. Slush hydrogen transfer lines should be designed to eliminate flow segregation and particles settling.

3.2 Solid State Hydrogen Storage Systems

In recent years, there has been increasing interest in using hydrides, especially metal hydrides for hydrogen storage due to the advantageous characteristics such as high volumetric density and better safety compared to conventional methods [26]. Solid state hydrogen storage provides compact storage in a form that is equal to or better than cryogenic liquid hydrogen on a volume basis [27]. Solid state hydrogen storage has developed into an important and extensive hydrogen storage method. There have been lots of solid state hydrogen storage systems, such as metal hydride storage system, complex hydride storage system, etc. There have also been some standards on solid state hydrogen storage such as ISO 16111: 2008 [28]. Considering the rapid development and wide application of solid state hydrogen storage technology, basic safety requirements and guidelines for solid state hydrogen storage systems are first included in the standard.

Factors involved in solid state hydrogen storage hazards are presented. Metal hydrides generally have relatively high heat of reactions and low thermal conductivity, which could result in overpressurization of storage system. Local stockpiling of hydride powders could also result in overpressurization, and hydride powders within hydrogen could be ignited if leak outside. Toxicity of some hydrides must be particularly concerned.

The standard also provides design and use guidelines for solid state hydrogen storage systems. Design of the storage systems should consider the unique pressure-temperature characteristics and reaction kinetics of hydrides. The storage vessels should be designed as heat exchange structure, such as concentric heat exchanger tubes equipped with fins and filled with flowing cooling fluid. Other design and use guidelines are also presented. Improvement of acceptability and safer use of solid state hydrogen storage systems are expected.

3.3 Hydrogen Production by Renewable Energy

Hydrogen production technology has made great progress in the past decade. As a kind of clean energy without carbon emission, it is perfect that hydrogen can be derived from renewable energy [29]. Hydrogen production by renewable energy mainly include solar-thermochemical method, solar energy splitting water, biology and water electrolysis powered by renewable energy, etc.

During the last decades, use of environment-friendly wind and solar energy has remained limited because of lack of a suitable and economic long term energy storage technology [30]. Hydrogen technology combined to wind and/or solar energy sources represents an attractive solution to overcome the difficult of storage and the stochastic character of wind and solar energy [31]. Thus, water electrolysis powered by renewable energy, especially by wind and/or solar energy, is considered as a relatively mature and promising hydrogen production method [32].

Comprehensive introductions for the existing main hydrogen production systems are provided in the standard. Typical hydrogen production systems are further introduced and the structure charts of those are presented as an informative annex. Fig.2 showed the structure chart of hydrogen production system by water electrolysis powered by wind and solar energy which is focused on and detailed in the standard. This kind of hydrogen production systems may achieve more effective energy utilization and overcome the shortcoming of wind and solar energy.

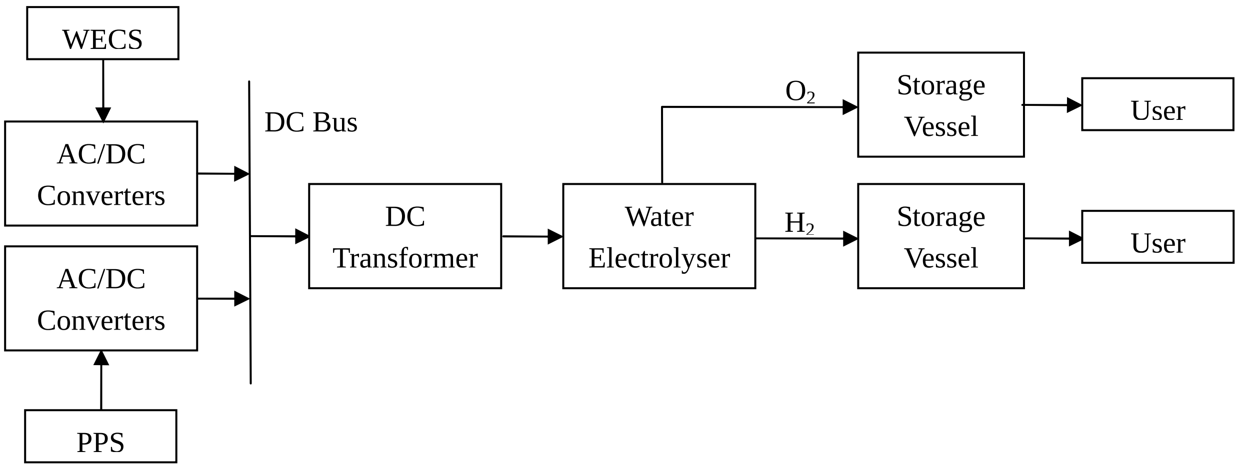

Figure 2. Structure chart of hydrogen production system by water electrolysis powered by wind and solar energy. WECS – Wind energy conversion system; PPS – Photovoltaic power system.

4.0 CONCLUSIONS

Factors involved in HE, flammability and explosion are discussed, as well as engineering control methods of those risks presented by the new standard. It was shown that metal hydrogen compatibility and risk control of flammability and explosion should be emphasized.

Features of the new standard consist of essential safety requirements and guidelines for slush hydrogen systems and solid state hydrogen storage systems, and introductions for hydrogen production by renewable energy. The intention of those is to try to cover all the safety aspects of hydrogen systems in the new standard and to reflect the state of the art.

As the first standard on safety of hydrogen systems in P.R. China, the new standard will have positive effects on the development of hydrogen technology and improvement of acceptance in market and society.

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