European Train the Trainer Programme for Responders

Lecture 4

Compatibility of hydrogen with different materials

LEVEL I

Firefighter

The information contained in this lecture is targeted at the level of Firefighter and above.

This topic is also available at level I-III.

This lecture is part of a training material package with materials at levels I – IV : Firefighter, crew commander, incident commander and specialist officer. Please see the lecture introduction regarding competence and learning expectations

Note: these materials are the property of the HyResponder Consortium and should be acknowledged accordingly, the outputs of HyResponse have been used as a basis

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

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Summary

The present lecture gives an overview of hydrogen interaction with different types of materials and hydrogen permeation, which are extremely relevant to hydrogen storage technologies. Although hydrogen is a non-corrosive gas, the reaction of hydrogen with some metals at high temperature may form corrosive hydrides, which then generates gas bubbles within the metal lattice, known as blistering. At low temperatures, some metal could become more brittle due to the change from ductile to brittle behaviour mode, which is called cold embrittlement. The interaction of hydrogen with polymer could also lead to swelling, blistering and deterioration of the polymer, increasing the permeation rate of hydrogen through the polymer matrix. The permeation rate of hydrogen through metallic containers (i. e. Type I and Type II) or containers with metallic liners (i. e. Type III) is negligible. However, the hydrogen permeation rate through Type IV containers must be correctly controlled to a very low value, to avoid the concentration of hydrogen reaching the LFL of hydrogen in air (4.0 vol. %).

Keywords

Hydrogen embrittlement, metal, polymer, blistering, hydrogen permeation, mitigation

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1. Target audience

The information contained in this lecture is targeted at LEVEL 1: Firefighter. Lectures are also available at levels II, III and IV: crew commander, incident commander and specialist officer.

The role description, competence level and learning expectations assumed at crew commander level are described below.

1.1 Roll description: Firefighter

A firefighter is responsible and expected to be capable of carrying out operations safely in personnel protective equipment including breathing apparatus using equipment provided, like vehicles, ladders, hose, extinguishers, communication and rescue tools, under any climatic conditions in areas and to emergency situations which can be reasonably anticipated as requiring a response.

1.2 Competence level: Firefighter

Trained in the safe and correct use of PPE, BA and other equipment which it is expected they will operate first responders must be supported by appropriate knowledge and practice. Behaviours that will keep them and other colleagues safe should be described by Standard Operating Procedures (SOP). Practiced ability to dynamically assess risk to self and others safety is required.

1.3 Prior learning: Firefighter

EQF 2 Basic factual knowledge of a field of work or study. Basic cognitive and practical skills required to use relevant information in order to carry out tasks and to solve routine problems using simple rules and tools. Work or study under supervision with some autonomy.

2. Introduction and objectives

The topic of hydrogen interaction and compatibility with different materials is vast. In this section of the lecture two different aspects will be considered: the interaction of hydrogen with metallic and polymeric materials, which are primarily used for the storage vessels. Due to the small size of its molecules and atoms, hydrogen can be easily absorbed by different materials including those used for hydrogen storage. This, in turn, leads to the degradation of the materials mechanical properties, which may result in unwanted hydrogen leaks and structural failures.

The aim here is to provide responders with sufficient knowledge to make relevant decisions. The interaction of hydrogen with the materials is pertinent to all FCH applications. However, in addition to being compatible with hydrogen, the materials used for storage are often subjected to high pressures, low temperatures, and cyclic or static loading. Thus, they must be selected accordingly. The selection of materials compatible with hydrogen is addressed in ISO standards applicable to FCH technologies (more detailed information on relevant RCS in the lecture of ‘Regulations, codes and standards for First Responders’ of the HyResponse project, http://www.hyresponse.eu/files/Lectures/RegulationCodesStandards_slides.pdf).

‘Hydrogen has a low viscosity and small atoms that can be absorbed into materials, so leaks and embrittlement of certain materials are possible, which can result in structural failure’ [1]. Mechanical degradation of structural materials under the influence of hydrogen is a serious problem and caused many incidents/accidents during production, storage, transportation and use [2]. The correct selection of suitable materials for the components is a crucial for safety of hydrogen storage systems. This relates to piping, walls of storage vessels, filling connectors, valves, fittings, etc. The silent movie produced in 1950s by Delft University illustrates how hydrogen bubbles emerge from steel at defects and other locations (https://www.youtube.com/watch?v=bv9ApdzalHM).

By the end of this lecture responders will be able to:

- Explain the mechanisms of hydrogen interaction with metallic and polymeric materials;
- Establish effect of hydrogen embrittlement on safety of hydrogen storage systems;
- Define the hydrogen permeation phenomena;
- Point out the safe permeation rate for hydrogen storages on-board of passenger cars and buses.

3. Interaction of hydrogen with metals

The compatibility of hydrogen with metals is affected by chemical interactions and physical effects, which include:

- Corrosion: dry corrosion (at high temperatures, *hydrogen attack*); wet corrosion (most common, caused by moisture); corrosion caused by impurities in a gas.
- Hydrogen embrittlement (HE).
- Embrittlement at low temperatures (‘cold embrittlement’).
- Violent reactions (e.g. ignition).

A whole range of factors influence the level of HE process [5]:

- Material:
    - Microstructure
    - Chemical composition
    - Heat treatment and mechanical properties
    - Welding
    - Cold working (strain hardening)
    - Non-metallic inclusions
- Environment:
    - Hydrogen purity
    - Hydrogen partial pressure
    - Temperature
    - Stress and deformation
    - Exposure time
- Design and surface conditions:
    - Stress level
    - Stress concentration
    - Surface defects

4. Interaction of hydrogen with polymeric materials

As it was mentioned earlier, the polymeric materials are increasingly being used for the liners and wrapping of hydrogen storage vessels. For the wrapping of composite tanks (Type III and IV) glass, aramide or carbon fibres can be used [3]. These fibres are characterized by their tensile modulus, tensile strength and elongation [3]. Polymers are also present in some fuel cells as a material for membranes. Please read about an incident occurred on a PEM FC [7]. Two phenomena often associated with polymeric materials used in FCH applications: a *permeation* of hydrogen through the materials and the *degradation of the mechanical properties* of the polymers. From material point of view, hydrogen storage represents quite a challenge. The materials used for hydrogen storage must be light in weight but also should be able to withstand extremely high pressures whilst maintaining their integrity. There are several unwanted effects of hydrogen on polymeric materials:

5. Limitation of hydrogen permeation

Permeation is an inherent phenomenon for all gases, which are in contact with polymers, and is the result of the hydrogen gas dissolution and diffusion in the polymer matrix. Due to a small size of its molecules hydrogen diffusion and thus the permeation are enhanced [3].

According to SAE J2578 (2009), permeation for CGH_2 systems could be defined as a diffusion of gas through the walls or interstices of a container vessel, piping or interface material [9]. It is worth noting that hydrogen in atomic form permeates metals, whilst for polymers permeation occurs in molecular form [10]. Current Type IV storage containers use a polymer liner, for example made of high-density polyethylene, typically overwrapped with carbon fibres set in a resin matrix. Other fibres such as glass or aramid may also be used, but most automotive systems use carbon fibre. The wrapping around the container varies in thickness, depending on the stress distribution. Type III or Type IV containers are used for most automotive applications.

6. A new standard for polymer hydrogen application compatibility

Today, there is a lack of test methods for evaluating polymer properties in hydrogen applications for determining design robustness. The polymer compatibility should occur on a material level. A new standard called “CHMC 2 – Test Methods for Evaluating Material Compatibility in Compressed Hydrogen Applications – Polymers” has been created and published (August 2019) by ANSI / CSA [15]. The results of these tests are intended to provide a basic comparison of polymer materials performance in applications utilizing compressed hydrogen. A list of priority test is proposed. The first one is the hydrogen permeation where the issue is to show if the polymer is unable to contain hydrogen through the material. The second one is the physical stability to check if the polymer is unable to maintain dimensions (swelling or shrinking) and/or mass. The third test is a rapid cycling test where the issue is material degradation (extrusion, cracks or blisters) due to hydrogen exposure. Dedicated tests have been selected to follow polymer property changes to check in the material is unable to maintain mechanical properties for design and compression. On test is rheologic. A dynamic frictional wear is dedicated to follow if the polymer is unable to maintain interface sealing and design with mating surface. Finally, the last critical test is material contamination test where the issue is materials release constituents causing impurity of the hydrogen.

Acknowledgement

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