

Fire & Explosion - General

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Fuel Cells - hazards and risk management

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Introduction

Since the start of the new millennium the interest and activity in hydrogen and fuel cell technology has been accelerating rapidly. The purpose of this note is to provide an introduction to the principal hazards that are likely to be present in fuel cell installations.

Basic Principles of fuel cell operation

In general terms a fuel cell is an electrochemical device that oxidises a hydrogen rich fuel and delivers a significant amount of the energy released as electricity. In virtually all fuel cells the oxidising agent employed is oxygen from the surrounding air and the most commonly used fuel at present is hydrogen, which may come from:

- cylinders of compressed gas
- cryogenic liquid storage
- metal hydride storage systems
- hydrocarbons e.g. LPG or methane
- methanol

The hydrogen produced from hydrocarbons and methanol is obtained using a high temperature catalytic reformer. This feeds a hydrogen stream directly into the fuel cell. In addition, cells are now being developed that can operate directly on methanol without the need for a reformer. The use of a liquid fuel simplifies storage and the elimination of a high temperature component is a significant safety advantage.

An extensive review of the main fuel cell types and typical uses is available in DIN TD5/045.

Hazards associated with fuel cell installations

All the fuels listed above present a significant fire and explosion hazard. In order to reduce the risks when storing and using these materials appropriate measures need to be taken. Hydrogen is, currently, the most common fuel for cells and in some ways is the most hazardous. The measures necessary to reduce the risks from hydrogen are discussed in detail below. The different or additional hazards arising from the other materials that may also be present in fuel cell installations are discussed separately later.

Fire and explosion hazards of hydrogen

Hydrogen is a flammable gas and readily forms an explosive mixture with air. The range of air/hydrogen concentrations that will explode is extremely wide. Mixtures containing from as little as 4% v/v hydrogen up to as much as 75% v/v will readily explode³. For the bulk of this range

(18-69% v/v) there is a significant risk that a confined hydrogen/air mixture will detonate.

The likelihood of an explosion occurring is further increased as a result of the very low ignition energy necessary to initiate a hydrogen/air explosion. The ignition energy for hydrogen/air mixtures is so low, 0.02 mJ, that the absence of ignition sources should not be relied upon as a basis of safety.

Hydrogen is very buoyant relative to air. Consequently, any leak of hydrogen will rapidly dissipate upwards. If the leak occurs in an open or well-ventilated area these properties will help to reduce the likelihood of a flammable atmosphere being formed. Conversely, there is a serious risk of explosion when hydrogen leaks occur within enclosed areas containing electrical equipment or other sources of ignition. The risk is particularly high when the source of ignition is close to a ceiling or other impervious high-level barrier.

Storage

Hydrogen will usually be supplied from high pressure compressed storage in cylinders and then fed into the fuel cell stack under very modest pressure (< 1 barg). Other modes of storage likely to be encountered include cryogenic storage of liquid hydrogen and, in the near future, absorption of hydrogen in metal hydrides.

When high pressure storage is used the cylinders should be located in secure outside storage in the open air. Indoor storage of hydrogen cylinders, although not recommended, is permissible provided that extensive safety measures; including effective ventilation, non-combustible construction and explosion relief, have been taken¹.

The cryogenic storage of liquid hydrogen for fuel cell use is likely to become more widespread in the future. Cryogenic storage installations should be constructed to an appropriate code and located in a suitable position in the open, not in a building³. Liquid hydrogen boils at -253 °C at atmospheric pressure. Consequently, hydrogen leaking from cryogenic storage will often sink initially, leading to the formation of flammable atmospheres at low level, before warming up and becoming buoyant and rising. This is in marked contrast to the situation with compressed hydrogen where the risk from the accumulation of flammable atmospheres is always at high level.

Care is necessary to prevent the condensation of oxygen-rich liquid air on uninsulated surfaces that are exposed to liquid hydrogen temperatures. It is particularly important not to have potentially flammable materials e.g. asphalt or tarmac beneath pipework where there is the risk of the condensation of oxygen-enriched air.

Research and development work on the storage of hydrogen in metal hydrides has been in progress for over 30 years, but the likelihood of encountering this type of storage "in the field" is at present very low. There are two main types of hydride storage system. The first involves the reversible absorption of hydrogen into the molecular lattice of transition metals. These are known as traditional hydrides. The finely divided metal is contained in a pressure vessel equipped with heating/cooling coils. The finely divided metal inside the pressure vessel is a flammable solid and in some cases could be pyrophoric.

The second type of hydride storage system uses sodium aluminium hydride and similar materials. These are known as complex hydrides and store hydrogen by undergoing reversible reactions. Complex hydrides are flammable solids and also react vigorously with water to produce hydrogen. The pressure of hydrogen in both types of storage system is dependant on storage temperature and the state of charge/discharge, but may often be in excess of 10 barg.

Supply

Hydrogen gas has a very low viscosity and it is, therefore, very difficult to prevent hydrogen systems from developing leaks. Pipework that was "leak-tight" when pressure tested with nitrogen will often be found to leak when used on hydrogen duty. Only appropriate pipework and fittings should be used for the supply of hydrogen. Copper and stainless steel are the preferred materials and joints should be brazed or welded. Flanged or screwed joints are acceptable but their use should be avoided if possible. Compression joints are generally not recommended.

Fuel cell enclosures

Fuel cells are often supplied as "stand alone" units contained in a dedicated enclosure. Large stationary power generation cell stacks are often supplied in skid-mounted "marine-transport"-size containers. The gaseous hydrogen supply equipment or reformer unit and fuel supply, electrical control systems, cooling water pumps and the d.c. output connections and bus bars are often present within the same enclosure. To prevent the risk of a

hydrogen/air explosion the internal arrangements within the enclosure must be to an appropriate design, correctly assembled and contain only electrical equipment suitable for use in a hazardous hydrogen atmosphere (gas group IIC). A hazardous area classification (electrical equipment zoning) study should have been completed for the installation. This should identify the extent and magnitude of the risk that flammable atmospheres present and will identify the specification of any electrical equipment necessary to ensure safe operation². It is essential that the upward migration of hydrogen is taken into account when carrying out this work.

Ventilation

Whenever reasonably practicable those areas of the fuel cell installation involving the use of flammable gases and liquids should be located in the open air. Where this is not practicable then effective ventilation should be provided to those areas of the installation where hydrogen or other flammable gases could accumulate in order to prevent the formation of an explosive atmosphere. The accumulation of hydrogen against impervious ceilings and high level bulkheads must be recognised as a significant hazard. The location of electrical equipment and the ventilation arrangements must be appropriate and recognise this hazard. The internal partitions and bulkheads present in some enclosures are intended to separate the hydrogen/natural gas handling areas from those areas where the likelihood of an incendive ignition source is high. Differential pressurisation of separate compartments is sometimes used to reduce the risk of a flammable atmosphere reaching identified ignition sources. Where this is the case it is important to ensure that the pressurisation air is drawn from a safe place.

When mechanical means are necessary to reduce the risk from the accumulation of flammable atmospheres it is important to ensure that appropriate alarm/shutdown systems are in place to detect and respond to the presence of flammable gases, equipment failure or the loss of ventilation or over-pressure. The alarm should sound when the concentration of hydrogen and or methane/LPG reaches 10% of the LEL; 0.4 %v/v in the case of hydrogen, and initiate the safe isolation of electrical ignition sources and the supply of flammable substances when the concentration reaches 25 % LEL; 1 %v/v for hydrogen. Additional guidance on the use of flammable gas detection/alarm systems is available in Reference ⁶.

Fuels other than hydrogen

Many commercially available cells use hydrogen that is produced using reformer-type technology located adjacent to the fuel cell stack. This usually involves passage of a hydrocarbon fuel (methane or LPG) and steam through a high (>300 °C) temperature catalyst bed. The reactions that take place within the reformer produce hydrogen for use in the cell and carbon dioxide, which is vented. Care is necessary to ensure that the carbon dioxide stream is effectively discharged and not allowed accumulate within the enclosure etc and become an asphyxiation risk.

Natural gas (methane) is lighter than air and will tend to diffuse upwards, but much more slowly than hydrogen. The explosive limits for natural gas (5-15% v/v) and LPG (2-10% v/v) are also much narrower than those for hydrogen. Consequently, in systems using hydrogen and methane, ventilation arrangements that are suitable for hydrogen will usually also prove adequate for methane. Sources of additional guidance on the safe use of natural gas are summarised in References ⁵ and ⁷.

LPG vapour is considerably heavier than air, especially when cold e.g. when taken directly from a liquid storage vessel rather than from a heated evaporator. In the event of a leak, LPG vapour can percolate downwards and may accumulate on the floor or in low-lying sumps producing a flammable atmosphere. Sources of additional guidance on the safe use and storage of LPG are summarised in Reference ⁷.

At present methanol is the only other fuel that can be used directly by fuel cells. Methanol is a highly flammable liquid that is also toxic, especially by skin absorption. When methanol is used as the fuel for the cell appropriate precautions should be taken to prevent the accumulation of flammable methanol/air atmospheres, e.g. containment and ventilation, and

to minimise the risk from ignition sources, e.g. through the use of appropriate electrical equipment.

Electrical hazards

It is very easy for operators of fuel cells to overlook the life-threatening hazard that electricity presents. Electrical hazards arise from two distinct areas within fuel cell installations; the normal 240 volt mains a.c. supply and the immediate output of the fuel cell stack. Although the voltages and currents produced by each element in the stack is very small, the total output from the stack can be of the order of 200-400 volts and 500 amps. Poor access control into dangerous areas, where unprotected bus bars etc are present, is a common area of concern that must be addressed by the operator.

References

1. "CP 8: The safe storage of gaseous hydrogen in seamless cylinders and similar containers." The British Compressed Gases Association.
2. "Area classification code for installations handling flammable fluids, part 15"; The Institute of Petroleum.
3. "Safety in storage, handling and distribution of liquid hydrogen"; IGC 06/93, Industrial Gases Council.
4. "Safety standard for hydrogen and hydrogen systems", NSS 1740.16 1997; National Aeronautics and Space Administration.
5. "Essential gas safety" second edition 2001: CORGI.
6. "Fixed flammable atmosphere detectors"; DIN TD5/035.
7. "Review of natural gas, LPG and fuel oil guidance"; DIN TD5/033.
8. "Guidance for the safe storage of transportable gas cylinders for industrial use, Revision 2. 1997." British Compressed Gases Association.
9. Draft IEC62282-2 March 2002 "Fuel cell technologies; Fuel cell modules".