

Chapter V: HYDROGEN SAFETY BARRIERS AND SAFETY MEASURES

Version 1.0 – May 2006



Table of content

1. Prevention measures	3
2. Safety procedures and training.....	3
3. Ventilation	3
Automatic shut down system (to be completed in future edition).....	5
4. Inerting	5
5. Inerting methods.....	7
6. Pressure-swing method.....	8
7. Flow-through method.....	9
8. Displacement inerting.....	9
9. Inerting control.....	9
Inferential method.....	10
10. Direct method.....	10
11. Disposal of inert-gas-hydrogen mixtures.....	10
12. Recombiners (FZJ).....	11
13. Control of ignition sources.....	12
14. Use of adequate electrical equipment.....	12
15. . Hot surfaces, flames and mechanical ignition (INERIS).....	16
16. Hot surfaces and mechanical ignition.....	16
17. Hot work and open flames.....	18
18. . Control of static electricity (INERIS).....	18
19. Igniters (to be completed in future editions).....	20
20. Knowledge, gaps and recent progress.....	20



1. PREVENTION MEASURES

2. Safety procedures and training

The following of safety procedures and training of professional personnel involved in the handling of hydrogen systems are probably the most important of prevention measures to reduce the occurrence of and potential consequences of incidents or accidents. Such procedures and training exist today in the chemical industry where hydrogen is produced, handled, stored and transported. Similar procedures are therefore to be developed for new applications of hydrogen such as transport or energy conversion, for professionals who come into contact with hydrogen. For the public, specific education courses are needed to address the specific properties of hydrogen, compared to other more familiar fuels such as natural gas or gasoline. Having a basic understanding of how hydrogen behaves when accidentally released into the environment is a prevention measure that all stakeholders of hydrogen must follow.

3. Ventilation

Whenever and wherever hydrogen is stored, or handled in confined spaces, ventilation must be provided. It is the most useful and common safety barrier to prevent the formation of explosive atmospheres in such environments, but to be effective; it needs to be adequately designed in terms of technique and performance. In some circumstances, limitations to the effectiveness of ventilation exist, and other prevention measures must be used.

The basic principle of ventilation is to bring fresh air into a room and to remove the inside air (this aspect is sometimes called extraction), thereby preventing the accumulation of explosive substances. The benefits of ventilation with respect to control of explosive atmospheres are threefold:

- Ventilation prevents the accumulation of explosive gas, by removing it;
- Ventilation limits the size of explosive volumes by dilution with fresh air, in that case it is sometimes called dilution ventilation; and
- Ventilation limits the resident time of explosive atmospheres, since it is active for a longer time than the duration of a leak of combustible gas.

Ventilation can be either forced (mechanical) or natural. The performance of natural ventilation fluctuates since it depends heavily on climatic conditions, whereas mechanical ventilation can provide a constant and controlled ventilation flow, and can be sized appropriately. However, there can be disadvantages associated with using mechanical ventilation rather than natural ventilation, as detailed below. First, let us describe natural ventilation techniques and recommendations.

For natural ventilation to be effective, openings at ground and ceiling levels should be provided. Natural ventilation is driven by temperature differences (inside vs. outside) and by wind or draughts. Typical natural ventilation rates expressed in terms of air change per hour (a.c.h) achieved through presence of cracks in structures, and gaps around windows and doors, are in the range of 0.2 a.c.h to 3 a.c.h. Some standards propose minimum openings to ensure sufficient ventilation (in terms of air intake and output). Experimental data which takes into account the specific physical properties of hydrogen, buoyancy and diffusion characteristics in particular, should be used to select and size ventilation openings and positions, especially for semi-confined areas where accumulation of unwanted gas pockets must be avoided.

As far as mechanical ventilation is concerned, the main question to be answered when using this measure as a protection barrier is how to size the ventilation rate, so that hazardous explosive

atmospheres cannot be formed in the event of non-catastrophic accidental leaks. Sizing can be determined

- Using “best practice” documents; or
- Using calculations based on assumed leakage rates; or
- be based on the hydrogen leak detection sensitivity.

As examples of best practices, (EUR 9689, 1985) recommends values of at least 20 a.c.h (air change per hour) for leaks of hydrogen in a room. In (FMGlobal, 2000) ventilation rates of at least 10 a.c.h are recommended for buildings, and values of about 25 a.c.h whenever hydrogen is detected. In (NSS 1740.16, 1997), typical ventilation rates of 6 a.c.h are recommended for rooms with ceiling height of about 3 m, and in general, it is mentioned that ventilation rates should be designed to ensure dilution of hydrogen down to 25% of the Lower Flammability Limit (LFL).

These best practices are always related to the volume of the room, but not the value of the leak rate. In conclusion, we can consider values of ventilation rates of 10 a.c.h as adequate ventilation rates in normal conditions, which should be increased to about 20 a.c.h in the event of an emergency (hydrogen detection).

Ventilation rates can also be calculated assuming a credible, non-catastrophic, leak rate, for example using the formula below:

$$Q_{vent} = \frac{10}{HL} Q_{leak} K_{safety}$$

where the ventilation and the leakage rates are given in terms of volumetric flows (m³/h). In such a formula, hydrogen concentrations are assumed homogeneous inside the room. K_{safety} is a safety factor, which in the case of hydrogen, should be either 4 (to ensure that the steady state concentration is 25% of the LFL, or 10 (to ensure a steady state concentration level of 10% LFL). This method of sizing the ventilation rate requires the anticipated leak rates to be known – and this can be achieved as part of a comprehensive risk assessment study which reviews all possible leak scenarios. An example of such a method to size ventilation can be found in the gas industry in the UK. Dilution ventilation is used in gas turbine acoustic enclosures, where the ventilation system is designed so as to dilute gas clouds from small leaks down to concentration below the Lower Explosive Limit (LEL). The system is not designed to cope with catastrophic failures. Care is needed to ensure that there are no stagnant zones, where gas can accumulate and create clouds with concentrations in the flammable range. It is sometimes erroneously assumed that high air change rates are needed, when in many cases the opposite is true. There is guidance on how to model dilution ventilation flows in acoustic enclosures housing natural gas fuelled gas turbine and select suitable leak sizes in documents published by Health and Safety Executive in the United Kingdom, (Ivings, 2004) and (Ivings, Lea and Ledin, 2004). Health and Safety Executive have also produced a Guidance Note PM84, which deals with the operation of gas turbines for power generation, (HSE, 2003).

The third method to size ventilation rates is to base it on the sensitivity of the hydrogen detection systems. These devices are used to trigger an automatic shut down process to stop a hydrogen leak. If the detectable leakage value is known, ventilation rates can be sized to ensure that any undetectable leak will not lead to hydrogen accumulation.

Although mechanical ventilation can provide a well controlled flow rate into the confined environment – for example in a tunnel, the downside of using active ventilation is that the gas cloud and the air will be more turbulent than if natural ventilation is used. This is not a problem in itself, except in situations where the gas cloud is ignited in which case the higher turbulence level could lead to a more severe explosion. There must also be some contingency for what to do should the fan(s) fail or not function properly. Natural ventilation, while cheaper to install and operate than mechanical ventilation, is also much less controllable, as it is dependent on the weather conditions at the openings

to the surrounding. A combination of natural and mechanical ventilation might be the most appropriate solution, but this will be tunnel or other structure dependent.

Finally, the ventilation of garages attached to or located near domestic dwellings is regulated in the Building Regulations, in the UK, and will differ from country to country, see (Miles, 2006). The regulations were drawn up prior to the advent of the introduction of hydrogen-fuelled vehicles and thus might need to be revised. The regulations are based on the build-up of petrol or diesel vapour, which is heavier than air, will accumulate near the floor, while hydrogen is highly buoyant will accumulate near the ceiling. New experimental work such as performed in HYSAFE (experiments in a well-instrumented garage facility) coupled to numerical simulations using CFD will prove valuable to reassess required ventilation rates for leaks of H₂ vehicles – or H₂ systems in general. Regulations concerning underground and multi-storey car parks and commercial garages may also need to be revised.

References:

BS 5925: 1991, Codes of practice for ventilation principles and designing of natural ventilation

EUR 9689, Commission des Communautés Européennes, Eléments pour un guide de sécurité hydrogène, Vol. 1 and Vol.2, 1985

FM Global, 2000, Property Data Sheets 7-91 « Hydrogen », September 2000

HSE 2003, Control of safety risks at gas turbines used for power generation, Plant and Machinery Guidance Note PM84, HSE Books (ISBN 0 7176 2193 6), 2003

Ivings, M.J. Lea, C.J. and Ledin, H.S., Outstanding safety questions concerning the use of gas turbines for power generation: Best Practice Guidelines for CFD, Health and Safety Laboratory Report No. CM/03/12, 2004

Ivings, M.J., Azhar, M., Carey, C, Lea, C., Ledin, S., Sinai, Y., Skinner, C., and Stephenson, P., Outstanding safety questions concerning the use of gas turbines for power generation: final report on the CFD modelling programme of work, Health and Safety Laboratory Report No. CM/03/08, 2004

Miles, S., HySafe Deliverable D49, 2006.

NSS 1740.16, National Aeronautics and Space Administration, “Safety standard for hydrogen and hydrogen systems”, Guidelines for hydrogen system design, materials selection, operations, storage, and transportation. February 1997

Automatic shut down system (to be completed in future edition)

4. Inerting

Inerting is defined as the replacement of a sufficient proportion of oxygen contained in a gaseous atmosphere by an inert gas, to make it impossible for the atmosphere to be ignited or a flame to propagate. It is an important way to prevent the formation of explosive atmospheres, particularly for hydrogenated atmospheres. However, it must not be forgotten that inerting can be dangerous for workers because of the asphyxiating property of inert gas. Although we will focus here only on injection of a gaseous inert gas, it must be mentioned that in some applications, foams can be used.

The latter has been designed for use on offshore installations for hot work, i.e. welding on process systems, (Anon, 1997).

The conditions which must be strictly complied with for a reliable and safe inerting are relative to the following features:

- the composition of atmospheres,
- the inerting procedures,
- the control of inerting.

These conditions are fully described in the European document entitled “Guidance on inerting for the prevention of explosions” (prEN/TR 15281, 2005). The conditions for an hydrogenated atmosphere to be inert can be derived from a triangular diagram representing the Hydrogen-Air-Inert mixtures. Such a schematic diagram is given on Figure 1.

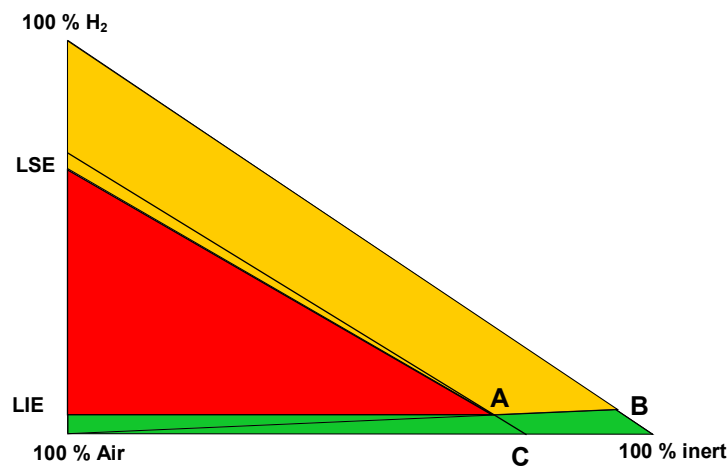


Figure 1: Triangular diagram for ternary Hydrogen-Air-Inert mixtures (schematic)

On this diagram, the apexes of the triangle correspond to one of the 3 pure gases:

- pure air at the bottom, on the left side,
- pure inert at the bottom, on the right side,
- pure hydrogen at the top.

The left side of the triangle corresponds to binary air-hydrogen mixtures : the currently accepted values for the Lower Explosion Limit (LEL) and the Upper Explosion Limit of hydrogen in air for normal atmospheric conditions have been placed on this side (LEL = 4 % vol. and UEL = 75 % vol.). The explosion area looks like a rectangular triangle (red area) : A is the apex of this area. Its lower side can be considered as parallel to the air-inert mixtures side. Its hypotenuse is almost parallel to hydrogen-inert mixtures side.

The following lines have been drawn:

- the parallel to the hydrogen-inert mixtures side drawn from A : the intersection of this line with the air-inert-mixtures side is C
- the line joining the air-apex and A : the intersection of this line with the hydrogen-nitrogen mixtures side is B

From the explosion diagram, the following concepts can be introduced

- Limiting Air Concentration (LAC)

- Limiting Oxygen Concentration (LOC)
- Relative and absolute inert mixtures

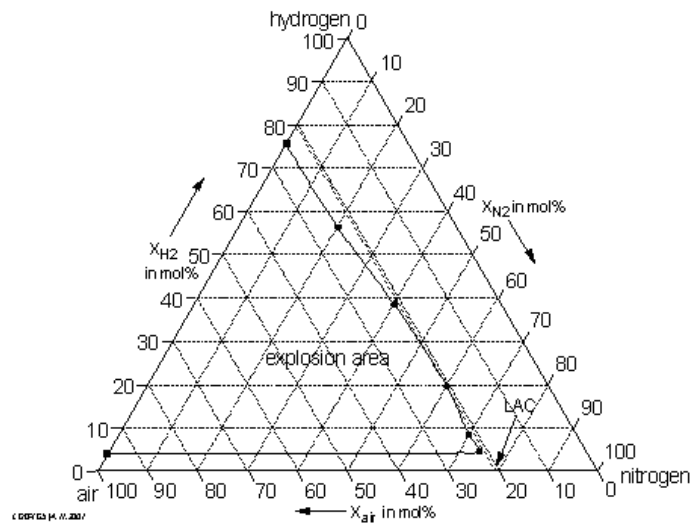
The Limiting Air Concentration (LAC) is the lowest air concentration of a hydrogen-air-inert mixture under which any hydrogen-air-inert mixture cannot be ignited : it corresponds to the air content of C and depends on the nature of the inert gas.

The Limiting Oxygen Concentration (LOC) is the lowest oxygen concentration of an hydrogen-air-inert mixture under which any hydrogen-air-inert mixture cannot be ignited and it can be derived from the concentration of oxygen in air : $LOC = 0,209 LAC$

The triangular diagram for ternary Hydrogen-Air-Inert mixtures comprises 3 coloured zones:

- red zone: it corresponds to the explosion area and contains all the representative points of explosive mixtures,
- orange zone: it corresponds to mixtures which are not explosive but which can get it if they are mixed with air : these mixtures are so called « relative inert »
- green zone: it corresponds to mixtures which are not explosive and which would not get it if they are mixed with air : these mixtures are so called « absolute inert ».

The ratio x_{inert}/x_{H_2} , calculated from the co-ordinates of B, corresponds to the limiting ratio for absolute inert mixtures. As an example, taking nitrogen as the inert gas, the ternary diagram for Hydrogen-Air-Nitrogen mixtures is given in Figure A2 of the standard prEN14756 “Determination of LOC for gases and vapours” (*prEN 14756, 2005*) for 20°C and ambient pressure. This diagram has been experimentally determined in a 14 litre sphere according to EN 1839 standard “Determination of explosion limits of gases and vapours” (*EN 1839, 2004*) as described in (Schröder, 2002).



On this diagram, the following values can be derived:

- $LAC = 21,2 \% \text{ vol.}$; then $LOC = 0,209 \times 21,2 = 4,4 \% \text{ vol.}$,
- the ratio x_{N_2}/x_{H_2} is equal to 20.

5. Inerting methods

Inerting consists in reducing the oxygen concentration of the atmosphere to be inerted to the lowest practical level, but it should always be less than the LOC. Typically for hydrogen, whatever the inert gas, an oxygen concentration equal to or less than 2% vol. should be used.

There are several methods of inerting systems where hydrogen is to be used and the main ones are:

- Pressure swing or vacuum swing method
- Flow-through method
- Displacement method

Further information on inerting methods in general are available in the in the CEN document (prEN/TR 15281, 2005). Where hydrogen is concerned, the requirements of the inerting system are more stringent due to several factors, including the extreme sensitivity of hydrogen to ignition, its very wide explosive limits, and its unusually low minimum oxygen for combustion. When inerting a system to contain hydrogen, it is best to use a technique which also leak tests the system as a routine part of the inerting. This can be accomplished by the use of a pressure or vacuum leak test as a part of the pressure or vacuum purging regime.

6. Pressure-swing method

This involves pressurising the system with inert gas, and relieving back to atmospheric pressure. A pressure test can be incorporated by isolating the inert gas supply after pressurising, and determining whether the pressure falls after a period of time. As hydrogen has a very small molecular size, it is best to use helium when leak testing, as it has a similar molecular size.

When pressure-swing inerting a system, it is best to measure the oxygen concentration after inerting to confirm that the required oxygen level has actually been reached. Depending on the complexity of the system, such as a branched system or several interconnected vessels, it may be necessary to measure the oxygen concentration at several points within the system, to ensure that adequate mixing of the inert gas and the air initially present. This also applies when removing hydrogen from a closed system prior to the admission of air.

Vacuum-swing inerting

This uses exactly the same principles as the pressure-swing inerting. It involves the evacuation of a closed system and restoration to atmospheric pressure by the admission of inert gas. It is useful where a system can withstand vacuum but cannot withstand pressure, such as glass vessels.

Instead of a pressure leak test, a vacuum leak test should be applied, by isolating the vacuum from the system and measuring the rate of pressure rise. Even the best systems will eventually allow some air in, so provision should be made for vacuum systems to have the oxygen content measured, so that the system can be re-inerted before the inevitable air in-leakage makes the atmosphere within the system explosive.

The number of pressure-swing or vacuum-swing cycles can be calculated from the equation (1):

$$C_n = C_i + (C_0 - C_i) \left(\frac{P_1}{P_2} \right)^n \quad (1)$$

where:

- n = number of pressure-swing or vacuum-swing cycles
- C_n = oxygen concentration after n purges
- C_i = oxygen concentration in the inert gas
- C_0 = initial oxygen concentration
- P_1 = lower purge pressure (absolute)
- P_2 = upper purge pressure (absolute)

7. Flow-through method

Where systems can be neither evacuated nor pressurised, a flow-through technique can be used, which involves the replacement of an oxidant by a continuous flow of inert gas into a system which is vented to atmosphere. This is less efficient, and great care is required to ensure that adequate purging is achieved. A high flow rate is required to ensure adequate mixing.

The time required to purge a given volume can be determined from the equation (2) :

$$t = F \frac{V}{Q} \ln \left(\frac{(C_i - C_0)}{(C_i - C_f)} \right) \quad (2)$$

where:

- t = time required for purging
 - V = system volume
 - Q = inert gas flowrate
 - F = safety factor for purging
 - C_f = oxygen content after flow purging
 - C_0 = initial oxygen content
 - C_i = oxygen content of inert gas
- t , V , and Q may be in any set of consistent units.

The inlet and outlet of the inert gas (place and geometry) should be chosen in order that :

- the molecules of the inert gas reach the part of the system which is the furthest from the inlet (this can be obtained if the inert gas is introduced into the system as a high speed jet, in a direction toward this furthest part),
- there is a sufficient distance between the inlet and the outlet

When using a flow-through technique, the safety factor can be determined by measurement of the oxygen concentration in the gas stream being vented. Typical values of the factor F would be 1 for a single straight pipe fed at one end and vented at the other, to a value of 5 or more for a complex vessel system with poor mixing. Where a system is branched, it will be necessary to vent from the ends of all the branches to ensure that no pockets of oxygen remain. This makes flow purging the worst method of all.

8. Displacement inerting

This method relies on using an inert gas of significantly different density to that which is to be purged, and where significant mixing does not take place. It is used typically on the inerting of very large vessels, where it would not be possible to ensure adequate mixing if an inert gas of substantially the same density were to be used.

9. *Inerting control*

There is no safe inerting if the inert state of the system is not controlled and it is particularly true for hydrogen. There are two types of method for ensuring that the inert state of the system is maintained :

- inferential method
- direct method

Inferential method

- some parameters linked to the oxygen concentration have to be measured (e.g. the number of swings and the value of P2 for the pressure swing, the number of swings, the value of P1 and the leak rate for the vacuum swing, the flow rate and flow duration for the flow through)
- moreover, one must be sure that the inert gas is always available.

This method infers that the atmosphere is inert by reference to some other parameter, which allows an inference to be drawn that the atmosphere is inert. An example of this is where a system is pressure-swing inerted using Equation (1). If the number of purges is carried out correctly it can be inferred that the oxygen concentration will be correct. This is probably adequate for a simple single vessel which is pressure-swing purged. However, where a complex, branched system is pressure-swing purged, it is quite feasible that the ends of some of the branches will not be adequately purged, as the pressurising inert gas simply compresses the air trapped in the branch without mixing, so that when the pressure is released, the air expands again. Consequently, although the correct number of purges may have been applied, the system has not been fully inerted.

This can be improved by venting the pressurised system through each branch, to ensure that all the air is swept out. This can be proved by the use of a portable oxygen analyser used to measure the oxygen concentration of the gas vented from each branch. Once a system has been successfully inerted and the oxygen content found to be sufficiently low at all points within it, then it can be inferred that using exactly the same purging regime will also reproduce the same inert conditions. The disadvantage with inferring that the inerting regime is the same is that not all changes may be noticed and recognised. Hence there is a danger that the inerting may not be satisfactory, yet there will be no information to suggest that it is not successful.

10. Direct method

- the oxygen concentration is continuously measured
- whatever the O₂ monitor, it needs to be **strictly maintained and calibrated**
- the sampling needs to be representative of the atmosphere

This method actually measures the oxygen content of the atmosphere using a suitable oxygen sensor, and hence if there is any in-leakage of air, it is immediately detected. There are several potential problems with direct measurement. Firstly, there is the potential to measure the oxygen content at a single point, so that in a branched or complex system the sensor may not detect a change in oxygen content elsewhere in the system. This can be overcome by the use of multiple sensors. Where there are multiple sensors, these can be configured such that each reads continuously, or sequentially, so that each sensor is polled periodically. Any increase of oxygen is then detected with a maximum delay of the time between sequential readings.

The sensors have to be suitable for the duty that they have to perform, so that they are not poisoned by materials within the system. Similarly, blockages in the sensors may reduce their sensitivity or response time. Ideally, sensors should be calibrated regularly and a duplicate sensor should be used during the calibration. The major advantage with direct measurement is that oxygen ingress is usually detected very quickly, allowing safety systems to shut down the process or re-inert the system. However, where a system is automatic and reliant on the detectors working correctly, it will be necessary to ensure that the reliability is adequate.

11. Disposal of inert-gas-hydrogen mixtures

Where hydrogen is routinely vented to atmosphere, it will be necessary to consider the potential for it to ignite. Unless it is diluted with inert gas until it is absolutely inert, it will be necessary to deal with the formation of an explosive atmosphere around the open end of the vent. As the minimum ignition energy is very low, it is likely that it will not be possible to exclude all potential ignition sources.

Consequently, it will be necessary to assume that the hydrogen-air mixture will ignite, and suitable precautions will need to be taken to deal with the over-pressure produced. This may involve determining the extent of the dilution

References

prEN/TR 15281 "Guidance on inerting for the prevention of explosions" (2005)

prEN 14756 "Determination of limiting oxygen concentration (LOC) for gases and vapours" Annex A2 (2005)

EN 1839 "Determination of explosion limits of gases and vapours" (2004)

Schröder, V. "Flammability limits of Hydrogen and Hydrogen/Methane mixtures" Nr. 253, NW Verlag, Bremerhaven 2002 (ISBN 3-89701-733-4)

Anon, Nitrogen Foam Inerting, BJ Services, 1997

12. Recoiners (FZJ)

A recombiner is a device that promotes the recombination of hydrogen with oxygen - usually available as a constituent of air - forming water. As such, this device provides a hydrogen sink and may serve to avoid, remove or at least to slow down the formation of flammable mixtures caused by the accidental ingress of hydrogen into a closed area.

Recombiners can generally be classified into active and passive devices. Active recombiners use heat to initiate the conversion. Passive recombiners make use of the effect that hydrogen and oxygen react already at low temperatures and even beyond conventional concentration limits in an exothermal reaction in the presence of catalysts such as platinum or palladium. Appropriate measures (e.g. system design) need to be taken to prevent the system temperatures from exceeding the self-ignition temperature. This might cause an unintended ignition due to the exothermal reaction at elevated hydrogen concentrations. Without appropriate measures, the use of recombiners is limited to mixtures below the ignition limit (K. LEDJEFF, 1987).

As of today, hydrogen is primarily used in industrial scale in designated areas where the risk of formation of flammable mixtures may be reduced by design or where venting can easily be applied. As a consequence, only few specific application fields exist where recombiners are used. Only very few systems available off the shelf. With the use of hydrogen in ,any surrounding in an increasing number of mobile applications an added need for specific recombiner systems may be expected.

Today, the main application fields are

- batteries
- nuclear reactors

New applications of recombiners or more generally catalytic recombination surfaces are also appearing, such as BMW's boil-off management system.

Batteries

During charging processes in batteries hydrogen and oxygen are produced and released. This may become a safety problem when



dealing with large battery sections or when using batteries in a closed area like for example submarines. Recombiner systems have been developed by VARTA for batteries (K. LEDJEFF, 1982) as well as for use in submarines providing conversion capacities of 200 L/h (VARTA, year unknown). Recombiners for batteries, so-called 'Hydrocaps' are also available from Hydrocap Corp. (USA). These catalytic caps replace battery cell caps and reduce water-loss of batteries as well as the risk of gas explosions outside the battery..

Nuclear reactors

In nuclear reactors recombiners are used to remove hydrogen that is produced in service (Boiling water reactors (BWR), active recombiners) or possibly released during a severe accident (Light water reactors, passive autocatalytic recombiners).

Active thermal recombiners are used with gas capacities of 100 m³/h. The inlet gas is heated up to 700°C and above initiating the recombining reaction. The product gas is cooled before leaving the device. Thermal recombiners are manufactured by Siemens (Germany) and AECL (Canada).

Catalytic recombiners for use in nuclear reactors are manufactured by the companies Framatome-ANP (France), NIS (Germany), AECL (Canada), and Electrowatt-Ekono AG (Switzerland).

Catalytic recombiners need usually a minimum concentration of about 0.5 vol.% for start-up. As passive recombiners are self-feeding devices, the conversion rate depends on the self-generated throughput that depends on the catalyst temperature. In known systems typical flow velocities are between 0.5 and 1.0 m/s. In order to keep the system active over long periods some devices propose to be kept in a sealed environment to prevent the catalyst from being spoiled (poisoned) by the atmosphere.

Detailed information on the long term research (qualifying tests, experimental studies) that has been performed in the nuclear field with extensive bibliographical references are given in (W. ZHONG, 2001) and (E. BACHELLERIE, 2002).

Reference and sources

K. Ledjeff. Elimination of hydrogen or oxygen from explosive mixtures by catalytic techniques. Int. J. Hydrogen Energy, Vol. 12, No. 5, pp. 361-367, 1987

K. Ledjeff, A. Winsel. Catalytic hydrogen/oxygen recombiner with self-limitation. J. Power Sources, Vol. 12, pp. 211-227, 1982

VARTA. Hydrogen elimination technology. Information brochure

W. Zhong (Ed.). Mitigation of hydrogen hazards in water cooled power reactors. IAEA-TECDOC-1196, IAEA, Vienna, ISSN 1011-4289, 2001

E. Bachellerie et al. State-of-the-art report on passive autocatalytic recombiners - Handbook guide for implementing catalytic recombiners. EC Project PARSOAR, Contract FIKS-CT1999-20002, Technicatome company report, Technical note TA-185706 Ind. A., June 2002

13. Control of ignition sources

14. Use of adequate electrical equipment

Protection principles

There are three basic methods of protection:

- **Explosion containment:** *this is the only method that allows the fire or explosion to occur but confines it to a well-defined area, thus avoiding the propagation to the surrounding atmosphere.*
- **Segregation:** *method that attempts to physically separate or isolate the electrical parts or hot surfaces from the explosive mixture. This method includes various techniques, such as pressurization, encapsulation, etc.*
- **Prevention:** *method that limits the energy content, both electrical and thermal, to safe levels under both normal operation and fault conditions.*

The choice of a specific protection method depends on the degree of safety needed for the type of hazardous location (Zone 0, Zone 1 or Zone 2) in order to have the lowest probability value for an eventual simultaneous presence of an adequate energy source and a dangerous concentration level of an hydrogen/air mixture.

None of the protection methods can provide absolute certainty of preventing an explosion. The most efficient precaution is to avoid electrical apparatus in hazardous locations. Only when there is no alternative should this application be allowed. Other important factors to be considered are the size of the apparatus to be protected, the flexibility of the system, the possibility of performing maintenance, the installation cost, etc.

Explosion-proof enclosure: this protection method is the only one based on the explosion containment concept: in this case, the energy source can come in contact with the hydrogen/air mixture. But, even if the explosion is allowed to take place, it will remain confined in an enclosure specially designed to resist the overpressure, and thus preventing the propagation to the surroundings. This kind of protection is applicable only to equipments located in Zone 1 & 2, not in Zone 0. In Europe, CENELEC and IEC standards refer to this protection methods with the symbol “Ex "d" ”. The reference standard is the EN 50018 (EN 50018, 2000).

Pressurization protection method: pressurization is a protection method based on the segregation concept. This method prevents the penetration of the hydrogen/air mixture into the enclosure containing all the electrical parts that might generate sparks or dangerous temperatures. A protective gas (clean air or inert gas) is contained inside the enclosure, with or without continuous flow, in order to maintain a pressure slightly greater than the external atmosphere. This kind of protection is applicable only to equipments located in Zone 1 & 2, not in Zone 0. In Europe, CENELEC and IEC standards refer to this protection methods with the symbol “Ex "p" ”. The reference standard is the EN 50016 (EN 50016, 2002).

Encapsulation protection method: the encapsulation protection method is based on the segregation of those electrical parts that can cause the ignition of a dangerous mixture, by putting them in resins that are resistant to the specific ambient conditions. This technique is often used as a complement to other protection methods. This kind of protection is applicable only to equipments located in Zone 1 & 2, not in Zone 0. In Europe, CENELEC and IEC standards refer to this protection methods with the symbol “Ex "m" ”. The reference standard is the EN 50028 (EN 50028, 1999).

Oil-immersion protection method: the oil-immersion protection method is based on the submersion of all electrical parts in oil, which prevents the external flammable hydrogen/air atmosphere from going

in contact with the electrical components. The most common application is for static electrical equipments, such as transformers, or where there are moving parts, such as transmitters. This method is not suitable for process instrumentation or for apparatus that requires frequent maintenance or inspections. This kind of protection is applicable only to equipments located in Zone 1 & 2, not in Zone 0. In Europe, CENELEC and IEC standards refer to this protection methods with the symbol “Ex "o" ”. The reference standard is the EN 50015 (EN 50015, 1998).

Powder-filling protection method: this protection method is similar to the oil-immersion one, except that the segregation is accomplished by filling the enclosure with powdered material so that an arc generated inside the enclosure will not result in the ignition of the dangerous atmosphere. The filling material that is generally used is quartz powder, and its granularity must comply with the standard. This kind of protection is applicable only to equipments located in Zone 1 & 2, not in Zone 0. In Europe, CENELEC and IEC standards refer to this protection method with the symbol “Ex "q" ”. The reference standard is the EN 50017 (EN 50017, 1998).

Increased safety protection method: this protection method is based on the prevention concept. Specific measures are applied to the electrical apparatus in order to prevent, with an high safety margin, the generation of excessive temperatures or of arcs and sparks inside and outside the apparatus during normal conditions. This technique can be used for the protection of terminals, electrical connections, lamp sockets and squirrel gauge motors, and is often used in combination with other methods of protection. This kind of protection is applicable only to equipment located in Zone 1 & 2, not in Zone 0. In Europe, CENELEC and IEC standards refer to this protection method with the symbol “Ex "e" ”. The reference standard is the EN 50019 (EN 50019, 2000).

Intrinsic safety protection method: intrinsic safety is the protection method most representative of the prevention concept and is based on the principle of limiting the energy stored in an electrical circuit. An intrinsically safe circuit is virtually incapable of generating arcs, sparks or thermal effects that are able to ignite an explosion of hydrogen/air mixture, both during normal operation and during specific fault conditions. According to the CENELEC EN 50020 standard, two categories of intrinsic safety (Ex "ia" and Ex "ib") are specified, defining the number of faults allowed for specific classifications and the safety coefficients to be applied during the design phase. The kind of protection Ex “ia” is applicable to equipment located in Zone 0, 1 & 2, while the Ex “ib” only to equipment located in Zone 1 & 2, but not in Zone 0. The reference standard is the EN 50020 (EN 50020, 2002).

Special protection method: originating in Germany and standardized in the United Kingdom, this protection method is not covered by any CENELEC or IEC standard and is not recognized in North America. It was developed to allow certification of apparatus that is not developed according to any of the existing protection methods, but can be considered safe for a specific hazardous location. This location must undergo appropriate tests or a detailed analysis of the design. The use of the special protection method is generally applied to Zone 1 & 2; however, Zone 0 certification is not excluded.

Mixed protection methods: in the process instrumentation field, the use of several protection methods applied to the same apparatus is a common practice. For example, circuits with intrinsically safe inputs can be mounted in pressurized or explosion-proof enclosures. Generally, this mixed system does not present installation difficulty if each of the protection methods is appropriately used and is in compliance with the respective standards.

Equipment categories

The categories of a piece of equipment, suitable for installation in a potentially explosive atmosphere, indicate its design safety level and requirements, as well as its allowed applications and locations (Zone). According to the ATEX Guidelines (ATEX Guidelines, 2000), for Group II (defined as “equipment intended for use in places different from underground parts of mines, and from those parts of surface installations of such mines), the category depends on the localization of the product (Zone) and whether a potentially explosive atmosphere, is always present, or is likely to occur for a long or a short period of time.

The following table shows the relationship between equipment category and safety requirements, as well as allowed applications and locations (Directive 1994/9/EC).

Category	Design safety	Design requirements	Application	Zone of use
1	Very high level of safety	Two independent means of protection or safe with two separate faults	Where explosive atmospheres are present continuously or for lengthy periods	Zone 0
2	High level of safety	Safe with frequently occurring disturbances or with an operating fault	Where explosive atmospheres are likely to occur	Zone 1
3	Normal level of safety	Safe in normal operation	Where explosive atmospheres are likely to occur infrequently and be of short duration	Zone 2

Table 0-1: ATEX Group II Categories and Application

References and sources

EN 50018, Electrical apparatus for potentially explosive atmospheres - Flameproof enclosure 'd', CENELEC, 2000.

EN 50016, Electrical apparatus for potentially explosive atmospheres - Pressurized apparatus "p", CENELEC, 2002.

EN 50028, Electrical apparatus for potentially explosive atmospheres - Encapsulation "m", CENELEC, 1999.

EN 50015, Electrical apparatus for potentially explosive atmospheres - Oil immersion "o", CENELEC, 1998.

EN 50017, Electrical apparatus for potentially explosive atmospheres - Powder filling "q", CENELEC, 1998.

EN 50020, Electrical apparatus for potentially explosive atmospheres – Intrinsic safety "i", CENELEC, 2002.

ATEX Guidelines (First Edition), Guidelines on the application of Council Directive 94/9/EC Of 23 March 1994 on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres, May 2000.

Directive 94/9/EC of the European Parliament and the Council of 23 March 1994 on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres, Official Journal L 100, 19/04/1994 P. 0001 - 0029.

15.. Hot surfaces, flames and mechanical ignition (INERIS)

A hot surface can exist during normal operations or may occur as a result of mechanical distress (friction) in machinery such as pumps or motors. “Hot surfaces” includes both hot spots and hot plate ignition. Ignition of a gas or vapour air mixture by a hot surface is a manifestation of auto-ignition. A boundary layer of this mixture in contact with the hot surface if heated sufficiently will result in a spontaneous ignition.

Apart from hot surfaces, open flames (and hot work) can also trigger an explosion. They will be dealt with in this chapter.

16. Hot surfaces and mechanical ignition

For ignition to occur on a hot surface, its temperature shall be greater than the gas auto-ignition temperature. Therefore, for hydrogen, hot surfaces or hot spots temperatures shall not go beyond 560°C. This value is rather high in comparison with most combustible gases and vapours. However, unlike most combustible gases, experience has shown (MECHEX EU project) that hydrogen/air ignition by hot surfaces will happen at temperature very close to the auto-ignition temperature even for a few mm² hot surface¹.

The control of hot surfaces during normal operations necessitate the selection of electrical and non-electrical equipment with care. Electrical and non-electrical equipment marking incorporates a temperature class (ranging from T1 to T6) as detailed in the table below.

Temperature Classes	Corresponding surface temperature (°C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

Table 2: Class temperature according to EN5014 or EN 60079-9?

As an example, surface temperatures of equipment belonging to the class T2 does not go beyond 300°C. In order to prevent ignition by hot surfaces, the surface or hot spot temperature of any equipment should not exceed the gas auto-ignition temperature. Hence, the maximum tolerable surface temperature when handling hydrogen is around 580°C. Therefore, equipment belonging to class 1 and above are appropriate for hydrogen use.

As far as mechanical ignitions are concerned, they are generally the result of mechanical distress (friction) under abnormal or fault conditions. Analysis of the physical processes that lead to mechanical ignition shows that there are at least three key stages from production of heat, transfer of heat to the surrounding explosive atmosphere and finally the ignition itself (Hawksworth).

In general, the friction processes that need to be considered are rubbing (long duration friction between surfaces producing a hot surface), grinding (long duration friction producing hot surfaces and

¹ For most combustible gases, hot spot temperature needs to be significantly greater than a surface temperature for auto-ignition to occur.

sparks) and impact (short duration friction producing short duration transient hot surfaces and sparks), or a combination of these.

Ignition by friction clearly depend on the temperature generated in the contact zone. For grinding and rubbing, the temperature at contact point depends on the rubbing speed and the contact pressure. Tests have demonstrated ignition down to speeds of 0.7 m/s (0.7 kW friction energy). In that case, ignition is triggered by the hot surface, few sparks being produced under these low speed conditions. (Hawksworth).

Control of mechanical ignition therefore necessitates careful design of equipment. It includes for instance to limit the rotating speed, to provide a sufficient distance between fixed and rotating parts. Temperature sensors may also be installed on mechanical equipment to detect any temperature deviation that necessitates to switch off the equipment.

European standards propose various design options to prevent ignition by mechanical equipment as detailed in the table below.

Type of protection	Concept	Standard	Title
fr: flow restricting enclosure	Restriction of flow inside the enclosure	EN 13463-1 (2001)	General requirements
d: flameproof enclosure	Enclosure which can withstand an explosion and prevents its propagation	EN 13463-2 (2004)	Protected by flow restricting enclosure 'fr'
g: inherent safety	Define the maximal criteria (speed, nature of materials, potential energies) so as there is no effective ignition source	EN 13463-3 (2005)	Protection by flameproof enclosure 'd'
c: constructional safety	Selection of components with no ignition source	EN 13463-5 (2003)	Protection by constructional safety 'c'
b: control of ignition source	Choose of control and monitoring devices which allow the de-energizing of equipment in case of failure	EN 13463-6 (2005)	Protection by control of ignition sources 'b'
p: pressurisation	Components protected by an enclosure which is pressurised with a protective gas at a higher pressure than the atmosphere	PrEN 13463-7 (2005)	Protection by pressurisation 'p'
k: liquid immersion	Components protected by an enclosure full of liquid	EN 13463-8 (2003)	Protection by liquid immersion 'k'

Table 3: Type of protection for mechanical apparatus used in potentially explosive atmosphere

For impact, experience indicates that impact energies as small as a couple of Joules are sufficient to ignite a hydrogen/air mixture. If we admit this rough evaluation it means that a solid object falling from man height could cause hydrogen ignition (Proust). Therefore, sufficient impact temperature can eventually result from the use of hand tools (falling tool, hammer...).

The use of hand tools made of bronze enriched with few percent of beryllium (to give them sufficient hardness) are known as spark free tools. They are of common use in gas industries (natural gas distribution). However, the absence of spark does not guarantee that hydrogen/air explosive atmosphere will not be ignited (guide hydrogène). Indeed, the temperature reached at the contact point is the main driving cause to trigger an ignition (even when sparks are produced).

Therefore, it is a very delicate issue to select the appropriate hand tool in location where hydrogen is handled. As a consequence, whatever the tool used, it is always recommended to purge hydrogen

before any intervention. Tools coated with shock absorbing materials can be a better option (as long as the coating material can not give rise to electrostatic sparks). Floors can also be covered with shock absorbing materials.

Finally the use of aluminium in contact with steel must be prohibited due to the highly energetic reaction that can take place whenever aluminium gets into contact with rusty steel.

17. Hot work and open flames

Hot work, like grinding ignition mechanisms have been detailed above. The only difference between hot work and grinding ignition mechanisms being that hot spots and sparks are not generated by a process mechanical failure but by human activity. Whenever hot work takes place (welding, grinding...) a hot work permit should be required. This permit assesses any fire or explosion hazards in connection with the planned work and proposes prevention and protection means for risk control. Prevention typically implies to switch off any gas supply and to purge equipment... Examples of protection means are to have fire fighting equipment available and organising breaks after work completion.

Beyond the delivery of a “hot work permit” people involved in hot work should be appropriately trained.

References

S Hawksworth & all, « Ignition of explosive atmosphere by mechanical equipment », CEN/TC 305/WG 2 N0433, SYMPOSIUM SERIES No. 150, 2005

EN 60079-9 (2004) , « Electrical apparatus for explosive gas atmosphere : General requirements ».

Norme EN 50014 : 1997 – Matériel électrique pour atmosphères explosibles – Règles générales

EN 50281-1-2 : Sélection, Installation et entretien : Tmax admissible = 2/3 Tnuage

ATEX Guide, TÜV Rheinland France

Eléments pour un guide de sécurité hydrogène – Expérimentations spécifiques, Choix d'appareils adaptés – Volume 1 – Annexe 1 : Protection contre les étincelles d'origine mécanique, Rapport EUR9689 FR, année 1985

18. . Control of static electricity (INERIS)

Different guidelines exist (CLC/TR 50404, NFPA 77) treating practical solutions in order to avoid the charge generation and accumulation phenomena and thus electrostatic discharge in various industrial situations. In a non-exhaustive way, we can recall the principle measures to adopt:

Avoid or restrict the charge generation

The first stage consists in avoiding, as far as possible, electric charge generation by one of the phenomena previously mentioned.

For the majority of nonconductive liquids, it is recommended not to exceed 1 m/s transport speeds, either by decreasing the flow of the pump, or by increasing the pipe diameter. This value will have however to be checked before its application in the case of hydrogen.

In the case of particles contained in a gas flow, it is not possible to prevent the electrical charging of these particles, but it is possible to prevent the accumulation phenomenon.

Remove or decrease the charge accumulation

The second stage consists in avoiding the use of insulating materials (supports, valves, coatings, etc) and in putting all the elements of the installation at the same potential and in grounding them.

The use of **insulating materials** must be **avoided**, as far as possible, whatever its size. Indeed, a simple bolt has a capacity of 1 PF and its setting with a potential of 10 kV would be enough to produce a spark discharge of 50 μ J, sufficiently to ignite an air-hydrogen ATEX.

In the same way, the use of certified materials according to the category corresponding to predefined ATEX zones allows the use of safety material. Thus, a material of category 1 and valid for IIC gas group, to which hydrogen is attached, should not include surfaces higher than 4 cm² of insulating material (according to EN 13463-1 standard).

Bonding will have to be made so as not have an insulated element able to accumulate electrical charges. The system **will be connected to the ground** in such way that the leakage resistance between an unspecified point of the installation and the ground will not exceed the threshold of 10⁶ Ω . In practice, for the metal elements, this resistance is normally much lower than this value.

Taking into account the electrostatic risk from the electrical charged operators in the hydrogen industry is to be considered as for the semiconductors industry. Indeed these are very sensitive to the electrostatic discharges which can strongly damage them. Thus, the same type of equipment can be carried by the involved personnel: grounded bracelet, conductive shoes, antistatic fabrics, etc. The leakage resistance between a person and the ground should not exceed 10⁸ Ω . However, it is important to note that the overriding principle with regard to personnel is that wherever possible, all precautions should be taken to ensure that they do not operate in an explosive atmosphere, or in an area where an explosive atmosphere is likely to occur.

Other measures (air humidification, ionisation), in order to limit the charge accumulation and discharge phenomena, exist but are not easily applicable in the case of installations handling liquid or gaseous hydrogen.

Organisational measurements

All measurements described in this paper would not be enough to prevent and protect the industrial installations from the electrostatic risk if the personnel were not trained accordingly and if technical improvements were not checked periodically. This step fits fully in the logic of the risks analysis required by 1999/92/CE European Directive transposed in each member state of the EU. The taking into account of the electrostatic risk is explicitly required there (1999/92/CE Directive, Annexe II §2.3), as well as the staff training concerned with ATEX risks (1999/92/CE Directive, Annexe II, §1.1).

Conclusion

The electrostatic charge and discharge phenomena are well-known for the majority of the combustible materials as for the various manufacturing processes and were briefly detailed above.

But the risks related to the intrinsic data of hydrogen (low MIE, low conductivity for liquid hydrogen) have not been studied in detail yet. The risks related to the accidental leak of compressed hydrogen is, a priori, one of the most probable sources of ignition for the ignition of air-hydrogen ATEX (Astbury and Hawksworth, 2005), but that remains to be shown.

19. Igniters (to be completed in future editions)

20. Knowledge, gaps and recent progress