TOPIC 5: Cross cutting themes - Safety

RISK ASSESSMENTS OF HYDROGEN REFUELLING STATION CONCEPTS BASED ON ONSITE PRODUCTION

Sandra Nilsen, Henrik Solgaard Andersen, Norsk Hydro ASA,
Company: Norsk Hydro ASA, Adress: P.O.Box 2560, Postal code: N-3907, City: Porsgrunn, Country: Norway
Phone: +47 35 92 39 66, Fax: +47 35 92 32 63
e-mail:sandra.nilsen@hydro.com

Gerd P. Haugom, Company: DNV
Address: Veritasveien 1, Postal code: N-1322, City: Høvik, Country: Norway
Phone: +47 67 57 92 67, Fax: +47 67 57 99 11

Harald Rikheim, Company: the Research Council of Norway
Address: Postboks 2700 St. Hanshaugen, Postal code: 0131 City: OSLO, Country: Norway

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Abstract
The paper describes risk assessments case studies undertaken on hydrogen refuelling stations. Several concepts with and without onsite production of hydrogen were assessed. This was done as a task in the EC funded research project European Integrated Hydrogen Project phase 2 (EIHP2). The EIHP2 shall provide input to regulatory activities on an EU and global level facilitating the safe development, introduction and daily operation of hydrogen fuelled vehicles on public roads and their refilling at public hydrogen refuelling stations. Hydrogen specific risk and safety analyses including comparative studies are an important part of the project's scope.

A common methodology for coarse risk assessments that take into account hydrogen specific issues, early concept phase and ensure similar results for the different concepts was adopted.

The main focus of the risk assessments were the hydrogen production elements of six different concepts for hydrogen refuelling stations, five with gaseous hydrogen and one with liquid hydrogen. The risk assessments identified safety aspects, compared the concepts and gave input for hydrogen related standards and regulations.

Conclusions were made regarding the assessed risk levels for the concepts and their comparison with the risk acceptance criteria in form of a risk matrix. The different refuelling station concepts are compared. The risk assessment methodology is also discussed.

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Introduction

Within the EC funded research project European Integrated Hydrogen Project phase 2 (EIHP2) see ref. /1/, risk assessment of several hydrogen refuelling station concepts were carried out. The EIHP2 project shall provide input to regulatory activities on a European and global level facilitating the safe development, introduction and daily operation of hydrogen fuelled vehicles on public roads and their refuelling at public hydrogen refuelling stations.

The main focus of the analyses was filling stations based on compressed gas, however liquefied systems were also briefly covered. The concepts analysed included hydrogen production by ammonia splitting, methanol steam reforming, natural gas reforming and water electrolysis. Hydrogen supply by truck – gaseous or liquefied – were also analysed. The results presented in this study cover gaseous hydrogen filling stations based on hydrogen production onsite.

The aim of the analyses was to identify hazards and to make a course risk evaluation of the concepts. Initially also the intention was to compare the risk of the concepts against each other and to compare the risk of hydrogen filling stations against the risk of conventional stations. The results were also used as input to development of standards and regulations.

Present at the analyses were technical experts among the EIHP2 partners and external technical experts, dependent on the concept being analysed.

Risk Assessment Methodology

A common methodology for coarse risk assessment, Rapid Risk Ranking (RRR), was adapted to take into account specific issues at a public hydrogen refuelling station, see ref. /2/ and /3/. This methodology is suitable for early concept risk evaluations, and further details about the methodology can be found in ref. /2/.

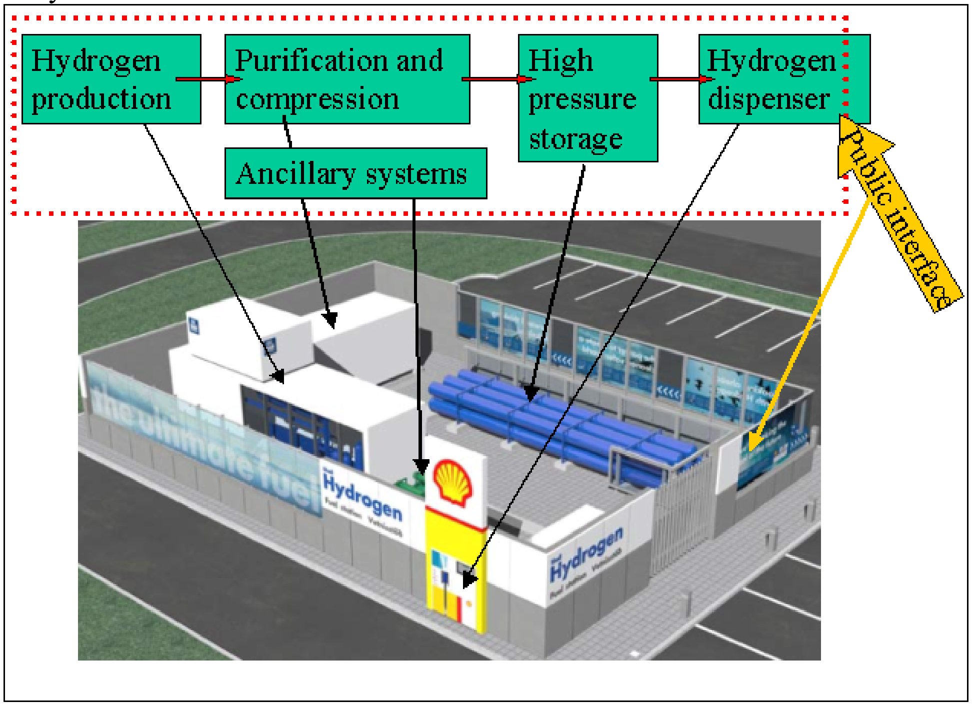
A RRR is carried out as a group session. The group consist of persons with expert knowledge of and experience with the item/process being analysed, representing different disciplines such as process, electronics and instrumentation, machinery etc. A person with risk analysis experience will usually lead the analysis and a secretary report the results.

During the group sessions hazards were identified, and assessed with regard to the probability of their occurrence and their consequences. The probability and consequences are categorised based on "semi quantitative" probability and consequence classes, - probabilities varies from "never heard of" to "occurs several times a year", whereas the consequence varies from "several fatalities" to "minor injury or annoyance". The resulting risk of the identified hazards, which is a combination of probability and consequences are then compared to a risk matrix, where the risk is classified as Unaccepatbly High, Medium or Acceptably Low, dependent on the probability/consequence combination. If the risk is High, a more detailed risk analysis should be carried out, and risk remedial actions might be required. For Medium risk, a more detailed risk analysis should also be carried out, for example a cost benefit analysis.

Description of refuelling station concepts

A gaseous hydrogen filling station based on onsite production of hydrogen can be divided into several main blocks, see illustration in figure 1:

Figure 1 Illustration of main blocks of a hydrogen filling station based on hydrogen production onsite. The 3D drawing is from the hydrogen filling station ECTOS at Reykjavik, ref. /4/. Hydrogen is produced onsite by water electrolysis and is used to fuel 3 Daimler Chrysler buses.



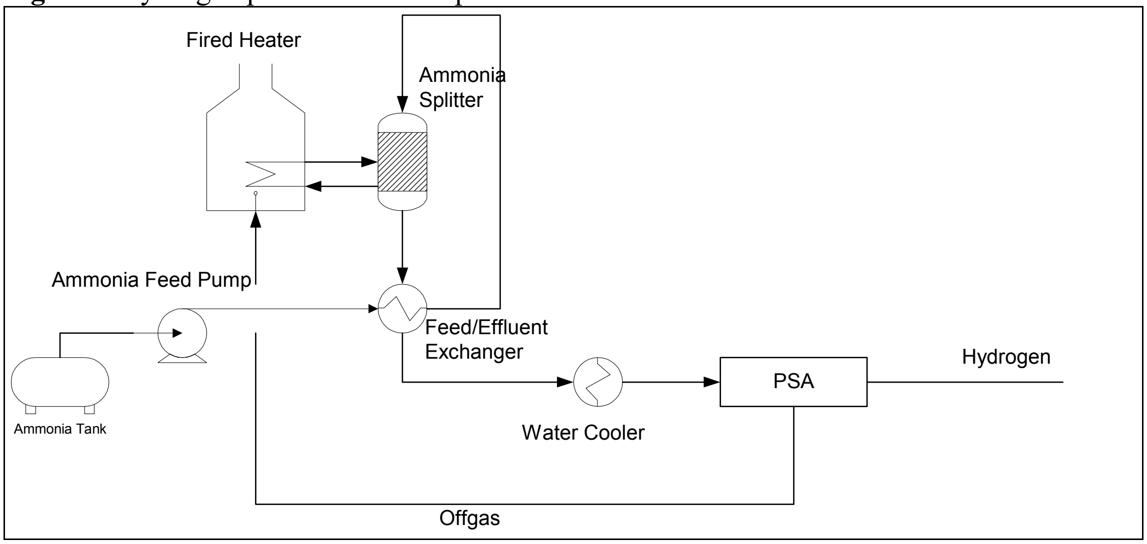
The only difference between the concepts analysed is the hydrogen production technology. Downstream the production unit the concepts were assumed to be similar, consisting of purification, compression, gas distribution, storage and dispenser.

The production capacity of hydrogen was assumed to be 60 Nm^3/hour (similar to the CUTE project (Clean Urban Transport in Europe) stations ref. /5/.

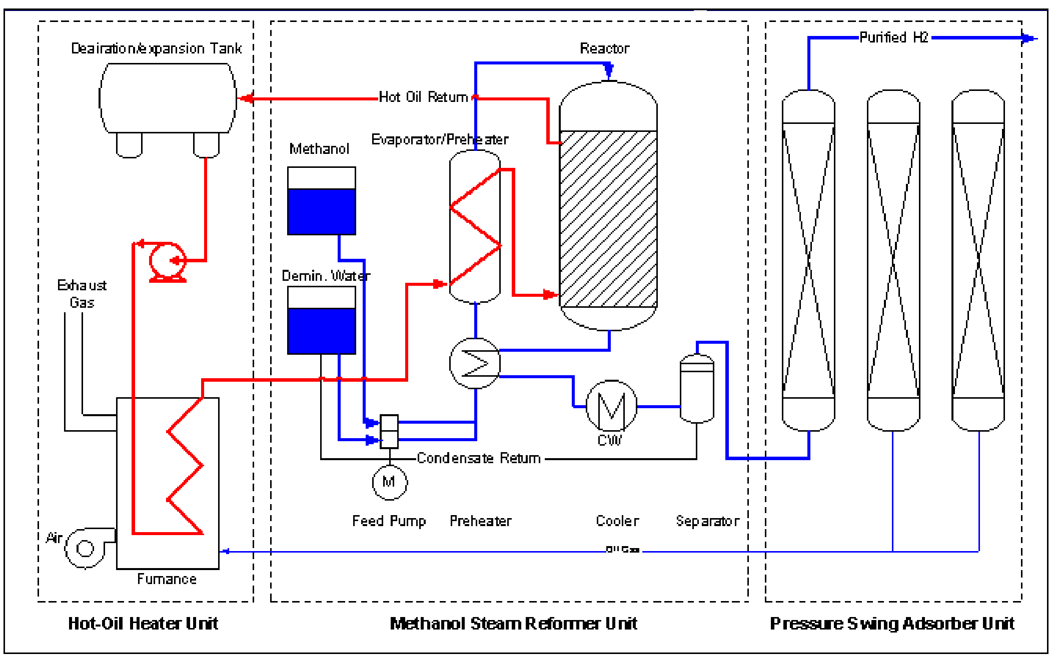
Production concepts

Illustrations of the production concepts are shown in figure 2 a) – 2d). More detailed information can be found in ref. /6/ /7/ /8/ and /9/.

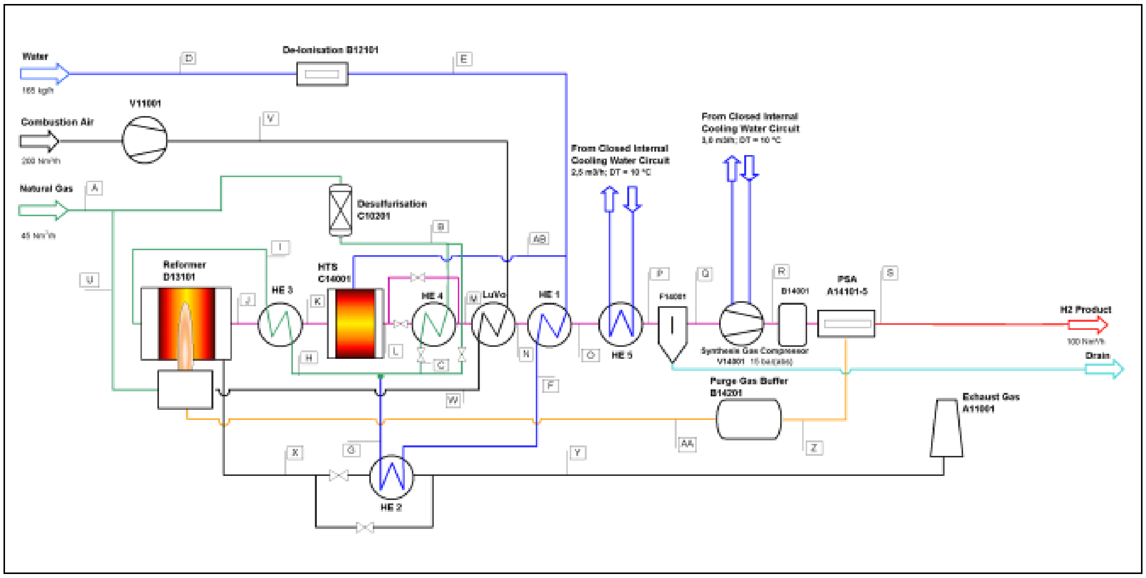
Figure 2 Hydrogen production concepts:



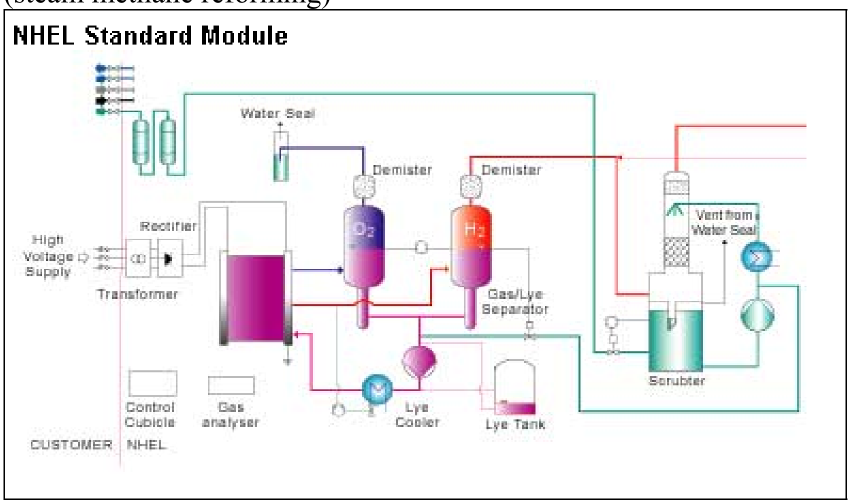
a) Concept 1: Simplified flow diagram for hydrogen production by ammonia splitting



b) Concept 2: Simplified flow diagram for hydrogen production by methanol steam reforming (MSR), including Hot-Oil Heater Unit and PSA unit.



c) Concept 3: simplified flow diagram for hydrogen production by natural gas reforming (steam methane reforming)

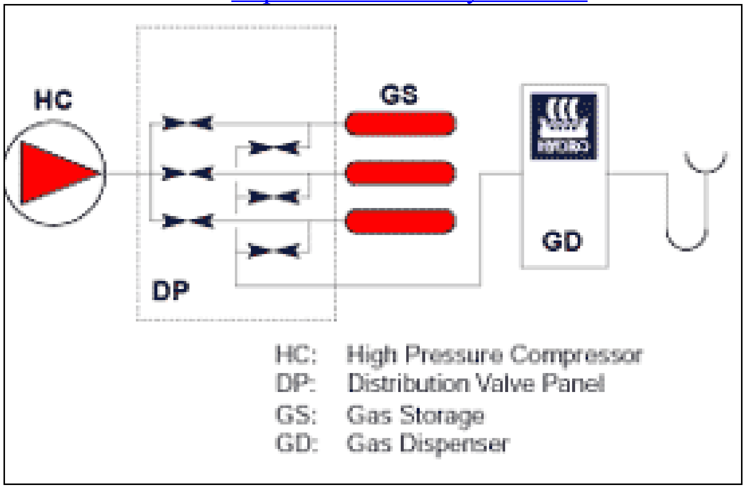


d) Concept 4: Simplified flow diagram for hydrogen production by water electrolysis. Sketch taken from http://www.electrolysers.com

Filling station downstream production unit

A principal sketch of the downstream units is shown in figure 3.

Figure 3 Principal sketch of a hydrogen filling station downstream gaseous hydrogen supply. Sketch taken from http://www.electrolysers.com



Compression

The produced hydrogen will after being dried and purified, be transferred to the compression unit where it will be compressed to about 450 bar (typical for the CUTE stations). The compressor(s) are expected to be located inside a container or some type of weather shed, see. Figure 1.

Storage

The produced and compressed hydrogen will be transported in a pipeline to high pressure storage vessels. The vessels are divided into several vessel banks, called the high pressure bank, the medium pressure bank and the low pressure bank to be able to carry out a three stage "cascade filling" of the vehicles. A two stage cascade filling system combined with a booster compressor, or a multiple stage cascade filling system with more than three pressure banks are other options. This is to ensure that the on-board vehicle storage tank reaches the optimum fill pressure within the required time. Each vessel bank is equipped with it's own pressure relief devices and pressure monitoring instruments

Typical storage pressure today is in the order of 350 – 450 bar, but it is expected that the storage pressure may be significantly higher in the near future (600 – 900 bar).

The storage cascades will be filled from the production side, one at a time, and the produced hydrogen will first flow to the high pressure bank, then to the medium pressure bank, and the low pressure bank will be the last filled vessel bank. This is to increase the efficiency of the filling process.

The storage and refuelling system assumed is based on cascade filling and high pressure storage. There may also be other alternatives.

Dispenser/refuelling

The Fuel Gas Dispenser is a "stand-alone" unit, which provides the mechanical interface between the hydrogen fuel station storage tanks and the vehicle together with safety features and metering equipment. The dispenser consists of a small enclosure where regulation and control valves are located. The filling sequence may be based on cascade filling or cascade filling combined with a booster compressor.   The compressed gas hydrogen dispenser will have a vent stack line to the atmosphere.

Purging system

Inert gas purging systems, which can be initiated automatically or manually will be an important ancillary part of the filling station. Inert gas purging systems may be used during start up and shutdown and in emergency situations.

Manning

Future hydrogen filling stations, including the production unit, may be fully automated and can be unattended. For demonstration stations, such as in the CUTE project, operation personnel will be located at a certain distance from the station or at the station. Remote monitoring will be carried out, and shut down to failsafe conditions may be carried out automatically or by emergency buttons at the filling station area or from a remote location.

Results

General observations

Very sparse technical input was available at the time of analyses. This was due to confidentiality aspects related to accident statistics and technical input. In addition the concepts were not finally designed and there is still some way to go until technical information is ready for some of the production units.

Purification units downstream the production unit, such as PSA (pressure swing absorption) units, were not analysed.

Identified risk of production units

The results from the RRR analyses were very dependent on the participants. A better basis for comparison of different concepts may have been achieved if all participants had been present at all analyses. This was not possible to achieve due to practical reasons. The risk results below can therefore not be used as a basis for comparison between production/supply concepts, but as a listing of potential hazards for the different concepts.

For all concepts the risk of releases of flammable gases inside confined areas should be addressed. Separation of units to prevent backflow from downstream units, gas and/or fire detection coupled to automatic shutdown and fast depressurisation and purging with inert gas will reduce the risk. Prevention of backflow inside a production enclosure/container from the high pressure sections in case of a hydrogen leak is a critical aspect; back flow **must** be prevented.

Identified hazards for the different production concepts are included in tables below.

Table 1
Results from risk assessment of production concept 1: Hydrogen production by ammonia splitting.

Process unit	Identified hazards/risks	Suggested risk reducing measures
Ammonia storage including filling of storage tank from truck	Rupture/large leak in ammonia filling hose, resulting in toxic heavy gas cloud exposing the surroundings. Risk for persons around the installation.	• Atmospheric refrigerated liquefied ammonia implies less risk than pressurized ammonia, transportation of refrigerated ammonia should be considered • Cordoned-off area during ammonia

		unloading • Filling hose designed to withstand external impact • Regular checks of rupture valves • Driver present during filling • Double walled storage tank with gas detection in shell coupled to a warning system should be evaluated
Ammonia splitting unit	Rupture of coil pipes inside ammonia splitting reactor, risk for material damage/downtime.	Installation of temperature control inside NH_3 splitter which will stop supply of ammonia
	Small leaks from inlet of ammonia splitting reactor due to wear out failure. Hydrogen gas will first be released followed by ammonia. May cause frequent smelling problems at filling station. Environmental risk.	Capacity of ammonia absorption process should be designed to minimize this problem
Compressor unit	Ammonia splitting not working properly due to circuit failure. Consequence may be liquid slugs in compressor. Risk for material damages/downtime.	• Install system for detection of failure coupled with shut down of NH_3 supply • Monitoring of ammonia content in hydrogen/nitrogen mixture or at outlet of reactor coupled to emergency shutdown

Table 2

Results from risk assessment of production concept 2: Hydrogen production by methanol steam reforming.

Process unit	Identified hazards/risks	Suggested risk reducing measures
Methanol storage	Rupture of methanol storage tank. Environmental risk.	Drainage systems should be designed for the whole tank capacity. Interceptor drainage (will be able to drain 7000 l effectively)
	Fire in methanol storage tank. Risk for people and environment.	▪ Tank is designed to withstand 2 hours fire exposure (standard) ▪ Flame arrestor ▪ Stage 1 vapour recovery. Pressure vacuum valve. ▪ Double walled tanks
MSR unit	Methanol/water leak to the hot oil system in vaporiser or reactor Material damages, downtime.	▪ Quality check of water and methanol
	Gas leaks (H_2, CO and CO_2) to atmosphere, risk for toxic exposure of persons, fire risk. Explosion risk especially if plant is placed in container.	▪ Isolation/segmentation valve ▪ CO detection ▪ Separation of units to prevent backflow from PSA unit. ▪ Fast depressurisation ▪ Explosion relief

Table 3
Results from risk assessment of production concept 3: Hydrogen production by natural gas reforming.

Process unit	**Identified hazards/risks**	**Suggested risk reducing measures**
Production unit	Tube rupture inside reformer caused by hotspot development on reformer tubes initiated by deactivation of reformer catalyst say by sulphur poisoning, risk for material damages.	▪ Cu-catalyst as sulphur guard in the bottom of ZnO bed. ▪ Pre-reforming upstream reformer ▪ Gas quality requirements to NG supplier
	Tube rupture inside reformer caused by hotspot formation on reformer tubes initiated by deactivation of reformer catalyst by coke formation from higher hydrocarbons (C_2+) in natural gas due to varying quality of natural gas, risk for material damages.	▪ Pre reforming ▪ Design with low inlet temperature to reformer, short connecting lines to reformer ▪ High S/C (Steam/Carbon) ratio
	NG leak in heat exchanger due to metal dusting, risk for material damages.	▪ High S/C ratio ▪ Appropriate material selection ▪ Improved design (use of boiling water and steam for cooling)
	Natural gas (NG) leak inside reformer due to metal dusting, material risk.	▪ High S/C ratio ▪ Appropriate material selection
	Pipe rupture caused by pressure explosion due to valve failure or human failure, risk for persons or equipment.	▪ Remote operated process will reduce the probability of human failure. ▪ Regularity requirements to suppliers of control system (PLC and valve operation)
	Large leak of flammable gas NG/H_2/CO-mixture inside container due to wear and tear or human failure, risk for material damages and for persons.	▪ Gas detection which activates: a) emergency ventilation, b) opening of ceiling an/or walls and c) closure of segmentation valves ▪ Segmentation valves should be located outside container in an area with good natural ventilation. ▪ Explosion relief of container

Table 4
Results from risk assessment of production concept 4: Hydrogen production by water electrolysis.

Process unit	Identified hazards/risks	Suggested risk reducing measures
Electrolyser unit	H_2 and O_2 gas mixture in electrolysis cell, local ignition causing pressure wave through electrolyser, material damages.	Continuous measurement of H_2 in O_2, critical H_2-concentration <LFL; controlled shutdown of installation.
	Imbalance in liquid level in separator.	Shutdown, separators min 50% water filled, level switches.
	Lye escaping through vent line, may expose persons and e.g vehicles outside the production unit.	Expanding vent line with water trap. Vent stack kept frost free by heating elements in container.
	Lye splash/exposure on personnel during maintenance.	Transparent cover for monitoring, full facial cover, including safety glasses) and personal protective equipment required.

Identified risk at gaseous hydrogen filling station downstream production unit

In the following scenarios identified to represent unacceptable risk are described and suggestions to risk reducing measures are briefly discussed. Aspects coupled to safety distances and protection against sabotage is also discussed.

Compressor unit

Ingress of air in suction side of compressor implies risk for internal fire or explosion and significant material damages. Special design for hydrogen compressors to prevent ingress of air (coupled to temperature and pressure indicators) will reduce the risk.

Compressors are units with high leak frequencies, and if located in confined areas, the risk of gas accumulation should be addressed and measures taken for control of such situations.

Leaks from high pressure

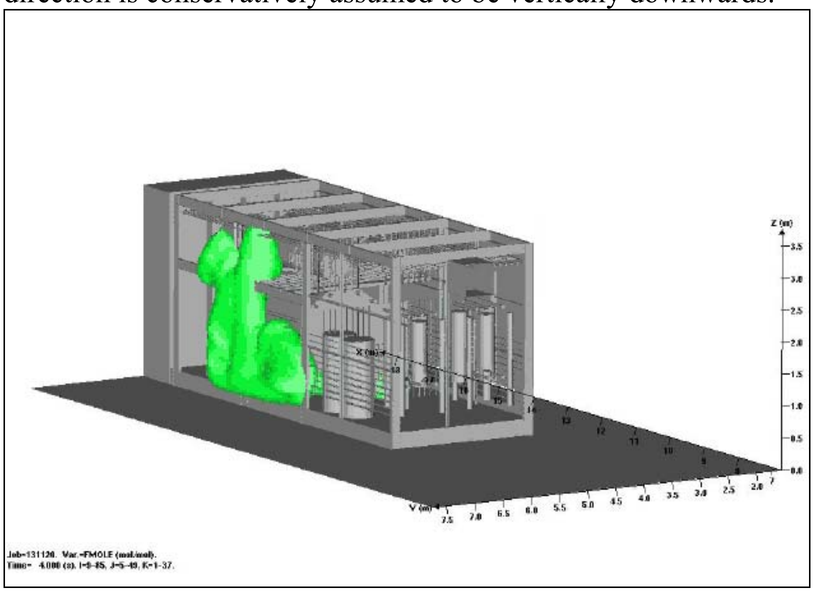
The high pressures in storage tanks and equipment downstream the compressor will, in case of a leak, lead to large release rates compared to leaks from systems with low pressure. Even if such releases are to take place outdoors in unconfined areas, and the conditions for dilution of hydrogen are good, this may lead to significant flammable gas clouds and hazard distances of several meters. The reason is that the impulse forces dominate above the negative gravity forces at a significant distance downwind the release source. The release direction plays an important role see ref. /10/. Since the ignition probability of hydrogen is high, see ref. /11/, and hydrogen fires are nearly invisible in daylight this scenario is a significant risk.

High pressure leaks in confined areas

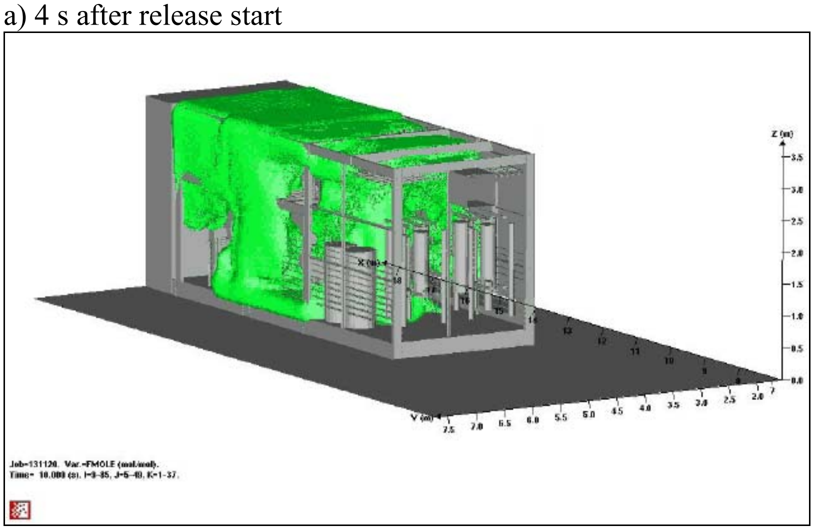
If high pressure hydrogen releases occur in a confined area (e.g. inside a container for compression or inside a confined storage area) impulse and buoyancy effects will influence on the dispersion. The confinement will trap the gas, the gas jet will impinge on walls, floor or other objects present, and loose velocity, and thus the impulse will be reduced. There may be special conditions related to the flow pattern inside the confined area, dependent of ventilation, extents and position of obstacles etc., that may lead to accumulation of hydrogen at lower levels. However, the released gas will usually rise to the ceiling.

The gas will accumulate, and large flammable gas envelopes may be created, if no measures are taken for shutdown of release or effective dilution and removal of the gas. A release scenario showing a 10 g/s release of hydrogen inside a process container of 40 m^2 is illustrated in figure 4. The calculations, carried out with the CFD code FLACS , ref. /12/, indicate that even large ventilation rates (300 volume changes per hour) will have limited effect on releases of this size.

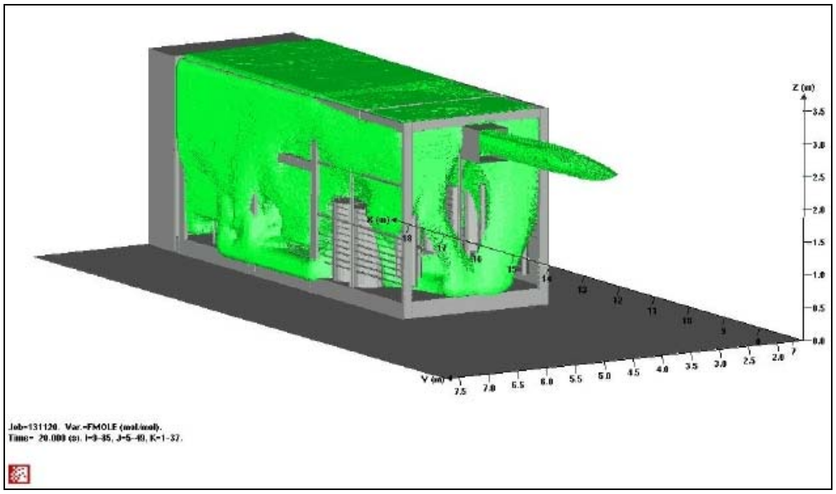
Figure 4 "Snapshot" of hydrogen gas cloud, showing the gas envelope with H_2-concentration in air > ½ LFL (2 vol%), at three different timesteps. Release rate 10 g/s, sonic velocity. Ventilation capacity 300 volume changes per hour. Release position is about 1.5 m above ground level, halfway between the end walls and close to one of the sidewalls. Release direction is conservatively assumed to be vertically downwards.



a) 4 s after release start



b) 10 s after release start



c) 20 s after release start

These results indicate that, whenever possible, hydrogen processing systems or storage at high pressures should be placed outdoors in well ventilated areas. If, for some reason, hydrogen systems have to be located indoors, it is very important that the risk of leaks and gas accumulation is assessed. If the risk is not acceptable risk reducing measures such as gas detection coupled to automatic activation of emergency ventilation, relief of hydrogen to safe area, purging etc. should be implemented.

Relief of hydrogen to atmosphere from safety valves

Hydrogen may be relived to atmosphere from time to time, caused by pressure build-up and opening of safety valves or by controlled ventilation in case of maintenance. Relief through safety valves may cause rather high release rates when the back pressure is high. The flammable gas cloud may reach several meters away from the outlet. It is therefore important that the relief point is located so that releases will not lead to hazards in the vicinity. This should especially be taken seriously in case of location in large cities with a high density of high buildings.

Hazards during refuelling

As pointed at, leaks from process equipment containing hydrogen at high pressures may lead to significant flammable gas clouds even in unconfined areas. Releases during refuelling where persons may be exposed to the gas jet were identified to represent a significant hazard. Hydrogen gas and hydrogen releases are virtually invisible in daylight. It is therefore very important that all precautions are taken to avoid hazardous situations during refuelling of vehicles where public customers may be exposed to the consequences of a leak in case of ignition. Risk reducing measures were suggested as follows:

- Only use high quality equipment that are documented for the expected pressure, temperatures, cycling etc.
- Regular inspection
- Fast leak detection and shutdown
- Design and layout so that the probability of hazardous situations close to the dispenser is reduced to a minimum
    - Automatic retraction of refuelling hose after refuelling
    - Design of drive in to minimise the probability of collisions

- No ignitions sources (smoking, open fire, mobile phones forbidden)
- Roof above dispenser should be avoided or designed so that released gas can not accumulate
- Grounding of car and refuelling hose, person refuelling at same electrical potential

Layout – Safety distances – Area limitations – Fire walls/protection

The high pressure is a significant challenge related to localisation in densely populated areas, where large safety distances may be impossible to achieve. Location in such areas should therefore imply strict requirements to quality, inspection and protection of refuelling stations against impact that may lead to leaks. Also sabotage should be taken into consideration.

Walls/fences around the units may lead to reduced safety distances requirements if they are designed so that flammable concentrations will not reach outside these fences. In design of such fences the following should be considered:

- Flow pattern, wake effects, increased probability of gas accumulation
- Larger probability of explosion or larger explosion pressure in case of ignition due to increased confinement
- Probability of flying debris in case of explosion
- Splint proof window panes

Conclusions

For all filling station concepts scenarios representing significant hazards and significant risk were identified. These scenarios need to be analysed in more detail to obtain a more accurate estimate of the actual risks. Common for all concepts are releases of hydrogen from high pressures leading to large hazard distances, and hydrogen releases in confined areas leading to risk of explosions. This is a challenge, especially in densely populated and crowded areas. Risk reducing measures are suggested and should be taken into consideration in the development of standards. Due to lack of experience and specific data, there is clearly a need for further research related to hydrogen hazards and development of safe systems.

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