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Hydrogen related accidents and lesson learned from events reported in the in east continental Asia

Abstract

Bin Wang[a] (Bin.Wang@bam,de), Pietro Moretto[b] (Pietro.MORETTO@ec.europa.eu), Georg Mair[a] (Georg.Mair@bam.de), Teresa Orellana Pérez[a] (Teresa.Orellana-Perez@bam.de)

[a] *Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany*

[b] *Joint Research Centre JRC, European Commission, Westerduinweg 3, Petten 1755 LE, Netherlands*

Hydrogen as an energy carrier plays an important role in carbon neutrality and energy transition. Hydrogen is the lightest element, with a density of only 0.08375 kg/m3 in gaseous form at standard temperature and pressure (STP); as a result, hydrogen is usually stored and transported in a highly compressed form. It is prone to leakage and has a very low ignition energy of 0.017 mJ. Safety remains a challenge in the use of hydrogen as an energy source. This paper examines approximately 20 hydrogen-related accidents in China over a 20-year period, focusing on the root causes, consequences of the accidents and responses to them. These accidents occurred in the production, storage, transport and application of hydrogen, with different causes in different locations and resulting in losses at different scales. Some statistical evaluations were conducted to learn lessons from the accidents. The main objective of this paper is (i) to retrieve a set of hydrogen related incidents from a region which is under-represented in incident repositories, (ii) to contribute to a generalised lesson learned from them, and (iii) to assist the definition of realistic scenarios for commonly occurring hydrogen accidents.

1 Introduction

1.1 Risks associated with hydrogen properties

Hydrogen is being increasingly used as an energy carrier because it is clean and can be produced from renewable sources. Due to its low density, hydrogen is often stored and transported in a highly compressed form in high pressure storages. One of the main risks associated with compressed hydrogen gas is the potential of rupture or leakage in the storage systems. If this were to happen, the high-pressure gas could rapidly escape, potentially causing an explosion or fire.

Hydrogen is highly flammable; it can ignite at concentrations from 4% to 75%. The common ignition sources for hydrogen gas are electrical sparks, open flames, hot surfaces. Hydrogen gas can be ignited even without obvious presence of an ignition source, so called autoignition. Furthermore, hydrogen gas has a low ignition energy, which means that it can ignite at relatively low temperatures or when exposed to a small spark or flame.

As mentioned, hydrogen has a small size and a low atomic weight, making it highly mobile and able to penetrate the surface of metals. The reactivity of hydrogen with metals can also be enhanced by factors such as high temperatures, pressures, or the presence of impurities. In addition, some metals are particularly susceptible to hydrogen embrittlement, such as high-strength steels, titanium, and aluminium alloys. Hydrogen embrittlement also contributes to the accidents related with hydrogen facilities.

1.2 Objectives of this work

Considering the limited flow of news on incidents coming from Asia, this work reports the results of an in-depth manual scan of public information on recent incidents. The information contained in the original sources has been structured according to incident 'descriptors' as described in the following chapter and assessed with the help of already available data. The individual return of experience of these incidents has been used to formulate qualitative and preliminary conclusions in the last chapter, hoping to contribute in this way to inform future improved safety strategies. All new events retrieved and presented in this paper will contribute to the population of the database HIAD 2.0 [2].

2 Methodology

The events presented in Chapter 3 come from publicly available sources, mainly from online news. Few of them are incident investigation reports mainly in Chinese.

The Event Descriptors adopted in this paper are based on those used by the database HIAD 2.0 [2]. Their number is however a smaller subset of the database ones, because of the intrinsic lack of technical information available for these events. Even with this smaller subset, it has not been possible to assign a value or a narrative to each Descriptor, due to the low quality typical of online news.

Table 1 - list of the Event Descriptors used in Chapter 3

Primary event descriptors ***('What did happen, and why?')***	**Systems descriptors** ***('Where did it happen?')***	**Consequences and emergency actions descriptors** **('*After the end of the incident*')**
Date *[day/month/year]* **Location** *[industrial area, inhabited centre, road, etc.]* **Event description** *[a narrative]* **Physical effects** [*classification in releases without ignition / fires / explosions*]	**Application** *[a description of the plant, unit, system affected]* **Location** [*open / confined / semi-confined*] **Operational condition** [*normal / abnormal such as repair,*	**Emergency actions** *[automatic, manual shutdown, fire brigade actions, etc.]* **Consequences** *[on persons, environment, materials]* **Corrective actions** *[modification of the operation / design /*

Cause *[immediate, intermediate / contributing, root cause, etc.]*	*maintenance, unexpected environmental conditions, etc.*]	*emergency adopted by the authority in charge to avoid repetition of the event]* **Lesson Learned** *[new knowledge from the specific event]*
Information source *[web link, literature reference]*		

Regarding the event description, we have tried to remain as near as possible to the original sources. However, news media, when reporting incidents, are affected by severe shortcoming, because event providers (journalists or ocular witnesses) do not have enough technical knowledge to provide an accurate description of the facility, the equipment involved and the sequence of events. The consequences are incomprehensible statements and evident contradictions. Moreover, the translation from the original language into English may contribute to the deterioration of the quality of the technical details. We have tried to improve the comprehension of the original texts with more pertinent and logic descriptions of the technical aspects, wherever possible based on information from multi-le sources.

The paper is not the place for a discussion on theoretical differences between *incident*, *accident* and *near miss*. We have adopted the definition of incident contained in ISO 19880-1, which considers *incident* and *accident* as equivalent. Unfortunately, there is no quantitative, unambiguous definition of *near miss.* Nevertheless, none of the events presented here could be classified as *near miss*. We have also adopted the term *explosion* in an almost common-sense meaning, without trying to specify or guess the underlying physical and chemical phenomena: almost in very specific cases it is possible to conclude *a posteriori* if an energy release involved a detonation or deflagration.

3 The individual accidents

3.1 Industrial incidents

3.1.1 Explosion at a hydro-treatment unit of a refinery

Source: "Electric horse" Web-news of 17 December 2021, available at https://mp.weixin.qq.com/s/VXAhZhm4BDdUrLuY9cN5kA (last retrieved 20.02.2023)

Location: industrial areas

Date: 13 December 2021

Event description: In a residual-oil hydrotreating (also called residual oil hydrogenation) plant, a hydrogenation unit caught fire with a huge bang, followed by a fireball in the form of a mushroom cloud. Black smoke began to billow up in the sky and was clearly visible from several kilometres away, (see Figure 1).

Application: residual oil hydrogenation unit in a refinery. Residual oil is the residue remaining after the distillation and processing of petroleum. "Oil hydrotreatment" refers to the purification of the oil from harmful impurities such as sulphur, nitrogen, and metals. In presence of a catalyst, the hydrogen reacts with these components, forming hydrogen sulphide, ammonia and metal sulphides. At the same time, some of the larger molecules of the residual oil are cracked and hydrogenated into smaller molecules, which also react to produce metal sulphides.

Classification of the physical effects: Explosion and fire

Causes**:** Both immediate and root causes are unknown. Although it is probable that hydrogen was at least one of the flammable gases contributing to the starting of the fire, without knowing the causes it is not possible to conclude on the role of hydrogen.

Emergency measures: the fire started at 9:43am, the city fire fighting service immediately responded, and the fire was extinguished at 11:20 am (in 1 hour 37 minutes).

Consequences**:** four persons lightly injured, no impact to air quality and environment.

Corrective actions: unknown

Lesson learned: unknown

Figure 1: Video still from videos taken at the scene of the accident (Source: Web-news of 17 December 2021, available at https://mp.weixin.qq.com/s/VXAhZhm4BDdUrLuY9cN5kA (last retrieved 20.02.2023)

3.1.2 Explosion of a flammable mixture in a petrochemical plant

Source: investigation report available at http://www.zhuhai.gov.cn/yjgl/gkmlpt/content/2/2608/mpost_2608730.html?from=groupmessage#2120 (last retrieved 20.02.2023)

Location: industrial area

Date: 14 January 2020

Event description: the incident occurred in a catalytic reforming unit. At 13:41, a leak occurred at the 90° elbow of a pressure pipe containing a mixture of hydrogen and naphtha. This pipe was located between the pre-hydrogenation heat exchanger and the pre-hydrogenation product tower heat exchanger. The flammable material leaking from the pipe burst into flames, and at 13:51 and 14:21 there were two more explosive combustions.

Some of the nearby towers, pipelines and other equipment and facilities affected by the following high temperature flames continued to burn, with varying degrees of damage or rupture and leakage of combustible materials. The intensified combustions and fire triggered two subsequent deflagrations, 10 minutes and 40 minutes later respectively, after the first explosions.

Application: Catalytic Reforming Unit of a petrochemical plant.

Classification of the physical effects: explosion and fire.

Causes: The immediate cause of the pipe rupture was corrosion. Due to corrosion, the wall thickness of the pressure pipe 90 ° elbow had become thinner and ruptured under an internal pressure of 0.2 MPa with an opening of about 950mm × 620mm. The hydrogen gas mixture ejected to form an explosive mixture. The friction between the ejected gas and the pipeline generated electrostatic sparks, which triggered a fire.

Regarding the root technical causes, the affected pipeline was continuously in an acidic environment. The company was not monitoring and analysing the acidic water in the pre-hydrogenation tank. The continued recycling of this acidic water led to increasing concentrations of H2S, HCl and NH3 and intensified the corrosion of the pipeline.

A contributing cause was the temperature of the pipeline. The operating temperature of the affected pipe was supposed to be 150°C, and the design temperature was 170°C. However, the actual operating temperature of the pipeline at the time of the accident was about 180°C, and this accelerated the corrosion process.

The investigation found also organisation causes in the failing of implementing preventive safety measures (see below at lesson learned).

Emergency measures: The municipality safety department intervened with 49 fire trucks and 121 firefighters. They acted according to the strategy: "first control, then elimination", and ""cooling and suppressing explosions, focusing on protection, and preventing spread", using equipment such as fire-fighting robots and mobile fire-fighting water cannons. The public security department dispatched 628 police officers to implement traffic control and maintain order at the scene. The health department dispatched 5 ambulances to stand by on site. Approximately 5 hours later, the fires were completely extinguished.

Consequences**:** The accident caused different degrees of damage to buildings, equipment and facilities in the pre-hydrogenation unit, reforming unit and product refining and separation unit of the catalytic reformer with no casualties.

Corrective actions: a legal action was started against the operator of the plant

Lesson learned: The investigation revealed sever shortcoming in the definition and execution of safety measures for the site:

(1) The safety management system of special equipment was not implemented, in particular the part related to corrosion monitoring and prevention. The operator did not execute the annual thickness measurement procedures. Also, they did not realise that measurements performed previously by an external inspection were demanding corrective actions.
(2) The procedures for the analysis of acid water quality were not well designed and not implemented.
(3) The pressure pipeline was not respecting the requirements of the more recent regulations, and therefore, de facto, illegal.
(4) The operator did not perform the regular (annual) inspection of all the special equipment on site.

3.1.3 Hydrogen fire on the generator of a power plant

Source: https://www.sohu.com/a/277222433_739772 (last retrieved 20.02.2023)

Location: power plant

Date: 7 November 2018

Event description: The incident occurred at a power generator during the shutdown of one reactor unit. Hydrogen leaked from the cooling circuit of the generator due to damaged sealing. The hydrogen ignited. The fire was extinguished after 1 hour 40 minutes.

Application: the turbine-generator system of the power plant (a non-nuclear area of the plant). Hydrogen is used as coolant of the system.

Causes: The immediate cause of the accident was the release of hydrogen from a sealing on the generator. The root cause is related to an electrical fault that caused the generator speed to suddenly rise from a still state to 1145 r/min, causing violent vibration of the generator rotor which lead to wear of the sealing leakage of hydrogen gas and the consequent hydrogen explosion. The cause of the ignition is probably an electrostatic spark.

Emergency measures: : unknown (probably just internal fire-fighting action).

Consequences: unknown

Corrective actions: unknown

Lesson learned: a stronger focus on safety management of equipment is needed. There are several incidents related to hydrogen explosions in a hydrogen-cooled generator in power plants, (for further examples see for example this Chinese online source https://www.gg-lb.com/asdisp-65b095fb-35521.html).

3.1.4 Explosion and fire at a diesel hydrogenation plant

Source: http://www.lcakzx.com/show.asp?id=798, ref [1], (last retrieved 20.02.2023)

A diesel hydrogenation plant is a process plant used to hydrogenate and upgrade petroleum products reacted with hydrogen under high pressures.

Location: petrochemical plan, industrial area

Date: 12 March 2018

Event description: the incident affected the raw material buffer tank (design pressure 0.38 MPa) of a diesel hydrogenation unit in a refinery. A buffer tank is located between the hydrogenation reactor and the raw material storage tank. During pressure fluctuations in the lubricating oil system of a hydrogen compressor, the operator handled the situation improperly, resulting in an abnormal shutdown of the compressor, causing the hydrogen feed pump to interlock and stop.

After the pump interlocked, the outlet valve was not closed in time and the two check valves failed. The high-pressure hydrogen gas in the system escaped into the tank. This caused an overpressure in the hydrogen buffer tank, which burst leading to a hydrogen-air explosion and a following fire, while diesel liquid spilled out to form a liquid pool on the ground.

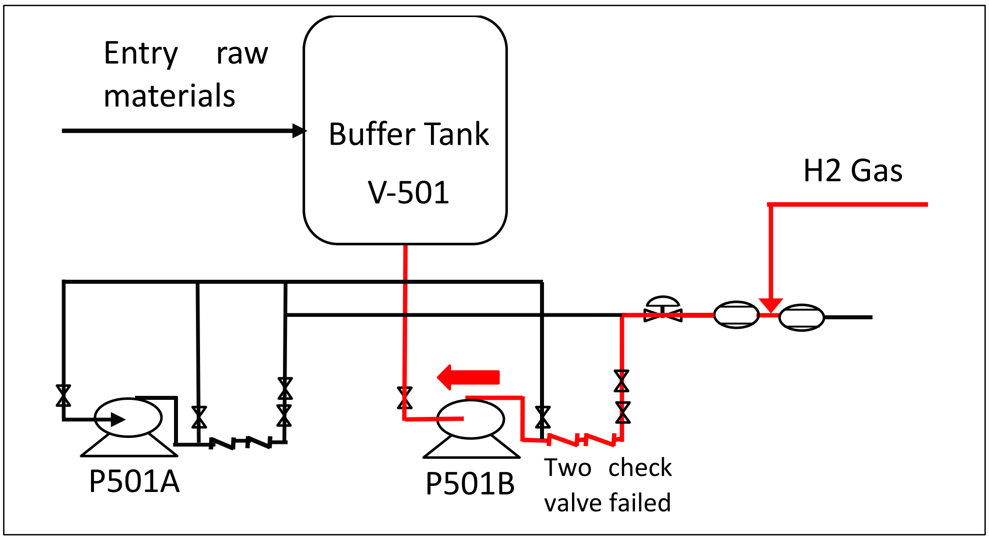

Figure 2: After the hydrogen compressor has stopped working, the high-pressure hydrogen of the reaction system is reversed through the outlet check valve P501B into the V501, ref [1].

Application: diesel hydrogenation unit (600,000 tonnes/year diesel) of a refinery.

Causes: The immediate cause of the explosion was due to the tank being erroneously filled up with hydrogen. Part of the root cause sequence was the wrongful operations of the operator. However, if an operator executes a wrong action, the root cause could be lack of instruction, lack of training, or shortcomings in the design.

Emergency measures: unknown

Consequences**:** 2 fatalities, 1 injured person， economic loss of about Euro 0.48 million.

Corrective actions: unknown

Lesson learned: unknown

Figure 3: Damaged tank shown in accident scene, ref [1].

3.1.5 Pressure vessel failure in a chemicals plant

Source: http://www.safehoo.com/Case/Case/Container/202104/5636635.shtml (last retrieved 20.02.2023)

Location: chemical factory near a city

Date: 28 June 2015

Event description: The vessel affected by the incident was a gas storage used for the desulphurisation process. The desulphurization gas had high hydrogen content. The vessels had cracks in the upper transverse fillet welds at the gas inlet which caused low stress brittle fractures. The cracks had been found during the maintenance, but not fixed. This eventually caused a gas release.

Approximately 2.5 hours after that a leak was detected and reported, a first explosion occurred. As the heat exchanger explosion was facing the desulphurisation pump room, the leaking desulphurisation gas gathered in the pump room, under the effect of the first explosion flame. 7 seconds later, a secondary explosion occurred in the desulphurisation pump room, resulting in 3 deaths. Due to the impact of debris from the first explosion and the high temperature of the open flame, a third explosion occurred in another cracked pressure pipe.

Application: desulphurization unit of an ammonia and fertilisers manufacturer.

Classification of the physical effects: explosion

Causes: the immediate cause was corrosion of a welded joint, with a low brittle fracture resistance. One of the root causes is lack of maintenance and repair.

Emergency measures: unknown

Consequences**:** three fatalities, six injured persons, and a direct economic loss of 100 million Euros.

Corrective actions: unknown

Lesson learned: unknown

3.1.6 Explosion in a refinery

Source: http://3g.k.sohu.com/t/n478449026 (last retrieved 20.02.2023)

Location: chemical plant, industrial area

Date: 18 March 2015

Event description: the explosion occurred inside the lower hydrogenation tower of a hydrogen peroxide unit, damaging the distribution tray inside the tower.

Application: Hydrogenation tower for hydrogen peroxide plant, chemical plant

The hydrogenation tower of a hydrogen peroxide plant is the equipment where hydrogen is produced, by letting hydrogen peroxide reacting with a catalyst. The hydrogenation tower is usually made up of a series of continuous reactors which consists of a catalyst bed and material pack bed. The catalyst bed is a special layer of material, usually a metal such as iron, nickel or copper, which is used to facilitate the hydrogen generation reaction.

Classification of the physical effects: fire and explosion, delayed ignition.

Causes: Immediate cause was the pure hydrogen inlet line shut-off valve leakage, and hydrogen gas was strung into the tower and mixed with the air entering from the upper manhole, which exploded when it met the ignition source. Contributing cause was the fact that the personnel of the enterprise did not take effective isolation and entered the lower tower of the hydrogenation tower to work. Root cause was a complete lack of risk management, no maintenance procedure, no risk assessment, no mitigation measures.

Possible ignition sources: one of the possible ignition sources is the ignition of non-explosion-proof tools in use. Operators carry non-explosion-proof steel socket spanners and steel tape measures into the tower, and there is a risk of hydrogen explosion due to impact and frictional ignition during use.

Emergency measures: unknown

Consequences**:** 4 fatalities, two injuries, a direct economic loss of 0.5 million Euro.

Corrective actions: unknown

Lesson learned: Equipment maintenance and management were not in place. Since the hydrogen peroxide plant was put into operation, no regular overhaul had been organised and no regular maintenance. During the event that internal leakage of the valves were found, no effective measures were taken in time, resulting in hydrogen being strung into the lower tower of the hydrogenation tower due to internal leakage of the valves.

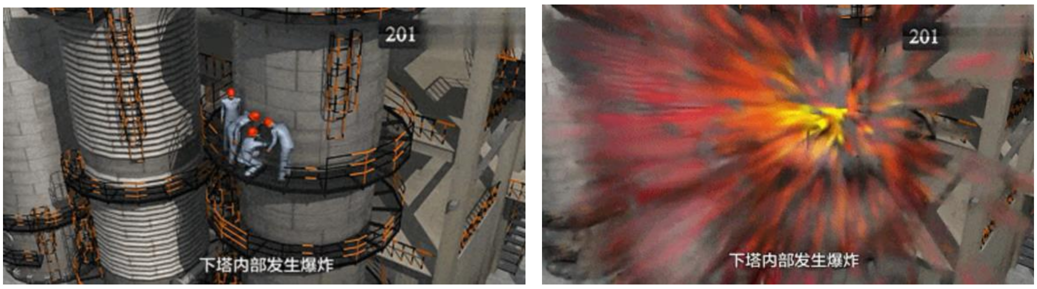

Figure 4: Video still from the accident scene simulation video (Source of the video: http://3g.k.sohu.com/t/n478449026)

3.1.7 Explosion at a methanation reactor

Source: https://www.renrendoc.com/paper/126162606.html (last retrieved 06.05.2021).

The methanation furnace works by reacting methane and steam at high temperatures and pressures to produce synthesis gas. Syngas is a mixture of gases, usually consisting of carbon monoxide and hydrogen.

Location: biochemical fertiliser, industrial area

Date: 23 April 2011

Event description: the day before the incident, the outlet pipe connected to methanation reactor started leaking gas, which contains hydrogen. The leak was temporarily eliminated by a pressurised plug. On the day of the incident, the pipe leaked again, and the same plugging method was still used to stop the leak. This occurred without shutting down the unit and taking safety measures. Approximately one hour later, a sudden explosion occurred at the inlet line of the methanation reactor. The welded joint of outlet pipes that connected to the methanation furnace was operating for a long time in the high temperature hydrogen containing medium. Under this condition, hydrogen embrittlement took place, producing local defects and eventually opening up. The released hydrogen ignited and exploded.

Application: methanation reactor of an agricultural chemicals plant.

Classification of the physical effects: explosion

Causes: the immediate cause was hydrogen corrosion which caused a crack and a gas release. Attempts to stop the leak by temporary measures were executed without stopping the operations and no additional safety measures being put in place were definitively part of the root causes.

Emergency measures: unknown

Consequences**:** 4 fatalities, 2 persons injured. Reactor destroyed, direct economic loss of over Euro 0.78 million.

Corrective actions: unknown

Lesson learned: In the petrochemical industry, leakage often occurs due to the increasing corrosion problems caused by the deterioration of processing raw materials, production, storage and transportation. Leak plugging technology is often being used to ensure the safe and long-term operation of the plant. However, leak plugging with pressure has high operating pressures, which makes it very easy for safety incidents to occur during operation. It is worthwhile to study how to carry out fast and effective leakage plugging under safe conditions, and to standardize the leak plugging technology with pressure.

Figure 5: Accident scene after the explosion (picture source: website https://www.renrendoc.com/paper/126162606.html).

3.1.8 Leakage and ignition of hydrogen from a pipeline

Source: https://www.mem.gov.cn/fw/jsxx/202106/t20210630_390326.shtml (last retrieved 20.02.2023)

Location: chemical plant, industrial area

Date: 22 July 2010

Event description: A mixture of carbon monoxide, carbon dioxide, hydrogen and nitrogen were released from a pipeline, generating a flammable mixture which ignited possibly due to static electricity.

Application: chemical plant, pipeline

Classification of the physical effects: fire and explosion

Causes: unknown

Emergency measures: unknown

Consequences**:** Eight fatalities and 3 injured persons

Corrective actions: unknown

Lesson learned: unknown

3.1.9 Explosion at a Petrochemical plant

Source: https://www.ichemsafe.com/info/3275.html (last retrieved 20.02.2023)

Location: chemical plant, industrial area

Date: 13 March 2006

Event description: a gas mixture (25% nitrogen, 73% of hydrogen, 2% methane) leaked, due to the ejection of the check valve from its connection with the inlet pipe. A large amount of the gas mixed with air and ignited, probably due to sparks generated by the ejected check hitting a metal pipe. It followed an explosion. Its pressure wave hit a gas pipeline causing its fracture and a fire. After about 1 hour and 30 minutes the fire was under control. The shockwave from the explosion caused a gas pipe at the back of the workshop to crack and leak, causing a large fire.

Application: the functions of the mentioned 'workshop' are unknown.

Classification of the physical effects: explosion and fire

Causes: The immediate cause of the incident is the sudden falling-off of the check valve, due to a large deviation of the dimension of the small diameter of the inner flange thread. Its diameter was too small and eventually lead to the separation of two connections. The root cause is related to quality control not properly done and failed inspection.

Emergency measures: unknown

Consequences**:** 2 fatalities, 11 injured persons (out of which 6 were severely injured). Damage estimated around 57K Euro.

Corrective actions: unknown

Lesson learned: The plant operator has to establish and implement a qualification system for purchased components. This will allow the early detection of wrong or not certified materials. Moreover, an inspection system has to be in place, to assess additional risks related to components replacements and repair.

Figure 6: Accident scene after the fire (picture source: website https://www.ichemsafe.com/info/3275.html (last retrieved 20.02.2023)

3.1.10 Explosion of a hydrogen tank in a steel manufacturing plant.

Source: [Causes Analysis and Lessons of An Explosion Accident of 10m3 Hydrogen-Holder](#) (last retrieved 20.02.2023)

Location: steel manufacturing, industrial area

Date: 28 February 2003

Event description: an explosion occurred in a hydrogen storage tank at the hydrogen station of the oxygen plant of the energy centre.

The 10 m^3 hydrogen storage tank at the hydrogen station belonging to the oxygen plant exploded during production operation. The hydrogen storage tank was installed and used by the plant in 1995, with a design pressure of 1,5 MPa, a volume of 10 m^3, a minimum wall thickness of 12 mm, a total length of 4576 mm (height) and an inner diameter of 1800 mm. After the explosion, there were no metal components left, except for the cement prefabricated foundation of the tank base. The main body of the hydrogen storage tank ruptured into 10 pieces, with most of the debris flying away from the site and all debris scattered separately within a 300m radius from the centre of the explosion; 46 pieces of debris were collected.

Application: the hydrogen production unit of a steel manufacturer, consisting of an electrolyser and a hydrogen storage vessel (60 kg, 10 m^3 at 0,6 MPa)

Classification of the physical effects: Explosion

Causes: The results of this test determined that the electrolytic cell was misconnected between positive and negative electrodes during inspection and maintenance (replacement) works. It is suspected that the electrician inverted the electrodes when replacing the cables. This led to an interchange in the hydrogen and oxygen production system.

Emergency measures: unknown (probably none).

Consequences**:** no one was injured. The buildings within approximately 200 m of the centre of the explosion glass was mostly broken. Windows and doors within approximately 100 m suffered varying degrees of damage of varying degrees. Nearly 10 m of the wall to the north-east of the centre of the explosion collapsed.

Corrective actions: unknown

Lesson learned: unknown

3.1.11 Explosion in a fertilisers production plant

Source: Knowledge Network Node -> link to accident report, (last retrieved 20.02.2023)

Location: chemical fertilizer plant, industrial area

Date: 27 February 2001

Event description: A gas (mixture of hydrogen and nitrogen) release occurred in the factory building. It occurred at the outlet valve, during works aiming to replace it. This caused the creation of an explosive gas mixture in the circulation room and surrounding spaces. The valve problem has been found since several years, the poor design and wear caused hydrogen gas leakage. The ignition took place with 9 minutes delay after initial leakage.

Application: circulation machine in a Fertilisers plant

Classification of the physical effects: delayed ignition, detonation.

Causes: the immediate cause was a leak of a mixture of hydrogen and nitrogen from a defective valve. Since the ignition occurred several minutes later, the hydrogen had the time to form a large flammable cloud within the building. The delayed ignition very possibly led to a detonation.

Causes of the ignition could be any of the following: electrostatic sparks generated during the hydrogen leak; high temperature on object surfaces; electrical sparks; personal electrostatic sparks or the air conditioning in an adjacent workshop. For this accident, air conditioning (spark) in the next adjacent workshop ignites the mixed gas.

Emergency measures: unknown

Consequences**:** five fatalities, 25 injured (one severely), explosion area about 680 m, 286k Euro damage.

Corrective actions: unknown

Lesson learned: effective safety measures should be immediately taken after leakage to prevent fire and explosion; valve should be replaced once the problem was found.

Figure 7 - Scene after the incident (source of the picture: [Knowledge Network Node -> link to accident report](), retrieved 20.02.2023).

3.1.12 Fire in a fertilizers plant

Source: https://www.bbaqw.com/al/3022.htm (last retrieved 20.02.2023)

Location: fertilizer plant, industrial area

Date: 13 March 1993

Event description: a gas leakage (approximately 70% hydrogen, 21% nitrogen and the rest carbon monoxide and other impurities) occurred at the connection between a temperature measurement casing and a flange in the carbonization workshop cleaning tower. The leakage was reported to the plant leader, who issued the request to the workers to use iron cards and rubber plates to plug the leak. The operation failed and the leakage continued.

At 17:00, at the request of the plant leader, the workers used a tire inner tube to wrap the leak. However, due to the high pressures in the tower the high-speed by which the gas was released, and the fact that that the rubber is an electrical isolator, electrostatic sparks were produced, which ignited the gas and started a fire.

Application: fertilisers production plant, carbonization workshop cleaning tower

Causes: The cause of the leak is unknown. The direct cause of this accident was the production of sparks when attempting to stop the leak... The contributing/root causes of the accident were, (i) the plant operator violated rules and regulations, issuing requests disregarding health and safety; (ii) the worker also did not take effective safety measures; (iii) a lack of emergency procedures, and probably a lack of risk assessment.

Ignition causes: this accident led to a fire because the conditions at the time were perfectly suited to electrostatic discharge causing a fire.

Emergency measures: According to the source (see References), the following safety actions and measures should be in place and followed when trying to stop a leakage:

(1) Safety technical measures and safety technical specifications such as fire prevention, explosion prevention, corrosion prevention, and heat radiation prevention shall be designed, implemented and enforced.

(2) The intervention team shall consist of a small number of very competent workers, with a strong sense of responsibility, familiar with the working conditions of the equipment and be equipped with one or two supervisors.

(3) These workers shall wear protection equipment appropriated for the working conditions of the facility, as prescribed by the regulations and have prepared the required supplies of repairing/replacing tools and equipment.

(4) Clean up the leakage plugging site, and take protective measures such as evacuation, drainage, ventilation and cover up if necessary for dangerous media according to their conditions and the nature of their media.

(5) To plug releases of flammable and/or explosive media, the welding plugging method shall be avoided as far as possible. The use of tools and operation methods that may cause sparks is prohibited. Copper tools, air guns, drills should be used, electrical equipment and electrical tools shall be avoided.

(6) Loose and tight bolts, union joints and other parts, after cleaning with kerosene, rust remover, etc., apply graphite and molybdenum disulfide to lubricate the thread, so that it can be operated gently and slowly to avoid bolts and wire buckles breaking.

(7) A platform should be set up for high-altitude work, and a lift, / machine, and crane should be used as a platform if the platform cannot be set up. Warning boards shall be used.

(8) Underwater plugging should comply with underwater operation regulations. The team shall wear impervious diving suits and ensure that the snorkel is intact and that safety measures are reliable.

(9) When operating indoors, in trenches, in underground and/or containers, preventive and rescue measures shall be in place to avoid intoxication and suffocation. The measures shall be in place and tested before accessing pits, wells, cellars or containers.

(10) The worker or the team of workers shall carry out the work according to the plan decided in advance and adopt a cautious approach. In case of abnormal phenomena during execution of the plan, they should not improvise or act upon subjective, individual opinion: they shall take time to reflect jointly, discuss and identify the best way forward.

Authors note: the following list of measures does not explicitly state the most obvious and most effective measure is the depressurisation of the leaking system/facility before starting any type of repair work. The measure (1) implies it, very generically.

Consequences**:** two fatalities and an economic loss of more than 43k Euro.

Corrective actions: unknown

3.1.13 Explosion of a hydrogen storage vessel

Source: Zhao Yun， Analysis of the causes of the explosion of the hydrogen storage tank， Journal of East China Power, 1990, 11.

Location: power plant, industrial area

Date: 8 September 1989

Event description: This incident occurred at the hydrogen production and storage unit of a power plant using hydrogen as a coolant of the turbine-generator system. Hydrogen was produced by water electrolysis and stored in 6 steel tanks.

One of the six hydrogen storage tanks exploded killing a staff member. The investigation results determined that a mixing of hydrogen and oxygen occurred in the tank. The needle valve of the hydrogen and oxygen pressure regulator as jammed, and the oxygen leaked into the hydrogen main supply line and entered the hydrogen tank.

The explosion was evaluated to be equivalent to a TNT explosion in the range of 64-125 kg of TNT. The tank which exploded was pulled off from its position, ripped open and completely destroyed. two other vessels fell due to the pressure wave caused by the explosion, and the other 3 were damaged in different degrees.

Application: hydrogen production and storage plant, the hydrogen storage system was of 6 stainless steel vessels (each $10m^3$, dimensions: inner diameter: 1500mm, height 6400mm, wall thickness 12mm)

Classification of the physical effects: explosion

Causes: the immediate cause was caused by a mixing of hydrogen and oxygen owing to the leakage of oxygen into the hydrogen main pipe and then flowed into the vessel. The leak of oxygen was resulted from the jam of needle valves in hydrogen and oxygen pressure regulator in hydrogen generation plant.

The cause of the ignition was very possibly a spark generated by the friction of the high-speed gas flow, which can reach 100m/s when opening the valve of the vessel, driven by a pressure difference of about 392kPa.

Since the needle valve had already jammed twice before, one additional cause could be related to lack of timely repair process. Also, it does not seem that a diagnostic system was in place, able to detect oxygen in the hydrogen stream (and vice versa) signalling accidental mixing and able prevent further escalation.

In conclusion, the root causes could have more than one reason: (i) the operator was not checking the purity of hydrogen; (ii) a poor design was allowing a single failure to escalate; (iii) lack of a learning process from previous near misses.

Emergency measures: unknown. Probably, due to the rapidity of the event, there had been no time to start emergency actions.

Consequences**:** An operator was killed at the site. the main pressure vessel was broken into 3 pieces, one of weighted 1000kg debris thrown to 29m away; other debris of 257kg flew to heights of 42m and hit the cooling tower and bounced back and damaged the brick fence wall. The brick wall surrounding the pressure vessels fell about 40m^2 in area. The window glass of building 30m away from explosion centre were almost all broken.

Corrective actions: The investigation formulated the following recommendations, but it is not known if they have been adopted:

1. When rebuilding the hydrogen production unit, a new type of pressure regulator shall be used, with a liquid level limit interlock protection device.
2. A hydrogen purity meter or an oxygen meter shall be installed on the hydrogen side to continuously monitor the hydrogen purity.
3. The management of equipment (monitoring, defect repair, replacement) shall be improved/strengthen. An immediately stop the operations shall be triggered to eliminate defects affecting hydrogen purity.
4. The equipment belonging to the hydrogen production unit shall be maintained once a year and overhauled every three years.
5. According to the requirements of "Fire Inspection Manual" and "Code for Design of Power Installations in Explosion and Fire Hazardous Environments", anti-static measures shall be in place.
6. Technical training and awareness shall be strengthened.

Lesson learned: it is necessary to develop a quality control or certification of subcomponents along the supply chain. Moreover, when there is a potential of mixing gas species with the risk of producing explosive mixture, gas detection and gas quality measurements must be continuously in place.

3.2 Hydrogen supply chain: production, transport and delivery

3.2.1 Release and fire at a flexible hose during hydrogen transfer

Source: Investigation Report on the "7-30" General Leakage and Fire Accident at Dongguan Juzhengyuan Technology Company Limited, Lixia Island, Shatian Town, Dongguan City.

Location: hydrogen production site, near a city

Date: 30 July 2020

Event description: A hydrogen leak occurred at a tube bundle container at the loading and unloading bay of a PSA (Pressure Swing Adsorption) hydrogen production plant. A PSA hydrogen production plant is a device that uses Pressure Swing Adsorption (PSA) technology to produce hydrogen. It is a commonly used method of hydrogen production, particularly in the industrial and chemical industries. During the hydrogen filling process, at 4:08:25 the worker in charge noticed the leak in the filling hose of trailer No. 6 after an abnormal noise. After 22s, at 4:08:47 the hose connected to trailer no. 6 broke, and moved rapidly towards trailer no. 4. At 04:13:25, the broken hose was flung in front of the trailer No. 4 and the leaking hydrogen gas started to burn (see Figure 8). At 04:13:31, hydrogen gas leaking from the loading and unloading ports on trailer No. 6 caught fire and burned.

The metal hose fractured, the hose was flung around, and hit an object, which caused the spark which ignited the hydrogen. This is a case of delayed ignition: from the moment in which the hydrogen leak was detected to the first ignition took 5 minutes.

The fire resulted in damage to the pipes, valves and other accessories of the two hydrogen bundle containers.

Application: hydrogen production plant

Causes: the immediate cause of the fire was the rupture of a flexible filling hose. The hose could not meet the working pressure of 22 MPa, the hose ruptured when it reached 17.473MPa and then broke off, causing a direct leak of hydrogen. The company bought and used metal hoses produced by a machinery fittings manufacturing company. They were cheap and burst when they were filled to 7.5MPa pressure. This reveals that the enterprise's quality and safety awareness was not strong, the risk assessment was not thoroughly performed, the control and the mitigation measure was not in place or not well-designed.

Event initiating system: hydrogen system

Emergency measures: emergency measures were taken effectively (can be extended). At around 05:24, the open fire was completely extinguished

Consequences**:** A direct economic loss of Euro 3,11. No injuries.

Corrective actions: unknown

Lesson learned: unknown

Figure 8 -A) Hydrogen leak from the hose in front of the trailer. No. 4 burst into flames; B) Hydrogen leaking from the loading and unloading ports on trailer No. 6 burst into flames (Source of the pictures: Investigation Report on the "7-30" General Leakage and Fire Accident at Dongguan Juzhengyuan Technology Company Limited, Lixia Island, Shatian Town, Dongguan City).

3.2.2 Hydrogen fire from a flexible hose

Source: qq news of 7 August 2021 available at https://new.qq.com/rain/a/20210807A02SN600 (last retrieved 20.02.2023)

Location: industrial area near a city

Date: 4 August 2021

Event description: A hose of a hydrogen trailer ruptured at a specialised chemicals company. The released hydrogen ignited and exploded, followed by a fire fed by the continuously leaking hydrogen, the hydrogen fire caused the tyres to burn and produce thick, black smoke.

The local fire rescue team rushed to the scene after receiving the alarm call. The fire was quickly brought under control and extinguished. Firefighters continued to cool the tank to avoid further problems. There were two hydrogen trailers parked at the accident site. The other trailer was not affected.

Applications: chemicals factory, hydrogen transport and distribution by road tanker.

Classification of the physical effects: explosion and fire

Causes: the immediate cause was a leak on the hose. It is not known if the hose was connected and a hydrogen delivery was taking place, or if the trailer was just parked there and the hose was detached from the stationary storage.

Therefore, nothing is known on the root cause. In general, it could be attributed to shortcomings in design or in operation (maintenance/inspection procedures and their execution).

Emergency actions: the command centre of local Fire and Rescue Department was alerted and the command centre immediately dispatched firefighting and rescue forces to the scene. The fire was put under control (time unknown) and was extinguished by water.

Consequences**:** no casualties.

Corrective actions: unknown

Lesson learned: unknown

Figure 9: Fire starts from trailer (Source of the pictures: https://new.qq.com/rain/a/20210807A02SN600, retrieved 20.02.2023).

3.2.3 Road crash of a tanker carrying hydrogen

Source: Link to the media (last retrieved 20.02.2023)

Location: high-speed motorway

Date: 1 December 2019

Event description: A tanker carrying 300 kg of hydrogen was rear ended by a semi-trailer, whereupon the tanker started leaking hydrogen which ignited, also involving the other vehicle.

Application: Hydrogen transport and distribution

Classification of the physical effects: fire

Causes: this is a classic road crash.

Emergency measures: The fire command centre mobilized four first responder teams and eight fire engines. The fire-fighters first secured the scene and immediately put out a water cannon to extinguish the fire in the semi-trailer and cooled the tanker body. After about one hour of supervision and disposal, the hydrogen tanker was no longer in danger of explosion.

Consequences: the semi-trailer was parked between the emergency lane and the third lane, the front passenger part of the vehicle was severely damaged, the co-driver was sent to the hospital for treatment, the driver was not injured. Nothing is known on the consequences of the hydrogen trailer.

Corrective actions: unknown

Lesson learned: unknown

Figure 10: Trailer carried hydrogen gas ended by a truck in motorway (source of the picture: Link to the media, retrieved 20.20.20123)

3.3 Miscellaneous accidents

3.3.1 Explosion in a university laboratory

Source: Baidu news of 18 December 2021 link to the media, (last retrieved 20.02.2023)

Location: laboratory of a university

Date: 18 December 2015

Event description: the explosion occurred when the postdoc was conducting a chemical experiment using hydrogen gas in the laboratory. A chemical fire started in the laboratory, involving a hydrogen cylinder made of steel, which exploded in a laboratory two to three metres away from a student’s workstation. The cylinder of about one metre, failed from the bottom, and after the explosion only the top half of the cylinder was left intact.

Application: chemistry department of a university

Classification of the physical effects: explosion (probably detonation)

Causes: Explosion caused by a malfunction of experimental equipment while a postdoc was conducting an experiment using hydrogen gas. The root cause was the wrongful storage of dangerous chemicals and of hydrogen gas cylinders. Laboratory safety management was not in place and the students' safety awareness was weak. It is also possible that the fire and explosion was related to tert-butyl lithium in the laboratory, a super-powerful base in organic synthesis, highly flammable and spontaneously combustible in air.

Emergency measures: teachers and students in and around the building were evacuated; the flame was quickly extinguished; because of the presence of harmful chemicals in the building, the responders measured and detected no harmful gases on the scene two hours after the explosion.

Consequences**:** one fatality. The windows of the laboratory were damaged in the explosion; iron cabinets and other furnishings in the laboratory were affected due to damaged windows downstairs. Several neighbouring rooms were also affected, with glass broken to varying degrees

Corrective actions: unknown

Lessons learned: unknown

Figure 11: Laboratory after the explosion (left) and external of eh university building during the fire (source of the pictures: Source: Link to the media, retrieved 20.02.2023)

3.3.2 Release from hydrogen storage cylinders

Source: https://news.ifeng.com/c/7fcqWhz3vB1 (last retrieved 20.02.2023)

Location: Shop in a town

Date: 03 August 2012

Event description: a hydrogen gas leak occurred at a stove shop. The city fire brigade arrived at the scene in time to avoid escalation. The shop bought hydrogen cylinders, filled them privately (it is not clear where the hydrogen gas came from), but did not know how to use them, causing the leak. The cylinder used for hydrogen was a modified natural gas cylinder.

When the firefighters arrived at the location where the hydrogen cylinder had been placed, they found it temporarily cooled with water in the shade of the bathroom.

Application: private use in shop. The shop was surrounded by private houses, with a large flow of people from the nearby streets and a kindergarten opposite. It is understood that the shop was a newly opened unlicensed shop, considering that children like to play with hydrogen balloons.

Classification of the physical effects: hydrogen release

Causes: the immediate cause is unknown. The root causes is in the lack of technical competence on to the correct handling of hydrogen gas.

Emergency measures: the Fire Brigade decided to transfer the hydrogen cylinder to the open space for depressurisation and to use the water from the fire engine to cool it. Two firemen went into the bathroom, wrapped the hydrogen cylinder with a wet quilt, then gently loaded it horizontally onto the police car, using multiple layers of wet rags underneath and a wet mat above to cover it, and then, with the police car in the way, went all the way to the open space. A fireman opened the valve of the hydrogen cylinder and started to slowly release the gas, while a fireman used a fire hose to cool the area with water spray.

Consequences: no consequence

Corrective actions: unknown

Lesson learned: unknown

4 Incidents assessment and general lessons learned

4.1 Evaluation of accidents

The figure 12 below shows the event consequence after a hydrogen leak, if the leaked hydrogen can be detected and isolated, it will not lead to damage. Otherwise, immediate ignition leads to jet fire, delayed ignition will cause explosion, respectively. If a leak cannot be detected, there is a possibility of a jet fire, explosion or non-ignition. Table 1 shows the percentage of accidents linked to delayed ignition and immediately ignition from “Major Hazard Incident Database Service of the Health and Safety Executive (UK)” [3] and the study of this paper. UK database shows 95% immediate ignition, the statistical data from accidents in this study shows only 60%. The results from later study show the more potential to take safety measures to react to the delayed ignition.

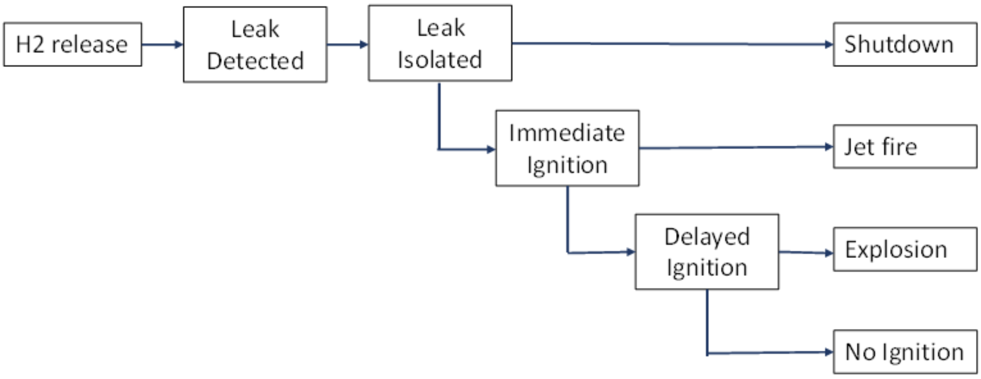

Figure 12: event consequence after a hydrogen leak [4]

Table 2: comparison of percentage of immediate ignition and delayed ignition from UK database and study in this paper.

	Major Hazard Incident Database Service of the Health and Safety Executive (UK):	**Hydrogen accidents over the last 20 years in China**
Incidents of hydrogen gas release	81	19
Delayed ignition	5%	40%
Immediately ignition	95%	60%
Ignition source cannot be identified	86,3%	10,5%

Some criteria from [2] are used to evaluate the accidents, such as sectors in the hydrogen value chain, root causes, severity of human damages; in additional, the cause of ignitions is put into the focus. Figure 13 shows the industrial sector in which the accidents are distributed, and most of them are in the chemical and petrochemical sector. From Figure 13, 26% of accidents are related to the storage of hydrogen, i.e. to the high pressure storage of hydrogen. This shows the importance of high-pressure hydrogen storage and its risks. It is worth noting that 17% of the accidents that occurred during the application of hydrogen, of which 3 involved air balloons, indicated the importance of managing the safety of the application of hydrogen when dealing with people who may lack expertise in hydrogen safety.

Casualties caused by accidents are shown in Figure 14, there were 35% of accidents with more than four fatalities and 35% of accidents with no fatalities, and it is worth noting that 35% of accidents still resulted in no injuries.

Figure 15 shows that the causes of fires from sparks due to impact, sparks due to friction and electric sparks exceed 70%, confirming the drawbacks of hydrogen as an energy carrier in terms of safety having a very small ignition energy, therefore being very prone to accidents.

Finally, Figure 16 shows the causes of accidents, with up to 37% of accidents being related to management. Theoretically, accidents that occur are directly and indirectly related to safety management. Therefore, it is important to strengthen the management of hydrogen safety.

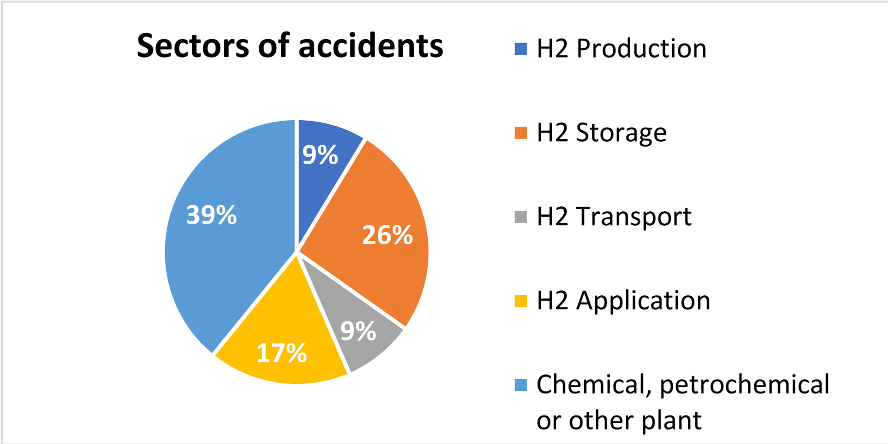

Figure 13: Accidents occurred in different industrial sectors

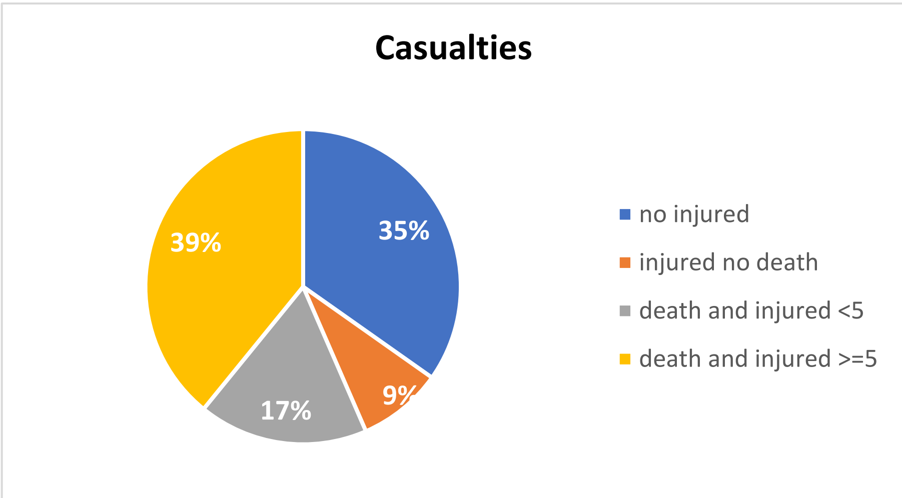

Figure 14: Casualties caused by accidents

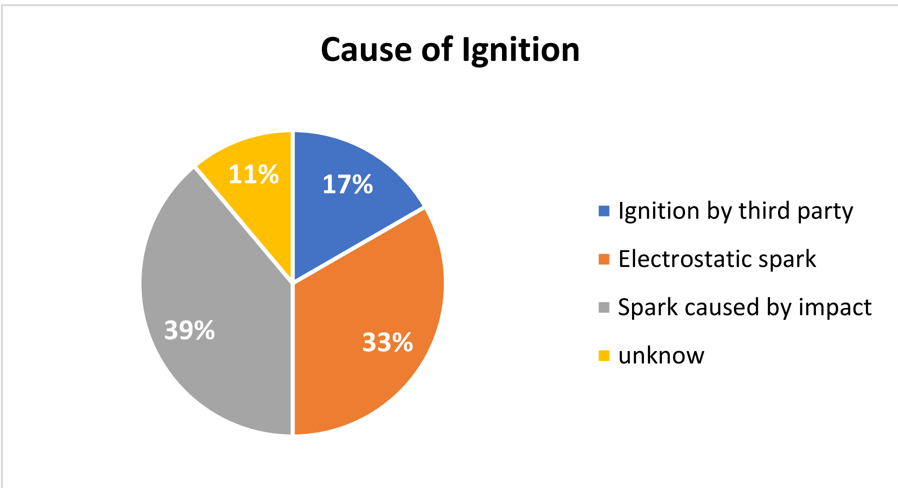

Figure 15: Cause of Ignition

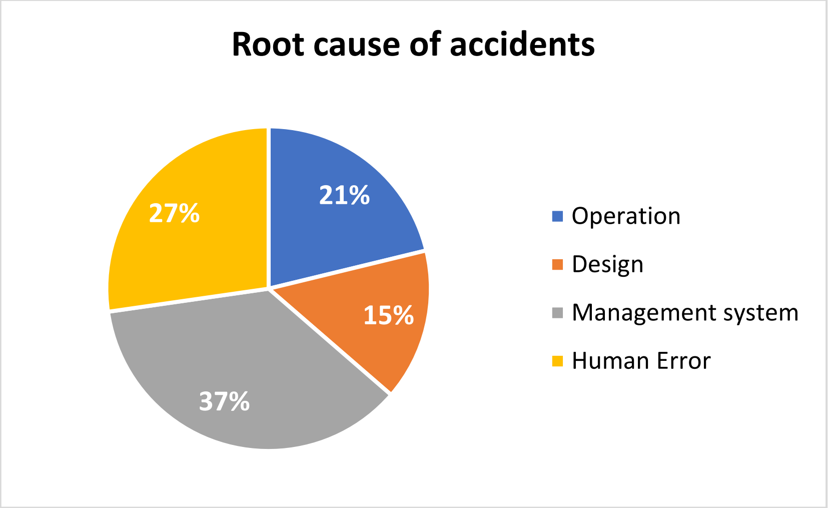

Figure 16: Root cause of accidents

4.2 Conclusions and lessons learned

A general discussion and conclusions on safety preventive and mitigating strategy and safety engineering are out of the scope of this paper. Nevertheless, the following narrative can assist more general and statistically more relevant recommendations:

- Not all hydrogen leaks result in serious damage, safety management measures and emergency response are important.
- In the case of delayed ignitions, the time delay is crucial to design safety measures able to react to leaks and prevent fire and explosion.
- Water is in the events analysed the predominant fluid used in case of fire. It is useful to cool down the affected component to reduce the possibility of a possible escalation due to temperature increases; however, if water is added to a hydrogen fire, it may contribute to the formation of an explosive gas mixtures and increasing the hazards for those operating near the fire.
- Removing ignition sources in a hydrogen environment is an important safety measure to prevent fires and explosions. This requires the definition of the 'hydrogen environment' area and the classification of it with the help of a risk assessment approach.
- Early identification of corrosion, fatigue, overpressure, thermal stress is required, assisted possibly by predictive maintenance methods.
- Safety management system (SMS) is important for hydrogen in all industrial environments.
- The development and adoption of advanced automatized, computer-controlled safety management systems should be promoted.
- Pressurised vessels for hydrogen storage are a recurring element in incidents. Development of alternative storage methods should be encouraged.

5 References:

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