Spontaneous ignition of hydrogen

Literature Review

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This report is part of a project funded by HSE to investigate the phenomena of spontaneous ignition of accidental hydrogen releases. Over the years there have been reports of hydrogen leaks igniting for no apparent reason, and a number of potential ignition mechanisms have been proposed. Investigations of these ignitions have often been superficial, with a mechanism postulated which, whilst appearing to satisfy the conditions prevailing at the time of the release, in general does not stand up to rigorous scientific analysis. Some of these proposed mechanisms have been simulated in the laboratory under superficially identical conditions and appear to be rigorous and scientific, but the simulated conditions often do not have the same large release rates or quantities, mainly because of physical constraints of a laboratory. With the advent wide spread use of high pressure hydrogen storage for vehicles and other applications, there is a clear need to try to understand the probability of this phenomena to occur and also the physical causes of these ignitions so that design guidance can be developed. The report reviews available literature that may be of use in the experimental phase of the above project. It includes a summary of the literature previously identified on this phenomena and identifies new literature/information that could have a bearing on this project.

HSE Books

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EXECUTIVE SUMMARY

Objectives

The aim of this review is to establish which available literature may be of use as part of the HSE funded project, which will investigate spontaneous ignition of accidental hydrogen releases (JR02071). It will identify phenomena that have the potential to cause spontaneous ignition of releases of pressured hydrogen and identify literature that may be of use when formulating the experimental program.

Main Findings

- The identification of important work that shows conclusive evidence of spontaneous ignition of hydrogen due to the failure of a boundary layer.

1   INTRODUCTION

Over the last century, there have been reports of hydrogen leaks igniting for no apparent reason, and a number of potential ignition mechanisms have been proposed. While there have been many leaks that have ignited, there are also reported leaks where no ignition has occurred. Investigations of these ignitions have often been superficial, with a mechanism postulated which, whilst appearing to satisfy the conditions prevailing at the time of the release, in general does not stand up to rigorous scientific analysis. Some of these proposed mechanisms have been simulated in a laboratory under superficially identical conditions and appear to be rigorous and scientific, but the simulated conditions often do not have the same large release rates or quantities, mainly because of physical constraints of a laboratory.

With the advent wide spread use of high pressure hydrogen storage for vehicles and other applications at pressures up to 700 bar, there is a clear need to try to understand:

- The probability of this phenomena to occur,

- The physical causes of these ignitions so that design guidance can be developed to minimize the probability of these phenomena occurring as hydrogen applications become more widely used.

This review is the first deliverable of a project funded by HSE (HIDSI5) to investigate this phenomena of spontaneous ignition of accidental hydrogen releases (JR02071). The objectives of the review are:

i.   To summarise the literature previously identified on this phenomena (recapping on Astbury and Hawksworth 2005[1])

ii.   To identify any new literature or information that may have a bearing on this project

iii.   Use the input from i. and ii. above to refine the experimental work programme of this project.

2 REVIEW OF LITERATURE

2.1 LITERATURE FROM ASTBURY AND HAWKSWORTH 2006

The starting point for this paper was a search was made using the Major Hazard Incident Database Service (MHIDAS) [2] to compare ignitions of hydrogen releases with non-hydrogen gaseous releases, to determine if there was a significant difference. The search revealed 81 incidents involving releases of hydrogen. Of those, a delay between release and ignition was reported for only 4 releases. It has to be assumed that the others ignited immediately. In 11 cases, the source of ignition was identified, but in the remainder, 86.3% of incidents, the source was not identified. This contrasts with the non-hydrogen releases, where 1.5% did not ignite, and only 65.5% of ignition sources were not identified. For hydrogen there were four incidents where there was a delay between release and ignition, yet no ignition source was identified. This does suggest that there is a difference in propensity for ignition between hydrogen and non-hydrogen gases when released. The summary of sources identified and their frequency is given in Table 1 of this publication. From this analysis a number of incidents involving apparent spontaneous hydrogen ignition and a detailed description of the event were identified and the postulated mechanisms discussed. In brief, these incidents are summarized below.

2.1.1 The 1922 Incident investigation

This incident and the subsequent investigation and research work was reported in Engineering [3], from work undertaken by Nusselt in Germany. After several spontaneous ignitions of hydrogen at 2.1 MPa being discharged to atmosphere had been reported, work was undertaken to determine the cause. Various experiments were undertaken on discharging hydrogen to atmosphere, but no ignitions occurred despite discharging though many different types of nozzle made from differing materials. However, cylinders had been noted for having quantities of iron oxide (rust) in them even though they were apparently dry, and it was thought that there was potential for electrostatic charging to occur. Despite many differing finely powdered materials being used, no ignitions occurred except for extremely finely ground iron oxide. Manganese dioxide also caused ignition, so it was thought that the rust was catalysing the oxidation of the hydrogen. Therefore, mixtures of hydrogen and oxygen were stored at an initial pressure of 1.1 MPa at various temperatures in the presence of iron oxide to determine whether the oxide catalysed the reaction. At ambient temperatures, no pressure changes occurred, even after a few weeks, but at temperatures above ambient, the pressure slowly fell, indicating that the oxidation reaction was occurring. The times were about 24 hours at 100°C, 9 hours at 200°C, and one hour at 380°C. There was no explosion at any time.

Subsequent experiments on discharging hydrogen into an open funnel fitted with a long pipe showed no ignitions except when the funnel was obstructed by an iron cap. The mechanism was not understood, so further trials were undertaken. Only when the trials were undertaken in the dark was a corona discharge observed. This was revealed when the hydrogen leaked out of a flange - the corona discharge was visible, which increased when the pipe was tapped to stir up dust. An ignition followed after the tapping. Further work showed that when sharpened copper wires were used to promote corona discharges, ignition occurred when the point was bent away from the gas direction, whereas no ignition occurred when the wire was pointing in the direction of flow. Consequently, it is apparent that a corona discharge was likely to have been the source of ignition in this case.

2.1.2   The 1926 and 1930 Incidents and Experiments

The first incident occurred in 1926, but was only reported by Fenning and Cotton [4] in 1930 after a second explosion occurred. As the cause of the ignition in both cases was obscure, experimental work was undertaken to try to establish the mechanism. The second explosion occurred when the isolation valve between a pressurised pipeline and a chromium plated vessel was opened to de-pressurise the line from about 4.9 MPa. The explosion occurred immediately, and traces of water were found in the previously dry vessel confirming that combustion had taken place. It was noticed that there was ample evidence of fine dust, presumably metal oxide, being present in the pipe-work during the examination after the explosion. This led Fenning and Cotton to surmise that the explosion had been initiated by an electrostatic discharge, presumed to have been generated by the fine dust being blown along the pipe by the high velocity hydrogen. However, despite many attempts, no ignition was achieved in their experiments.

The first explosion was not investigated at the time, but as the same workers were involved, they reviewed the circumstances. In this first explosion, the pressure was only about 6.6 kPa above atmospheric pressure in a glass vessel. No obvious source of ignition was present, but it was observed that a fine jet or spray of mercury may have been projected into the gas mixture. The mixture was said to have been "...a sample of a 'complete combustion' hydrogen-air mixture...", which can be taken to mean a stoichiometric mixture. Again, there is a suggestion that an electrostatic ignition mechanism is possible.

2.1.3   Incidents reported by Bond

Bond [5] reports two incidents, sourced from a private communication, where hydrogen ignited. In the first incident, hydrogen at a pressure of 11.1 MPa was leaking from a gasket between two flanges. The hydrogen had not ignited at the time when the fitters arrived to tighten the bolts. It was reported that on the second strike of the hammer wrench that was being used to tighten the bolts, there was an ignition. It is not apparent whether the ignition source was an impact spark from a hammer wrench being used to tighten the bolts on the joint, or attributed to the mechanism of diffusion ignition. The second incident refers to a cylinder of hydrogen being connected to a piece of laboratory apparatus. The laboratory technician cracked the valve open to clear any dirt out of the connection, and when he did so, the escaping gas ignited immediately. Bond attributes this ignition to the phenomenon of diffusion ignition. Whilst no pressure of gas is quoted in this second incident, it can be assumed that the pressure would have been the typical full cylinder pressure of 23 MPa.

2.1.4   Jackass Flats Incident, 1964

This incident, reported by Reider, Otway and Knight [6], involved the deliberate release of a large quantity of hydrogen to determine the sound pressure levels. The hydrogen was released from storage at an initial pressure of 23.6 MPa and an initial rate of 54.4 kg s^{-1}, for a period of 10 seconds. The gas was transferred through a 200 mm nominal bore pipe and a 150 mm bore ball valve to a cylindrical vessel fitted with a convergent-divergent nozzle venting to atmosphere. The intention was to discharge the gas without combustion and again with deliberate combustion, so that the sound level due to the combustion could be measured. In the run where the gas was not deliberately ignited, after 10 seconds, the 150 mm diameter valve was being closed, and three seconds after starting to close the valve, ignition occurred.

Prior to the experimental discharge, three potential ignition mechanisms were examined, as it was recognised that ignition during a "non-ignition" would require the run to be aborted. The three potential ignition mechanisms examined were electrification of the gas; electrification of

particles in the gas; and metal particles abrading a metal bar welded across the mouth of the nozzle. Of these, the first was discounted as pure gases are known to have negligible electrostatic charging. The second was considered, but as the system had been thoroughly cleaned out and blown down prior to the test, it was considered that there would not be any particles present. However, the velocity of the gas being discharged, at 1216 m s^{-1}, was far higher during the run than had been used before, so this potential mechanism could not be discounted. The third mechanism was considered as a possibility as the discharge velocity was high - possibly dislodging particles, and impacting them on the bar. This too could not be discounted. After the ignition, it was found that the bar had been torn loose at one end, and this may have presented a possible ignition source which had not been foreseen.

2.2 POSTULATED MECHANISMS

The paper by Astbury and Hawksworth [1] also contains an analysis of postulated ignition mechanisms and these are summarised below.

2.2.1 Reverse Joule-Thomson Effect

When a compressed gas is vented to atmosphere through a nozzle, the gas expands. If it is below the Joule-Thomson inversion temperature, then the gas cools on expansion. The inversion temperature for air is about 325°C, so air at ambient temperature and above atmospheric pressure will cool on expansion. Hydrogen on the other hand has a Joule-Thomson inversion temperature of about 193 K (-80°C) [7], so compressed hydrogen at ambient temperature will heat up on expansion to atmospheric pressure. Calculations in the paper show that for initial conditions of 50 MPa and 9°C a rise in temperature of between 9 K and 18 K is likely to occur which is hardly conducive to autoignition. since the autoignition temperature of hydrogen is 585°C [8]. At higher pressures and temperatures, the Mollier [10] diagram shows that isenthalpic lines become very non-linear, so the temperature rise on expansion is likely to be much larger. However, data for the Joule-Thomson coefficient for hydrogen at pressures up to 250 MPa and 150 °C is given by Michels et al. [9] and shows that it is unlikely to lead to ignition at the pressures in most of the incidents quoted above.

Although on its own it would appear that the Joule-Thomson expansion would not raise the temperature of any hydrogen to its normal autoignition temperature, it should be borne in mind that it will raise the temperature of the gas above ambient. This alone is unlikely to cause ignition, but in combination with other effects may be sufficient to initiate spontaneous ignition. This is discussed later.

2.2.2 Electrostatic Ignition

A stoichiometric mixture of hydrogen with air has a very low minimum ignition energy of 0.017 mJ [11]. This makes it far more sensitive to ignition than most other gaseous or vaporised flammable materials, and therefore the potential for electrostatic ignition is much greater. There are three main types of electrostatic discharge to consider - spark discharges, brush discharges and corona discharges.

Spark discharges from isolated conductors.

These are characterised by a single plasma channel between the high potential conductor and an earthed conductor. The discharge is completed in a very short time, and almost all the charge is transferred in a single spark. Calculations in the paper show that even when quenching effects are taken into account, an energy of 0.164 mJ at 2kV is more than sufficient to ignite the stoichiometric hydrogen-air mixture. Consequently, whilst electrostatic charging of people

refuelling vehicles with petrol rarely gives rise to ignitions, it is significant that the voltage required for hydrogen to be ignited is below 2 kV. While this discussion focused on people, the same applies to other isolated conductors. This voltage can be generated easily, without their being aware of it, on people standing on an insulating surface so there is a potential for personnel to ignite hydrogen leaks very easily, without any apparent ignition source being present.

Brush discharges

These are typified by a discharge between a charged insulator and a conducting earthed point. They are characterised by many separate plasma channels, combining at the conductor, and are typical of those from insulating plastics. As the charged surface is a non-conductor, a capacitance and hence energy cannot be determined. Typical equivalent energies were found to be about 4 mJ [12, 13] for brush discharges from flat polyethylene sheets.

Corona discharges

These are silent, usually continuous discharges which are characterised by a current but no plasma channel. A corona discharge is able to ignite a hydrogen-air mixture without there being a discrete spark or single discharge event. This is a known potential ignition source, particularly from atmospheric electrical activity. Where a potential exists some distance from an earthed surface, an electric field will be present. This field will be linear between a pair of parallel plates. However, if a small point is placed on one of the plates, it will modify the field, and concentrate the lines towards the point. If the local concentrated field strength exceeds the breakdown strength of the air, then a current will pass in the form of a corona. Where vents discharge hydrogen to atmosphere, it has been known for the gas at the vents to ignite for no apparent reason. Studies undertaken many years ago on hydrogen vents [14, 15, 16] showed that ignition was rare during fine weather, but was more frequent during thunderstorms, sleet, falling snow, and on cold frosty nights.

2.2.3 Diffusion Ignition

The phenomenon of diffusion ignition has been postulated by Wolański and Wójcicki [17], who demonstrated that ignition occurred when high pressure hydrogen was admitted to a shock tube filled with air or oxygen. They found that ignition could be achieved even if the temperature was below the autoignition temperature of the hydrogen. They calculated that ammonia synthesis gas, composed of a 3:1 mixture of hydrogen and nitrogen would ignite in air if the shock wave exceeded a Mach Number of 2.8 at a temperature of 575 K. Although they confirmed their calculations using the shock tube, there is no experimental work undertaken with releases to an unconfined atmosphere, such as would be the case for a leak from high pressure direct to atmosphere. They also stated that the autoignition temperature for ammonia synthesis gas containing 75% v/v hydrogen, with a balance of nitrogen, had an autoignition temperature of 685 ± 30 K (412 ± 30°C). This autoignition temperature seems unduly low compared to that reported by other workers, notably the 585°C by NASA [7] and 560°C quoted by IEC 60079-20:2000 [18], although the NFPA [19] reports 500°C. There is no indication whether their autoignition temperature was measured at the expected final pressure in the shock tube, or at atmospheric pressure. Although their shock tube experiments produced ignition, their initial temperature was rather high at 575 K (302°C), requiring an increase of only 110 K to reach their autoignition temperature of hydrogen.

2.2.4   Sudden Adiabatic Compression

This occurs when a gas is compressed adiabatically. If a gas obeys the ideal gas laws, then compressing it at constant entropy would increase the pressure due to the compression in accordance with the relationship:

$$PV^{\gamma} = k \tag{1}$$

In the paper the authors calculate the compression required to give ignition assuming behaviour as a perfect gas and demonstrate that a compression ratio of 80 would be required to heat a hydrogen-air mixture to 750°C and that experimental work produced ignition at lower pressures indicating that another ignition mechanism is present.

2.2.5   Hot Surface Ignition

This is a phenomenon shared by most flammable gas or vapour air mixtures, in that providing the surroundings are at a high enough temperature, the rate of oxidation generates more heat than is being lost to the surroundings, so allowing the oxidation chain-reaction to progress. This is the usual method of determining autoignition temperatures, and the value obtained is very dependent on the apparatus used. For example, NASA [7] report values for stoichiometric gaseous hydrogen-air mixtures at 101.3 kPa, of between 773 K and 850 K, and at reduced pressures of 20 to 50 kPa, ignitions have occurred at temperatures as low as 620 K (347°C).

An abstract of work by Neer [20] indicates that ignitions under shock conditions occurred at much lower temperatures than those resulting from classical static conditions, and concludes that a more realistic measurement is to use the term *ignition speed* rather than ignition temperature to take account of this. At temperatures approaching the classical thermal ignition temperature for stationary mixtures, the ignition delay is short, becoming longer as the temperature drops. Neer postulates that the onset of ignition is favoured by higher densities in the lower region of the boundary layer, higher wall temperatures, higher flow speeds and longer test times. He also suggests that charged particles which are generated by the high speed flow over the walls are responsible for the ignitions.

However, work by Bulewicz [21] showed that the position and mode of heating a hot plate had an effect. He used a slow-heating method where free-convection was important, and a time delay between exposure and ignition was apparent, depending on the rate of temperature rise. The orientation of the heating surface also affected the delay, with a longer delay with the heated surface pointing down than when the heated surface was pointing up. During the delay period, H and OH radicals slowly increased in concentration, until the concentration reached a certain level, at which point ignition was observed with a violent increase in the temperature. This correlated well with their theory. They also looked at heating the plate impulsively using a capacitor bank to discharge through the plate, heating it resistively. The ignition temperatures were higher when heated impulsively than when heated by a slow temperature rise, with ignition temperatures of typically 1600 K to 2500 K.

2.3 SUMMARY OF FINDINGS

To summarise the findings from the paper by Astbury and Hawksworth, they concluded:

- Hydrogen does not necessarily ignite spontaneously when released at high pressure.
- Compression ignition, Joule-Thomson expansion, diffusion ignition and hot surface ignition are unlikely ignition mechanisms for most accidental releases of hydrogen at ambient temperature.
- The postulated mechanisms described in the literature and discussed above do not account for all the reported ignitions and non-ignitions of hydrogen releases.
- There is the possibility that when hydrogen does ignite on release, two or more of the postulated mechanisms are present together.
- It is possible that some form of electrostatic charging is a part of the mechanism where spontaneous ignition of leaks of hydrogen from high pressure has occurred at ambient temperature.
- Further work is required to establish the conditions under which hydrogen releases ignite, particularly with respect to electrostatic phenomena.

3 OTHER RECENT WORK

A further more recent examination of the literature has revealed three interesting pieces of work, which are discussed below.

3.1 GOLUB ET AL ,2006)

This paper (Golub et al 2006 [22]) presents experimental and modeling work to investigate the phenomena of self-ignition as a result of shock wave formation in front of a cold expanding gas jet. The work used a shock tube to simulate high pressure releases into a vacuum chamber. The work looked at the effects of pressure and release orifice size on the propensisty for ignition to take place.

The report concluded that a possible cause of ignition could be the contact surface separating discharging gas from the surrounding heated oxidizer as a result of the primary shock wave.

It was found that an increase in temperature of the shock wave leads to a greater risk of spontaneous ignition. For example, ignition occurs if the initial hydrogen pressure is between 150 and 400bar, the temperature of the hydrogen and air is 300K, and the orifice size >3mm. It was concluded that the process was strongly dependant upon the initial temperature of the hydrogen and air, as can be seen from the results achieved if the temperature is increased by 100K to 400K. Here, with an initial hydrogen pressure of 200bar, the size of orifice required to produce ignition is reduced in size to 2mm.

3.2 DRYER ET AL, 2006

This paper (Dryer et al, 2006 [23]) presents an experimental demonstration of the spontaneous ignition from sudden compressed hydrogen releases to simulate vessel or piping failure. In addition to being significant as probably the first experimental piece of work to demonstrate ignition of releases into "normal" everyday type of environments, it is important in that it also identifies the importance of down stream obstructions.

The work used open ended flow geometries downstream of a standard commercial, screw union type, straight-through burst disk holder with 1/2" NPT female connections (1.83 cm ID) on both sides of the holder as shown in Figure 1a below, and T type disc holders as shown in Figure 1b.
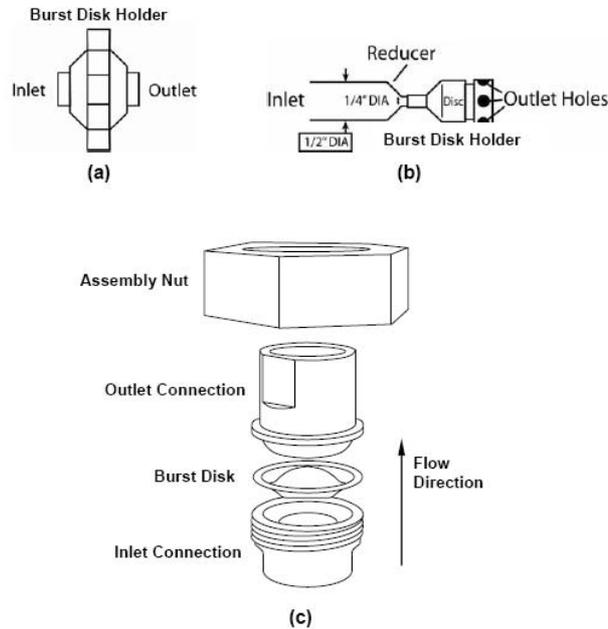
Figures

Figure 1

Both commercial and in-house-manufactured burst disks with different failure pressures were used in the experiments. Failure of each burst disk was induced by slowly raising the flammable gas supply pressure to the burst disk failure pressure. The majority of the experiments, particularly those at failure pressures higher than about 40 atm (~600 psia) were performed in open air, out of doors. Ambient air temperatures for the experiments ranged between 280 K and 305 K, with relative humidity levels between 60 and 90%.

The list below (taken from Dryer et al conclusion) highlights the most significant findings from the work by Dryer et al:

- The present work conclusively establishes that within the storage and pipeline pressures used today and/or contemplated in the future for hydrogen, transient shock processes associated with rapid pressure boundary failure have the capacity to produce spontaneous ignition of the compressed flammable released into air, provided sufficient mixing is also present.

- Pressure boundary failure geometry, multi-dimensional shock-boundary, and shock-shock interactions in addition to molecular diffusion can provide the necessary short mixing time scales. Turbulent free jet hydrogen flames can be stabilized at sufficiently high jet velocities to result in continued combustion.

- Experimental observations identify that the minimum compressed gas pressure (relative to atmospheric pressure air) at which spontaneous ignition occurs is dictated by reflected shock and shock-shock interactions. The repeatable nature of

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the ignition and its characteristic time scale suggest that proposed ignition alternatives (e.g. electrostatic discharge) are not contributory to the present observations.

- Further experiments are needed to quantitatively define the experimental parameter ranges of gas temperature, pressure, pressure boundary thickness and structure, and pressure boundary local geometry that contribute to determining the envelope of design parameters over which shock induced inflammation will or will not result.

- These works need to include the analysis of external boundary failure and shock reflection from surrounding structures to encompass compressed pressure vessel and high pressure pipe failure modes inside enclosures.

- There is no doubt, however, that this phenomenon has been a cause of past fire incidents involving sudden releases of compressed hydrogen gas into air (e.g. National Research Council, 1995).

- Simple 1-D shock calculations suggest that sudden compressed methane and natural gas discharges into air may cause similar reflected shock and focused shock-shock induced spontaneous ignition, but at considerably higher compression pressures (relative to hydrogen).

- To date, it appears that this phenomenon has escaped consideration in the analysis of most accidental fires and in the development of piping and storage safety codes both for hydrogen and natural gas.

- Moreover, an important observation is that downstream flow geometry or objects in the path of exiting jets formed by the sudden discharge of compressed flammable gases into air have impact on whether shock induced spontaneous ignition.

- Methodologies to enhance or mitigate continued combustion likely exist and such options need to be identified and characterized by more detailed measurements so that safe storage and distribution systems can be interfaced with general consumer use of compressed hydrogen.

4   SUMMARY

The dryer paper is particularly relevant to the current HSE project looking into spontaneous ignitions of accidental hydrogen releases (JR02071). For the first time conclusive evidence of spontaneous ignition was shown to occur from sudden releases of compressed hydrogen to atmosphere. More importantly these ignitions were found to occur at pressures used in current and future (predicated) hydrogen systems. The work identified certain downstream geometries that have been found to cause spontaneous ignitions when there is a sudden failure of the boundary layer.

Information from dryer's report combined with postulated ignition mechanisms discussed by Astbury and Hawksorth will be used as a basis for the first phase of experimental work that will be performed as part of JR02071.

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