

SPONTANEOUS IGNITION OF HYDROGEN LEAKS: A REVIEW OF POSTULATED MECHANISMS

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ABSTRACT

Over the last century, there have been reports of high pressure hydrogen leaks igniting for no apparent reason, and several ignition mechanisms have been proposed. Although many leaks have ignited, there are also reported leaks where no ignition has occurred. Investigations of ignitions where no apparent ignition source was present have often been superficial, with a mechanism postulated which, whilst appearing to satisfy the conditions prevailing at the time of the release, simply 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. Also, some of the release scenarios carried out or simulated in laboratories are totally divorced from the realistic situation of most actual leaks. Clearly there are gaps in the knowledge of the exact ignition mechanism for releases of hydrogen, particularly at the high pressures likely to be involved in future storage and use. Mechanisms which have been proposed in the past are the reverse Joule-Thomson effect; electrostatic charge generation; diffusion ignition; sudden adiabatic compression; and hot surface ignition. Of these, some have been characterized by means of computer simulation rather than by actual experiment, and hence are not validated. Consequently there are discrepancies between the theories, releases known to have ignited, and releases which are known to have not ignited. From this, postulated ignition mechanisms which are worthy of further study have been identified, and the gaps in information have been highlighted. As a result, the direction for future research into the potential for ignition of hydrogen escapes has been identified.

1. NOMENCLATURE

<i>C</i>	capacitance, Farads
<i>C</i>	specific heat of gas
<i>e</i>	energy stored in capacitor, J
<i>k</i>	a constant
<i>n</i>	number of moles of perfect gas
<i>P</i>	pressure
<i>R</i>	universal gas constant
<i>T</i>	absolute temperature
<i>V</i>	voltage, volts
<i>V</i>	volume

Greek:

γ	ratio of specific heats of gas, C_p/C_v
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Subscripts

1	initial conditions
2	final conditions
<i>p</i>	constant pressure

r ratio
v constant volume

2. INTRODUCTION

Since hydrogen has a reputation for spontaneous ignition, a search was made using the Major Hazard Incident Database Service (MHIDAS) [1] 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 below. It is worthy of note that since this is a major hazard incident database, releases of hydrogen which simply dispersed and did not involve fire, explosion or other major hazard are not recorded, so the non-ignition being reported as zero is not necessarily an indication that all hydrogen releases ignited.

Table 1. Frequency of occurrence of ignition sources

Ignition source	Hydrogen incidents		Non-hydrogen incidents	
	Number	%	Number	%
Arson	0		37	2.6
Collision	2	2.5	121	8.4
Flame	3	3.7	113	7.9
Hot Surface	2	2.5	56	3.9
Electric	2	2.5	114	7.9
Friction Spark	2	2.5	33	2.3
Not identified	70	86.3	942	65.5
Non-ignition	0	0	21	1.5
Total	81	100.0	1437	100.0

Several descriptions of hydrogen ignitions are reported in the literature, and these postulate various mechanisms. Also there is other work on specific ignition mechanisms which were not related directly to hydrogen, but were as a result of other incidents. These hydrogen ignition incidents are discussed. Possible ignition sources are reviewed and their potential applicability to hydrogen is reviewed.

3. SUMMARY OF SPECIFIC INCIDENTS

3.1 The 1922 Incident investigation

This incident and the subsequent investigation and research work was reported in Engineering [2], from work undertaken by Nusselt in Germany. The discussions in this paper are based on the findings summarised and reported in Engineering . 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 through 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.

3.2 The 1926 and 1930 Incidents and Experiments

The first incident occurred in 1926, but was only reported by Fenning and Cotton [3] 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.

3.3 Incidents reported by Bond

Bond [4] 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 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.

3.4 Jackass Flats Incident, 1964

This incident, reported by Reider, Otway and Knight [5], 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.

3.5 Hydrogen Releases at Health and Safety Laboratory, Buxton

Work yet to be reported has been undertaken at Buxton on the dispersion of releases of hydrogen from cylinders at a pressure of 15 MPa, through various shaped and sized orifices from 1 mm to 12 mm. Of all the runs, none ignited, showing that high pressure releases do not necessarily ignite. Hence spontaneous ignition of hydrogen is not a foregone conclusion, and no ignition mechanism was present during these tests.

4. POSTULATED MECHANISMS

4.1 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) [6], so compressed hydrogen at ambient temperature will heat up on expansion to atmospheric pressure. Data from a Mollier diagram [7] can determine the rise, which for initial conditions of 50 MPa and 9°C will give a rise in temperature of between 9 K and 18 K. This is hardly conducive to autoignition since the autoignition temperature of hydrogen is 585°C [6]. At higher pressures and temperatures, the Mollier 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. [8], and shows that at 100 MPa and temperatures up to 150°C , the Joule-Thomson coefficient does not exceed 0.53 K MPa, so ignition by this mechanism is unlikely at the pressures in most of the incidents quoted above. However, the data for the Joule-Thomson coefficient quoted by Michels et al are calculated partly from experimental data, partly from others' work and partly by extrapolation and calculation from other measured parameters. For example, using their data for an initial pressure of 250 MPa at 25°C and their worst-case coefficient of 0.53 K MPa, would produce a peak temperature rise of

$250 \times 0.53 = 132.5$ K, or a maximum temperature of 157.5°C . This assumes that the Joule-Thomson coefficient is constant over the whole pressure and temperature range, which it is not. Thus where extrapolation is used, it is possible that the values may be erroneous, particularly at the boundaries of the available data, since the quoted coefficients cannot be constant at both isothermal and isenthalpic conditions. Thus any calculation has to be approximate unless the Joule-Thomson coefficient can be characterized over the whole range of temperature and pressure.

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.

4.2 Electrostatic Ignition

A stoichiometric mixture of hydrogen with air has a very low minimum ignition energy of 0.017 mJ [9]. 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.

4.2.1 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. The energy is calculable from the equation $e = \frac{1}{2}CV^2$. In considering

spark discharges, there are two factors to take into account. Firstly, the energy stored in the capacitance of the item, and secondly the potential difference between the charged item and earth. If the capacitance is low, a high potential is required to store sufficient energy. As an example, a person has a capacitance of about 100 pF, depending on body size, the area of their feet and the construction and thickness of the soles of their footwear. First it is prudent to consider a typical hydrocarbon-air mixture. Taking a typical value of 100 pF as the capacitance of a person, and a minimum ignition energy of 0.29 mJ for a hydrocarbon atmosphere of say propane, then the voltage required to produce

a spark of sufficient energy to ignite the atmosphere is given by re-arranging the equation $e = \frac{1}{2}CV^2$

as $V = \sqrt{\frac{2e}{C}}$. Substituting gives $V = \sqrt{\frac{2 \times 0.29 \times 10^{-3}}{100 \times 10^{-12}}} = 2408$ volts. There is then the electrical

breakdown of the air to consider. For air, the dielectric strength is about 30 kV cm^{-1} , so for 2400 volts, the gap required between the charged conductor and the earthed point for breakdown to occur would

be $\frac{2400}{30 \times 10^3} = 0.08 \text{ cm}$ or 0.8 mm. People typically cannot feel an electrostatic shock of less than

about 1 mJ, so would be unaware of the potential to ignite a hydrocarbon-air mixture. Whilst this would suggest that ignition is inevitable, it has to be borne in mind that the gap over which the spark passes from a person to earth is rarely of a form which has pointed electrodes. Typically a finger has a tip radius of about 6 mm, so a finger-tip approaching a flat earthed metal surface, though having a gap of 0.8 mm, would actually present a large almost flat area around the point at which the spark passes. This would tend to quench any ignition. This phenomenon of a spark not igniting a flammable mixture between two parallel plates is discussed by Metzler [10] with relation to the prediction of minimum ignition energy. The quenching of flames by parallel surfaces in close proximity has also been investigated by Potter [11], who found that hydrocarbons have quenching distances of 2 to 3 mm. Similarly, the breakdown strength of air is not constant at small gaps, as discussed by Glor [12], but for the purposes of this illustration, it can be assumed to be constant at the distances and potentials under discussion. Thus, theoretically, any ignition would not propagate from the plasma channel of

the spark at such a low voltage. With a breakdown strength of 30 kV cm^{-1} , and a gap of 2 mm which would just allow the flame to propagate, a potential of 6 kV would be required for a spark to occur.

If hydrogen is now considered, the corresponding voltages and gaps are much reduced. Although the dielectric strength for air is about 30 kV cm^{-1} , the dielectric strength of hydrogen atmospheres is only 17.5 kV cm^{-1} [13] and its quenching distance is only 0.69 mm. The variation of dielectric strength with concentration of hydrogen in air mixtures is unknown, but as a simple case, it could be assumed to be linear within a specified narrow concentration range, so the theoretical dielectric strength of an about stoichiometric mixture of 30% would be $0.3 \times 17.5 + 0.7 \times 30 = 26.25 \text{ kV cm}^{-1}$. With a quenching distance of 0.69 mm, and a dielectric strength of 26.25 kV cm^{-1} the breakdown potential would correspond to a voltage of $26.25 \times 0.069 = 1.81 \text{ kV}$, which corresponds to a stored energy of $0.5 \times [100 \times 10^{-12}] \times [1.81 \times 10^3]^2 = 1.638 \times 10^{-4} \text{ Joule}$, i.e. 0.164 mJ, which 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. 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.

4.2.2 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. Work by Gibson and Harper [14] introduced the term of incendivity or equivalent energy which is where the brush discharge has the ability to ignite an atmosphere, with the same minimum ignition energy as a spark which will just ignite the flammable atmosphere. Typical equivalent energies were found to be about 4 mJ for brush discharges from flat polyethylene sheets. However, Ackroyd et al [15] found that certain more modern plastics, and thin plastic coatings on earthed metal, had higher equivalent energies.

4.2.3 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. If the field spreads out rapidly, as it would in the case of a point locally modifying the field, then a spark will not pass, simply because the field strength remote from the point is too low to break down. This has been described by Cross [16], who gives an equation to determine the voltage required for a corona to start from a point given its tip-radius.

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 [17] showed that ignition was rare during fine weather, but was more frequent during thunderstorms, sleet, falling snow, and on cold frosty nights. These weather conditions correspond to high electrical field strengths in the atmosphere, as described by Schaefer [18], Camp [19], and Burrows and Hobbs [20]. From this it can be appreciated that under some circumstances, hydrogen ignitions could be due to atmospheric electrical effects. The prevention of ignition of hydrogen deliberately vented to atmosphere has been described before by using a polished toroidal ring at the end of the vent [21] to ensure that the effective tip-radius is large. The intention is that by having a large radius, the field strength is less than that required to form a corona, and hence ignition could be prevented. In practice, corrosion and dirt

deposits are effectively small radius protrusions, so anything which affects the polished finish could create small radius protrusions which would still have an effect. Further work is required on the atmospheric effects required to initiate combustion of hydrogen atmospheres, and the frequency of such effects occurring.

4.3 Diffusion Ignition

The phenomenon of diffusion ignition has been postulated by Wolański and Wójcicki [22], 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. A shock-wave of this Mach Number would be produced by an upstream pressure of 3.9 MN m^{-2} , which is typical of the pressure and temperature conditions in an ammonia synthesizer plant. They also calculated that ignition would occur at a lower Mach Number of only 1.7, corresponding to an upstream pressure of 1.3 MN m^{-2} , when the shock wave was reflected by an obstacle. They confirmed their results using a shock tube, which was totally enclosed.

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 $685 \pm 30 \text{ K}$ ($412 \pm 30^\circ\text{C}$). This autoignition temperature seems unduly low compared to that reported by other workers, notably the 585°C by NASA [6] and 560°C quoted by IEC 60079-20:2000 [23], although the NFPA [24] 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.

4.4 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:

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

For a compression ratio of say 10 to 1, from atmospheric pressure and 273 K, then for hydrogen where γ equals 1.410 [25], and it is assumed to behave ideally, the pressure rise ratio would be:

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma = (10)^{1.41} = 25.7 \tag{2}$$

Since for a perfect gas the relationship $PV = nRT$ holds, then the new temperature can be calculated using:

$$T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = \frac{25.7 \times 1 \times 273}{10} = 701.6 \text{ K} \tag{3}$$

These two equations may be combined to determine the adiabatic temperature rise due to compression as:

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad (4)$$

Since most diatomic gases have a specific heat ratio of about 1.4, an air-hydrogen mixture would have similar properties, and therefore the same magnitude of temperature rise would occur. However, this assumes adiabatic compression, which is unlikely to be realised in practice. In experiments conducted by Pan et al [26], the actual measured temperature realised by a compression ratio of 28 times was only 149 K. This compares to a theoretical estimate of 453 K for a plug-flow model where no mixing takes place, and 108 K for a fully mixed system. Thus isentropic compression is unlikely to occur in practice.

Work by Cain [27] however, indicates that compression ignition of hydrogen-oxygen-helium mixtures occurs at a relatively constant temperature of 1050 K, at pressure rise ratios of 35 to 70 starting at 300 K at atmospheric pressure. Reverse calculation using Equations (2) and (3) combined and re-arranged in terms of ratios, indicates that a temperature rise from 300 to 1050 K would require a pressure rise ratio of:

$$P_r = (T_r)^{\left(\frac{\gamma}{\gamma-1}\right)} = \left(\frac{1050}{300}\right)^{\left(\frac{1.4}{1.4-1}\right)} = 80.2 \quad (5)$$

where P_r - pressure rise ratio; T_r - absolute temperature ratio. This required pressure rise ratio is greater than that measured by Cain, suggesting that there is another ignition mechanism present.

4.5 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 [6] 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 [28] 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 [29] 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.

5. DISCUSSION

From the above, it appears that no one mechanism is able to explain all of the recorded incidents. One was reported at substantially atmospheric pressure, but the rest all involved discharges of hydrogen stored at high pressure. In several incidents, there is a suggestion in the reports that electrostatic effects may have been responsible. In particular, the second incident reported by Fenning and Cotton involved only a fine stream of mercury, with no other potential ignition sources inside the closed system. The potential for drops and bursting bubbles to generate electrostatic charges has been proposed by Blanchard [30], and the ability of such charges to ignite sensitive atmospheres has been illustrated by Pratt [31]. Therefore it would appear that there is a potential for such bubble and drop formation in a fine stream of mercury to generate sufficient charge to ignite a sensitive mixture. A "complete combustion" mixture, if taken to be a stoichiometric mixture, would be at its lowest ignition energy, and therefore extremely sensitive to ignition.

The ignition of flammable materials by a hot surface is well documented, both for hydrogen and for other materials such as hydrocarbons, with most researchers showing the lowest temperatures for ignition being associated with large volumes and surface areas [32]. The trends reported show smaller heated surfaces require higher temperatures [33], downward facing surfaces showing longer induction times [29], and surfaces at the top of the enclosure having longer induction times [34]. Consequently, any mixture of hydrogen and air within the flammable range is liable to be ignited by a heated surface, but the temperature and the delay before ignition will depend on the size, geometry and orientation of the enclosure. Clearly, release of hydrogen direct to atmosphere would not be enclosed, so only if the gas were to impact on a heated surface would ignition from this mechanism be likely.

Where ignition has occurred due to a high pressure discharge direct to atmosphere, two mechanisms have been proposed. The first, the Joule-Thomson effect has been described above, and whilst it is a possible mechanism where the initial conditions are well above ambient temperature, it would appear to be an unlikely mechanism for ignition on its own. The diffusion ignition mechanism also seems to be likely only when the initial temperature is high. However, where valves on cylinders are briefly opened direct to atmosphere, presumably to clear any debris from the cylinder, ignition has occurred. This may be due to the Joule-Thomson effect or the diffusion ignition effect, but the diffusion ignition effect appears to be reproducible in a shock-tube apparatus or similar closed equipment, and Wolański and Wójcicki appear to have only carried out work using a hydrogen-nitrogen mixture. Nothing in their theory has any reference to properties specific to hydrogen, so it would be reasonable to assume that other gases would also behave similarly. However, it does not appear that gases other than hydrogen show similar ignition phenomena when subjected to shock. Hence it may not be an adequate theory for discharges direct to atmosphere.

Similarly, the adiabatic compression phenomenon of ignition is known to have ignited an ethylene pipeline [35], so it would be difficult to separate the exact differences between diffusion ignition and compression ignition, but both would appear to require a degree of confinement not present in all the incidents where a release to atmosphere occurred.

In terms of electrostatic ignition, it is generally recognised that pure gases do not become electrostatically charged under normal conditions [36], but this refers generally to low velocities and pressures. Where gases are released at very high pressures, the flow becomes sonic and the propensity of electrostatic charging occurring is not known. It is known that pure gases tend not to charge, but particles within the gas stream are known to become electrostatically charged. In the incident reported in Engineering [2], a corona discharge was observed. Such a corona would be capable of igniting a flammable hydrogen atmosphere, as the ignition energy of the hydrogen-air mixture is low enough. Clearly in this case, the corona was produced by the particles impacting on the funnel or the cap within the pipe. However, the ignition at Jackass Flats took place some three seconds after the valve to stop the flow had been actuated. The maximum flow rate of hydrogen leaving the nozzle would have occurred during the 10 second full-flow period, and the flow would already be diminishing when ignition occurred. It is unlikely that the bar across the nozzle would have broken loose during the

shut-off stage, and hence any charge associated directly with the breaking of the bar would have been expected to dissipate by the time that the gas ignited.

Of all the high pressure releases, the common effect is that there is somewhere a restriction across which a high pressure-drop occurs, be this a valve, nozzle, gasket or fitting. Hence with a high pressure drop there is a very high local velocity. With a sharp-edged orifice, it is likely that the flow through the orifice would be sonic, and only through a properly shaped convergent-divergent nozzle would the flow become supersonic. In all cases except the Jackass Flats incident, supersonic flow would be very unlikely, but the discharge orifice would probably be convoluted and not in a straight line. This would require the hydrogen to discharge through one or more bends, which would potentially allow materials on the surface of the pipes to be eroded and form particles which could become electrostatically charged. This would need to be verified. In the case of the Jackass Flats incident, at the time of ignition, the shut-off valve was partially closed, so again, the flow velocity would be highest through the valve itself, again suggesting a non-straight line discharge. This is the only common feature apparent in all the high-pressure releases.

There is also the potential for two or more potential mechanisms to work together. It is known that the minimum ignition energy of gases and vapours decreases with increases in temperature [37], so expanding hydrogen would increase in temperature due to the reverse Joule-Thomson effect, and hence its ignition energy would reduce. However, this could be countered by the increase in ignition energy with pressure, but once expanded to atmospheric pressure, the ignition energy would be expected to be lower overall. Similarly, if particles were to be abraded from the walls of any pipe-work, the required energy for ignition from a corona discharge would be lower, so it is likely that less corona charging current would be required to ignite the hydrogen.

Thus it can be seen that whilst no one postulated theory would account for the spontaneous ignition of hydrogen, there are possibilities that several mechanisms are possible, either alone or in combination. Further work is required to determine the potential for very high velocities to generate electrostatic charges, alone as a pure gas, or by abrasion of surfaces by the sonic velocity of the gas. Work is also required to determine the magnitude of these charges and their propensity to ignite hydrogen.

6. CONCLUSIONS

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.

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.

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.

Further work is required to establish the conditions under which hydrogen releases ignite, particularly with respect to electrostatic phenomena.

7. REFERENCES

- 1 <http://www.hse.gov.uk/infoserv/mhidas.htm>.
- 2 Anon., Spontaneous Ignition of Hydrogen, *Engineering*, 113, April 21, 1922, p. 502.

- 3 Fenning, R.W., and Cotton, F.T., Two Unexpected Hydrogen-Air Explosions, *Engineering*, **130**, August 22nd 1930, p. 252.
- 4 Bond, J., Sources of Ignition: Flammability Characteristics of Chemicals and Products, 1991, Butterworth Heinemann, Oxford.
- 5 Reider, R., Otway, H.J., and Knight, H.T., An Unconfined Large Volume Hydrogen/Air Explosion, *Pyrodynamics*, **2**, 1965, p. 249.
- 6 National Aeronautics and Space Administration Report, Safety Standard for Hydrogen and Hydrogen Systems, Report NSS 1740.16, 1997, p. A-16.
- 7 Perry, J.H., Chemical Engineers' Handbook, 4th Ed., Figure 3-28, 1963, McGraw-Hill Book Co.
- 8 Michels, A., de Graaf, W. and Wolkers, G.J., Thermodynamic Properties of Hydrogen and Deuterium between -175°C and 150°C and at Pressures up to 2500 Atmospheres, *Appl. Sci. Res.*, Part A, **12**, 1963, pp. 9-32.
- 9 International Standards Organisation Technical Report ISO/TR 15916:2000, Basic considerations for the safety of hydrogen systems, p.41 Table B.2
- 10 Metzler, A.J., Minimum Ignition Energies of Six Pure Hydrocarbon Fuels, NACA Report RM E52 F27 1952.
- 11 Potter, A.E., "Flame Quenching", *Prog. Comb. Sci. & Tech.*, **1**, 1960, pp. 145-181.
- 12 Glor, M., quoted by Lees, F. P., Loss Prevention in the Process Industries, Vol 1, 2nd Ed., 1996, Butterworth Heinemann, Oxford, p. 16/93.
- 13 Cassutt, L., Biron, D. and Vonnegut, B., Electrostatic Hazards Associated with the Transfer and Storage of Liquid Hydrogen, *Advances in Cryogenic Engineering*, **7**, 1962, pp. 327-335.
- 14 Gibson, N. and Harper, D.J., Parameters for Assessing Electrostatic Risk from Non-Conductors - A Discussion, *J. Electrostatics*, **21**, 1988, pp. 27-36.
- 15 Ackroyd, G.P., and Newton, S.G., An investigation of the electrostatic ignition risks associated with a plastic coated metal, *J. Electrostatics*, **59**, 2003, pp. 143-151.
- 16 Cross, Jean A., Electrostatics Principles, Problems and Applications, 1987, Adam Hilger, Bristol.
- 17 Personal communication to G.R. Astbury from D. McBrien at ICI, Manchester.
- 18 Schaefer, V.J., Properties of Particles of Snow and the Electrical Effects They Produce in Storms, *EOS Transactions*, **28**, No.4, 1947, pp. 587-614.
- 19 Camp, P. R., Charge, Morphology, and pH of Natural Snow, *J. Geophysical Research*, **81**, No.9, 1976, pp. 1589-92.
- 20 Burrows, D.A., and Hobbs, P.V. Electrical Charges on Snow Particles, *J. Geophysical Research*, **75**, No.24, 1970, pp. 4499-505.
- 21 Techlink No. 218, Ministry of Technology, HMSO (1968)
- 22 Wolański, P., and Wójcicki, S., Investigation into the Mechanism of the Diffusion Ignition of a Combustible Gas Flowing into an Oxidising Atmosphere, 14th Symp. (Int.) on Combustion, The Combustion Institute, Pennsylvania State University, 1973, pp. 1217-1223.
- 23 International Electrotechnical Commission, Electrical apparatus for explosive gas atmospheres - Part 20: Data for flammable gases and vapours, relating to the use of electrical apparatus, Standard IEC 60079-20:2000
- 24 National Fire Protection Association, Fire Protection Guide on Hazardous Materials, 325M, 9th Edition, 1986, Massachusetts, p. 59.
- 25 International Critical Tables, **5**, McGraw-Hill Book Co., New York, 1933, p. 80.
- 26 Pan, L., Fisher, S.A., Jayanti, S. and Hewitt, G.F., Measurement and Prediction of Temperature rise Following Sudden Compression in a High-Pressure Pipeline, *Trans. I.Chem.E.*, **73**, Part B, 1995, pp. 18-20.
- 27 Cain, T.M., Autoignition of Hydrogen at High Pressure, *Combustion and Flame*, **111**, 1997, pp. 124-132.

- 28 Neer, M. E., An Investigation into Spontaneous Ignitions in Flowing Hydrogen Air Mixtures, PhD Thesis, Ohio State University, 1972, abstracted in *Diss. Abstr. Int. B.*, **33**, 1972, p. 686.
- 29 Bulewicz, E.M., et al, Zapłon mieszaniny wodorowo-tlenowej od gorącej powierzchni (The ignition of hydrogen-oxygen mixtures from a hot surface), *Archiwum Termodynamiki i palania*, **8**, No.1, 1977, pp. 85-93.
- 30 Blanchard, D.C., Electrification of the Atmosphere by Particles from Bubbles in the Sea, *Progress in Oceanography*, **1**, 1963, pp. 71-202
- 31 Pratt, T. H., Electrostatic Ignitions in Enriched Oxygen Atmospheres: A Case History, *Process Safety Prog.*, **12**, 1993, pp. 203-5.
- 32 Snee, T.J., and Griffiths, J.F., Criteria for Spontaneous Ignition in Exothermic, Autocatalytic Reactions: Chain Branching and Self-Heating in the Oxidation of Cyclohexane in Closed Vessels, *Combustion and Flame*, **75**, 1989, pp. 381-95.
- 33 Silver, R.S., The Ignition of Gaseous Mixtures by Hot Particles, *Phil. Mag.*, 7th Ser., **23**, No.156, 1937, pp. 633-57.
- 34 Ungut, A. and James, H., Autoignition of gaseous fuel-air mixtures near a hot surface, *I.Chem.E. Symposium Series* No. 148, 2001, pp. 487-502.
- 35 Britton, L.G., Loss case histories in pressurised ethylene systems, *Process Safety Progress*, **13**, No.3, 1994, pp.128-138.
- 36 IEC Published Technical Report: Electrostatics - Code of practice for the avoidance of hazards due to static electricity, TR 50404: 2002
- 37 Moorehouse, J., Williams, A., and Maddison, T.E., An investigation of the minimum ignition energies of some C₁ to C₇ hydrocarbons, *Combustion and Flame*, **23**, 1974, pp. 203 et seq.

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