EXPERIMENTAL RELEASES OF LIQUID HYDROGEN

Hooker[1], P., Willoughby[1], D.B., Royle[2], M.
[1]Health & Safety Laboratory UK
[2]Health and Safety Executive UK

Health and Safety Laboratory, Buxton, Derbyshire, SK17 9JN, United Kingdom,
Tel 01298 218120, Fax 01298 218162, Deborah.willoughby@hsl.gov.uk

ABSTRACT

If the hydrogen economy is to progress, more hydrogen refuelling stations are required. In the short term, in the absence of a hydrogen distribution network, the most likely means of supplying the refuelling stations will be by liquid hydrogen road tanker. This development will clearly increase the number of tanker offloading operations significantly and these may need to be performed in more challenging environments with close proximity to the general public.

The work described in this paper was commissioned in order to determine the hazards associated with liquid hydrogen spills onto the ground at rates typical for a tanker hose failure during offloading.

Experiments have been performed to investigate spills of liquid hydrogen at a rate of 60 litres per minute. Measurements were made on both unignited and ignited releases. These include:

- Concentration of hydrogen in air, thermal gradient in the concrete substrate, liquid pool formation, and temperatures within the pool
- Flame velocity within the cloud, thermal radiation, IR and visible spectrum video records.
- Sound pressure measurements
- An estimation of the extent of the flammable cloud was made from visual observation, video, IR camera footage and use of a variable position ignition source

Keywords: Flame speed, Thermal radiation, Hydrogen concentration, Flammable cloud, Liquid pool

1.0 INTRODUCTION

Cryogenic liquid storage and transfer has been safely executed for many years in secure and regulated industrial sites. However, its use in relatively congested, highly populated urban areas presents a new set of problems in relation to security, safety and associated planning. Research is needed to identify and address safety issues relating to bulk liquid hydrogen storage and transfer facilities associated with hydrogen refuelling stations located in urban environments.

Liquid hydrogen has significantly different properties to other more common cryogenic gases, as can be seen from the values presented in Table 1.

Table 1: Properties of liquid hydrogen and other common cryogenic gases[1]

	Hydrogen	Nitrogen	Oxygen	Methane
Liquid density (kg/m^3)	70.8[3]	804	1142	424
Gas density at boiling point (kg/m^3)	1.34[3]	4.61	4.48	1.80
Boiling point (K)	20.28	77.35	90.18	109.15
Freezing point (K)	14.01	63.29	54.75	90.67

It can be seen from these properties that attempting to simulate the release behaviour of liquid hydrogen with other more easily handled cryogens is unlikely to yield useful results. The liquid phase has very low density compared to the other industrial cryogenic liquids and the vapour phase at the boiling temperature is only just negatively buoyant in ambient air (air density approximately 1.2 kg/m^3)[1]. Furthermore, a release of liquid hydrogen can result in significant cooling of the surroundings causing condensation of nitrogen and oxygen from the air and even the freezing of these gases to produce a solid.

In addition, the general combustion properties, such as flame speed and ignition behaviour, for a cool, dense vapour cloud of hydrogen with high proportions of condensed water present are unknown and therefore needs to be studied.

This paper gives an overview of experimental work to investigate the behaviour of liquid hydrogen released to atmosphere in both un-ignited and ignited scenarios.

2.0 EXPERIMENTAL AIMS

A number of distinct areas of spill behaviour were investigated:

- Hydrogen dispersion from unignited spills
- On ground liquid spill formation
- Spills into free air
- Spill behaviour with respect to specific storage conditions
- Flame speed and extent from ignited spills
- Thermal radiation from ignited spills
- Sound pressure level measurement from ignited hydrogen clouds

All the releases made were chosen to replicate a reasonably foreseeable release from the failure of a transfer hose coupling during product transfer. Catastrophic failure of the containment vessel was not investigated, as it is considered to be a highly unlikely event.

3.0 EXPERIMENTAL RELEASES

All the releases in this work were made from hydrogen stored in a road tanker provided by BOC UK. The liquid hydrogen was piped from the tanker to the release point through a 25mm diameter vacuum insulated flexible line. Most of the releases were made from a nominal storage pressure of 1bar(g) this gave a nominal release rate of 60 litres per minute of liquid hydrogen. A schematic of the release system is shown in Figure 1 and a photograph of the test area with tanker and pipe-work in Figures 2 and 3. The release system comprised the liquid hydrogen tanker, 20 metres of 25mm bore vacuum insulated hose, a release valve station with bypass, purge and release valves and a 6 m high vent stack to vent excess hydrogen. The tanker contains up to 2.5 tonnes of hydrogen in a vacuum insulated internal tank surrounded by an outer jacket containing liquid nitrogen. The tanker is equipped with vent valves such that the pressure within the tanker can be lowered. It is also fitted with a liquid hydrogen / air heat exchanger such that the pressure in the tanker can be raised. To raise the pressure within the tanker LH2 is allowed to flow into the heat exchanger where it vaporises; this vapour is then fed into the vapour space in the tanker in order to pressurise the liquid hydrogen. The tanker is fitted with a bursting disc rated at 12 bar to protect against over-pressurisation. The storage conditions of the liquid hydrogen are important if consistent results are to be obtained. As the pressure of hydrogen delivered in the tanker was up to 5 bar, the vapour space of the tanker was first depressured and then re-pressurised to approximately 1 bar before each series of releases. This was carried out in order to achieve consistency and to obtain a liquid spill without significant flash vaporisation.

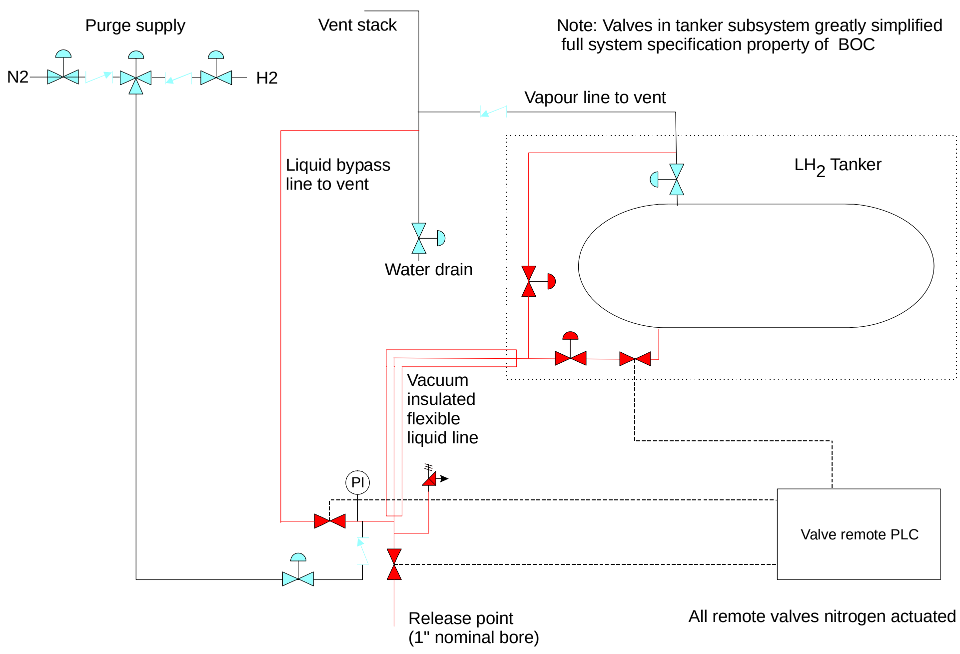

Figure 1. Schematic of release system

Figure 2. Test area and tanker

Figure 3. Release pipework

The releases were made onto or above a concrete surface. For unignited releases the following measurements were made:

- Storage pressure – the pressure in the tanker during the release, this remained constant, as the amount of liquid being withdrawn was small compared to the overall volume of the tanker
- Release pressure – this was the pressure measured just upstream of the final release valve
- Pool size – the extent of any pool of liquid formed on the ground, this was determined by a combination of video and thermocouple measurements – twenty four 1mm type E thermocouples were deployed in contact with the ground (see Figure 4)
- Hydrogen concentration – this was determined from temperature measurements within the cloud using an adiabatic mixing assumption. A total of thirty 1mm type E thermocouples were deployed (see Figure 5)
- Pool temperature – the temperature of the hydrogen being released and that forming a pool on the ground was determined by thermocouple measurements
- Substrate temperature – the temperature within the concrete pad in the vicinity of the release was measured with three thermocouples embedded in the concrete at depths of 10, 20 and 30 mm
- Meteorological measurements – including wind-speed, wind direction, air temperature and humidity were determined at release height and 2.5 metres above the ground at the edge of the release area

For ignited releases additional measurements were made of:

- Flame speed – by high speed video recording and thermal imaging
- Thermal radiation – using Medtherm fast response ellipsoidal radiometers
- Pressure – using Kulite pressure transducers
- Sound pressure level measurement

Figure 4. Pool thermocouples

Figure 5. Concentration measurements

4.0 TEST PROGRAMME

The work plan involved releases of liquid hydrogen at a nominal rate of 60 litres per minute for different durations and different orientations. For all of the tests the liquid hydrogen was released through a 1inch nominal bore Schedule 40 pipe, which gave an internal diameter at the orifice of 26.3 mm.

A number of tests were performed in which LH2 was released in one of the following ways; a) horizontally along the ground, b) vertically downwards from 100mm above the ground, c) horizontally at a height of 860mm above the ground. The nominal storage pressure was 1 bar and the nominal release pressure was 0.2 bar for all the releases reported here.

5.0 RESULTS

A report containing the full set of results with full details of sensor position and meterological measurements can be obtained by contacting the authors. However, a summary of the results is given below.

5.1 UNIGNITED TESTS

The tests which impinged hydrogen onto the ground all produced a pool of liquid once the ground had cooled sufficiently, usually about 2 minutes into the release. In addition a large solid deposit, which had the appearance of "snow", was produced. Both the liquid and the "snow" persisted for several minutes after the release ended.

The thermocouple measurements taken in contact with the ground during the release are shown in Figure 6. These show a degree of sub-cooling is occurring as the hydrogen is released and evaporates with temperatures as low as 16K being recorded. In addition steps are evident in the temperature traces as the temperature increases after the release has ended. This is indicative of the melting and boiling of the condensed air.

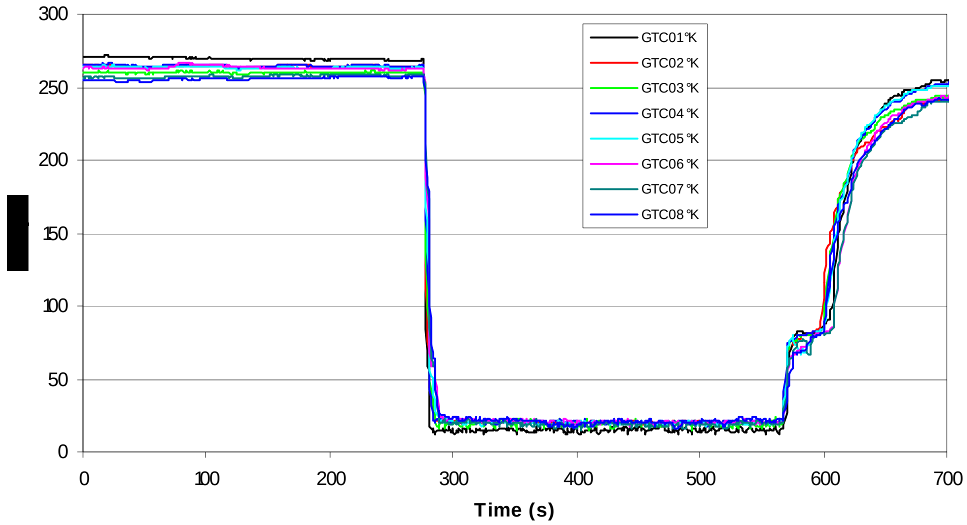

Figure 6. Surface concrete temperatures for the first eight sensors during the release

The temperatures typically recorded in the concrete layer underneath the release point are shown in Figure 7 at depths of 10, 20 and 30 mm.

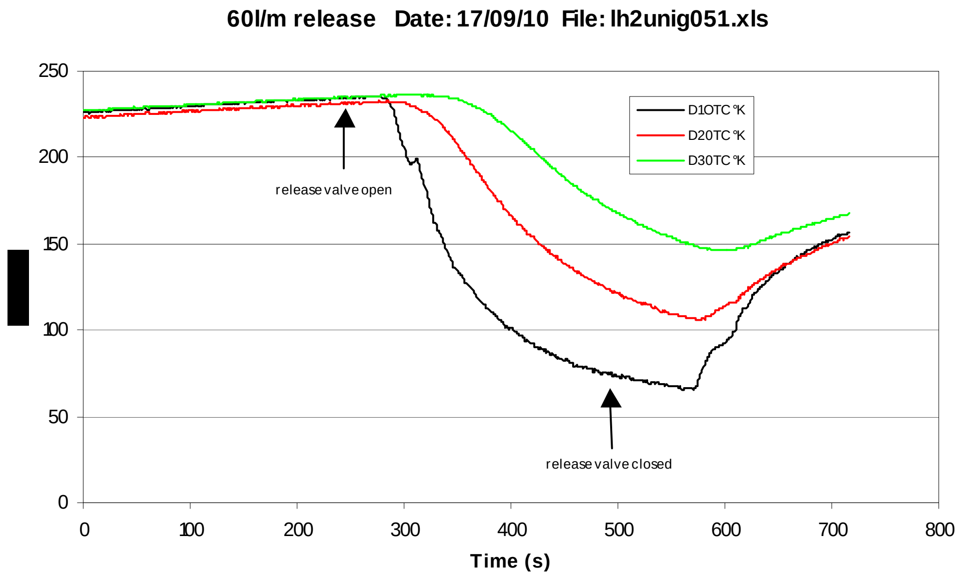

Figure 7. Concrete temperatures during the release

The cloud of hydrogen vapour is visible during the release due to condensation of water within the cloud. A photograph showing a typical hydrogen cloud formed by a release is shown in Figure 8.

Figure 8. Hydrogen cloud

A concentration contour graph is shown in Figure 9 representing a snapshot of experimental data from a typical horizontal release at ground level. The graph was generated using measured hydrogen concentration data at various heights and distances from the release point. The red line represents the 4% concentration contour (LFL) and the green line the 30% concentration contour (stoichiometric). The graph gives an estimate of hydrogen concentrations at a specific time during the release when the wind direction was such that the hydrogen cloud passed through the sensors.

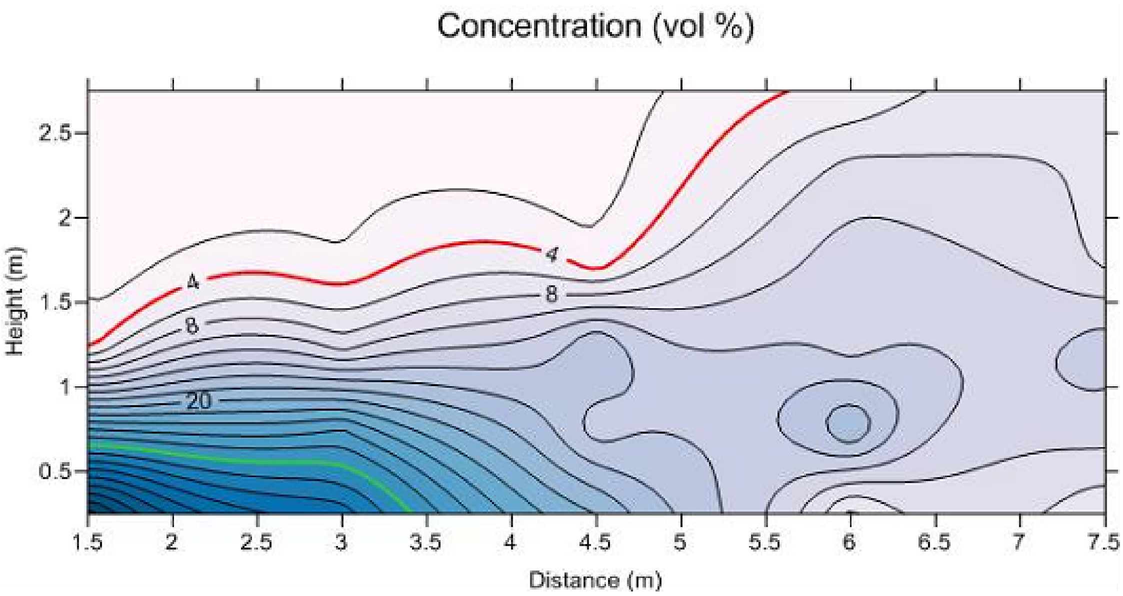

Figure 9. Concentration contour graph

A photograph of the pool of liquid produced during a release is shown in Figure 10. A solid deposit can also be seen close to the release point. A close up photograph of the solid deposit is shown in Figure 11.

Figure 10. Pool and solid

Figure 11. Solid deposit 3 minutes after release

This solid persisted for some time after the release, appearing to co-exist with a boiling pool of liquid. The solid deposit appeared to sublime rather than melt, possibly due to the relatively close melting and boiling points compared to ambient temperature.

After one of the tests an attempt was made to ignite the vapour above the snow deposit, ignition occurred and a vigorous flame ensued.

Initial thoughts are that the solid deposit is a mixture of solid nitrogen and oxygen with some liquid hydrogen trapped within the matrix similar to that observed when butane forms hydrates with water Allen 2000[2].

5.2 IGNITED RELEASES

A number of ignited releases were performed with varying parameters. The release rate and pressure were the same as for the unignited releases. All the ignited releases performed to date have been made with the hydrogen released horizontally at ground level. A number of releases were made at night to enable the flame to be more easily visualised. It should be noted that the clouds of hydrogen produced by the release of liquid hydrogen were fairly difficult to ignite. On one occasion the hydrogen cloud failed to ignite even after four 1 kJ chemical igniters were fired within it.

The first ignited release (see Figure 12) was performed with the ignition timed immediately after the release had stabilised and before any pool or solid had accumulated on the ground. On ignition there was a soft report followed by a low rumble and then a gentle jet flame as the hydrogen issuing from the release pipe burned. The ignition was approximately 9 m from the release point and at 1 m high. The flame speed was measured from the high speed video and was approximately 30 m/s.

There was some evidence of sudden, energetic combustion occurring close to the release point after LH2 had been released at ground level for about 4 minutes and a solid deposit had formed. The phenomenon occurred after the hydrogen cloud had been ignited and had burned back to the release point. It is considered likely that this is related to the formation and subsequent reaction of an oxygen-rich slurry of solidified air and LH2[3].

Figure 12. Ignited cloud

6.0 MAIN FINDINGS

The release of liquid hydrogen in contact with a concrete surface can give rise to pooling of liquid once the substrate is sufficiently cooled.

Release of liquid hydrogen in close proximity to a concrete surface can result in subcooling due to vaporisation.

The release of liquid hydrogen at a rate consistent with the failure of a 1 inch transfer line produces a flammable mixture at least nine metres downwind of the release point.

The release of hydrogen in contact with a concrete surface produces a solid deposit of oxygen and nitrogen once the substrate is sufficiently cooled.

REFERENCES

[1] CRC Handbook of Chemistry and Physics, 58th Ed.

[2] Allen, J.T., Characteristics of impinging flashing jets, HSL report FS/00/02, 2000

[3] NASA document NSS 1740.16 : "Hydrogen and Hydrogen Systems, Guidelines for Hydrogen System Design, Materials Selection, Operations, Storage, and Transportation"