Handling the cryo-factor

John Frame has created and delivered LNG Fire Response training courses and also produced the original book *LNG Fire Protection & Emergency Response*, available from the IChemE. In this article, he focuses on LNG incident hazards and likely scenarios with a view to assisting emergency responders who may be called upon to react to incidents at LNG facilities.

Above: the Methane Pioneer loading at Lake Charles. Note the cars parked and the basic facilities – we have come a long way since then! Right: modern LNG carrier, British Trader. © BP plc.

Potential LNG emergency responders may already be aware of a particularly catastrophic failure of an LNG tank in Cleveland, Ohio, USA, on 20th October, 1944, which was followed by further tank failures and fires.

Much has been written about the incident, but briefly, the LNG tanks were spherical, with an inner tank constructed of steel with only 3.5% nickel composition, insulated with cork between this tank and finally an outer tank of only carbon steel. Since LNG is a cryogenic liquid it means temperatures as low as -162°C. At such temperatures, carbon steel loses its ductility, becomes brittle and can easily crack under stress. The effects of cryogenic liquid contact on carbon steel and resultant embrittlement were already very well known in 1944. Today, it's normal to use around 9% nickel in steel for LNG storage tanks, to prevent embrittlement (no tank using this has failed). The embrittlement effects of using only 3.5% nickel should have been known, but the reasons for its use in 1944 remain unclear. One hypothesis is that since it was built during WWII, nickel was scarce, but if true, the tanks should still not have been constructed given the then knowledge of steel embrittlement with such a low nickel content.

Due to cracks in the sphere steel, possibly caused by vibration from a nearby railroad, one of the tanks failed catastrophically and the liquid overflowed the two metre high bund walls, flowed outside of the site, entered public drains and housing basements and other low level areas and was ignited as vapourisation increased in confined spaces. The resultant explosions and fires killed 128 and injured between 200 and 400 people. The fire completely destroyed the LNG plant as well as business and residential blocks in the town. Although this major disaster had a profound impact on the LNG industry, and led to fear of LNG storage facilities until the 1960s, there have been no recorded incidents involving tank failures since this time, more than 60 years ago, which is testament to a very effective and safe tank containment construction which uses 9.5% nickel steel.

After this catastrophe, in time honoured fashion, lessons were learned, codes and standards improved and much better defined requirements and greater enforcement put into place as a result – which if we think about it, is the history of the any advancement and improvements in fire protection and emergency response through the decades.

With the scale of this particular catastrophe, it is obvious that emergency responders could do little except limit fire spread beyond the area of catastrophe and then carrying out a belated search and rescue for casualties as they doused secondary fires. Although an incredible incident, it is one the industry and regulators alike have focused on to ensure that any impact is limited to on-site areas only. In other words, assumptions that it is not a credible incident for consideration in risk assessment is not acceptable.

Given this approach, the intention of this article is to look at the associated hazards for responders and the more likely incident scenarios, strategies and tactics which should be considered. We may term these as "intervention-possible" LNG incidents.

A short history of LNG

Readers will know that Liquefied Natural Gas, sometimes known as liquid natural gas (LNG) is firmly established as the "new" fuel for the 21st Century. However, Methane was first liquefied around 125 years ago, as an experiment in Europe, and was therefore the earliest version of LNG. Commercially, LNG has been available since the first half of the 20th Century. In 1912, the first LNG plant was built in West Virginia, USA and in 1914 a patent was placed for a barge to carry LNG, complete with a very rudimentary insulation system. In 1959, the first LNG sea tanker voyage was made from Lake Charles, Louisiana, USA to Canvey Island, Essex, UK: this was the "Methane Pioneer", a Converted World War 2 Liberty Ship, which took 5,000 M^3 of LNG in Aluminum Prismatic tanks. Now LNG has become a world wide phenomenon and the number of LNG import terminals has rocketed in consumer countries in the rush for cleaner energy.

LNG HAZARDS FOR EMERGENCY RESPONDERS

An example of frostbite, something that immersion in a cryogenic liquid would cause rapidly. Sensations in the finger tips are lost forever.

The basics

LNG is lighter than and will therefore "float" on water (it will also vapourise rapidly on water). LNG cold vapour is heavier than air, and then as it warms becomes neutrally buoyant, before becoming lighter than air (due to mainly Methane content). The vapour flammable range is usually quoted as 5% to 15%, but is more accurately 5.3% to 14%. Like other flammable gases, if LNG vapour is confined and within flammable range on ignition, there will be an explosion. However, unconfined vapour clouds of LNG have not, to date, exploded to cause overpressures, mainly due to slow flame speeds through the cloud (this creates a deflagration and not a detonation). LNG vapour is not toxic, but where O2 displacement occurs, will obviously be an asphyxiant.

Cryo factor

LNG is a cryogenic liquid, the word taken from the ancient Greek "Kryos", meaning cold/frost/freezing, and genic meaning "relating to production", thus Cryogenics is the production of very low temperatures.

As a cryogenic liquid, alone, it is hazardous to personnel in terms of skin or body contact. While small infrequent droplets are not a serious hazard if PPE is worn, immersion of hands, feet or other parts of the body, or prolonged skin contact will result in rapid freezing and serious injury. The term "ice burn" or "cryogenic burn", in fact a misnomer, describes the sensation experienced when liquids or materials at cryogenic temperatures come into contact with the skin. This happens because the nerve endings in the skin cannot easily distinguish between temperature extremes – high heat and freezing creates similar sensations. For cryogenic "burns", unlike heat burns, the freezing and sub-cooling of flesh produces embrittlement of the affected area, because of its water content. Bunker gear will give responders some protection against LNG fire radiant heat, but not against sustained liquid contact/immersion.

Vapourisation rate

When any LNG is spilled, there will be a high vapourisation rate initially (around 3cu.m^3/min/m^2) vapour from liquid) due to the inherent heat of either ground or water, which rapidly boils the liquid. In a contained pit and assuming the ground has been chilled down/frozen by the liquid, the vapourisation rate will settle down and stabilise (to around 0.3 m^3/min/m^2). A coarse rule of thumb for responders is that for 0.3m depth of liquid at stable vapourising conditions, it can take around 10 hours to vapourise completely. This is obviously a significant length of time for a vapour hazard on a site, although the vapour cloud will not be so great as initial vapourisation while the ground chills down.

A spill on an expanse of unconfined water is different due to the LNG being unable to chill down water in span and depth. Therefore, there is no true stabilisation (as there is with, for instance, a ground pit) with high vapourisation (around 15 m^3/min/m^2 vapour from liquid) lasting much longer. With a spill on shallow water which is itself confined (small pond or pit), the water at the bottom of the pit will rise and then freeze due to the cryo impact and create an ice layer on

An Atlantic LNG 122 storage tank, Trinidad and Tobago. © BP plc.

top, to some degree acting as an insulator, but not preventing vapourisation, although this is less than with open water rates and more like the spill on land (around 0.3 m^3/min/m^2). Obviously, the upshot of all this is if a significant spill occurs on open water, the generated vapour cloud will be greater for a longer period.

Burn off rate

LNG burn off rate is approximately 12.5mm per minute. This compares with gasoline liquid which has a burn off rate of approximately 4mm per minute. Assuming an LNG depth of say 1 metre, it may take about 1 hour 20 minutes to burn out – a significant time for radiant heat impact.

Icing hazards on open, porous ground

If a serious LNG spill occurs into/on open porous ground where moisture/water is in the soil, there will usually be tell-tale icing on the surface at some distance from the actual liquid spill, which indicates the ground around the area is porous: in other words, the cold vapour is migrating through the soil. If this happens, care must be taken to prevent responders moving over the area where are small ice particles, because if ignition occurs, fire will occur where the ice is present, outside of where the liquid spill can be seen, as the ice indicates LNG sub-zero vapours.

Flammable vapour cloud indications

A liquid spill of most cryogenic liquids results in a vapour/air mixture temperature which typically is less than the moisture dew point of air. Therefore, atmospheric condensation will be formed on the outer fringes of an LNG vapour cloud, giving the appearance of fog. Obviously, this can help to identify the general hazard area of the spill and immediate vapour cloud visible limits and the potential downwind drift direction. However, it does not indicate where the gas cloud flammable limits are and must not be relied on for that purpose. It is therefore only a clear indication of a cold LNG vapour release. It must always be remembered that flammable vapour exists outside this visible fog and in some cases could be tens of metres beyond the cloud.

Rapid phase transition (RPT)

Often termed a "flameless" explosion. As a coarse description, when liquid droplets are dropped on to a hot surface, the evaporation rate is so rapid and great that each liquid droplet is supported by an invisible film from the continuing vapour and the liquid droplet does not actually touch the hot surface.

An LNG liquid spill on water has a sufficient temperature difference as well as surface tension to produce large droplets, or in some cases, puddles of LNG supported above the water by a continually produced film of evaporating vapour. When LNG is spilled on land or water, the LNG is initially around -162°C. The land or water surface is therefore, by comparison, very hot. (Even if the ground temperature is say, -12°C, this is still 150°C above the LNG!) This high temperature difference creates LNG boiling and because the difference in temperature is initially so high, a vapour film is formed at the contact point between the LNG and the underlying spill surface. The liquid is therefore supported above the hot surface by the vapour film.

This vapour film exists until the spill surface cools sufficiently, or until the LNG temperature becomes warm enough. So long as the vapour film exists, heat transfer is greatly reduced because the vapour layer is also acting as an insulator. When the difference in temperature between the LNG and the spill surface reduces, the vapour film disappears and a more rapid heat transfer occurs. Heat exchange between the cold LNG and the warmer surface area is now far greater because there is no vapour film in place. When this happens, the LNG is heated almost immediately, creating a Rapid Phase Transition (RPT) from liquid to vapour. Once this RPT is initiated, it proceeds through the heated LNG, almost instantly, in some cases involving potentially large amounts of LNG.

RPTs have caused overpressures although these have not been recorded as comparable to say, oil industry vapour cloud explosions in congested areas or chemical explosions. Yet the size and energy can cause damage. RPTs have been recorded as ranging in size from minor "puffs" to larger events which have damaged lightweight structures.

An interesting incident also occurred at Foz-sur-Mer in France in the 1990s when, during demonstration/use of a vehicle mounted dry chemical system monitor to extinguish a 25m^2 LNG pool fire, an RPT occurred because the contents of a water puddle between the vehicle and the LNG pool was blown into the burning LNG by the pressure from the dry chemical/nitrogen stream. A fireball arose from the burning LNG pool fire, doubling fire size for several seconds. The fire was extinguished as part of the dry chemical system demonstration, but it illustrated very well the hazards of RPTs where water and LNG make contact. Note that it has been stated that where very high Methane content LNG has spilled (>98%), there have been no recorded RPTs. For emergency responders, common sense advises that all LNG spills on water or with water introduction should be treated with the same caution. For this reason, use of water streams directly into LNG is not recommended in the field. This is a tactic some may consider beneficial since this increases vapourisation, and therefore the vapour hazard will be over much quicker.

In the next issue John Frame will be focussing on "rollover" (the rapid release of LNG vapours); international standards; and likely incident scenarios – including refrigeration, jetties cargo operations, tankage and piping.

LNG's terminology

LNG can sometimes be confused with NGL and so for clarity on terminology, LNG is the processed gas which is liquefied after recovery from oil/gas reservoirs and is mainly of Methane content. NGL's (Natural Gas Liquids) are mostly, though not wholly, removed from reservoir gas to either reduce liquefaction problems or to ensure gas quality/purity or to provide the feed for other petrochemical products. NGL's, from the heaviest upward, are either Hexane (C6), Pentane (C5), Butane (C4) Propane (C3) or Ethane (C2).

LNG is typically made up of anything from around 88% to 99% Methane, with varying Ethane, Propane and very small quantities of C4 making up the total. For most end users, the lack of any smoke from the LNG when burning indicates a very high Methane content, whereas smoke indicates a higher presence of Ethane and Propane.