Liquefied gas over water : an experimental approach at medium scale to assess gas/water interactions and vapor dispersion

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Liquefied Gas Over Water : An Experimental Approach at Medium Scale to assess gas/water interactions and vapor dispersion

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1.   Introduction

In case of a marine accident, gas or liquid substances could be released from the damaged ship and generate important risks for the crew, for the approaching emergency services and even for the population if the damage occurs close to the sea coast. In particular, some delayed hazardous phenomena may occur, like ignition of the spilled gas leading to a fire (jet fire, pool fire) or an explosion (overpressure added to flash fire effects), instantaneous vaporisation of liquefied gas still confined (BLEVE) or toxic effects due to evaporation of spreading pools over water. Even though improvements have been made in ship structures and safety equipments, the increasing volume and number of marine tankers in the recent years make this threat more acute.

The behaviour of spilled cryogenic hazardous gases like Liquefied Natural Gas – LNG – onto or under water has been studied in the late 70s (e.g. Atallah & Schneider, 1983; Opschoor, 1980) and some new studies have been recently published (e.g. Cormier et al., 2009; Fay, 2007; Luketa-Hanlin, 2006) due to the revival of interest in natural gas in the last few years. However the interaction mechanisms between the water surface and a refrigerated or pressurised gas spilled at sea are quite complex and still need to be studied to improve their understanding.

This paper presents the main observations from experimental tests carried out at INERIS (Verneuil-en-Halatte, France) to study the behaviour of refrigerated liquefied gas and liquids spilled over or below a water surface. The main topics addressed with this experimental approach at medium scale are:

- the vaporisation of the liquefied gas,

- the spreading of the pool, with potential freezing effects at the surface for cryogen substances,

- the evaporation of the liquid pool. The tests with pentane are not discussed in this paper.

In Section 2, we present the test device. Section 3 is dedicated to the observations and their analysis.

2.   Test device and protocol

2.1   Test device and instrumentation

The test device consists of a 10 m×10 m-pool of water with 1 m depth, in which some liquid or liquefied gases have been spilled (see Figure 1). The release point is located at the centre of the basin. The spilled materials are refrigerated liquefied nitrogen (boiling temperature T_{eb}=-196°C) as a safe substitute to LNG, pressurized liquefied propane (T_{eb}=-42°C) and

butane (T_{eb}=-1°C) and finally liquid pentane (T_{eb}=36°C) as a more persistent substance. The nozzle is connected to the storage tank by a 8-m flexible heat insulated hose of internal diameter 20 mm for liquefied gases and by a 8-m simple hose of internal diameter 4 mm for pentane. The nozzle diameter could be adjusted. In all the trials except in trial 8, the gases were spilled vertically downward 20 cm onto water. In test 8, the gas was spilled 10 cm below the waterline in order to observe how the water and the liquefied gas mix together and how the gas then vaporizes to the atmosphere.

Instrumented masts are immersed into the basin, equipped with temperature sensors (thermocouples) at different depths. A line of thermocouples floats at the water surface in order to detect a surface pool of spilled gas and its evolution (Figure 2). Three instrumented aboveground masts are placed downwind of the basin between 5 m and 11 m from the release point on a quite flat and open area, for measuring some properties of the dispersing cloud: gas concentration, temperature, velocity and turbulence level from 20 cm up to 3 m above the ground (Figure 3). The concentration measurements are made by means of a O_2-analyser with regular sampling of the atmospheric cloud. Several cameras are immersed into the basin to visualize the interaction between spilled gas and water. All trials have also been filmed with a normal camera and an infrared camera.

As wind direction is quite variable on the test site, two large fans have been placed upwind of the basin in order to channel the atmospheric flow towards the flat measurement area.

Figure 1: Experimental device

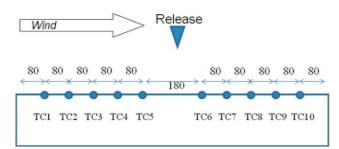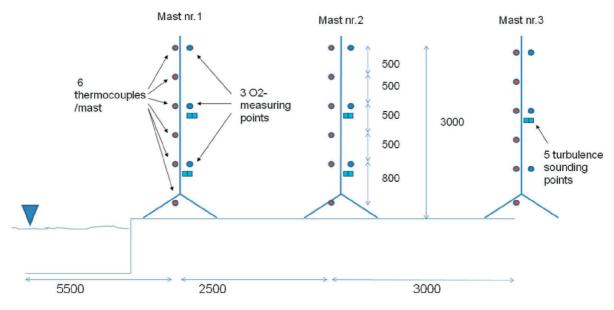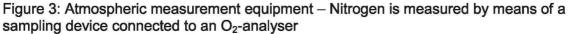Figure 2: Thermocouples floating at the water surface

Figure 3: Atmospheric measurement equipment – Nitrogen is measured by means of a sampling device connected to an O_2-analyser

2.2 Test protocol

The characteristics of all trials are given in Table 1. The indicated release pressure values give an estimation of initial pressures in the storage tank. It appeared in the trials that the pressure dropped significantly during the release, especially for the highest spill rate, since the gas vaporization into the tank could not be fast enough to compensate the decreasing volume of gas in the tank. Thus the estimated release rate given in the table is a mean value.

The four trials (No. 17 to 20) with pentane are not discussed in this paper.

Table 1: List of trials and release conditions, where T_{water}: ambient water temperature, T_{air}: ambient air temperature, RH: ambient relative humidity, T_{dew}: dew point temperature, P_{init}: estimated initial release pressure, $M_{spilled}$: mass of material spilled, d_{nozzle}: nozzle diameter, Δt: spill duration, Q_{mean}: mean release rate.
*release below the waterline.

Trial	Gas	T_{water} (°C)	T_{air} (°C)	RH (%)	T_{dew} (°C)	P_{init} (bara)	$M_{spilled}$ (kg)	d_{nozzle} (mm)	Δt (s)	Q_{mean} (kg/s)
6	N_2	10.5	11.3	98	10.9	4	172	20	215	0.8
7	N_2	10.5	12.1	84	10.3	4	103	20	115	0.9
8*	N_2	11.0	12.0	94	11.1	4	90	20	184	0.49
9	N_2	10.0	12.1	93.1	11.0	4	100	16	213	0.47
12	C_3H_8	6.5	11.1	54	2.3	10	57	10	140	0.41
13	C_3H_8	5.0	7.4	81	4.2	7	59	9	121	0.49
14	C_4H_{10}	5.5	1.2	88	-0.5	4	39	9	58	0.68
15	C_4H_{10}	4.5	4.6	83	1.8	2	46	9	74	0.63
16	C_4H_{10}	4.5	4.6	83	2.4	2	22	9	32	0.69
17	C_5h_{12}	3.0	1.6	92.1	0.6	-	0.8	2.5	360	8.5 g/s
18	C_5h_{12}	3.0	1.5	95.5	0.7	-	1.5	2.5	194	8.5 g/s
19	C_5h_{12}	3.0	1	99.9	1.1	-	1.7	2.5	205	8.5 g/s
20	C_5h_{12}	3.0	1	99.9	1.1	-	1.2	2.5	140	8.5 g/s

3.   Observations and analysis

An first analysis of the test results is discussed in the next paragraphs, mostly on the basis of trial No.7 (LN$_2$ spilled at a rate of 0,9 kg/s).

3.1   Interaction liquefied gas-water

Water surface temperature data from trial No.7 show a significant temperature decrease at water surface close to the release point (approximately -8°C at TC 6, Figure not shown). The other thermocouples do not measure temperature variations higher than 1°C. These variations are negligible compared to the boiling temperature of liquid nitrogen close to -200°C. Thus it is probable that evaporation does not take place at water surface but into the water. By direct observation with traditional video camera (Figure 4b), one sees a plume produced at the water surface inside a circle from approximately 1 m to 1,5 m of diameter.

The image extracted from the thermal imaging camera (Figure 4a) confirms that the water surface temperature shows negligible variations out of this "circle of emission". One can also notice that the order of magnitude of the temperature of the emitted vapors roughly deduced from this thermal video is -50°C and the order of magnitude of the temperature of the cloud when reaching the first mast is between 0 and 10°C. These values are rather close to those extracted from the analysis of the measurements (not shown).

(a)   (b)
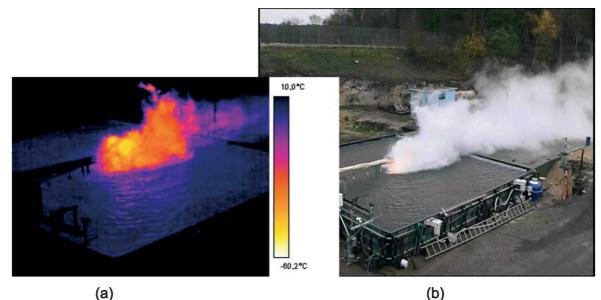
Figure 4: Images extracted from (a) thermal and (b) traditional videos of trial No.7

Underwater cameras did not allow perceiving the presence of a pool of nitrogen at the water surface further than 1 m from the release point.

Figure 5 shows snapshots – in a vertical cut – of penetrating jets of liquefied gases into the water. In trial No.7, the penetrating jet of nitrogen produces a mixing cone with a depth of about 75 cm and a diameter of about 40 to 50 cm at water surface. The penetration depth appears to be correlated to the release rate.

Nitrogen−20mm	Nitrogen−16mm	C_3H_8 − 9mm	C_4H_{10} − 9mm
H : 75cm	H : 30cm	H : 25cm	H : 50cm
Q : 0,9 kg/s	Q : 0,5 kg/s	Q : 0,5 kg/s	Q : 0,7 kg/s

Figure 5: Underwater mixing cones for different test cases. H: cone depth − Images extracted from trials No.7, 9, 13 and 16 respectively.

These pictures suggest that this intense underwater mixing leads to the important vaporization of liquefied gas with bubbles rising to the surface. We can believe that a part of the neighboring water cooled by the strong vaporization is also entrained by the bubbles rising to the surface. This current of cooler water at the surface could explain the slight decrease of temperature (less than 1°C) detected by surface thermocouples out of the "circle of emission" previously discussed. As the base of the atmospheric cloud observed above the basin has a size comparable to the base of the vaporization cone under the waterline, we can deduce that most of the heat transfer and the vaporization process take place in the mixing cone under water. This strong underwater mixing let suppose that some water droplets would be entrained into the vapor cloud in the atmosphere.

3.2 Short-range atmospheric dispersion

We first focus on the temperature in the atmospheric plume. On the one hand we tried to evaluate the local density of the cloud to assess the incidence of the gravity forces in the dispersion process. On the other hand we examined the nature of the mixture (adiabatic or not) between the vapors from the basin and the atmosphere. In a previous study, the degree of adiabaticity of a plume which is formed above an evaporating pool was studied. It appears that the evolution of temperature in the plume is very mainly induced by the mass transfer between vapor and atmosphere rather than by heat transfer with the ground. Consequently it seems reasonable to consider that the mixture vapor/ambient air occurs in an adiabatic way, i.e. the enthalpy is preserved. With this assumption, one can obtain an approximate mathematical expression for the mass concentration C of spilled gas in the plume, depending on the measured temperature and the water content in the atmosphere. It reads:

$$C = [C_{p\text{-air}} (T_{amb}-T_m) + L_{H2O}xf_{H2O}]/[C_{p\text{-g}} (T_m-T_{ge})] \tag{1}$$

where

C: mass concentration of spilled gas (N_2)

$C_{p\text{-air}}$, $C_{p\text{-g}}$: respectively, heat capacity of air and spilled gas

T_m, T_{ge}, T_{amb}: respectively measured temperature in the cloud, temperature of gas when emitted from the pool, ambient temperature

L_{H2O} : latent heat for (atmospheric) water

f_{H2O}: mass fraction of condensable water in the atmosphere.

The temperature of the vapor emitted from the pool, T_{ge}, can be estimated from the measurement of gas concentrations in the cloud at the first mast. The estimated value of T_{ge}

is then applied to all data at aerial masts. Figure 6 presents the comparison between the concentrations deduced from formulation (1) and measured by means of O_2-analyser for trial No.7. They appear to be fairly consistent once the temperature T_{ge} well estimated.
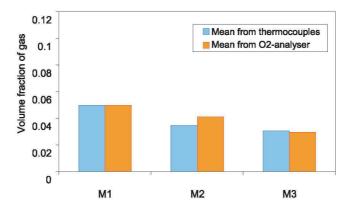

Figure 6: Comparison of the averages of nitrogen concentrations measured and deduced from formulation (1) for trial No.7

The estimated values of T_{ge} are given in Table 2. It appears that T_{ge} can be very different from the boiling temperature. This confirms that the boiling transition occurs essentially in the underwater mixing zone and not at the water surface, as explained before. In trial No.8, where the release happens below the waterline, the value of temperature T_{ge} of the emitted gas at the water surface is significantly higher than temperatures obtained for trials No.6 and 7. This is consistent with what was expected since the underwater mixing with water is strongly increased in this case. The comparison of emission temperatures for trial No.6/7 and No.9 indicates that the deeper the jet penetrates into the water, the lower the emission temperature is. We can also notice that the temperature of -45°C obtained for Trial No.7 are in good agreement with the thermal infrared image presented in Figure 4a.

Table 2: Properties of gas cloud and atmosphere for trials No.6, 7, 8, 12, 13, 14, 15, and 16. T_{ge}: temperature of the gas emitted from the pool, deduced from comparison between thermocouple measurements and concentration measurements, $T_{boiling}$: boiling temperature of considered material. *release below the waterline.

Trial	Gas	$T_{boiling}$ (°C)	T_{water} (°C)	T_{air} (°C)	RH (%)	T_{dew} (°C)	T_{ge} (°C)
6	N_2	-196	10.5	11.3	98	10.9	-45
7	N_2	-196	10.5	12.1	84	10.3	-45
8*	N_2	-196	11.0	12.0	94	11.1	-15
9	N_2	-196	10.0	12.1	93.1	11.0	-70
12	C_3H_8	-42	6.5	11.1	54	2.3	-16
13	C_3H_8	-42	5.0	7.4	81	4.2	-23
14	C_4H_{10}	-0.9	5.5	1.2	88	-0.5	0
15	C_4H_{10}	-0.9	4.5	4.6	83	1.8	0
16	C_4H_{10}	-0.9	4.5	4.6	83	2.4	0

Thermocouples measure at a very higher frequency than the O_2-analyser. Consequently the analysis of the behavior of the cloud is based on the data from thermocouples converted to nitrogen concentrations – based on the estimation of T_{ge} and formulation (1). From trial No.7, we can observe from these mean concentrations (Figure 7) that at mast M1 the cloud of nitrogen is highly concentrated in the first meter above the ground and then concentration decreases rapidly with height, whereas further at masts 2 and 3 the concentration decreases more regularly with height. This highlights the decrease of the density in the cloud with the

distance to the source: the cloud is dense close to the source due to its low temperature – and also water condensation – and then is gradually heated by the ambient air entrained.
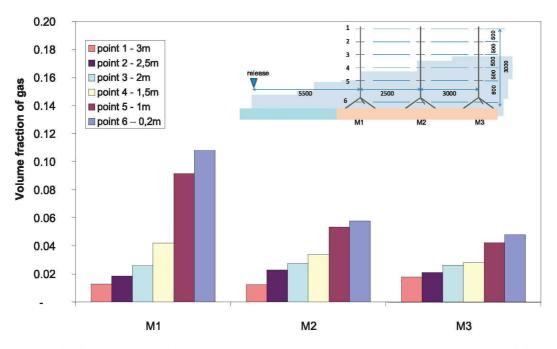

Figure 7: Calculated mean N_2 concentrations at the three atmospheric masts for trial No.7.

From wind speed and turbulence data measured in the cloud (not shown), it arises that no reduction of ambient vertical turbulent mixing or wind speed modification due to the presence of the dense cloud can be seen at this scale. These effects should be visible with larger clouds as it had been clearly observed in Burro and Falcon experiments (Koopman & Ermak, 2007). We also suspect that these effects could have been masked by the quite high level of ambient turbulence induced by fans used to guide the wind flow.

Finally, Figure 8 shows the visible plumes from nitrogen, propane and butane spills. These images and the measured concentrations (not shown) confirm that it cannot be assumed that the flammable region of a cloud should necessarily be included in the visible part of the cloud. Naturally, the visible part of a cloud depends on the cloud temperature and the dew point of atmospheric water, which is related to ambient temperature and relative humidity. For example, the butane spill in trial No.14 (Figure 8c) leads to no visible plume whereas measured concentrations at mast M1 are higher than the lower flammable limit of butane (1,3 %v/v). In this case, it appears that emitted vapours are close to 0°C whereas the dew temperature is around -0.5°C (cf. Table 2): atmospheric humidity cannot condense when mixed in the cloud, so the flammable cloud is not visible.

(a) Nitrogen – 20mm – 0,9 kg/s   (b) C_3H_8 – 9mm – 0,5 kg/s   (c) C_4H_{10} – 9mm – 0,7 kg/s
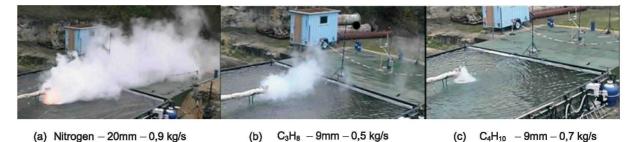
Figure 8: Comparison of the atmospheric plume sizes for three test cases. Images extracted from trials No.7 nitrogen (a), 13 propane (b) and 14 butane (c).

4. Conclusions

This medium-scale experiment allowed validating a measuring setup that permits to assess the behaviour of spilled hazardous liquid/liquefied gases over water. Only the spills of liquefied gas have been discussed. It appears that most of the gas vaporization occurs below the water line in the mixing cone produced when the jet penetrates vertically into the water. The temperature of the emitted vapors at the water surface could be estimated and is shown to be significantly different from the boiling point in some cases. Thus the dispersing cloud may be less cold and less dense than it would be expected for a cloud vaporizing from a still pool spreading at water surface. The physical process observed in our experiment is not taken into account by common consequence models, which usually consider that liquefied gas form a boiling pool at water surface. We thus expect that these consequence models used for safety studies would give conservative results when mixing under water is important, since it can be expected that a lighter cloud would lead to shorter safety distances. Anyway, it is clear from the atmospheric measurements that the cloud is very dense close to the source, even though the ambient flow (turbulence and mean wind velocity) has not shown to be disturbed by the presence of the cold cloud of nitrogen – used as a substitute to LNG in the experiments – at this scale. Otherwise it was verified that the visible part of a cloud and its flammable part do not usually match, as the size of the visible cloud strongly depends on cloud and air temperatures and relative humidity.

Globally, these experiments suggest that release conditions – over water, under water, impinging water surface,...– strongly determine the actual hazardous areas.

These trials can be seen as a first experimental step towards large-scale experiments of liquefied gas releases at sea needed to assess the behaviour of large hazardous dense clouds over water and to validate accidental dispersion models.

5. Acknowledgements

6. References

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