ELSEVIER

Journal of Loss Prevention in the Process Industries 14 (2001) 349–355

Journal of Loss Prevention in the process industries

www.elsevier.com/locate/jlp

Effectiveness of water curtains to protect firemen in case of an accidental release of ammonia: comparison of the effectiveness for two different release rates of ammonia

Aurélia Dandrieux [a,*], Gilles Dusserre [a], James Ollivier [a], Henri Fournet [b]

[a] *Laboratoire Génie de l'Environnement Industriel, Ecole des Mines d'Alès, 6 Avenue de Clavières, 30319 Alès Cedex, France*
[b] *Département Sécurité-Environnement, Grande Paroisse S.A., ATO, 92062 Paris La Défense Cedex, France*

Abstract

This paper presents the results of some dispersion experiments of liquefied ammonia in the presence of peacock tail water curtains. The aim of this paper is to evaluate the effectiveness of water barriers to counteract a weak release of ammonia under pressure (0.25 kg/s). The dissolution of ammonia in the water curtain is rather poor (about 15%), but at 10 m behind the curtain the effectiveness can reach levels as high as 90%. The results of the effectiveness obtained with ammonia releases of 0.25 kg/s are compared with results from those obtained from a release of ammonia half the size.

Keywords: Ammonia leakage; Water spray; Mitigation; Field experiments

1. Introduction

This paper deals with field experiments on the open dispersion of ammonia and its dispersion in the presence of water curtains. This study substantiates research on heavy gas dispersion at the medium scale. Previous studies have not often utilised field experiments, particularly with regard to the use of water curtains.

The most recent field experiments on ammonia were parts of the Fladis project (Nielsen et al., 1997) and the INERIS study (Bouet, 1999). Experiments on ammonia have been mostly carried out in wind tunnel studies where meteorological conditions can be fixed (Papaspyros, Papanicolaou, Kastrinakis, & Nychas, 1996). Field experiments are of prime interest to increase current knowledge on the efficiency of water curtains to mitigate the consequences of a toxic gas release.

Due to its thermodynamic properties, ammonia is frequently used in the chemical industry as a cooling agent. Being a toxic gas, its inhalation at high concentrations causes acute irritation of the respiratory system (INRS, 1992; Griffiths & Megson, 1984). Therefore, one must be able to deal with potential hazards due to the increasing transportation and storage of ammonia (Nyborg, Lunde, & Conley, 1991). Despite its low molecular weight (vapour density=0.6), ammonia behaves in some circumstances like a mixture with a higher density than air (Griffiths & Kaiser, 1982). The mixing and dispersing of heavy gas clouds are often much slower than those of buoyant clouds, and consequently it is desirable to enhance their natural dispersion by increasing their rate of dilution (Moodie, 1985). Water curtains represent a low cost method for controlling the spread of such clouds and mitigate their effects by the abatement of the concentrations.

Water curtains with an upward flow have been shown to be more effective than those with a downward flow (Fthenakis, Schatz, Rohatgi, & Zakkay, 1993). Peacock tail sprays used by the French fire services, which are considered in this paper, belong to the first category.

The aim of this study is to evaluate the behaviour of water curtains to counteract a leakage of ammonia of 0.25 kg/s and to compare the results with those obtained with releases of 0.1 kg/s (Bara & Dusserre, 1997).

* Corresponding author: Tel.: +33-04-66-78-27-61; fax: +33-04-66-78-27-01.
E-mail address: aurelia.dandrieux@ema.fr (A. Dandrieux).

0950-4230/01/$ - see front matter
PII: S0950-4230(01)00021-3

2. Experimental facilities

2.1. Test site

The experiments took place in Champclauson (Gard, France) during the winter of 1998–1999. The trials were based on the release of ammonia in the presence and in the absence of water curtains. Eleven trials were performed.

2.2. Release system

Liquefied ammonia was stored under pressure in steel bottles (B84 of L'Air Liquide) at its vapour saturation pressure (7.7 bars for a temperature of 17°C). Two bottles were set up side-by-side, the nozzle facing downwards, in order to produce a release in the horizontal downwind direction. The release height was 15 cm above ground level and lasted for 90 or 120 s. The experimental discharges were evaluated by weighing each bottle separately before and after each release and by timing the duration of the tests. On average and according to the storage temperature, the release rates were about 0.25 kg/s.

These release rates are representative of leaks which can occur in small tanks used for transportation or as storage for ordinary consumers.

2.3. Sensors distribution and concentration measurement

Concentration sensors were distributed on arcs at 15, 25, 35 and 50 m from the emission source during Trials 1 and 4; at 10, 20 and 30 m as shown in Fig. 1 for Trials 2, 3, 5 and 6. The concentrations are based on ground level sampling (10 cm from the ground).

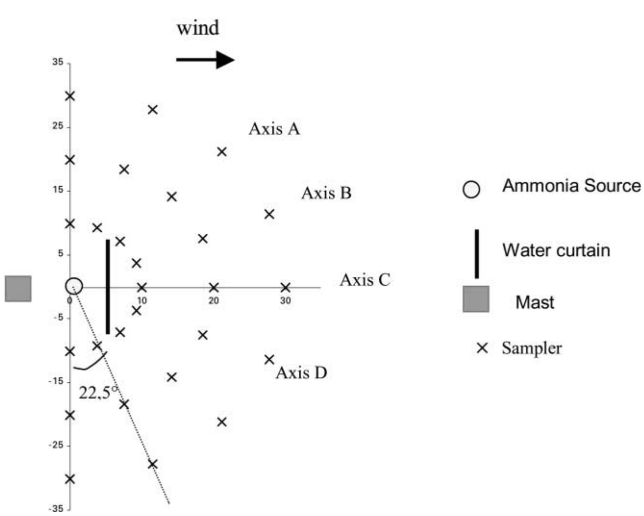

Fig. 1. Experimental facilities.

The sampling was performed by pumping the ammonia–air mixture up and capturing the mixture in an hydrochloric acid solution (0.1 M). Thirty seconds after the beginning of the release of ammonia, the pumps were started. This was to ensure that the cloud had reached all the sampling points before sampling commenced. The ammonia concentration was measured by means of UV–visible spectrophotometry with the Nessler reagent.

2.4. Meteorological measurements

Meteorological data were provided by a meteorological mast (with a Leader model 05106 station). Wind speed and wind direction measurements were made at a height of 6 m from ground level. Relative humidity and temperature of ambient air were measured by means of sensors located on the mast. These meteorological data were averaged for the duration of each trial.

2.5. The water curtain

The water curtain used was a peacock tail spray (Pons DSP65). Water is directed upwards, forming a fan as shown in Fig. 2. The flow rate of water was measured and found to have an average value of 730 l/min.

The vertical and horizontal dimensions of the screen are 8 and 20 m, respectively. The functioning pressure was 8 bars.

3. Experimental results

3.1. The experiments

A preliminary trial involved a study of ammonia dispersion in the absence of the water curtain. This allowed comparison of the concentrations measured in the atmosphere in the absence and in the presence of the water screen, and therefore evaluation of the effectiveness in reducing the concentrations.

The study comprised 11 trials, three of free dispersion and eight in the presence of water curtains. Table 1 contains the brief characteristics of tests 1–7, trials presenting conditions acceptable to the study of the water curtain efficiency.

3.2. Source rate results

The bottles were placed head down so the leakage was situated beneath the liquid level of ammonia. The release rates were measured and calculated by the Bernoulli equation (for liquid releases) with a discharge coefficient (C_d) of 0.8. We considered that ammonia was at ambient temperature. Experimental and theoretical values are given in Fig. 3. The release rate of ammonia was also calculated with the formulation of UIC (Union des

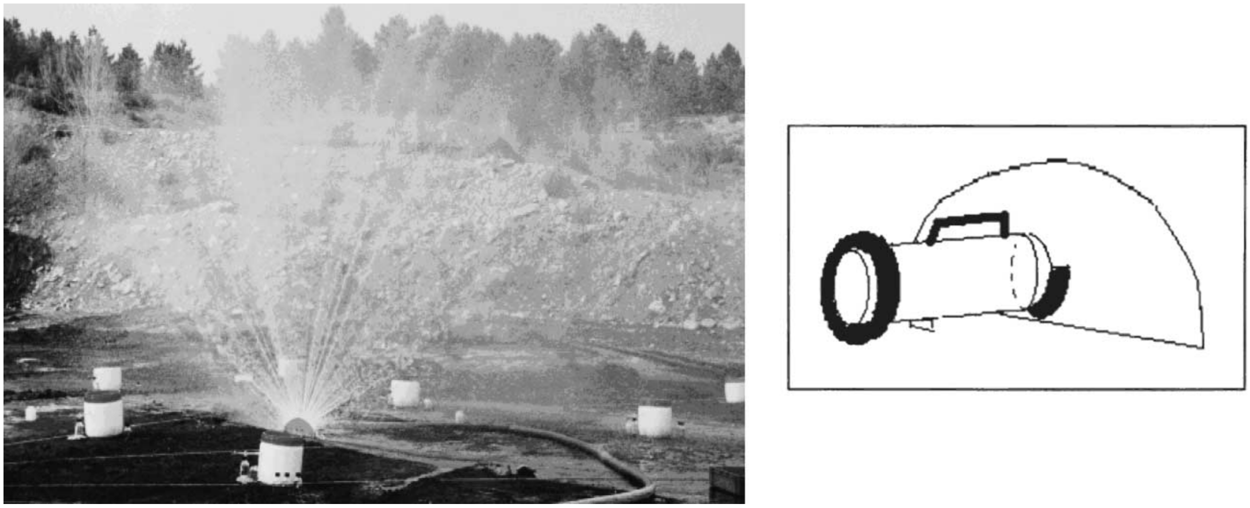

Fig. 2. Fan spray.

Table 1
Experimental conditions

Trial	1	2	3	4	5	6	7	A	B
Release rate (kg/min)	14.1	14.6	13.2	15.4	13.5	13.5	13.5	8.6	6.5
V (m/s)	0.8	3	1.9	0.3	2.8	2.8	4.4	2.0	6.0
Relative humidity (%)	65	50	60	65	50	50	60	30	60
Temperature (°C)	5	16	21	5	17	17	20	22	16
Source–curtain distance	no	no	no	6 m	6 m	6m	5 m	8 m	6 m

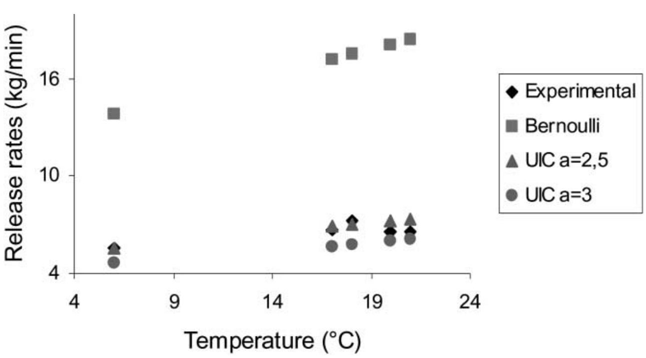

Fig. 3. Measured and calculated release rates.

Industries Chimiques) using the Bernoulli equation but with a correction factor (UIC, 1987). This method is a very simple way to evaluate two-phase releases. The calculation is given by Eq. (1).

$$Q_{2\ \mathrm{phaserelease}}\ (\mathrm{kg/s}) = \frac{Q_{\mathrm{Bernouilli\ liquid}}\ (\mathrm{kg/s})}{a} \quad (1)$$

where a is an empirical parameter varying between 2.5 and 3.

3.3. Results on dispersion

Each trial presented the same relative characteristics: immediately after the bottles were opened, a white plume with well defined contours was observed (Resplandy, 1969). At the nozzle exit, the liquid was instantaneously vaporised. A very small spill of ammonia was formed and quickly disappeared.

3.4. Results concerning the dilution rate and the effectiveness of the water barrier

The dilution rate of the water curtain characterises the reduction of concentration in the presence of the water spray. It is defined as the ratio between the concentrations measured during the dispersion in the absence of the water curtain (C_{free}) and the concentrations measured in the presence of the water screen (C_{curtain}). It is dependent on various interacting factors. External conditions, such as wind direction and speed, relative humidity etc., have a great influence on the dilution rate. Parameters specific to the spray which determine the rate of the mitigation are: the distance between the screen and the point source; the size and distribution of spray droplets; the water/gas ratio ... (Fthenakis & Blewitt, 1995). The influence of the ammonia release rate is studied in this paper. The same water curtain has been used with ammonia release rates varying from 0.10 to 0.25 kg/s.

Table 2 shows the results in terms of relative concentrations and dilution rate.

We defined the effectiveness (%) of the peacock tail by the following relationship (Eq. (2)). The effectiveness is calculated for the axes where the higher concentrations were observed during free dispersion and dispersion in the presence of the water curtain:

$$Eff=\frac{(C_{\mathrm{free}})-(C_{\mathrm{curtain}})}{(C_{\mathrm{free}})}\times 100 \qquad (2)$$

where C_{free} is the relative concentration (ppm) measured without the water curtain, and C_{curtain} is the relative concentration (ppm) recorded behind the water screen.

The calculation is applicable for the same meteorological conditions. To take into account the different release rates of ammonia this formula can be developed further to:

$$Eff_{\mathrm{pond}}=\frac{(C_{\mathrm{free}})-(C_{\mathrm{curtain}})_{\mathrm{pond}}}{(C_{\mathrm{free}})}\times 100 \qquad (3)$$

$$(C_{\mathrm{curtain}})_{\mathrm{pond}}=C_{\mathrm{curtain}}\times\frac{(\text{Release rate})_{\text{free dispersion}}}{(\text{Release rate})_{\text{dispersion with water curtain}}} \qquad (4)$$

The effectiveness for Trials 5 and 7 is reported (Fig. 4) and compared with effectiveness obtained previously for two experiments (Trials A and B) performed in Champclauson's site with weaker release rates of ammonia. The features of these experiments are given in Table 1.

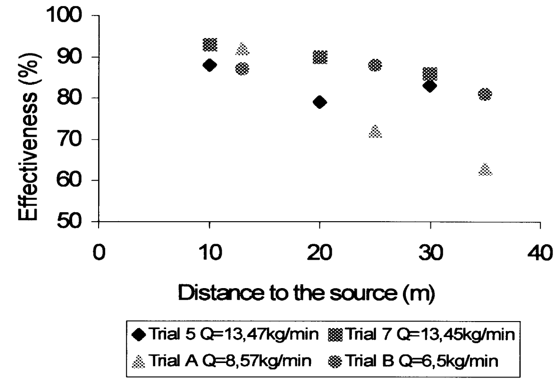

Fig. 4. Comparison of effectiveness behind the curtain for different release rates of ammonia.

3.5. Results concerning the dissolution of ammonia

The water curtain can absorb a significant amount of ammonia via a physico-chemical phenomenon. It is therefore of great interest to quantify this effect. The percentage of dissolution of ammonia can be defined as:

$$\text{Dissolution}=\frac{M_{\text{present in water}}\ (\text{kg})}{M_{\text{released in atmosphere}}\ (\text{kg})}\times 100 \qquad (5)$$

where $M_{\text{in the water}}$ is the mass (kg) of ammonia present in the water from the water curtain, and $M_{\text{released in atmosphere}}$ is the total mass (kg) of ammonia released during the trial.

In order to collect the total volume of water used, a ground sheet was utilised and a representative sample was analysed. The amount of ammonia dissolved is calculated from the water flow rate, the duration of the water screen and the concentration of ammonia in the sample. Table 3 gives the results of ammonia dissolution with fan sprays.

Table 2
Relative concentrations (ppm) and dilution rate

Axis	Distance from the source (m)	Trial 2 C_{F} (ppm)	Trial 5 C_{c} (ppm)	DR ($C_{\mathrm{F}}/C_{\mathrm{C}}$)	Trial 3 C_{F} (ppm)	Trial 7 C_{f}c (ppm)	DR ($C_{\mathrm{F}}/C_{\mathrm{C}}$)
A	10	200	900	0.2	180	1000	0.2
A	20	30	300	0.1	710	1130	0.6
A	30	10	80	0.1	640	670	1.0
B	10				4050	2650	1.5
B	20	17,780	3440	5.2		1550	
B	30	13,380	2060	6.5	1940	1310	1.5
C	10	26,150	2990	8.7	35,550	2770	12.8
C	20	10,910	1720	6.3	15,400	670	23.0
C	30	340	80	4.3	8880	230	38.6
D	10	30	1070	0.0	20	170	0.1
D	20	10	180	0.1	10	50	0.2
D	30	20	80	0.3	10	0	

Table 3
Percentage of dissolution of ammonia[a]

	Trial 4	Trial 5	Trial 6
Quantity of NH_3 in the water (kg)	5.2	2.2	1.7
Quantity released in the air (kg)	24.7	20.3	20.2
Dissolution of NH_3 %	21.2	11.0	8.2
Concentrationof NH_3 (g/l)	5.81	1.43	1.90

[a] Solubility of NH_3 in the water (20°C): 529 g/l.

4. Discussion

4.1. Source rate discussion

Release rates are for a discharge coefficient (C_d) of 0.8, about 2.5 times higher than the experimental results (Fig. 3). Consequently, it is not a purely liquid but a two-phase release. These results are comparable with those of Gühler, Hannemann, and Sallet (1979) who demonstrated that if the diameter is sufficiently small and the storage pressure sufficiently large, the breach release is always a two-phase process. These results confirm also the formulation of UIC using the Bernoulli equation for two-phase leakage when the factor a is equal to 2.5 as a reasonable approach.

4.2. Discussion on dispersion in the presence of water curtains

4.2.1. Dilution rate

The effect of the water screen is substantial: concentrations behind the curtain are more than eight times lower at 10 m behind it and still four times lower at 30 m downwind for Trial 5 (Table 2).

On the other hand, the forced dispersion generates a significant rise of concentrations on the axes situated on the edges of the water curtain (dilution rate <1). The explanation lies in the fact that when the cloud collides with an obstacle, its lateral and vertical dimensions become larger, and a portion of the cloud passes through the edges of the curtain.

Barriers must be far larger than the dimensions of the plume in order to protect the fire services. Moreover, the wind direction is scarcely constant and so larger curtains are required. A solution consists of using a barrier of several curtains, one possibility is to arrange them in a half-circle to anticipate a change in wind direction. One must keep in mind that the possible interaction between the flows of the water curtains can create an ineffective zone to mitigate concentrations. Furthermore, the main drawback of such configurations is the great increase of water consumption.

4.2.2. Effectiveness of the water curtain

Effectiveness for Trials 5 and 7 (Fig. 4) are relatively equal to those for leakages of half the size (Trials A and B) and similar experimental conditions. Effectiveness of Trial A is globally less important; it may be due to the relative humidity which is very low for Trial A (relative humidity of 30%), in comparison to Trials 5–7 and B (relative humidity reaches 50–60%). Therefore, the effectiveness of fan sprays is quite similar for release rates varying from 0.1 to 0.25 kg/s of ammonia.

However, the dilution rate or the effectiveness are relative to the concentrations measured for the free dispersion. Despite a high dilution rate, however, the concentrations behind the curtain are still high and exceed the toxic limits.

4.2.3. Dissolution rate

The mean percentage of dissolution was found to be approximately 15% as shown in Table 3; 15% is a poor value for ammonia as it has a high solubility in water. In theory, with a solubility of 0.529 g/g, solubility of ammonia for 20°C (L'Air Liquide, 1976), the possible mass of ammonia which could be dissolved with the mean amount of water used reaches 579 kg (20°C was chosen as a temperature as solubility decreases with a rise in temperature, and this value predicts a weaker solubility in comparison with temperatures measured in real situations). The concentrations of ammonia dissolved in water for Trials 4–6 are given in Table 3. They depend on the water flow rate, the functioning duration of the water curtain in relation to the release duration … A less important dissolution rate was measured for Trials 5 and 6 compared to Trial 4. This may be due to the influence of wind on the shape of the water curtain and on the time of contact between the gas and the curtain which is reduced for Trials 5 and 6.

The concentrations measured are far from saturation. In fact, a part of the cloud passes through the edges of the curtain. In consequence it is never in contact with the water curtain. Above all, the relative coarse spray of this kind of water curtain reduces the absorption processes. Indeed, the mass transfer between two phases (water and gas) is partially controlled by the interface properties (such as transfer time, interfacial area …) (Griolet, 1996).

In conclusion, the weak absorption of ammonia in the water curtain may not be relative to the saturation, but partially caused by a too small interfacial area and by a too short contact time between the droplets and the cloud.

Thus, the global effectiveness has been found to be 90%, the percentage of dissolution rising from 15%; the enhancement of dispersion (mechanical dilution effect) is more important than the physico-chemical inhibition.

The predominance of the mechanical effect of the water screen leads to the conservation of almost the entire pollutant mass in the cloud. This is the reason why elevated concentrations for the axes on the sides of the curtain were recorded. The loss of ammonia by dissolution or vertical dispersion is not sufficiently marked to reduce ground level concentrations below toxic levels (IDLH concentration for ammonia being 500 ppm) (Buchlin, 1994).

Even if the water barriers are effective in diluting ammonia vapour cloud (high dilution rate behind the water screen), the concentrations are still higher than the toxic limit. To improve downwind concentrations mitigation, either the dilution rate or the ammonia dissolution rate can be increased.

Petersen and Diener tested, in wind tunnel experiments, various configurations of solid obstacles (Petersen & Diener, 1990). The main objective was to study how these barriers mitigate the consequences of accidental releases of heavier than air vapour clouds and enhance their natural dispersion. Solid barriers could be substituted with water curtains for the configuration which gave the higher dilution rate. Concentration measurements and the calculation of the dilution rate will or will not confirm the greater mitigation of the concentrations in this configuration.

With regard to the improvement of ammonia dissolution in the water curtain, a solution involves the use of a spray composed of fine droplets, or even a water mist.

Due to a larger interfacial area of contact between water and ammonia, it will probably increase the absorption of ammonia in the water curtain. Small droplets of a spray, which have a lower speed than bigger drops, stay in contact with the gas for a longer time (Griolet, 1996). This allows an increase of the absorption ability, but this kind of spray is more sensitive to wind effects.

A compromise between a water curtain giving a high dilution rate and a water curtain favourable to the absorption mechanism (small droplets) will lead to lower concentrations behind the water barrier.

5. Conclusions

The effectiveness of peacock tail sprays has been proven when the discharge rate of ammonia is doubled (0.25 kg/s instead of 0.1 kg/s). Water curtains can still reduce, with an effectiveness of more than 90%, the concentrations at 10 m behind the water curtain. The dilution rate is mainly due to the mechanical effect, dissolution of ammonia being quite poor. Favourable wind conditions (stability of wind direction) are, however, required to maximise effectiveness.

Nevertheless, attention must be drawn to the relatively high concentrations behind and on the edges of the curtain, in so far as toxicity limits are exceeded. Therefore, new water spray systems to mitigate concentrations under lower levels must be perfected. A possible solution consists of the coupling of fine sprays to increase the surface area and then absorption and coarser sprays to enhance vertical dispersion. These parameters are to be examined in future experiments.

Acknowledgements

The work reported in this paper has been supported by the French Ministry of Environment. The authors would like to thank the fire services of Alès and la Grand Combe, without whom these experiments would not have been possible. They provided us with their logistic means and their knowledge of intervention in crisis situation.

References

Bara, A., & Dusserre, G. (1997). The use of water curtains to protect firemen in case of heavy gas dispersion. *Journal of Loss Prevention in the Process Industries*, *10* (3), 179–183.

Bouet, R. (1999). *Rapport final ammoniac — essais de dispersion atmosphérique à grande échelle.* Ministère de l'Aménagement du Territoire et de l'Environnement (in French).

Buchlin, J. M. (1994). Mitigation of problem clouds. *Journal of Loss Prevention in the Process Industries*, *7* (2), 167–174.

Fthenakis, V. M., & Blewitt, D. N. (1995). Modelling mitigation of releases of hazardous gases. *Journal of Loss Prevention in the Process Industries*, *8* (2), 71–77.

Fthenakis, V. M., Schatz, K. W., Rohatgi, U. S., & Zakkay, V. (1993). Computation of flow fields induced by water spraying of an unconfined gaseous plume. *Journal of Fluids Engineering*, *115* (4), 742–750.

Griffiths, R. F., & Kaiser, G. D. (1982). Production of dense gas mixtures from ammonia releases — a review. *Journal of Hazardous Materials*, *6*, 197–212.

Griffiths, R. F., & Megson, L. C. (1984). The effect of uncertainties in human toxic response on hazard range estimation for ammonia and chlorine. *Atmospheric Environment*, *18* (6), 1195–1206.

Griolet, F. (1996). *Dimensionnement des rideaux d'eau. Modélisation et applications industrielles*. Thesis, Université Claude Bernard, Lyon (in French).

Gühler, M., Hannemann, R. J., & Sallet, D. W. (1979). Unsteady two-phase blowdown of a flashing liquid from a finite reservoir. In *Two-phase Momentum Heat and Mass Transfer in Chemical Process and Energy Engineering Systems, Seminar, September 1978, Dubrovnik: Vol. 2* (pp. 781–795).

INRS (1992). Ammoniac et solutions aqueuses. In *Fiche toxicologique n°16.* (in French).

L'Air Liquide (1976). *Gas encyclopaedia.* Amsterdam: Elsevier Science Publishers BV (in French).

Moodie, K. (1985). The use of water spray barriers to disperse spills of heavy gases. *Plant/Operation Progress*, *4*, 234–241.

Nielsen, M., Ott, S., Jorgensen, H. E., Bengtsson, R., Nyrén, K., Winter, S., Ride, D., & Jones, C. (1997). Field experiments with dispersion of pressure liquefied ammonia. *Journal of Hazardous Materials*, *56* (1–2), 59–105.

Nyborg, R., Lunde, L., & Conley, M. (1991). Integrity of ammonia storage vessels — life prediction based on SCC experience. *Material Selection and Design*, *30* (11), 61–65.

Papaspyros, J. N. E., Papanicolaou, P. N., Kastrinakis, E. G., & Nychas, S. G. (1996). Wind tunnel simulation of ammonia gas release transport processes. *Journal of Hazardous Materials*, *46* (2-3), 241–252.

Petersen, R. L., & Diener, R. (1990). Vapour barrier assessment programme for delaying and diluting heavier-than-air HF vapour clouds a wind tunnel modelling evaluation. *Journal of Loss Prevention in the Process Industries*, *3*, 187–196.

Resplandy, A. (1969). Etude expérimentale des propriétés de l'ammmoniac. *Chimie et Industrie-Génie Chimique*, *102* (6), 691–702 (in French).

UIC (Union des Industries Chimiques) (1987). Cahier de sécurité n°11. Emission à la brèche d'une capacité — débit en phase gazeuse, débit en phase liquide, formation et vaporisation des flaques. In *Edition Chimie Promotion*, *Paris* (in French).